

Difference between metallic and electrolytic conduction

S.No.	Metallic conduction	Electrolytic conduction
(i)	Flow of electricity takes place without the decomposition of the substance	Flow of electricity takes place by chemical changes at electrodes.
(ii)	No transfer of matter takes place.	Transfer of matter takes place in the form of ions
(iii)	The resistance to the flow of current increases with the increase in temperature and hence the increase in temperature decreases the conduction.	The resistance to the flow of current decreases with the increase in temperature and hence increase in temperature increases the conduction.

ELECTROLYSIS

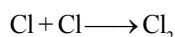
The process of decomposition of an electrolyte by the passage of electricity is called electrolysis or electrolytic dissociation. It is carried out in electrolytic cell where electrical energy is converted into chemical energy. For electrolysis to take place two suitable electrodes are immersed in the liquid. The solution of an electrolyte contains ions. When an electric potential is applied between the electrodes, the positively charged ions move towards the cathode and negatively ions move towards the anode, when a cation reaches the cathode, it takes up electron(s) and thus gets its charge neutralised. Thus the gain of electrons (decrease in oxidation number) means reduction takes place at the cathode.

Similarly an anion when it reaches the anode, gives up electron(s) and thus gets discharged. Loss of electrons (Increase in oxidation number) means oxidation takes place at anode.

- The tendency of an electrode to loose electrons is known as the oxidation potential.
- The tendency of an electrode to gain electrons is known as the reduction potential.

(a) Electrolysis of fused sodium chloride :

When fused sodium chloride is electrolysed, Na^+ ions moves towards the cathode and Cl^- ions moves towards the anode. At cathode Na^+ ions accept electrons to form sodium metal. At anode each Cl^- ion loses an electron to form Cl_2 gas.



(b) Electrolysis of aqueous solution of NaCl

The solution of NaCl contain Na^+ , Cl^- and small amounts of H^+ , OH^- (due to small dissociation of water)

- If more than one types of ions are present at a given electrode, then the one ion is the liberated which requires least energy. The energy required to liberate an ion is provided by the applied potential between electrodes. This potential is called discharge or deposition potential.

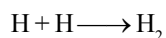
ORDER OF DISCHARGE POTENTIAL

Higher be the discharge potential, lower will be the tendency of ion to get discharged at the respective electrode. The decreasing order of discharge potential or increasing order of deposition of some of ions are given below :

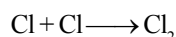
For cations : K^+ , Na^+ , Ca^{2+} , Mg^{2+} , Al^{3+} , Zn^{2+} , H^+ , Cu^+ , Ag^{2+} , Ag^+

For anions : SO_4^- , NO_3^- , OH^- , Cl^- , Br^- , I^-

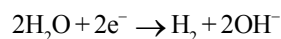
At cathode $H^+ \xrightarrow{+e^-} H$



At anode $Cl^- \xrightarrow{-e^-} Cl$



Na^+ ions move towards the cathode and combine with OH^- ions furnished by feebly ionised water to form NaOH.



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)	Dilute HCl	Pt or Graphite	Cl_2	H_2
(vii)	Dilute H_2SO_4	Pt or Graphite	O_2	H_2
(viii)	Aqueous $AgNO_3$	Pt or Graphite	O_2	Ag

ELECTROLYTIC CONDUCTANCE

- (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 current following(**I**).

$$R = \frac{V}{I} \quad \bullet \quad R \text{ is expressed in ohms.}$$

- (b) **Conductance (C)** : The conductance of a conductor is equal to reciprocal of resistance

$$C = \frac{1}{R} \quad \bullet \quad C \text{ is expressed in mho.}$$

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

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

where ρ is a constant and called resistivity or specific resistance.

When $\ell = 1$, $A = 1$, then $\rho = R$ thus the specific resistance may be defined as the resistance of a conductor of unit length and unit area of cross section.

- Unit of $\rho \rightarrow$ ohm.cm

(d) **Specific conductance (κ):**

It is defined as the reciprocal of specific resistance

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

The above definitions apply to metallic conductors and electrolytes.

- In the case of solution of electrolytes, the resistance offered by the solution to the flow of current is –
- Directly proportional to the distance between the electrodes

$$R \propto \ell$$

- Inversely proportional to the area of cross section of the electrodes

$$R \propto \frac{1}{A} \quad R = \rho \frac{\ell}{A}$$

The conductance $C = \frac{A}{\rho \ell}$

$$\therefore \frac{1}{\rho} = \kappa \text{ so } \kappa = \frac{C \ell}{A}$$

If $\ell = 1 \text{ cm}$ and $A = 1 \text{ cm}^2$ then

$$\kappa = C$$

Hence specific conductivity of a solution is defined as the conductance of one centimeter cube of the solution of the electrolyte.

- $\kappa = \frac{C \ell}{A}$

Where $\frac{\ell}{A} = \text{cell constant}$

- Cell constant (x) is a fixed quantity for a particular cell and is defined as the distance between two parallel electrodes of a cell divided by the area of cross section of the electrodes.

$$\kappa = C \times \text{cell constant}$$

$$\text{cell constant} = \frac{\kappa}{C} = \kappa R = \text{Specific conductivity} \times \text{resistance}$$

- Unit of $\kappa \rightarrow \text{ohm}^{-1} \text{ cm}^{-1}$

(e) **Equivalent Conductance (λ_{eq}):** It is defined as the product of specific conductance (κ) and the volume (V in mL) of the solution which contain one gram equivalent of the electrolyte.

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

If concentration of solution is C - gram equivalent per litre then $\lambda_{eq} = \frac{\kappa \times 1000}{C}$

- Unit $\rightarrow \text{ohm}^{-1} \text{ cm}^2$ per gram equivalent

Ex. The resistance of a 1N solution of salt is 50Ω . 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 cm^2 .

Sol.

$$\kappa = \frac{1}{\rho} = \frac{1}{R} \left(\frac{\ell}{A} \right)$$

$$= \frac{1}{50} \times \frac{2.1}{4.2} = \frac{1}{100}$$

and $\lambda_{eq.} = \frac{\kappa \times 1000}{N} = \frac{1}{100} \times \frac{1000}{1} = 10$

(f) Molar conductance : (λ_m or μ)

It is defined as the product of specific conductance (κ) and the volume (V in mL) in which contains one mole of the electrolyte.

$$\lambda_m = \mu = \kappa \times v$$

and
$$\lambda_m = \frac{\kappa \times 1000}{M}$$

Unit \rightarrow ohm⁻¹ cm² per mole

Ex. Which of the following have maximum molar conductivity.

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

(ii) 0.1M solution and its resistivity is 50 $\Omega \text{ cm}$.

Sol. **(i)**
$$\lambda_M = \frac{\kappa \times 1000}{M} = 2 \times 10^{-2} \times \frac{1000}{0.08} = 250 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

(ii)
$$\lambda_M = \frac{\kappa \times 1000}{M}$$

$$\therefore \kappa = \frac{1}{\rho}$$

$$\therefore \lambda_M = \frac{1}{50} \times \frac{1000}{0.1} = 200 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

So, the molar conductivity of 0.08M solution will be greater than 0.1M solution.

- Relation between $\lambda_{eq.}$ and λ_M :**

$$\lambda_M = \frac{\kappa \times 1000}{M} \quad \text{and} \quad \lambda_{eq.} = \frac{\kappa \times 1000}{N}$$

We know that

$$\text{Normality} = \text{Valency Factor} \times \text{Molarity}$$

or
$$N = n \times M \quad \text{so} \quad \lambda_{eq.} = \frac{\lambda_M}{V.F.}$$

Ex. If resistivity of 0.8 M KCl solution is $2.5 \times 10^3 \Omega \text{ cm}$ calculate λ_m of the solution.

Sol.
$$\rho = 2.5 \times 10^3 \Omega \text{ cm}$$

$$\kappa = \frac{10^3}{2.5} = 4 \times 10^2$$

$$\lambda_m = \frac{4 \times 10^2 \times 1000 \times 10}{0.8} = 5 \times 10^5 \Omega^{-1} \text{ cm}^2 \text{ mole}^{-1}$$

FACTORS INFLUENCING THE CONDUCTIVITY OF ELECTROLYTES

(a) Inter ionic attraction :

If inter ionic attraction between solute is more, then the conductivity will be less.

(b) Polarity of solvent :

If the solvent is greater polarized then the ionization and conductivity will be more.

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(c) **Viscosity of medium :**

By increasing the viscosity of medium, the conductivity decreases.

(d) **Temperature :**

As the temperature of electrolyte solution is increased, the conductivity increases because K.E. of ions increases and all type of attraction forces decreases and the viscosity of medium decreases.

(e) **Dilution :**

(i) The degree of ionisation increases with the increase of dilution of the solution the conductivity is increases due to increasing the number of ions.

(ii) Effect of dilution on specific conductance :

Specific conductance decreases with the increase of dilution of the solution due to the presence of no. of ions in 1cm^3 solution decreases.

(iii) Effect of dilution on equivalent/molar conductivity :

The equivalent/molar conductivity increases with dilution. This is due to the fact that degree of ionisation increases with dilution.

- When the whole of the electrolyte has ionised, further addition of the water bring a small change in the value of equivalent/molar conductance. This stage is called infinite dilution.
- The ratio of equivalent conductivity at any dilution to equivalent conductivity at infinite dilution is called conductivity ratio or degree of dissociation of solute -

$$\alpha = \frac{\lambda}{\lambda_{\infty}}$$

Ex. The equivalent conductivity of H_2SO_4 at infinite dilution is $384 \Omega^{-1} \text{cm}^2 \text{eq}^{-1}$. If 49 g H_2SO_4 per litre is present in solution and specific resistance is 18.4Ω then calculate the degree of dissociation.

Sol. Equivalent of $\text{H}_2\text{SO}_4 = \frac{49}{49} = 1\text{N}$

$$\text{specific conductance} = \frac{1}{\text{specific resistance}} = \frac{1}{18.4} \Rightarrow \lambda_{\text{eq.}} = \frac{1000 \times \kappa}{\text{N}} = \frac{1000 \times 1}{18.4} = 55$$

$$\text{Degree of dissociation } (\alpha) = \frac{\lambda_{\text{eq.}}^{\text{C}}}{\lambda_{\text{eq.}}^{\infty}} = \frac{55}{384} = 0.14 \Rightarrow \alpha \% = 14\%$$

KOHLRAUSCH LAW :

This law states that the equivalent conductivity of any electrolyte at infinite dilution ($\lambda_{\text{eq.}}^{\infty}$) is the sum of ionic conductances of the cation and anion given by the electrolytes at infinite dilution.

$$\lambda_{\text{eq}}^{\infty} = \lambda_{\text{a}}^{\infty} + \lambda_{\text{c}}^{\infty}$$

consider a salt NaCl, its equivalent conductivity at infinite dilution is the sum of two terms i.e.

$$\lambda_{\text{eq}}^{\infty} = \lambda_{\text{Na}^+}^{\infty} + \lambda_{\text{Cl}^-}^{\infty}$$

These terms are known as ionic mobilities of anion and cation.

For A_xB_y type solution :-

$$\lambda_{\text{eq}}^{\infty} = \frac{1}{Z^+} \lambda_{\text{c}}^{\infty} + \frac{1}{Z^-} \lambda_{\text{a}}^{\infty}$$

here c = cation & a = anion and Z^+ , Z^- are the charges on the cation and anion respectively.

Ex. At infinite dilution the equivalent conductance of Al^{+3} and SO_4^{-2} ion are 189 and $160 \Omega^{-1} \text{cm}^2 \text{eq}^{-1}$ respectively. Calculate the equivalent and molar conductivity at infinite dilute of $\text{Al}_2(\text{SO}_4)_3$.

