Chapter 03

Electro Chemistry

CONTENT

INTRODUCTION:

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

• CONDUCTOR AND NON-CONDUCTORS

➢ Substance which do not allow electric current to pass through them are called **Non-Conductors** or insulators.

Example: Pure water, Ice, Glass, Rubber etc.

➢ Substances which allow electric current to pass through them are called **Conductors.**

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

Conductors are of two types : -

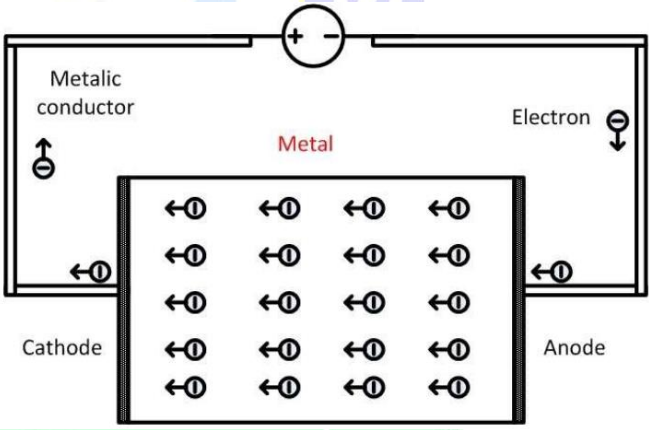
(i) Metallic conductors or Electronic conductors

(ii) Electrolytic conductors or ionic conductors

(i) METALLIC CONDUCTORS :-

➢ The conductors which conduct electric current by movement of electrons without undergoing any chemical change are known as metallic conductors.

Ex : Metals (Cu, Ag, Fe, Al etc), non-metals (graphite) and various alloys and minerals.



Conduction current flow through a metallic conductor.

(ii) ELECTROLYTIC CONDUCTORS :-

➢ Those substances which conduct the electric current through ions in aqueous solution or molten state are called electrolytic conductor.

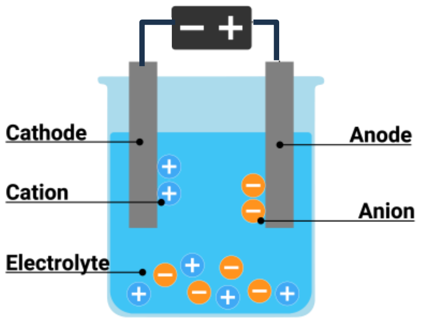
Ex : Strong acid, strong base, salt.

➢ **STRONG ELECTROLYTE :**Electrolytes which are completely ionized in aqueous solution or in their molten state; are called strong electrolyte.

Example : all salts, strong acids and strong bases

➢ **WEAK ELECTROLYTE :**Electrolytes which are not completely ionized in aqueous solution or in their molten state; are called weak electrolytes.

Examples : All carbonic acids (except sulphonic acid), CH_3COOH, HCN, NH_3, amine, etc.



Electrolytic Conduction

DIFFERENCE BETWEEN METALLIC AND ELECTROLYTIC CONDUCTOR

	Metallic conduction	**Electrolytic conduction**
(i)	Charge carrier are free electrons.	Charge carrier 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 at the electrodes
(iv)	Resistance is due to vibrations 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.

ELECTROCHEMICAL CELL :

A device which convert electrical energy to chemical energy and vice versa.

Electrochemical cell

Galvanic or Voltaic cell
- A spontaneous chemical reaction generates an electric current.

Electrolytic cell.
- An electric current drives a non spontaneous reaction.

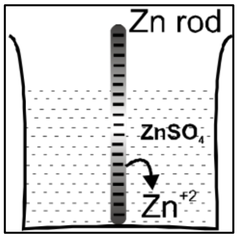
GALVANIC CELL: WORKING PRINCIPLE

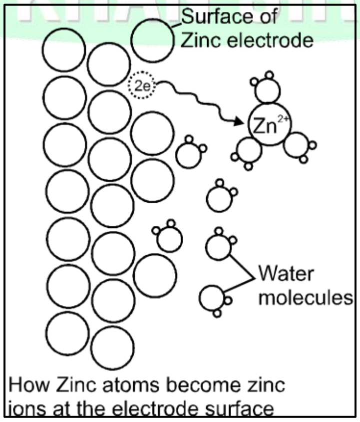
Whenever a metal strip is put in its electrolytic salt solution then a potential difference created between the metal and the liquid phase (Electrolytic salt).

ANODE:

➢ Some metals (which are reactive) are found to have tendency to go into the solution phase when these are placed in contact with their ions or their salt solutions.

For Example: Zn rod is placed in $ZnSO_4$ solution.





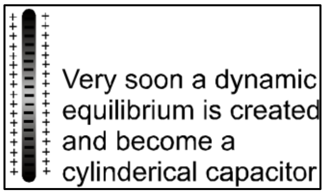


Figure : 1 **Figure : 2** **Figure : 3**

- The Zn atom or metal atoms will move in the solution to form Zn^{+2}. After some time following equilibrium will be established.

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

- There will be accumulation of sufficient negative charge on the rod which will not allow extra zinc ions to move in the solution. i.e. solution will be saturated with Zn^{+2} ions.
- The extra positive charge of the solution will be more concentrated around the negatively charged rod.
- An electrical double layer is developed in the system and hence a potential is created between the rod and the solution which is known as electrode potential.

  *Oxidation takes place at anode.

CATHODE :

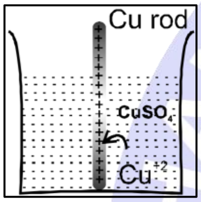


Figure : 1

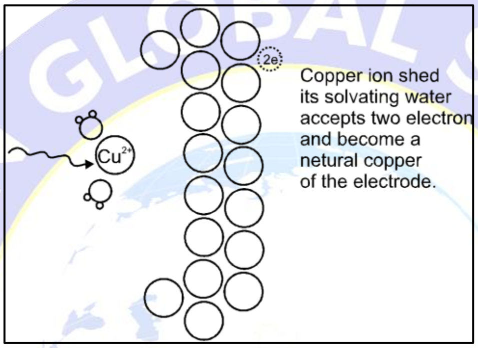


Figure : 2

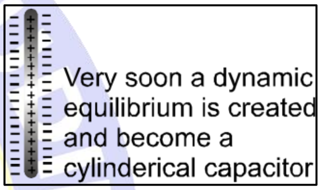


Figure : 3

- Some metals (Cu, Ag, Au etc.,) are found to have the opposite tendency i.e. when placed in contact with their aqueous ions, the ions from the solution will get deposited on the metal rod.
- The following equilibrium will be established :

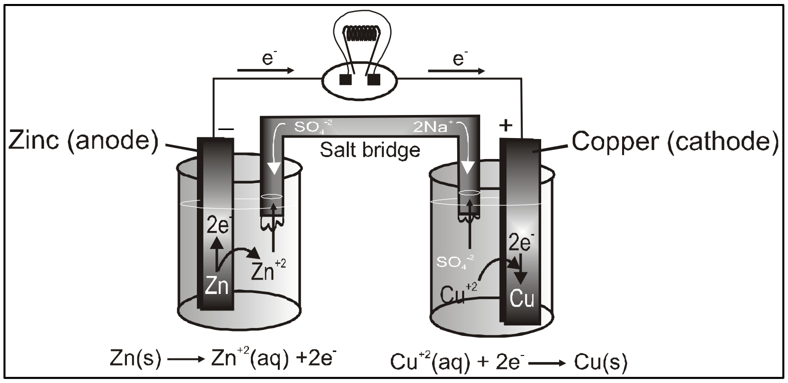
  $$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$$

- So rod will have deficiency of electron (become positive charge).
- Extra negative charge will surround this positively charged rod and form double layer.
- An electrical double layer is developed in the system and hence a potential is created between the rod and the solution which is known as electrode potential.

  * Reduction takes place at cathode.

CONSTRUCTION OF 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 a **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- Shaped 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.

  Example: KCl, KNO_3, NH_4NO_3
- If Ag^+, Hg_2^{+2}, Pb^{+2}, $T\ell^+$ 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 $T\ell C\ell$.

  Functions :
  - It connects the solution of two half-cell 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 brought in contact with each other.

CELL REPRESENTATION :

We require two half cells to produce an electrochemical 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. (II).
- The significant features of the substance like pressure of a gas, concentration of ions etc. are indicated in brackets immediately after writing the substance.