Sol.
$$\lambda_{\text{eq}}^{\infty}[\text{Al}_2(\text{SO}_4)_3] = \frac{1}{3}\lambda_{\text{Al}^{3+}}^{\infty} + \frac{1}{2}\lambda_{\text{SO}_4^{2-}}^{\infty}$$

$$= \frac{1}{3} \times 189 + \frac{1}{2} \times 160 = 143 \Omega^{-1} \text{ cm}^2 \text{ eq}^{-1}$$

Molar conductivity = $\lambda_{\text{eq}} \times \text{V.F.} = 143 \times 6 = 858 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$

Application :

This law can be used to

- (a) Determine the equivalent conductivities of weak electrolytes at infinite dilution.
 (b) Determination of degree of dissociation, since α , the degree of dissociation of an electrolyte at the dilution V is

given by $\alpha = \frac{\lambda}{\lambda_{\infty}}$ where $\lambda_{\infty} = \lambda_a^{\infty} + \lambda_c^{\infty}$

Ex. $\lambda_{\text{m}}^0 \text{Na}^+ = 150 \Omega^{-1} \text{ cm}^2 \text{ mole}^{-1}$; $\lambda_{\text{eq}}^0 \text{Ba}^{2+} = 100 \Omega^{-1} \text{ cm}^2 \text{ eq}^{-1}$
 $\lambda_{\text{eq}}^0 \text{SO}_4^{2-} = 125 \Omega^{-1} \text{ cm}^2 \text{ eq}^{-1}$; $\lambda_{\text{m}}^0 \text{Al}^{3+} = 300 \Omega^{-1} \text{ cm}^2 \text{ mole}^{-1}$
 $\lambda_{\text{m}}^0 \text{NH}_4^+ = 200 \Omega^{-1} \text{ cm}^2 \text{ mole}^{-1}$; $\lambda_{\text{m}}^0, \text{Cl}^- = 150 \Omega^{-1} \text{ cm}^2 \text{ mole}^{-1}$

Then calculate

- (a) $\lambda_{\text{eq}}^0, \text{Al}^{3+}$ (b) $\lambda_{\text{eq}}^0 \text{Al}_2(\text{SO}_4)_3$ (c) $\lambda_{\text{m}}^0 (\text{NH}_4)_2\text{SO}_4$
 (d) $\lambda_{\text{m}}^0 \text{NaCl}, \text{BaCl}_2 \cdot 6\text{H}_2\text{O}$ (e) $\lambda_{\text{m}}^0, (\text{NH}_4)_2 \text{SO}_4 \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ (f) $\lambda_{\text{eq}}^0 \text{NaCl}$

Sol. (a) $\lambda_{\text{eq}}^0 \text{Al}^{3+} = \frac{300}{3} = 100$ (b) $\lambda_{\text{eq}}^0 \text{Al}_2(\text{SO}_4)_3 = 100 + 125 = 225$

(c) $\lambda_{\text{m}}^0 (\text{NH}_4)_2\text{SO}_4 = 2 \times 200 + 2 \times 125 = 650$

(d) $\lambda_{\text{m}}^0 \text{NaCl} \cdot \text{BaCl}_2 \cdot 6\text{H}_2\text{O} = 150 + 200 + 3 \times 150 = 800 \text{ r}^{-1}$

(e) $\lambda_{\text{m}}^0, (\text{NH}_4)_2 \text{SO}_4 \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O} \lambda_{\text{m}}^0 (\text{NH}_4)_2 = 400 + 600 + 4 \times 250 = 2000$

(f) $\lambda_{\text{eq}}^0 \text{NaCl} = 300 \Omega^{-1} \text{ cm}^2 \text{ eq}^{-1}$

Ex. To calculate λ_{m}^0 or λ_{eq}^0 of weak electrolyte

$$\lambda_{\text{mCH}_3\text{COOH}}^0 = \lambda_{\text{mCH}_3\text{COO}^-}^0 + \lambda_{\text{mH}^+}^0$$

$$= (\lambda_{\text{mCH}_3\text{COO}^-}^0 + \lambda_{\text{mNa}^+}^0) - \lambda_{\text{mNa}^+}^0 + \lambda_{\text{mH}^+}^0 + \lambda_{\text{mCl}^+}^0 - \lambda_{\text{mCl}^-}^0$$

$$\lambda_{\text{CH}_3\text{COOH}}^0 = \lambda_{\text{mCH}_3\text{COONa}}^0 + \lambda_{\text{mHCl}}^0 - \lambda_{\text{mNaCl}}^0$$

Ex. Calculate λ_{m}^0 of oxalic acid, given that

$$\lambda_{\text{eq}}^0 \text{Na}_2\text{C}_2\text{O}_4 = 400 \Omega^{-1} \text{ cm}^2 \text{ eq}^{-1}$$

$$\lambda_{\text{m}}^0 \text{H}_2\text{SO}_4 = 700 \Omega^{-1} \text{ cm}^2 \text{ mole}^{-1}$$

$$\lambda_{\text{eq}}^0 \text{Na}_2\text{SO}_4 = 450 \Omega^{-1} \text{ cm}^2 \text{ eq}^{-1}$$

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Sol. $\lambda_m^0 \text{H}_2\text{C}_2\text{O}_4 = 700 + 800 - 900 = 600 \Omega^{-1} \text{cm}^2 \text{mole}^{-1}$

$$\lambda_{\text{eq}}^0 = 400 + \frac{700}{2} - 450$$

$$\frac{\lambda_m}{2} = 350 - 50 = 300$$

$$\lambda_m = 600$$

Ex. If conductivity of water used to make saturated solution of AgCl is found to be $3.1 \times 10^{-5} \Omega^{-1} \text{cm}^{-1}$ and conductance of the solution of AgCl = $4.5 \times 10^{-5} \Omega^{-1} \text{cm}^{-1}$

If $\lambda_M^0 \text{AgNO}_3 = 200 \Omega^{-1} \text{cm}^2 \text{mole}^{-1}$

$\lambda_M^0 \text{NaNO}_3 = 310 \Omega^{-1} \text{cm}^2 \text{mole}^{-1}$

calculate K_{sp} of AgCl

Sol. $\lambda_M^0 \text{AgCl} = 140$

Total conductance = 10^{-5}

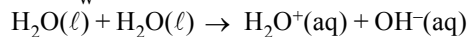
$$S = \frac{140 \times 4 \times 10^{-5} \times 1000}{140}$$

$$= \frac{1.4 \times 10^{-4}}{14}$$

$$S = 5.4 \times 10^{-4}$$

$$S^2 = 1 \times 10^{-8}$$

Ex. To calculate K_w of water



$$\lambda_m = \lambda_{\text{M,H}_2\text{O}}^0 = \lambda_M^0 \text{H}^+ + \lambda_M^0 \text{OH}^-$$

$$= \frac{K \times 1000}{\text{molarity}} - \text{Concentration of water molecules 100\% dissociated Ask}$$

$$\text{molarity} = [\text{H}^+] = [\text{OH}^-] = \frac{K \times 1000}{\lambda_M^0}$$

$$K_w = [\text{H}^+][\text{OH}^-] = \left[\frac{K \times 1000}{\lambda_M^0} \right]^2 \quad K_a \quad \text{or} \quad K_b = \frac{[\text{H}^+][\text{OH}^-]}{\text{H}_2\text{O}}$$

CONCENTRATION CELLS :

- A concentration cell consists of two electrodes of the same material, each electrode dipping in a solution of its own ions and the solution being at different concentrations.
- The two solutions are separated by a salt bridge.

e.g. $\text{Ag}(s) | \text{Ag}^+(a_1) || \text{Ag}^+(a_2) | \text{Ag}(s)$ ($a_1 < a_2$) a_1, a_2 are concentrations of each half cell

At LHS electrode Anode : $\text{Ag}(s) \longrightarrow \text{Ag}^+(a_1) + e^-$

At RHS electrode Cathode : $\text{Ag}^+(a_2) + e^- \longrightarrow \text{Ag}(s)$

The net cell reaction is : $\text{Ag}^+(a_2) \longrightarrow \text{Ag}^+(a_1)$

The Nernst eq. is

$$E_{\text{cell}} = -\frac{0.059}{n} \log \frac{a_1}{a_2} \quad (\text{Here } n = 1, \text{ Temp, } 298 \text{ K})$$

- Likewise, the e.m.f. of the cell consisting of two hydrogen electrodes operating at different pressure P_1 and P_2 ($P_1 > P_2$) and dipping into a solution HCl is :

$$E_{\text{cell}} = \frac{0.059}{2} \log \frac{P_1}{P_2} \quad (\text{at } 298 \text{ K})$$

Solubility product and EMF (Metal Insoluble Salt Electrode) :

- A half cell containing metal M and its sparingly soluble salt MA in a saturated solution. i.e. $M(s) | MA(\text{satd})$ or a metal, its sparingly soluble salt in contact with a solution of a soluble salt NaA of the same anion, i.e. $M(s) | MA(s) | NaA$ is set up.
- The solubility product of a sparingly soluble salt is a kind of equilibrium constant.



At Anode

At Cathode



$$E^\circ_{\text{cell}} = E^\circ_{\text{red}} - E^\circ_{\text{ox}}$$

From thermodynamics $\Delta G^\circ = -nFE^\circ$

$$\Delta G^\circ = -2.303 RT \log K_{\text{sp}}$$

combining both equations $-2.303 RT \log K_{\text{sp}} = -nFE^\circ$

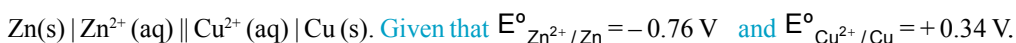
or $E^\circ = \frac{2.303 RT}{nF} \log K_{\text{sp}}$

$$E^\circ = \frac{0.0591}{n} \log K_{\text{sp}} \quad \text{at } 25^\circ\text{C}$$

Work done by a cell :

- 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 \times Potential = nFE
- Work done by cell = Decrease in free energy
so $-\Delta G = nFE$
or $W_{\text{max}} = +nFE^\circ$ where E° is standard EMF of the cell

Ex. Calculate the maximum work that can be obtained from the Daniell cell given below -



Sol. Cell reaction is : $Zn(s) + Cu^{2+}(aq) \longrightarrow Cu(s) + Zn^{2+}(aq)$ Here $n = 2$

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} \quad (\text{On the basis of reduction potential})$$

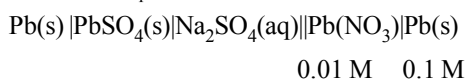
$$= +0.34 - (-0.76) = 1.10 \text{ V}$$

We know that : $W_{\text{max}} = \Delta G^\circ = -nFE^\circ$

$$= -(2 \text{ mol}) \times (96500 \text{ C mol}) \times (1.10 \text{ V}) = -212300 \text{ C.V.} = -212300 \text{ J}$$

or $W_{\text{max}} = -212300 \text{ J}$

Ex. Calculate K_{sp} if $(PbSO_4)$ E_{cell} at 298 K of this electrode is 0.236 V

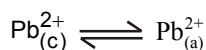
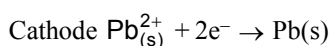
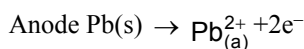


Sol. I $E_{cell} = E_{cell}^0 - \frac{0.059}{2} \log \left[\frac{0.01}{0.1} \right]$

$$0.236 = E_{cell}^0 + \frac{0.059}{2}$$

$$E_{cell}^0 = 0.236 - 0.03 = 0.206 - 0.059 \log [K_{sp}]$$

Sol. II Let it be conc. cell



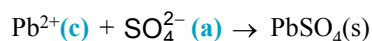
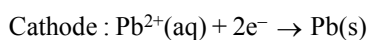
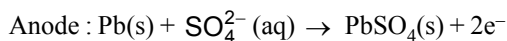
$$E_{cell} = E_{cell}^0 - \frac{0.059}{2} \log \left[\frac{(Pb^{2+})_a}{(Pb^{2+})_c} \right]$$

$$0.236 = \frac{0.059}{2} \log \left[\frac{(Pb^{2+})_a}{(Pb^{2+})_c} \right]$$

$$(Pb^{2+})_a = 10^{-9} M$$

$$K_{sp} = (Pb^{2+})_a (SO_4^{2-})_a = 10^{-11}$$

Let if it is not a conc cell



$$E_{cell}^0 = E_{Pb^{2+}/Pb}^0 - E_{SO_4^{2-}|PbSO_4|Pb}^0 = E_{Pb^{2+}/Pb}^0 - \left[E_{Pb^{2+}/Pb}^0 + \frac{0.059}{2} \log K_{sp} \right]$$

$$E_{cell}^0 = -\frac{0.059}{2} \log K_{sp}$$

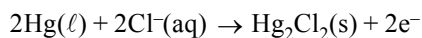
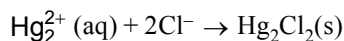
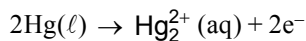
$$0.236 = \frac{0.059}{2} \log K_{sp} - \frac{0.059}{2} \log \left[\frac{1}{(Pb^{2+})_c (SO_4^{2-})_a} \right] = \log \left[\frac{K_{sp}}{0.1 \times 0.01} \right] = \log \left[\frac{K_{sp}}{10^{-3}} \right] \log 10^{-8}$$

$$K_{sp} = 10^{-11}$$

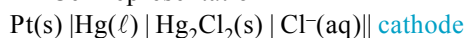
Calomel Electrode :