  $Zn(s)\ |\ ZnSO_4(aq)\ ||\ CuSO_4(aq)\ |\ Cu(s)$

• 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 1M 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 $M(s) \rightarrow M^{+n}(aq) + ne^-$
- 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 $M^{+n}(aq) + ne^- \rightarrow M(s)$
- Tendency to get reduced.
- **Greater the R.P. greater will be the tendency to get reduced.**
- Electrode potential depends upon:
  (i) Concentration of the solution (ii) Nature of the metal (iii) Pressure & 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.
- There are two types of reference electrodes.

(a) PRIMARY REFERENCE ELECTRODES :

Standard hydrogen electrode (SHE)

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

When acts as anode

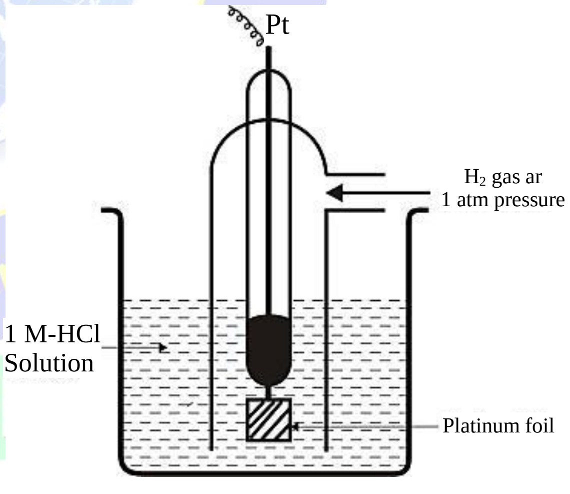
$$H_2(g) \rightleftharpoons 2H^+ + 2e^-$$

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

When acts as cathode

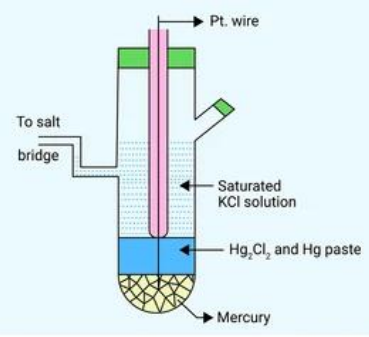
$$2H^+ + 2e^- \rightleftharpoons H_2(g)$$

$$E^o_{H^+/H_2(g)} = SRP$$



Standard Hydrogen Electrode

- For SHE electrode potential is taken to be zero at all temperature.
  SOP = –SRP = 0 for SHE.
- To calculate standard potential of any other electrode a cell is coupled with **Standard Hydrogen Electrode (SHE)** and it's potential is measured that gives the value of electrode potential of that electrode.



Calomel Electrode

(b) SECONDARY REFERENCE ELECTRODE:

(i) CALOMEL ELECTRODE (Hg_2Cl_2):

Representation:

$Pt|Hg\text{-}Hg_2Cl_2|KCl(aq)$

When acts as cathode

$Hg_2^{2+} + 2e^- \rightarrow 2Hg$

$Hg_2Cl_2 \rightarrow Hg_2^{2+} + 2Cl^-$

Overall reaction:

$Hg_2Cl_2 + 2e^- \rightarrow 2Hg(l) + 2Cl^-$ (Reduction reaction)

When acts as anode

$2Hg(l) \rightarrow Hg_2^{2+} + 2e^-$

$Hg_2^{2+} + 2Cl^- \rightarrow Hg_2Cl_2$

Overall reaction:

$2Hg + 2Cl^- \rightarrow Hg_2Cl_2 + 2e^-$ (Oxidation reaction)

(ii) SILVER-SILVER CHLORIDE ELECTRODE :

Representation : $Pt \mid Ag\text{-}AgCl_{(s)} \mid KCl_{(aq)}$

When acts as cathode $AgCl_{(s)} + e^- \rightarrow Ag_{(s)} + Cl^-_{(aq)}$

When acts as anode $Ag_{(s)} + Cl^-_{(aq)} \rightarrow AgCl_{(s)} + e^-$

CELL POTENTIAL ($E°_{cell}$) :

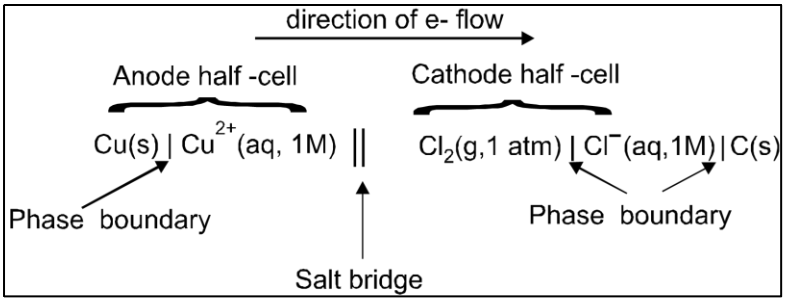
$E°_{cell}$ = SRP of cathode – SRP of anode

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

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

Shorthand Notation for Galvanic Cell

- We require two half cells to produce an electrochemical 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 viz. pressure of a gas, concentration of ions etc. are indicated in brackets immediately after writing the substance.
- For a gas electrode, the gas is indicated after the electrode for anode and before the electrode in case of cathode. (i.e Pt H_2 / H^+ or H^+ /H_2 Pt)



Example: 1 What does a negative E.M.F. for a cell indicate?

(1) Electrons flow through the external circuit in the reverse direction

(2) The opposite half-cell reactions take place spontaneously

(3) The reactions as written are not spontaneous

(4) All of the above

Answer. **(4)**

- **ELECTROCHEMICAL SERIES :**

Arrangement of different elements in increasing order of SRP 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	$Mg^{+2} + 2e^- \rightarrow Mg(s)$	– 2.37 V
Al	$Al^{3+} + 3e^- \rightarrow Al$	– 1.66 V
Mn	$Mn^{+2} + 2e^- \rightarrow Mn$	– 1.18 V
H_2O	$H_2O(l) + e^- \rightarrow ½H_2 + OH^-$	– 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	$Ni^{+2} + 2e^- \rightarrow Ni(s)$	– 0.24 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	$Br_2 + 2e^{-} \rightarrow 2Br^{-}$	1.06 V
Pt	$Pt^{+2} + 2e^{-} \rightarrow Pt$	1.20 V
O_2	$\frac{1}{2}O_2 + 2H^{+} + 2e^{-} \rightarrow H_2O(l)$	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

APPLICATIONS OF ELECTROCHEMICAL SERIES

(i) OXIDISING AND REDUCING POWER :-

Oxidising power $\propto$ SRP $\propto \frac{1}{\text{SOP}}$ Reducing power $\propto$ SOP $\propto \frac{1}{\text{SRP}}$

(ii) REACTIVITY OF METALS :-

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

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

(iii) REACTIVITY OF NON-METAL :-

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

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

(iv) DISPLACEMENT REACTIONS IN SOLUTION :-

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

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

(vi) TO CALCULATE STANDARD EMF OF CELL $\left(E^{o}_{Cell}\right)$:-

$\left(E^{o}_{Cell}\right)$ = SRP of cathode – SRP of anode = SRP of cathode + SOP of anode = SOP of anode – SOP of cathode

Example: 2 The calomel electrode is reversible with respect to

(1) Mercury (2) H^+ (3) Hg^{2+} (4) Cl^-

Solution: (4)

Since half cell reaction

$$Hg_2Cl_2(aq.) + 2e \rightleftharpoons 2Hg(\ell) + 2Cl^-$$

Example: 3 A galvanic cell is composed of two hydrogen electrodes, one of which is a standard one. in which of the following solutions should the other electrode be immersed to get maximum EMF.

(1) 0.01 M HCl (2) 0.1 M CH_3COOH (3) 0.1 M H_3PO_4 (4) 0.1 M H_2SO_4

Solution: (4)

H_2SO_4 will furnish maximum H^+

Example: 4 E° for the reaction Fe + Zn^{2+} = Zn + Fe^{2+} is – 0.35 V. The given cell reaction is

(1) Feasible (2) Not feasible (3) In equilibrium (4) None

Solution: (2)

Since EMF of the cell is negative i.e., Gibbs free energy change will be positive so cell reaction will not be feasible

Example: 5 Consider the following relations for emf of a electrochemical cell :

(a) emf of cell =(Oxidation potential of anode) – (Reduction potential of cathode)

(b) emf of cell = (Oxidation potential of anode) + (Reduction potential of cathode)

(c) emf of cell = (Reductional potential of anode) + (Reduction potential of cathode)

(d) emf of cell = (Oxidation potential of anode) – (Oxidation potential of cathode)

Which of the above relations are correct :

Options :

(1) (a) and (b) (2) (c) and (d) (3) (b) and (d) (4) (c) and (a)