- A calomel cell consists of a platinum electrode dipping into mercury in contact with calomel (dimercury (II) chloride, Hg_2Cl_2) and potassium chloride solution.
- Usually the solution is saturated with potassium chloride.
- The cell has $E^0 = 0.28$ V (with respect of SHE) at $25^\circ C$

Standard (normal) calomel electrode when $[Cl^-] = 1M = 1N$

At Anode

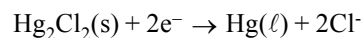
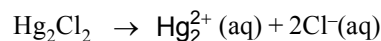
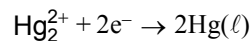
- Cell representation



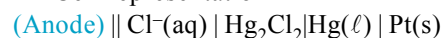
$$E_{Pt|Hg|Hg_2Cl_2+Cl^-}^0 = SOP$$

$$E_{Cl^-/Hg_2Cl_2/Hg} = E_{Cl^-/Hg_2Cl_2/Hg}^0 - \frac{RT}{F} \ln[Cl^-]$$

$$E_{M^{n+}/M(Hg)Pt} = E_{M^{n+}/M(Hg)Pt}^0 - \frac{RT}{F} \ln\left[\frac{1}{M^{n+}}\right]$$

At Cathode

- Cell representation



$$E_{Cl^-|Hg_2Cl_2|Hg(\ell)}^0 = SRP$$

THERMODYNAMICS OF CELL POTENTIAL

We know that :

$$\Delta G^0 = -nF E_{cell}^0$$

$$\Delta G = -nF E_{cell}$$

$$G = H - TS$$

From thermodynamics $H = E + PV$ enthalpy function.

Substituting $G = E + PV - TS$

By partial differentiation

$$\partial G = \partial E + P \partial V + V \partial P - T \partial S - S \partial T \quad \dots (i)$$

according to **1st law** of thermodynamics

$$E = q + W \quad dW = -PdV$$

$$\partial E = \partial q - PdV$$

$$\partial q = \partial E + P \partial V \quad \dots (ii)$$

according to **2nd law**

$$ds = \frac{dq}{T} = dq = Tds \quad \dots (iii)$$

From (i), (ii) and (iii)

$$dG = V \partial P - S \partial T$$

at constant pressure, which is actually the condition for all normal cell reaction.

$$dG = -S \partial T$$

$$S = -\frac{\partial G}{\partial T}$$

$$\Delta S = -\frac{\partial(\Delta G)}{\partial T}$$

$$\Delta G = -nF E_{cell}$$

$$\Delta S = +nF \frac{\partial E_{\text{cell}}}{\partial T}$$

$$\frac{\partial E_{\text{cell}}}{\partial T} = \text{temperature coefficient of cell reaction.}$$

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta H = -nF E_{\text{cell}} + nFT \frac{\partial E_{\text{cell}}}{\partial T}$$

Kirchoff's equation

$$\Delta C_p = \frac{\partial}{\partial T} (\Delta H)$$

$$C_p (\text{of products}) - C_p (\text{of reactants}) = \frac{-nF\partial E_{\text{cell}}}{\partial T} + nFT \frac{\partial^2 E_{\text{cell}}}{\partial T^2} + \frac{-nF\partial E_{\text{cell}}}{\partial T}$$

$$\Delta C_p = nFT \frac{\partial^2 E_{\text{cell}}}{\partial T^2}$$

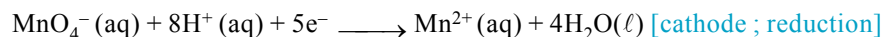
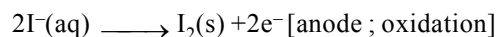
ELECTROLYSIS & ELECTROLYTIC CELL

ELECTROLYSIS

- Electrolyte is a combination of cations and anions which in fused state can conduct electricity.
- This is possible due to the movement of ions from which it is made of and electrolyte.
- The process of using an electric current to bring about chemical change is called electrolysis.
- Electrolysis is a process of oxidation and reduction due to current in the electrolyte.
- The product obtained during electrolysis depends on following factors.
 - The nature of the electrolyte
 - The concentration of electrolyte
 - The charge density flowing during electrolysis.
 - The nature of the electrode

ACTIVE v/s INACTIVE ELECTRODES

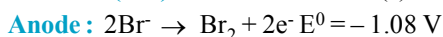
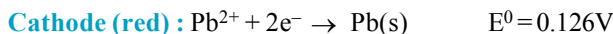
- The metal electrodes in the cell that are active because the metals themselves are components of the half reactions.
- As the cell operates, the mass of the zinc electrode gradually decreases, and the $[\text{Zn}^{2+}]$ in the anode half – cell increases. At the same time, the mass of the copper electrode increases and the $[\text{Cu}^{2+}]$ in the cathode half – cell decreases; we say that the Cu^{2+} „plates out" on the electrode.
- For many redox reactions, however, there are no reactants or products capable of serving as electrodes. Inactive electrodes are used, most commonly rods of graphite or platinum, materials that conduct electrons into or out of the cell but cannot take part in the half -reactions.
- In a voltaic cell based on the following half reactions, for instance, the species cannot act as electrodes :



Therefore, each half – cell consists of inactive electrodes immersed in an electrolyte solution that contains all the species involved in that half -reaction. In the anode half-cell, I^- ions are oxidized to solid I_2 . The electrons released flow into the graphite anode, through the wire, and into the graphite cathode. From there, the electrons are consumed by MnO_4^- ions as they are reduced to Mn^{2+} ions.

Examples of Electrolysis

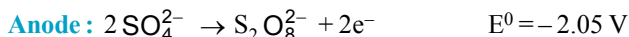
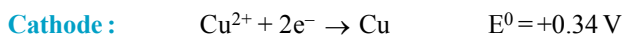
- Using inert (pt/graphite) electrodes.



$$E_{\text{cell}} = -0.126 - (0.108) \times 10 = -1.206\text{V}$$

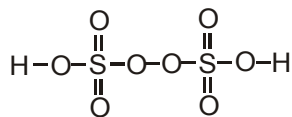
$$E_{\text{ext}} > 1.206\text{V}$$

- Electrolysis of CuSO_4 molten

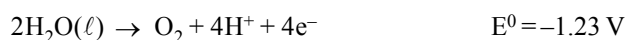
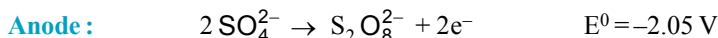
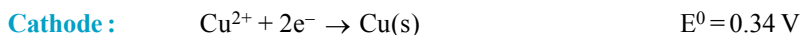


$\text{H}_2\text{S}_2\text{O}_8$ – Marshall's acid peroxy disulphuric acid.

$$E_{\text{cell}} = 0.34 - (2.05) = -1.71\text{V} \text{ (negative } \therefore \text{ not feasible)}$$



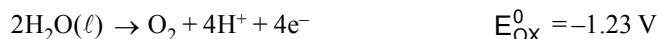
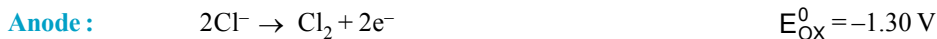
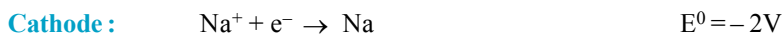
- Electrolysis of aq CuSO_4



- Electrolysis of aq NaBr solution (initially $\text{PH} = 7$)



- Electrolysis of aq NaCl



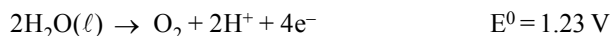
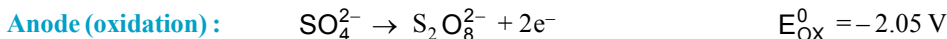
Rate of production of Cl_2 is more than rate of production of O_2 gas.

KEY POINTS

According to thermodynamics, oxidation of H_2O to produce O_2 should take place on anode but experimentally (experiment from chemical kinetics) the rate of oxidation of water is found to be very slow. To increase its rate, the greater potential difference is applied called over voltage or over potential but because of this oxidation of Cl^- ions also become feasible and this takes place on anode.

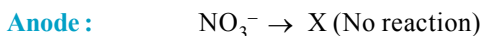
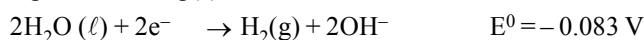
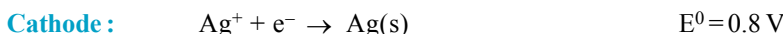
Electrolysis using attackable (reactive) electrodes.

- Electrolysis of aq. CuSO_4 using Cu electrode.



electrolytic refining

- $\text{AgNO}_3(\text{aq})$ using Cu cathode & Ag anode.



FARADAY'S LAWS OF ELECTROLYSIS :

Michael Faraday deduced two important law :

(a) FARADAY'S FIRST LAW OF ELECTROLYSIS

This law states that "The amount of a substance deposited or dissolved at an electrode is directly proportional to the charge passing through the electrolytes.

If a current of I amperes is passed for t seconds, the quantity of charge Q in coulombs. If W, gram of substances is deposited by Q coulombs of electricity, then

$$W \propto Q \propto It$$

$$W = Z It = \frac{E}{96500} It$$

Where Z is constant of proportionality and is known as electrochemical equivalent.

- When $Q = 1$ coulomb, $W = Z$

thus electro chemical equivalent may be defined as the weight in grams of an element liberated by the passage of 1 coulomb of electricity.

Ex. How many cc of chlorine will be deposited by 100 amp. current flowing for 5 hours through melted NaCl.

Sol. $Q = It = 100 \times 5 \times 60 \times 60 = 18 \times 10^5$

$$W = ZQ = \frac{E}{96500} \times 18 \times 10^5 = \frac{18E}{96500} \times 10^5 = \frac{18 \times 35.5}{965} \times 10^3 = 662.2 \text{ g}$$

\therefore Volume of 71 g Cl_2 at NTP = 22.4 L

\therefore volume of 662.2 g Cl_2 at NTP = $\frac{22.4}{71} \times 662.2 = 208.9 \text{ L}$

Ex. The time required to coat a metal surface of 80 cm^2 with 0.005 mm thick layer of silver (density = 10.5 g cm^{-3}) with the passage of 3 A current through silver nitrate solution is –

Sol. \therefore Volume of layer of silver = $0.005 \times 10^{-1} \times 80 = 0.04 \text{ cm}^3$

$$\therefore \text{Mass} = \text{Density} \times \text{volume} = 10.5 \times 0.04 = 0.42 \text{ g}$$

$$\text{So } w = \frac{E}{96500} \times It \Rightarrow 0.42 = \frac{108}{96500} \times 3 \times t$$

$$t = \frac{0.42 \times 96500}{108 \times 3} = 125.09 \text{ seconds.}$$

(b) FARADAY'S SECOND LAW :

This law states that the amounts of different substances deposited at electrodes by passage of the same quantity of electricity are proportional to their chemical equivalent (**E**).

$$W \propto E$$

If W_1 and W_2 be the amounts of two different substances deposited at electrodes and E_1 and E_2 be the equivalent weights then -

$$\frac{W_1}{W_2} = \frac{E_1}{E_2}$$

combining the two laws

$$W \propto It \quad E \quad W = \frac{ItE}{F} \quad \text{Where } \frac{1}{F} \text{ is proportionality constant and } F \text{ is called faraday.}$$

when $It = F$ then $W = E$

Hence faraday (**F**) is the quantity of charge in coulombs required to deposit one g equivalent of any substance.

The Faraday (**F**) is also the quantity of charge carried by one mole of electrons.

$$F = e \times N = 1.6 \times 10^{-19} \times 6.023 \times 10^{23} = 96500 \text{ coulombs.}$$

Ex. The same current if passed through solution of silver nitrate and cupric salt connected in series. If the weight of silver deposited is 1.08 g . Calculate the weight of copper deposited

Sol. According to faradays second law

$$\frac{W_1}{W_2} = \frac{E_1}{E_2} \Rightarrow \frac{1.08}{W_2} = \frac{108}{31.75} \Rightarrow W_2 = 0.3175 \text{ g}$$

CURRENT EFFICIENCY

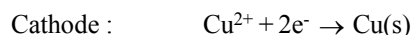
$$\text{current efficiency} = \frac{\text{charge actually used in electricity}}{\text{charge passed}} \times 100$$

$$\text{current efficiency} = \frac{\text{mass actually produced}}{\text{mass that should have been produced}} \times 100$$

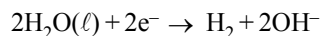
Ex. Calculate volume of the gases liberated at STP if 1 L of 0.2 molar solution of CuSO_4 is electrolysed by 5.79 A current for 10000 seconds .

CHEMISTRY FOR JEE MAIN & ADVANCED

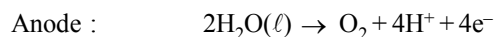
Sol. No. of moles of $e^- = \frac{5.79 \times 10000}{96500} = \frac{579}{965} = 0.6$



0.2 mole 0.4 mole



0.2 mole of $e^- \rightarrow 0.1$ mole of H_2 at S.T.P.



4 mole of $e^- \rightarrow 1$ mole of O_2

0.6 mole of $e^- \rightarrow 0.15$ mole of O_2

so, total moles = 0.25 mole

Total volume = 5.6 Ltr.

Ex. The electrochemical equivalent of copper is 0.0003296 g coulomb $^{-1}$. Calculate the amount of copper deposited by a current of 0.5 ampere flowing through copper sulphate solution for 50 minutes.

Sol. According to Faraday's first law, $W = 2 \text{ It}$.

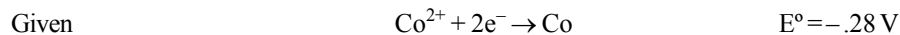
$$W = 0.5 \times 50 \times 60 \times 0.0003296 = 0.4944 \text{ g}$$

Ex. An electric current is passed through three cells connected in series containing ZnSO_4 , acidulated water and CuSO_4 respectively. What amount of Zn and H_2 are liberated when 6.25 g of Cu is deposited? Eq. wt. of Cu and Zn are 31.70 and 32.6 respectively.

Sol. \therefore Eq. of Cu = Eq. of Zn = Eq. of H_2

$$\frac{6.25}{31.70} = \frac{W_{\text{Zn}}}{32.6} = \frac{W_{\text{H}_2}}{1}$$

Ex. The cell consists of three compartments separated by porous barriers. The first contains a cobalt electrode in 5.00 L of 0.100 M cobalt (II) nitrate; the second contains 5.00 L of 0.100 M AgNO_3 . Assuming that the current within the cell is carried equally by the positive and negative ions, tabulate the concentrations of ions of each type in each compartment of the cell after the passage of 0.100 mole electrons.



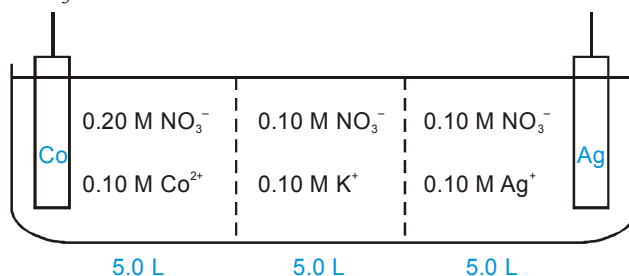
Spontaneous reaction is : $2\text{Ag}^+ + \text{Co} \rightarrow \text{Co}^{2+} + 2\text{Ag}$ $E^\circ = 1.08 \text{ V}$

Sol. In the left compartment. Cobalt will be oxidized to cobalt (II) ion. In the right compartment, silver ion will be reduced to silver. The passage of 0.100 mol electrons will cause the following quantities of change.

	Compartment 1	Compartment 2	Compartment 3
Effect of electrode	+ 0.0500 mol Co^{3+}	- 0.100 mol Ag^+	
Positive ion movement	- 0.0250 mol Co^{2+}	+ 0.0250 mol Co^{2+}	+ 0.0500 mol K^+
		- 0.0500 mol K^+	
Negative ion movement	+ 0.0500 mol NO_3^-		- 0.0500 mol NO_3^-

Changing the numbers of mol to concentrators in 5.0 L compartments and adding or subtracting yields the following results :

Final concentrations (M) Co^{2+}	0.015	Co^{2+}	0.00500	Ag^+	0.0800
NO_3^-	0.210	K^+	0.090	NO_3^-	0.0900
NO_3^-	0.100	K^+	0.0100		



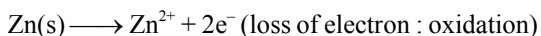
ELECTRO CHEMICAL CELL/GALVANAIC CELL/ VOLTAIC CELL

Example – Daniel Cell

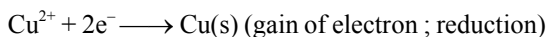
- A cell in which the chemical energy is transformed into electrical energy.
- The chemical reaction occurring in a galvanic cell is always a redox reaction.
- During the chemical process, the reduction in free energy will obtain as a result in the form of electrical energy.

Galvanic cell is made up of two half cells i.e., anodic and cathodic. The cell reaction is of redox kind. Oxidation takes place at anode and reduction at cathode. It is also known as **voltaic cell**. It may be represented as shown in fig. Zinc rod immersed in ZnSO_4 behaves as anode and copper rod immersed in CuSO_4 behaves as cathode.

Oxidation takes place at anode :



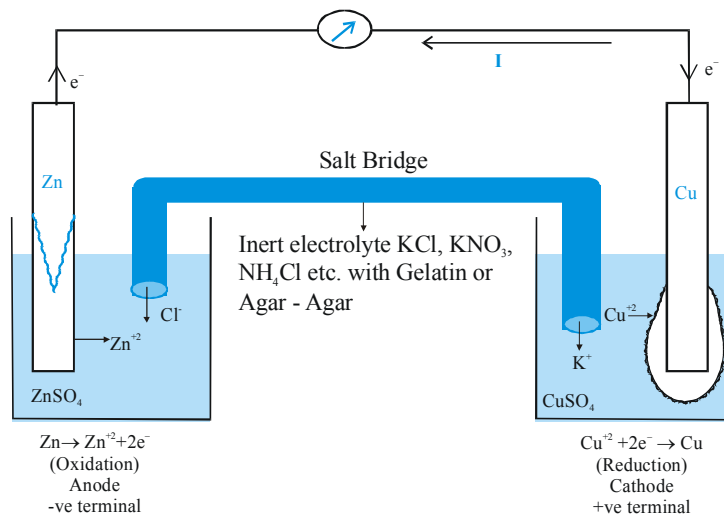
Reduction takes place at cathode :



Over all process :



In galvanic cell like Daniell cell ; electrons flow from anode (zinc rod) to the cathode (copper rod) through external circuit ; zinc dissolves as Zn^{2+} ; Cu^{2+} ion in the cathode cell picks up two electron and become deposited at cathode.



Salt bridge :

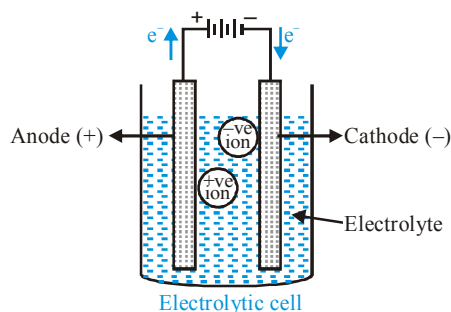
1. It allows to flow of current by completing the circuit.
2. It maintains electrical neutrality of electrolytes in two half cells.

Characteristics of electrolyte used in salt bridge :

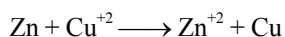
1. The electrolyte should be inert
2. The cations and anions of the electrolyte used should be of the same ionic mobility.

ELECTROLYTIC CELL

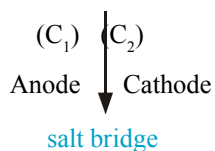
This cell converts electric energy into chemical energy. The entire assembly except that of the external battery is known as the electrolytic cell.



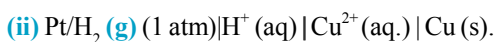
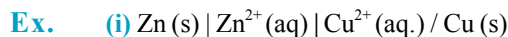
Cell reaction :



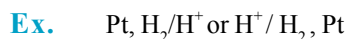
Representation of Galvanic cell.



Representation of electrochemical cell :



1. First of all, the anode is written.
2. After anode, the electrolyte of the anode should be written with its concentration in the bracket.
3. A slash (/) is put between anode and electrolyte to denote the surface barrier between the two as they exist in different phases.
4. Then we denote salt bridge by two vertical parallel lines. **(II)**.
5. Then, we write the electrolyte of cathode (negative electrode) followed by its concentration in bracket.
6. Finally, after a slash, we write the cathode.
7. In case of gas, the gas is to be indicated after the electrode in case of anode and before the electrode in case of cathode.



ELECTRODE POTENTIAL

When a strip of metal is brought in contact with the solution containing its own ions then the strip of metal gets positively charged or negatively charged and results into a potential being developed between the metallic strip and its solution which is known as electrode potential.

At anode



At cathode



The value of electrode potential depends upon :

- (1) the nature of electrode
- (2) the concentration of solution
- (3) the temperature

STANDARD ELECTRODE POTENTIAL (E^0):

If the concentration of ions is unity, temperature is 25°C and pressure is 1 atm (standard conditions), the potential of the electrode is called standard electrode potential.

The given value of electrode potential be regarded as reduction potential unless it is specifically mentioned that it is an oxidation potential.

ELECTRO MOTIVE FORCE OF CELL OR CELL VOLTAGE:

The difference in the electrode potentials of the two electrodes of the cell is termed as electro motive force [EMF] or cell voltage.

$$E_{\text{cell}} = E_{\text{red}} (\text{cathode}) - E_{\text{red}} (\text{anode})$$

or
$$E_{\text{cell}} = E_{\text{oxi.}} (\text{anode}) - E_{\text{oxi.}} (\text{Cathode})$$

or
$$E_{\text{cell}} = E_{\text{oxi.}} (\text{anode}) + E_{\text{red}} (\text{cathode})$$

Ex. Write short hand notation for the following reaction, $\text{Sn}^{2+} (\text{aq}) + 2\text{Ag}^+ (\text{aq}) \rightarrow \text{Sn}^{4+} (\text{aq}) + 2\text{Ag}(\text{s})$.