Sol: **(3)**

Fact

Example: 6 E value for the cell reaction

Cu | Cu^{2+} (0.001 M) || Cu^{2+}(0.1 M) | Cu is :-

(1) $-\frac{RT}{2F}\ln(0.01)$ (2) $-\frac{RT}{2F}\ln(0.1)$ (3) $+\frac{RT}{F}\ln(0.01)$

(4) $\frac{RT}{F}\ln(0.1)$

Sol: (1)

$$E_{cell} = E^0_{cell} - \frac{RT}{nF}\ln\frac{0.001}{0.1}$$

$$E_{cell} = -\frac{RT}{2F}\ln(0.01)$$

NERNST EQUATION

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

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

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

Where ΔG and $\Delta G°$ free energy change and standard free energy change; ‘Q’ is reaction quotient.

$\therefore -\Delta G = nFE$ and $-\Delta G° = nFE°$

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

$$E = E° - \frac{2.303RT}{nF}\log Q$$

Where $E°$ = standard electrode potential, R = gas constant,

T = temperature (in K), F = Faraday (96500 coulomb mol^{-1}),

n = number of e^- gained or lost in balanced equation.

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

$$\boxed{E = E° - \frac{0.0591}{n}\log\frac{[P]}{[R]}}$$

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

$$aA + bB \longrightarrow cC + dD$$

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

APPLICATIONS OF NERNST EQUATION

(i) CALCULATION OF ELECTRODE POTENTIAL (E_{RP} or E_{OP}) :-

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

$\boxed{E_{RP} = E^o_{RP} - \frac{0.0591}{n}\log\frac{1}{[M^{+n}]}}$ If $[M^{+n}]$ increases, then E_{RP} increases.

(ii) CALCULATION OF ELECTRODE POTENTIAL AND pH OF HYDROGEN ELECTRODE :-

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

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

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

$E_{RP} = 0.0591 \log [H^+]$ $\boxed{E_{RP} = -0.0591\,pH}$ $\boxed{E_{OP} = +0.0591\,pH}$

(iii) CALCULATION OF EMF OF CELL (E_{cell}) :-

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

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

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

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

(iv) PREDICTION AND FEASIBILITY OF A CELL REACTION:-

For a feasible cell reaction

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

$E_{cell} = +ve$

Example: 7 The metal that cannot be produced on reduction of its oxide by aluminium is

(1) K (2) Mn (3) Cr (4) Fe

Solution: **(1)**

$E°_{OP}$ of K > $E°_{OP}$ of Al.

Example: 8 $Zn|Zn^{2+}(C_1)||Zn^{2+}(C_2)|$ Zn. For this cell ΔG is negative if

(1) $C_1 = C_2$ (2) $C_1 > C_2$ (3) $C_2 > C_1$ (4) None

Solution: **(3)**

$$E = E° - \frac{0.0591}{2}\log\left(\frac{C_1}{C_2}\right) = \frac{0.0591}{2}\log\frac{C_2}{C_1}$$

To make $\Delta G = -\Delta ve$

E = + ve

Hence $C_2 > C_1$

Example: 9 Determine potential for the cell $Pt\left|Fe^{+2}, Fe^{+3}\right|\left|Cr_2O_7^{-2}, Cr^{+3}, \right|H^+\ Pt$ in which $[Fe^{+2}]$ and $[Fe^{+3}]$ are 0.5 M and 0.75 M respectively and $[Cr_2O_7^{-2}]$, $[Cr^{+3}]$ and $[H^+]$ are 2 M , 4 M and 1 M respectively.

Given : $Fe^{+3} + e^- \longrightarrow Fe^{+2}$ $E° = 0.770$ V

and $14H^+ + 6e^- + Cr_2O_7^{-2} \longrightarrow 2Cr^{+3} + 7H_2O$ $E° = 1.35$ V

(1) 0.60 V (2) 0.62 V (3) 0.56 V (4) 0.50 V

Solution: $\because$ $E°_{OPFe^{+2}/Fe^{+3}} > E_{Cr^{+3}/Cr_2^{+6}}$

$\therefore$ Redox change will be

Anode : $Fe^{+2} \rightarrow Fe^{+3} + e$

Cathode : $14H^+ + 6e + Cr_2O_7^{-2} \longrightarrow 2Cr^{+3} + 7H_2O$

$$E°_{cell} = E°_{OPFe^{+2}/Fe^{+3}} - E_{Cr^{+3}/Cr_2^{+6}} = 0.58$$

$$E°_{cell} = E°_{cell} - \frac{0.059}{6}\log\frac{(0.75)^6(4)^2}{(2)(1)^{14}(0.5)^6} = 0.58 - \frac{0.059}{6}\log\frac{(0.75)^6(4)^2}{(2)(1)^{14}(0.5)^6} = 0.58 - \frac{0.059}{6}\log(91.125)$$