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

ELECTRO CHEMICAL SERIES

Standard Aqueous Electrode potentials at 298K

'The Electrochemical series'

Element	Electrode Reduction Reaction	Standard electrode Reduction potential E^0 , Volts
Li	$\text{Li}^+ + e^- \rightarrow \text{Li}$	-3.05
K	$\text{K}^+ + e^- \rightarrow \text{K}$	-2.93
Ba	$\text{Ba}^{+2} + 2e^- \rightarrow \text{Ba}$	-2.90
Ca	$\text{Ca}^{+2} + 2e^- \rightarrow \text{Ca}$	-2.87
Na	$\text{Na}^+ + e^- \rightarrow \text{Na}$	-2.71
Mg	$\text{Mg}^{+2} + 2e^- \rightarrow \text{Mg}$	-2.37
Al	$\text{Al}^{+3} + 3e^- \rightarrow \text{Al}$	-1.66
Mn	$\text{Mn}^{+2} + 2e^- \rightarrow \text{Mn}$	-1.18
Zn	$\text{Zn}^{+2} + 2e^- \rightarrow \text{Zn}$	-0.76
Cr	$\text{Cr}^{+3} + 3e^- \rightarrow \text{Cr}$	-0.74
Fe	$\text{Fe}^{+2} + 2e^- \rightarrow \text{Fe}$	-0.44
Cd	$\text{Cd}^{+2} + 2e^- \rightarrow \text{Cd}$	-0.40
Ni	$\text{Ni}^{+2} + 2e^- \rightarrow \text{Ni}$	-0.25
Sn	$\text{Sn}^{+2} + 2e^- \rightarrow \text{Sn}$	-0.14
Pb	$\text{Pb}^{+2} + 2e^- \rightarrow \text{Pb}$	-0.13
H ₂	$2\text{H}^+ + 2e^- \rightarrow \text{H}_2$	0
Cu	$\text{Cu}^{+2} + 2e^- \rightarrow \text{Cu}$	0.34
I ₂	$\text{I}_2 + 2e^- \rightarrow 2\text{I}^-$	0.54
Hg	$\text{Hg}_2^{+2} + 2e^- \rightarrow 2\text{Hg}$	0.79
Ag	$\text{Ag}^+ + e^- \rightarrow \text{Ag}$	0.8
Hg	$\text{Hg}^{+2} + 2e^- \rightarrow \text{Hg}$	0.85
Br ₂	$\text{Br}_2 + 2e^- \rightarrow 2\text{Br}^-$	1.08
Cl ₂	$\text{Cl}_2 + 2e^- \rightarrow 2\text{Cl}^-$	1.36
Pt	$\text{Pt}^{+2} + 2e^- \rightarrow \text{Pt}$	1.2
Au	$\text{Au}^{+3} + 3e^- \rightarrow \text{Au}$	1.5
F ₂	$\text{F}_2 + 2e^- \rightarrow 2\text{F}^-$	2.87

Ex. Calculate E^0_{cell} of (at 298 K),



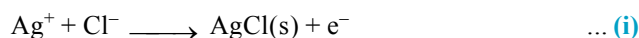
given that $E^0_{\text{Zn/Zn}^{2+}(\text{aq})} = 0.76 \text{ V}$
 $E^0_{\text{Cu(s)/Cu}^{2+}(\text{aq})} = -0.34 \text{ V}$

Sol. $E^0_{\text{cell}} = (\text{S.R.P})_{\text{cathode}} - (\text{S.R.P})_{\text{anode}}$
 $= 0.34 - (-0.76) = 1.1 \text{ V}$

- Ex.** Given the cell $\text{Ag} | \text{AgCl(s)} | \text{NaCl (0.05 M)} || \text{AgNO}_3 (0.30) | \text{Ag}$
- (a) Write half reaction occurring at the anode. (b) Write half reaction occurring at the cathode.
 (c) Write the net ionic equation of the reaction. (d) calculate E°_{cell} at 25°C .
 (e) Does the cell reaction go spontaneous as written ?

(Given $E^\circ_{\text{AgCl,Cl}} = +0.22$ volt) ; $E^\circ_{\text{Ag}^+/\text{Ag}} = +0.80$ volt)

- Sol.** (a) LHS electrode is anode and half reaction is oxidation.



- (b) RHS electrode is cathode and half reaction is reduction.



- (c) From equation (i) and (ii) cell reaction is : $\text{Cl}^- (0.05 \text{ M}) + \text{Ag}^+ (0.30 \text{ M}) \longrightarrow \text{AgCl(s)}$

(d) $E^\circ_{\text{cell}} = E^\circ_{\text{right}} - E^\circ_{\text{left}}$
 $= (0.80 - 0.22 \text{ volt}) = 0.58 \text{ volt}$

- (e) Yes, the e.m.f. value is positive, the reaction will be spontaneous as written in the cell reaction.

- Ex.** An aqueous solution containing Na^+ , Sn^{2+} , Cl^- & SO_4^{2-} ions, all at unit concentration, is electrolysed between a silver anode and a platinum cathode. What changes occur at the electrodes when current is passed through the cell ? Given : $E^\circ_{\text{Ag}^+|\text{Ag}} = 0.799 \text{ V}$,

$$E^\circ_{\text{Sn}^{2+}|\text{Sn}} = -0.14 \text{ V}, E^\circ_{\text{Cl}_2|\text{Cl}^-} = 1.36 \text{ V}, E^\circ_{\text{S}_2\text{O}_8^{2-}|\text{SO}_4^{2-}} = 2 \text{ V}, E^\circ_{\text{Sn}^{4+}|\text{Sn}^{2+}} = 0.13 \text{ V}$$

- (A) Sn^{2+} is reduced and Cl^- is oxidized (B) Ag is oxidized and Sn^{2+} is reduced
 (C) Sn^{2+} is reduced and Sn^{2+} is oxidized (D) H^+ is reduced and Sn^{2+} is oxidised

- Sol.** At anode either Ag can be oxidised to Ag^+ or Sn^{2+} to Sn^{4+} or Cl^- to Cl_2 or SO_4^{2-} to $\text{S}_2\text{O}_8^{2-}$. Their respective oxidation potential values are -0.799 V , 0.13 V , -1.36 V and -2 V . From these values, it is evident that Sn^{2+} would be oxidised first, followed by Ag at anode. At cathode, either Na^+ can get reduced to Na. or Sn^{2+} to Sn or H^+ to H_2 . The reduction potential value for Na^+ is highly negative while for $\text{Sn}^{2+} | \text{Sn}$ is -0.14 V and for

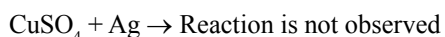
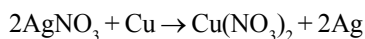
$$\text{H}^+ + e^- \longrightarrow 1/2 \text{ H}_2 \left(E_{\text{H}^+|\text{H}_2} = 0.059 \log \frac{1}{10^{-7}} \right) \text{ is } -0.413 \text{ V. Thus } \text{Sn}^{2+} \text{ will get reduced at cathode}$$

followed by H^+ \therefore (C)

IMPORTANT POINTS ABOUT SERIES :

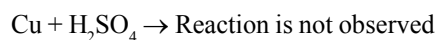
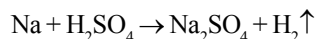
1. Electrode whose standard reduction potential (SRP) is less, act as anode, and other one which has high reduction potential acts as cathode.
2. Metals near the top of the series are strongly electropositive.
3. Metals near the top of the series can displace more electronegative metal below them from their salt.

For example :



4. Metal above hydrogen can displace H_2 from dilute acid

For example -



5. Hydroxides of metal in the upper part of series are strongly basic while hydroxides of a metal in lower part are weakly basic.
6. The activity of non metals increases from top to bottom.
7. The metals which come below copper, form unstable oxides i.e., these are decomposed on heating.

NERNST EQUATION

With the help of Nernst equation, we can calculate the electrode potential of electrode or EMF of cell.

$$E_{\text{cell}} = E^{\circ} - \frac{RT}{nF} \log_e \frac{[\text{Product}]}{[\text{Reactant}]}$$

Where - E° = standard electrode potential

R = gas constant

T = temperature (in K)

F = Faraday (96500 coulomb mol^{-1})

n = no. of e^- gained or loosed in balanced equation.

or

$$E_{\text{cell}} = E^{\circ} - \frac{0.0591}{n} \log_{10} \frac{[\text{Product}]}{[\text{Reactant}]} = E^{\circ} - \frac{0.0591}{n} \log Q$$

Let, in the cell :



for this reaction –

$$E_{\text{oxi}} = E_{\text{oxi}}^{\circ} - \frac{0.0591}{n} \log_{10} \frac{[M_1^{+n}]}{[M_1]} \quad \dots(1)$$



for this reaction –

$$E_{\text{red.}} = E_{\text{red.}}^{\circ} - \frac{0.0591}{n} \log_{10} \frac{[M_2]}{[M_2^{+n}]} \quad \dots(2)$$

Note : Concentration of solid taken as unity.

so $[M_1] = [M_2] = 1$

We know that EMF of cell is

$$\text{EMF} = \underset{\text{(Anode)}}{E_{\text{oxi}}} + \underset{\text{(Cathode)}}{E_{\text{red.}}}$$

By adding equation (1) & (2) we get :

$$\text{EMF} = E_{\text{oxi}}^{\circ} - \frac{0.0591}{n} \log [M_1^{+n}] + E_{\text{red.}}^{\circ} - \frac{0.0591}{n} \log \frac{1}{[M_2^{+n}]}$$

$$(E_{\text{oxi}}^{\circ} + E_{\text{red.}}^{\circ}) - \frac{0.0591}{n} [\log [M_1^{+n}] - \log [M_2^{+n}]]$$

$$\boxed{\text{EMF} = E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{n} \log \frac{[M_1^{+n}]}{[M_2^{+n}]}}$$

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

Sol. $\text{Cu}^{+2} + 2e^{-} \rightarrow \text{Cu}$

$$E_{\text{red}} = E_{\text{red}}^{\circ} - \frac{0.0591}{n} \log \frac{[\text{Product}]}{[\text{Reactant}]}$$

here $n = 2$

$$\begin{aligned} \text{so } E &= 0.34 - \frac{0.0591}{2} \log 10 \\ &= 0.34 - 0.03 = 0.31 \text{ Volts} \end{aligned}$$

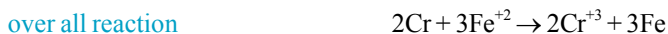
Ex. The EMF of the cell



(Given $E^{\circ} \text{Cr}^{+3}/\text{Cr} = -0.75\text{V}$

$E^{\circ} \text{Fe}^{+2}/\text{Fe} = -0.45\text{V}$)

Sol. Half cell reactions are :



E_{cell}° = oxidation pot. + Reduction pot.

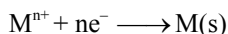
$$= 0.75 + (-0.45) = 0.30$$

$$E_{\text{cell}} = E^{\circ} - \frac{0.0591}{n} \log \frac{[\text{Product}]}{[\text{Reactant}]}$$

$$= 0.30 - \frac{0.0591}{6} \log \frac{[\text{Cr}^{+3}]^2}{[\text{Fe}^{+2}]^3} = 0.30 - \frac{0.0591}{6} \log \frac{[0.1]^2}{[0.01]^3} = 0.30 - \frac{0.24}{6} = 0.26 \text{ Volt.}$$

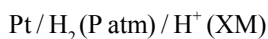
DIFFERENT TYPES OF ELECTRODES :

1. Metal - Metal ion electrode M/M^{n+}

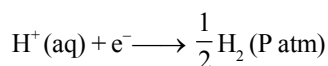


$$E = E^{\circ} + \frac{0.0591}{n} \log [M^{n+}]$$

2. Gas - ion Electrode

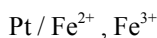


as a reduction electrode

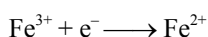


$$E = E^{\circ} - 0.0591 \log \frac{P_{H_2}^{\frac{1}{2}}}{[H^{+}]}$$

3. Oxidation - reduction Electrode

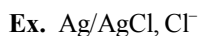


as a reduction electrode

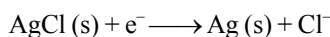


$$E = E^{\circ} - 0.0591 \log \frac{[Fe^{2+}]}{[Fe^{3+}]}$$

4. Metal - Metal insoluble salt electrode



as a reduction electrode



$$E_{Cl^{-}/AgCl/Ag} = E_{Cl^{-}/AgCl/Ag}^{\circ} - 0.0591 \log [Cl^{-}]$$

Note :

1. The value of electrode potential does not depend on stoichiometry of half reactions.
2. In electrolytic cell, cathode is negative terminal whereas in Galvanic cell cathode is positive terminal.
3. Work obtained by electro chemical cell = -free energy of cell

$$\Delta G = -nFE_{\text{cell}} \quad \Delta G^{\circ} = -nFE_{\text{cell}}^{\circ}$$

4. Cell reaction is spontaneous, if

$$\Delta G = -ve \quad \text{or} \quad E_{\text{cell}} = +ve$$

5. Cell reaction will be in equilibrium

Ex. $\Delta G = 0 \quad \text{or} \quad -nFE_{\text{cell}} = 0 \quad \text{or} \quad E_{\text{cell}} = 0$

6. In nernst equation

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{n} \log_{10} \frac{[\text{Product}]}{[\text{Reactant}]}$$

If $E_{\text{cell}} = 0$, then

$$E_{\text{cell}}^{\circ} = \frac{0.0591}{n} \log_{10} \frac{[\text{Product}]}{[\text{Reactant}]}$$

$$\text{or } E_{\text{cell}}^0 = \frac{0.0591}{n} \log_{10} K \quad \text{or } E_{\text{cell}}^0 = \frac{RT}{nF} \log_e K$$

put the value of E_{cell}^0 in

$$\Delta G^\circ = -nFE_{\text{cell}}^0$$

$$\text{we get } \Delta G^\circ = -nF \frac{RT}{nF} \log_e K \Rightarrow \Delta G^\circ = -RT \log_e K$$

Ex. Calculate R.P. of hydrogen electrode at 298K which is prepared with the help of aq. solution of acetic acid with 0.1 M conc at 1 atm pressure $K_a = 1.8 \times 10^{-5}$.

Sol. $[H^+] = \sqrt{K_a \times c} = \sqrt{1.8 \times 10^{-5} \times 10^{-1}} = \sqrt{1.8 \times 10^{-6}}$
 $2H^+ + 2e^- \rightarrow H_2$

$$E_{\text{Redn}} = E_{\text{red}}^0 - \frac{0.059}{2} \log \frac{P_{H_2}}{[H^+]^2} \quad (E_{\text{Reduction}}^0 = 0)$$

$$E_{\text{Redn}} = -\frac{0.059}{2} \log \left(\frac{1}{1.8 \times 10^{-6}} \right) = -\frac{0.059}{2} [6 - \log(1.8)]$$

$$E_{\text{Redn}} = -\frac{0.059}{2} \times 5.74 = -0.169 \text{ V}$$

Ex. Which is stronger oxidizing agent

(i) $K_2Cr_2O_7$ in solution in which

$$[Cr_2O_7^{2-}] = 0.1 \text{ M}, [Cr^{3+}] = 10^{-2} \text{ M and } [H^+] = 10^{-1} \text{ M}$$

(ii) $KMnO_4$ in a solution in which

$$[MnO_4^-] = 10^{-1} \text{ M}, [Mn^{2+}] = 10^{-2} \text{ M}, [H^+] = 10^{-2} \text{ M}$$

$$E_{Cr_2O_7^{2-}/Cr^{3+}}^0 = 1.33 \text{ V} \quad E_{MnO_4^-/Mn^{2+}}^0 = 1.51 \text{ V}$$

Sol. (i) $14H^+ + Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + 7H_2O + 6e^-$

$$E_{\text{Redn}} = 1.33 - \frac{0.059}{6} \log \left[\frac{10^{-4} \times 10}{10^{-14}} \right] = 1.33 - \frac{0.059}{6} \times 11$$

$$E_{\text{Redn}} = 1.33 - \frac{0.649}{6} = 1.330 - 0.108 = 1.222 \text{ V}$$

(ii) $5e^- + 8H^+ + MnO_4^- \rightarrow Mn^{2+} + 4H_2O$

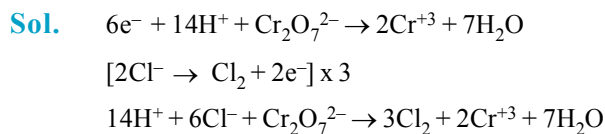
$$E_{\text{Redn}} = 1.51 - \frac{0.059}{5} \log \left[\frac{10^{-2}}{10^{-16} \times 10^{-1}} \right] = 1.51 - 0.059 \times 3 = 1.51 - 0.18 = 1.33 \text{ V}$$

$E_{\text{Reduction}}$ is more so, good oxidising agent

Ex. Calculate E_{cell} of $Pt(s) \left| Cl_2(g) \right| Cl^-(aq) \left| Cr_2O_7^{2-}, Cr^{3+} (in H_2SO_4) = 0.05M \right|$
 $\left| 0.1atm \right| 10^{-2}M \left| 0.01M \quad 0.1M \right|$

given that $E_{Cr_2O_7^{2-}/Cr^{3+}}^0 = 1.33 \text{ V}$

$$E^0 Cl^- | Cl_2 = -1.36 \text{ V}$$



$$E_{\text{cell}}^0 = 1.33 - (+1.36) = -0.03$$

$$E_{\text{cell}} = -0.03 - \frac{0.059}{6} \log \frac{[Cr^{3+}]^2 [P_{Cl_2}]^3}{[H^+]^{14} [Cl^-]^6 [Cr_2O_7^{2-}]} = -0.03 - \frac{0.059 \times 23}{6}$$

$$E_{\text{cell}} = -0.26 \text{ V}$$

Ex. The E_{cell}^0 for the reaction $Fe + Zn^{2+} \rightleftharpoons Zn + Fe^{2+}$, is -0.32 volt at 25°C . What will be the equilibrium concentration of Fe^{2+} , when a piece of iron is placed in a $1 \text{ M } Zn^{2+}$ solution ?

Sol. We have the Nernst equation at equilibrium at 25°C

$$E^0 = \frac{0.0591}{n} \log K \quad \dots \text{(i)}$$

Since E_{cell}^0 for the given reaction is negative, therefore, the reverse reaction is feasible for which E_{cell}^0 will be $+0.32 \text{ V}$, Thus for $Zn + Fe^{2+} \rightleftharpoons Fe + Zn^{2+}$; $E_{\text{cell}}^0 + 0.32 \text{ V}$

$$\text{Now, } E^0 = \frac{0.0591}{n} \log \frac{[Zn^{2+}]}{[Fe^{2+}]} \text{ or } 0.32 = \frac{0.0591}{2} \log \frac{1}{[Fe^{2+}]}$$

$$\log [Fe^{2+}] = -10.829 \quad \text{Taking antilog,}$$

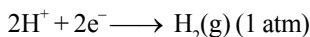
$$[Fe^{2+}] = 1.483 \times 10^{-11} \text{ M}$$

REFERENCE ELECTRODE

An electrode used to calculate the electrode potential of other electrodes.

(a) Standard Hydrogen Electrode (SHE) :

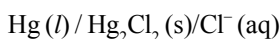
It consist of a platinum electrode over which H_2 gas (1 atm pressure) is bubbled and the electrode is immersed in a solution that is 1 M in H^+ at 25°C .



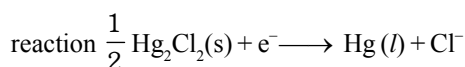
(1M)

the potential of this electrode at 25°C is taken as Zero volt.

(b) Calomel Electrode :



It is prepared by a Pt wire in contact with a paste of Hg and Hg_2Cl_2 present in a KCl solution.



$$E = E^0 - 0.0591 \log [Cl^-].$$

HEAT OF REACTION INSIDE THE CELL

Let n Faraday charge flows out of a cell of e.m.f. E , then

$$-\Delta G = nFE \quad \text{.....(i)}$$

Gibbs Helmholtz equation (from thermodynamics) may be given as,

$$\Delta G = \Delta H + T \left[\frac{\partial \Delta G}{\partial T} \right]_p \quad \text{.....(ii)}$$

From Eqs. (i) and (ii), we have

$$-nFE = \Delta H + T \left[\frac{\partial(-nFE)}{\partial T} \right]_p = \Delta H - nFT \left[\frac{\partial E}{\partial T} \right]_p$$

$$\therefore \Delta H = -nFE + nFT \left[\frac{\partial E}{\partial T} \right]_p$$

ENTROPY CHANGE INSIDE THE CELL

We know that $G = H - TS$ or $\Delta G = \Delta H - T\Delta S$...**(i)**

where ΔG = Free energy change, ΔH = Enthalpy change and ΔS = entropy change.

According to Gibbs Helmholtz equation,

$$\Delta G = \Delta H + T \left[\frac{\partial \Delta G}{\partial T} \right]_p \quad \text{.....(ii)}$$

From Eqs. (i) and (ii), we have

$$-T\Delta S = T \left[\frac{\partial \Delta G}{\partial T} \right]_p \quad \text{or} \quad \Delta S = - \left[\frac{\partial \Delta G}{\partial T} \right]_p$$

$$\text{or} \quad \Delta S = nF \left[\frac{\partial E}{\partial T} \right]_p$$

where $\left[\frac{\partial E}{\partial T} \right]_p$ is called temperature coefficient of e.m.f. of the cell.

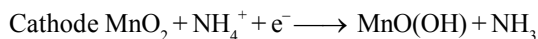
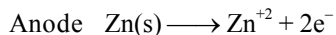
SOME COMMERCIAL BATTERIES

Any battery or cell that we use as a source of electrical energy is basically an electrochemical cell where oxidising and reducing agents are made to react by using a suitable device. In principle, any redox reaction can be used as the basis of an electrochemical cell, but there are limitations to the use of most reactions as the basis of practical batteries. A battery should be reasonably light and compact and its voltage should not vary appreciably during the use.

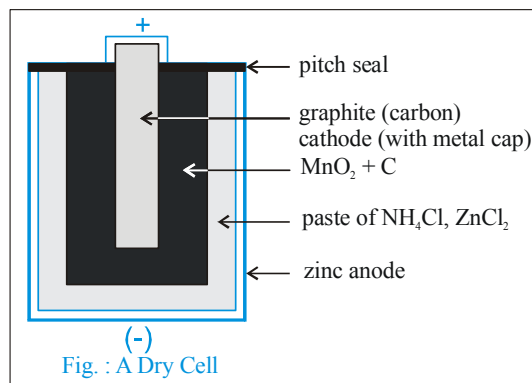
There are mainly two types of cells : **(i)** primary cells and **(ii)** secondary cells. In primary cells, the reaction occurs only once and the battery then becomes dead over a period of time and cannot be used again. (For example, dry cell, mercury cell.) Contrary to this, secondary cells can be recharged by passing a current through them so that they can be used again and again. (For example, lead storage battery, nickel-cadmium storage cell.)

PRIMARY CELLS

The most familiar type of battery is the dry cell which is a compact of Leclanche cell known after its discover 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.



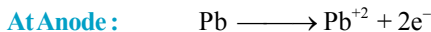
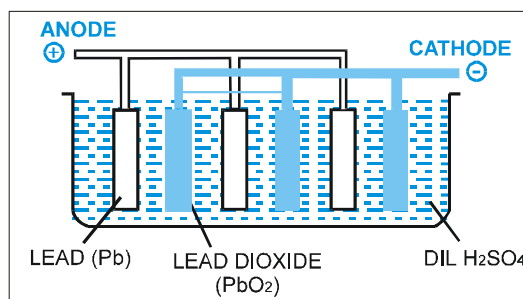
In the cathode reaction, manganese is reduced from the +4 oxidation state to the +3 state. Ammonia is not liberated as a gas but combines with Zn^{2+} to form $Zn(NH_3)_4^{2+}$ ion.



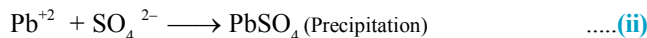
SECONDARY CELLS

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 g 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.

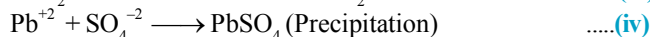
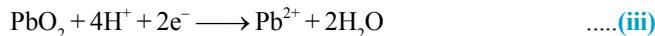


Pb^{+2} ions combine with sulphate ions of solution to form insoluble lead sulphate $PbSO_4$, when begins to coat lead electrode

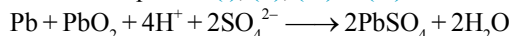


The electrons given by Pb are used at cathode (PbO_2 electrode)

At Cathode:



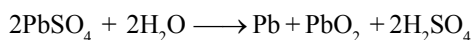
Over all cell reaction \rightarrow add equation (i), (ii), (iii) & (iv)



$$E_{\text{cell}} \text{ is } 2.041 \text{ volt}$$

(A 12 V lead storage battery is generally used which consist of 6 cells each producing 2 volt)

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 electrodes reactions are reverse of those that occur during discharge :



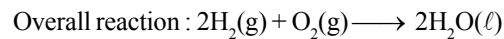
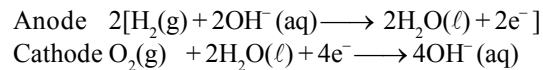
It is clear that H_2SO_4 is used up during the discharge & produced during recharging reaction of cell.