$= 0.58 - 0.0192 = 0.56$ V

Example: 10 On the basis of the following E° values, the strongest oxidizing agent is :-

$[Fe(CN)_6]^{4-} \rightarrow [Fe(CN)_6]^{3-} + e^{-1}, E° = -0.35V$

$Fe^{2+} \rightarrow Fe^{3+} + e^{-1}$; $E° = -0.77V$

(1) Fe^{3+} (2) $[Fe(CN)_6]^{3-}$ (3) $[Fe(CN)_6]^{4-}$ (4) Fe^{2+}

Solution: **(1)**

Strongest oxidizing agent = oxidizing potential should be least.

The oxidizing Potential of Fe^{+2} is less than that of $[Fe(CN)_6]^{4-}$, Fe^{+2} is stronger oxidizing agent than $[Fe(CN)_6]^{4-}$. The stronger oxidizing agent should easily reduce itself, Fe^{+3} is easily reduced than Fe^{+2}, Fe^{+3} is the stronger oxidizing agent.

Example: 11 Given :

(i) $Cu^{2+} + 2e^- \rightarrow Cu$, $E° = 0.337$ V

(ii) $Cu^{2+} + e^- \rightarrow Cu^+$, $E° = 0.153$ V

Electrode potential, E° for the reaction,

$Cu^+ + e^- \rightarrow Cu$, will be :-

(1) 0.38 V (2) 0.52 V (3) 0.90 V (4) 0.30V

Solution: **(2)**

$\Delta G° = -nFE°$

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

$\Delta G° = 2 \times F \times 0.337$ ————(I)

For the reaction $Cu^+ \rightarrow Cu^{2+} + e^-$

$\Delta G° = 1 \times F \times 0.153$ ————(II)

So adding both the equations we get –

$Cu^+ + e^- \longrightarrow Cu \qquad \Delta G° = -0.521\ F$

$\Delta G° = -\ nFE°$

$\Delta E° = 0.52\ V$

(v) CALCULATION OF EQUILIBRIUM CONSTANT (K_{eq}) and ΔG° :-

From Nernst equation -$E_{cell} = E°_{cell} - \dfrac{0.0591}{n}\log\dfrac{[P]}{[R]}$

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

$$\boxed{E^o_{cell} = \frac{0.0591}{n}\log K_{eq}} \qquad E^o_{cell} = \frac{2.303RT}{nF}\log K_{eq}$$

$$nFE°_{cell} = 2.303\ RT\ \log K_{eq} \qquad \boxed{\Delta G° = -2.303RT\log K_{eq}}$$

SPOT LIGHT

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

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

  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

    $W_{max} = -\Delta G$

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

SOME SPECIAL CELLS

(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 $\mathbf{E^\circ_{cell} = 0}$.

eg. Pt, $H_2(g)$ (P_1atm) | $H^+(C_1)$ || $H^+(C_2)$ | $H_2(g)$ (P_2atm), Pt

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

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

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

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

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

Case 1 : f $P_1 = P_2 = 1$ atm $E_{cell} = -\dfrac{0.0591}{2}\log\left[\dfrac{C_1}{C_2}\right]^2$

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

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

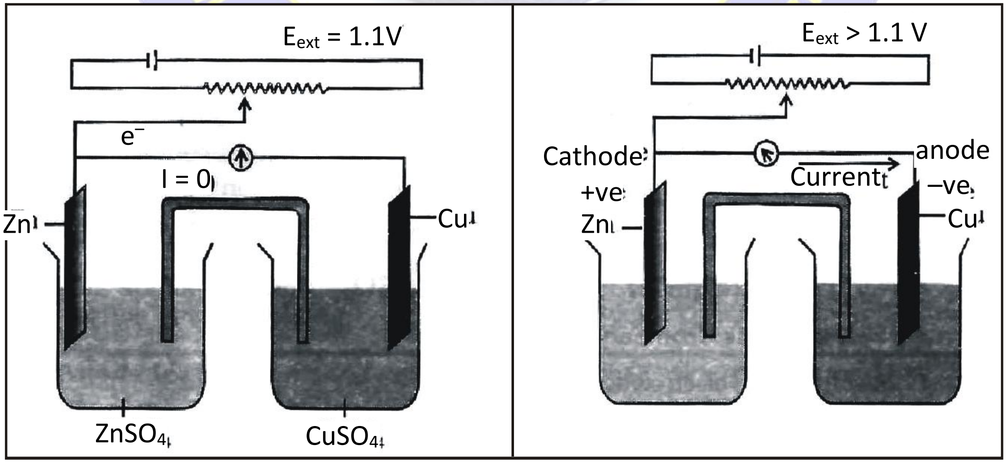
Case 2 : If $C_1 = C_2 E_{cell} = -\dfrac{0.0591}{2}\log\left[\dfrac{P_2}{P_1}\right]$