Another secondary cell is the nickel-cadmium storage cell which has a longer life than the lead storage cell but it is more expensive to manufacture.

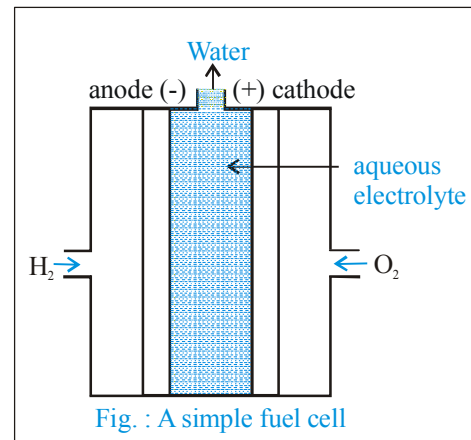
FUEL CELLS

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 Apollo space programme. The water vapour produced was condensed and added to the drinking water supply for the astronauts.

In the cell (fig.) 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 :



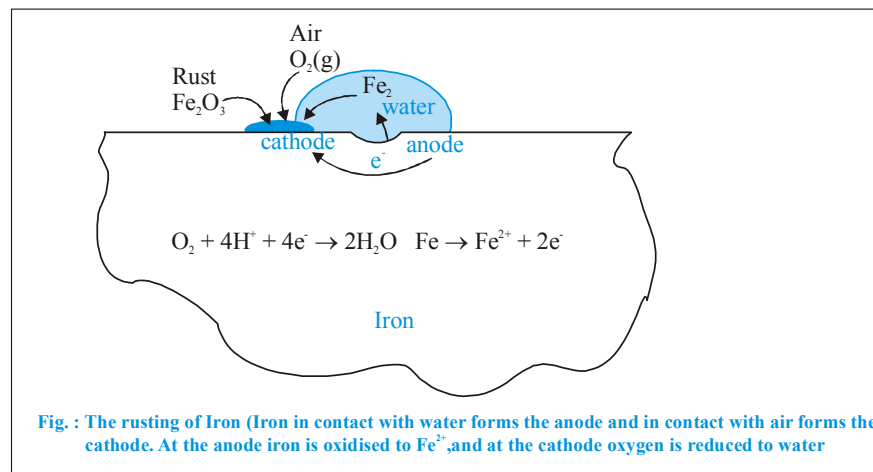
This cell runs continuously as long as the reactants are supplied.



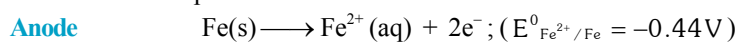
CORROSION

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.

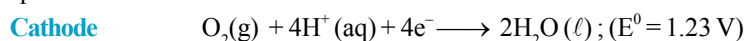
In corrosion, a metal is oxidised by loss of electrons to oxygen and forms metal oxide. Corrosion of iron (which is commonly known as rusting) occurs in presence of water and oxygen (air).



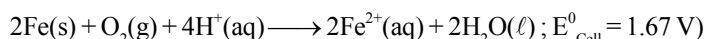
Although the chemistry of corrosion is complex but it is understood that at one spot of an iron object oxidation occurs and that spot behaves as an anode.



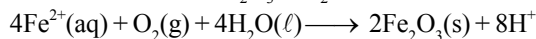
Electrons released at anode move through the metal and go to another spot on the metal and reduce the oxygen in presence of H^+ ions (which is believed to be available from H_2CO_3 formed due to dissolution of CO_2 in water). This spot works as a cathode :



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 :



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 $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$.

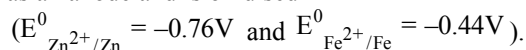


H^+ ions produced in the above reaction help further in rusting.

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

PREVENTION FROM CORROSION

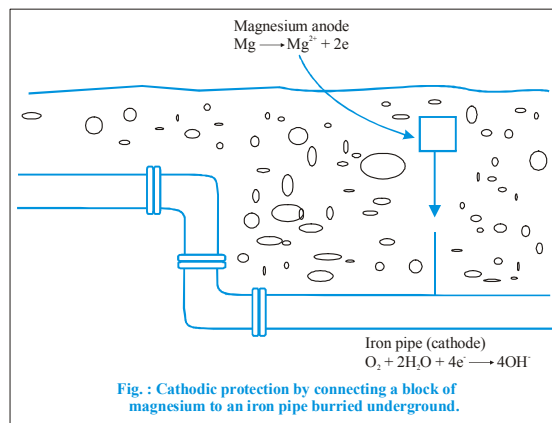
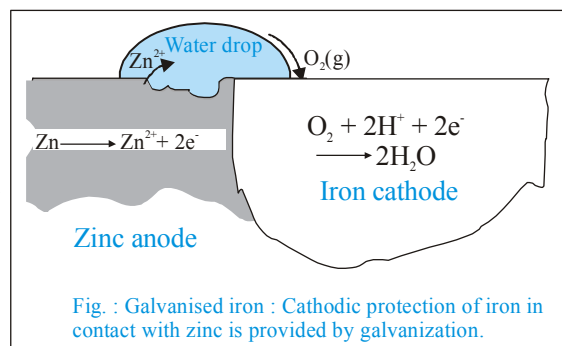
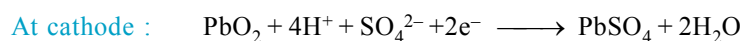
Corrosion of a metal is prevented by applying protective coating (such as grease, paint or metal coatings) on its (metals) surface. In case of iron this coating is done in two ways : (i) electrolysis (Cr, Ni and Cd coating) (ii) dipping iron objects in a molten metal (Zn and Sn coating). Use of zinc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



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 ($E_{\text{Sn}^{2+}/\text{Sn}}^0 = -0.14\text{V}$). 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 ($E_{\text{Cu}^{2+}/\text{Cu}}^0 = 0.34\text{V}$). Instead of coating more reactive metals 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 buried beside the iron pipe or tank and connected to it by wires.

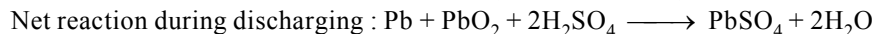
Here iron becomes **cathode** and more reactive metal becomes **anode**. The reactive metal anode is sacrificed to protect the iron. Since these reactive metal plates are oxidised quickly, they are replaced from time to time which is easy to do.

Ex. During the discharge of a lead storage battery the density of H_2SO_4 falls from ρ_1 g/cc to ρ_2 g/C, H_2SO_4 of density of ρ_1 g/C. C is X% by weight and that of density of ρ_2 g/c.c is Y% by weight. The battery holds V litre of acid before discharging. Calculate the total charge released at anode of the battery. The reactions occurring during discharging are.



Sol. Mass of acid solution before discharge of lead storage battery (LSB) = $(V \times 10^3 \times \rho_1) \text{ g}$
 $= (1000 \times V \rho_1) \text{ g}$

$$\text{Mass of H}_2\text{SO}_4 \text{ before discharge of LSB} = \left(1000 \times V \rho_1 \times \frac{X}{100} \right) \text{ g} = (10 \times V \rho_1 X) \text{ g}$$



From the reaction, it is evident that the moles of electron exchanged (lost at anode and gain at cathode) is equal to the moles of H_2SO_4 consumed or moles of H_2O produced. Let the moles of H_2SO_4 produced be x , then

$$\text{Mass of H}_2\text{O produced during discharge of LSB} = (18x) \text{ g}$$

$$\text{Mass of H}_2\text{SO}_4 \text{ consumed during discharge of LSB} = (98x) \text{ g}$$

$$\therefore \text{Mass of H}_2\text{SO}_4 \text{ after discharge of LSB} = [(10 V \rho_1 X)] - 98x] \text{ g}$$

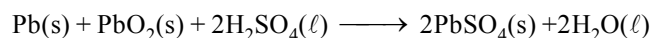
$$\text{Mass of acid solution after discharge of LSB} = [(1000 V \rho_1) - 98x + 18x] = [(1000 V \rho_1) - 80x] \text{ g}$$

$$\therefore \% \text{ of H}_2\text{SO}_4 \text{ after discharge of LSB} = \frac{\text{Mass of H}_2\text{SO}_4 \text{ after discharge}}{\text{Mass of acid solution after discharge}} \times 100$$

$$Y = \frac{[(1000 \times V \rho_1) - 98x]}{[(1000 \times V \rho_1) - 80x]} \times 100 \quad x \text{ can be calculated as all other quantities are known.}$$

$$\therefore \text{Total charge released at cathode, } Q = nF = xF.$$

Ex. A lead storage cell is discharged which causes the H_2SO_4 electrolyte to change from a concentration of 34.6% by weight (density 1.261 g ml^{-1} at 25°C) to one of 27% by weight. The original volume of electrolyte is one litre. Calculate the total charge released at anode of the battery. Note that the water is produced by the cell reaction as H_2SO_4 is used up. Over all reaction is.



Sol. Before the discharge of lead storage battery,

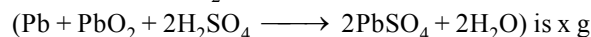
$$\text{Mass of solution} = 1000 \times 1.261 = 1261 \text{ g}$$

$$\text{Mass of H}_2\text{SO}_4 = \frac{1261 \times 34.6}{100} = 436.3 \text{ g.}$$

$$\text{Mass of water} = 1261 - 436.3 = 824.7 \text{ g}$$

After the discharge of lead storage battery,

Let the mass of H_2O produce as a result of net reaction during discharge



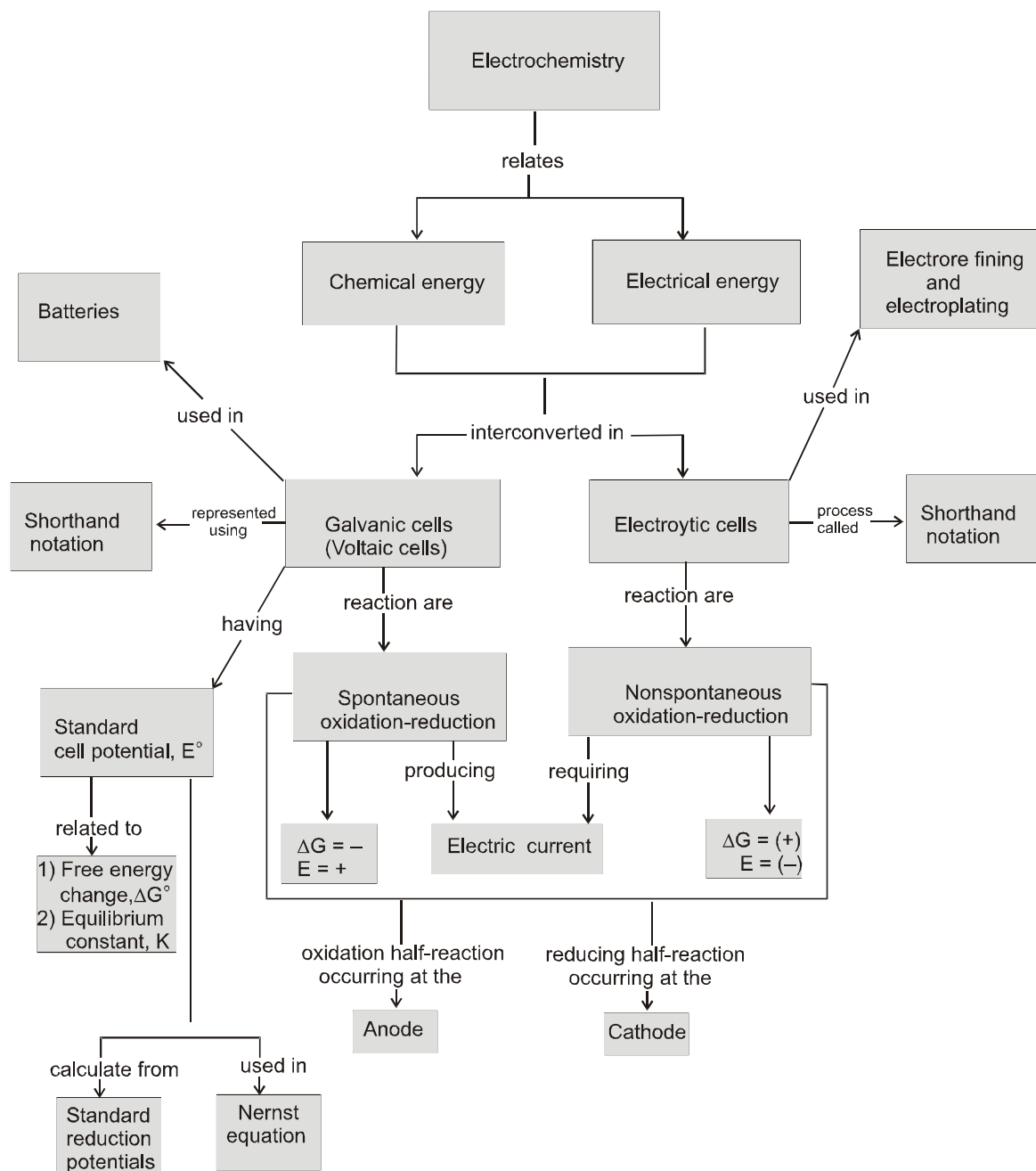
$$\therefore \text{Moles of H}_2\text{O produced} = \frac{x}{18} = \text{moles of H}_2\text{SO}_4 \text{ consumed}$$

$$\text{Mass of H}_2\text{SO}_4 \text{ consumed} = \frac{x}{18} \times 98$$

$$\text{Now, mass of solution after discharge} = 1261 - \frac{98x}{18} + x$$

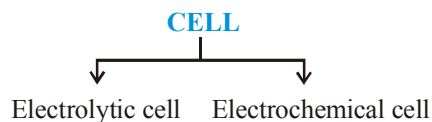
$$\% \text{ by the mass of H}_2\text{SO}_4 \text{ after discharge} = \frac{\text{Mass of H}_2\text{SO}_4 \text{ left}}{\text{Mass of solution after discharge}} \times 100 = 27$$

$$= \frac{436.3 - \frac{98x}{18}}{1261 - \frac{98x}{18} + x} \times 100 = 27 \quad \therefore x = 22.59 \text{ g}$$

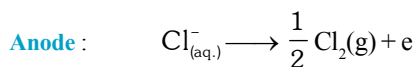
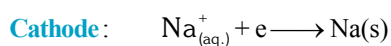
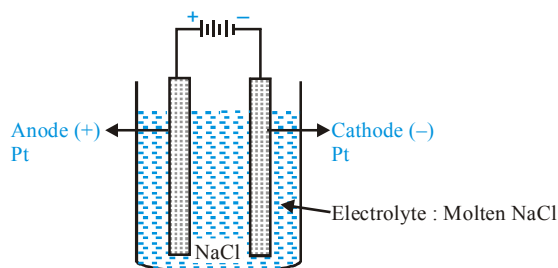


$$E = E^\circ - \frac{.0592}{n} \log \frac{(\text{Products})}{(\text{Reactants})} \Rightarrow E = E^\circ - \frac{.0592}{n} \log \frac{(\text{Anodic ion concentration})}{(\text{Cathodic ion concentration})}$$

Tips



- (1) Electrolytic cell : Converts electrical energy into chemical energy



- (2) **Deposition of material at any electrode follow faraday's law of electrolysis.**

Faraday's Ist Law :

$$w = Z it$$

$$w = \frac{M}{n - \text{factor} \times 96500} \times it$$

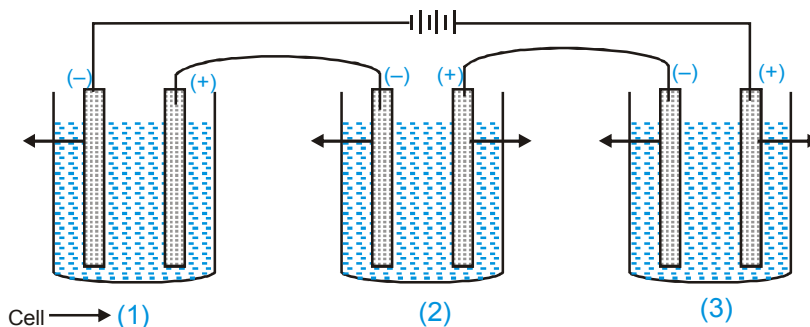
where w = mass deposit (gm)

M = molar mass

i = current (Amp.)

t = time (sec.)

Faraday's second law :



- (3) At any electrode for material deposited.

$$\frac{W_1}{E_1} = \frac{W_2}{E_2} = \frac{W_3}{E_3}$$

Note : Order of discharge potential.

CHEMISTRY FOR JEE MAIN & ADVANCED

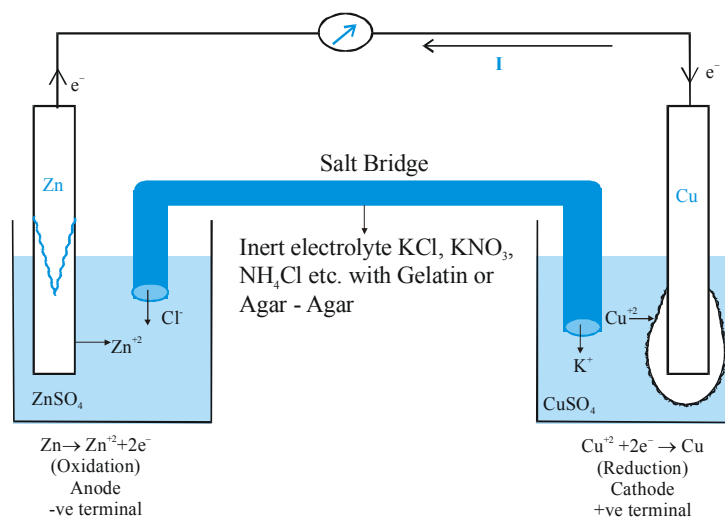
Cathode : $\text{Au}^{+3} > \text{Ag}^{+} > \text{Cu}^{+2} > \text{Zn}^{+2} > \text{H}_2\text{O} > \text{Al}^{+3} > \text{Mg}^{+2} > \text{Na}^{+} > \text{Li}^{+}$

Anode : $\text{SO}_4^{2-} < \text{NO}_3^{-} < \text{H}_2\text{O} < \text{Cl}^{-} < \text{Br}^{-} < \text{I}^{-}$

PRODUCTS OF ELECTROLYSIS OF SOME ELECTROLYTES

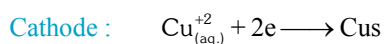
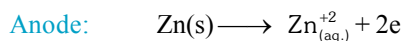
S.No.	Electrolyte	Electrode	Product obtained at anode	Product obtained at cathode
(i)	Aqueous NaCl	Pt or Graphite	Cl_2	H_2
(ii)	Fused NaCl	Pt or Graphite	Cl_2	Na
(iii)	Aqueous NaOH	Pt or Graphite	O_2	H_2
(iv)	Fused NaOH	Pt or Graphite	O_2	Na
(v)	Aqueous CuSO_4	Pt or Graphite	O_2	Cu
(vi)	Dilute HCl	Pt or Graphite	Cl_2	H_2
(vii)	Dilute H_2SO_4	Pt or Graphite	O_2	H_2
(viii)	Aqueous AgNO_3	Pt or Graphite	O_2	Ag

- (4) **Electrochemical Cell** : converts chemical energy into electrical energy.



- (5) $E^\circ_{\text{Cell}} = \text{SRP}_{\text{cathode}} - \text{SRP}_{\text{anode}}$
 $= \text{SRP}_{\text{cathode}} + \text{SOP}_{\text{at anode}}$

Half cell reaction :



- (6) **Cell reaction :** $\text{Zn}(\text{s}) + \text{Cu}_{(\text{aq.})}^{+2} \longrightarrow \text{Zn}_{(\text{aq.})}^{+2} + \text{Cu}(\text{s})$

$$Q = \frac{[\text{Zn}^{+2}]}{[\text{Cu}^{+2}]}; n = 2$$

- (7) **Nearest equation :** $E_{\text{Cell}} = E^\circ_{\text{Cell}} - \frac{0.059}{n} \log Q$ at 298 K

- (8) Max electrical work done = $nFE^\circ = -\Delta G^\circ$
 electrical work done = $nFE = -\Delta G$

Different type of electrodes/half cell

Type	Example	Half-cell reaction	Half-cell reaction
Metal - Metal ion	M/M ⁿ⁺	M ⁿ⁺ + n e ⁻ → M(s)	$E = E^{\circ} + \frac{0.0591}{n} \log[M^{n+}]$
Gas - ion	Pt / H ₂ (P atm) / H ⁺ (XM)	H ⁺ (aq) + e ⁻ → $\frac{1}{2}$ H ₂ (P atm)	$E = E^{\circ} - 0.0591 \log \frac{\sqrt{P_{H_2}}}{[H^+]}$
Oxidation - reduction	Pt / Fe ²⁺ , Fe ³⁺	Fe ³⁺ + e ⁻ → Fe ²⁺	$E = E^{\circ} - 0.0591 \log \frac{[Fe^{2+}]}{[Fe^{3+}]}$
Metal - insoluble salt Anion	Ag/AgCl, Cl ⁻	AgCl (s) + e ⁻ → Ag (s) + Cl ⁻	$E_{Cl^-/AgCl/Ag} = E_{Cl^-/AgCl/Ag}^{\circ} + 0.0591 \log [Cl^-]$
Calomel electrode	Cl ⁻ (aq)/Hg/Hg ₂ Cl ₂	Hg ₂ Cl ₂ (s) + 2e ⁻ → 2Hg(l) + 2Cl ⁻ (aq.)	$E = E^{\circ} - 0.0591 \log [Cl^-]$

(9) Gibb's Helmholtz equation :

$$\Delta G = \Delta H + T \left[\frac{\partial \Delta G}{\partial T} \right]$$

$$\Rightarrow \Delta H = -nFE + nFT \left[\frac{\partial \Delta G}{\partial T} \right]_P$$

CONDUCTION IN ELECTROLYTES

	Conductance	Specific Conductivity	Molar Conductivity
Symbol	C	k	Λ _m
Unit	Ω ⁻¹	Ω ⁻¹ cm ⁻¹	Ω ⁻¹ cm ² mol ⁻¹
Specific	Conductance of volume within electrode	Conductance of unit volume	Conductance of that volume which contain exactly one mole
Change with concentration	Decrease with in concentration	Decrease with in concentration	Increase with in concentration
Formula	$C = \frac{1}{R}$	k = C × cell constant	k = Λ _m = K × V V = Volume of solution contain 1 mole of electrolyte
Factors	(i) Nature of electrolyte (ii) Concentration of electrolyte (iii) Type of cell.	(i) Nature of electrolyte (ii) Concentration of electrolyte	(i) Nature of electrolyte (ii) Concentration of electrolyte

(10) KOHLRAUSEH'S LAW :

$$\Lambda_m^\infty(A_x B_y) = x\lambda_+^\infty + y\lambda_-^\infty$$

$$\Lambda_m^\infty(K_2SO_4) = 2\lambda_+^\infty + \lambda_-^\infty$$

$$\Lambda_m^\infty(Na_3PO_4) = 3\lambda_+^\infty + \lambda_-^\infty$$

$$\Lambda_m^\infty[Fe_2(SO_4)_3] = 2\lambda_+^\infty + 3\lambda_-^\infty$$

(11) **FORMULA**

$$(1) R = \rho \times \frac{\ell}{A}$$

$$(2) \lambda_m = k \times \frac{1000}{M}$$

$$(3) \lambda_{eq.} = k \times \frac{1000}{N}$$

$$(4) \text{ for strong electrolyte } \lambda_m = \lambda_{m_\infty} - b\sqrt{C}$$