$P_1 \neq P_2$

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

(B) REVERSIBLE CELLS :

- Those cell's in which chemical reactions are reversed by applying external emf in opposite directions are 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 reversed
  (ii) When $E_{ext} = 1.1$ V (emf of Daniel cell); equilibrium will be established.
  In general secondary cells are reversible in nature.



When $E_{ext} = 1.1$ V
(i) No flow of electron or current
(ii) No chemical reaction

When $E_{ext} = 1.1$ V
(i) Electron flow from Cu to Zn and current flow from Zn to Cu.
(ii) Zinc is deposited at the zinc electrode and Cu is oxidised at Cu electrode.

◆◆◆

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 flowing(I).

$\boxed{R = \frac{V}{I}}$ R is expressed in **ohms (Ω)**.

(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)

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

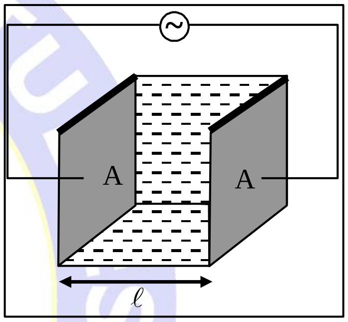
$$R = \rho.\frac{\ell}{A}; \qquad \rho = R.\frac{A}{\ell}$$

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

$\because V = A \times \ell = 1\ cm^3$

Resistance offered by 1cm^3 electrolytic solution is known as resistivity.

$\boxed{\text{Unit of } \rho : \text{ohm cm}}$



(d) **SPECIFIC CONDUCTANCE / CONDUCTIVITY (κ) :-** It is defined as the reciprocal of specific resistance, $\kappa = \frac{1}{\rho}$

$R = \rho\frac{\ell}{A}$ $\qquad \frac{1}{\rho} = \frac{1}{R}.\frac{\ell}{A}$ $\qquad \boxed{\kappa = G \times G^*}$ $\qquad$ **Cell constant :** $G^* = \frac{\ell}{A}$; Its unit is cm^{-1}

Specific conductance = Conductance × Cell constant

Hence specific conductivity of a solution is defined as the conductance offered by 1 cm^3 of electrolytic solution.

(e) **MOLAR CONDUCTANCE :- (Λ_m or λ_m** or μ**):** 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 mole of electrolyte.

If concentration of solution is M (mol/L) then

$$\Lambda_m = \frac{\kappa \times 1000}{M} \quad \boxed{\text{Unit}: \text{ohm}^{-1}\ \text{cm}^2\ \text{mol}^{-1}}$$

(f) 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.

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

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

If concentration of solution is N (gm eq/L) then

$$\Lambda_{eq} = \frac{\kappa \times 1000}{N} \qquad \boxed{\text{Unit : ohm}^{-1}\ \text{cm}^2\ \text{eq}^{-1}}$$

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 Normality = Valency Factor × Molarity. So $\boxed{\Lambda_{eq} = \frac{\Lambda_m}{\text{V.F.}}}$

• FACTORS AFFECTING ELECTROLYTIC CONDUCTANCE :

(a) INTER IONIC ATTRACTION : If inter ionic attraction between ions of solute is more, then the conductivity will be less.

(b) POLARITY OF SOLVENT : If the solvent has high dielectric constant then the ionization and conductivity will be more

(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, all type of attraction forces decreases and the viscosity of medium also decreases.

(e) DILUTION :

(i) On increasing dilution conductance (G) increases

- ➢ For strong electrolyte with dilution inter ionic force of attraction decreases therefore conductance increases.
- ➢ For weak electrolyte with dilution degree of dissociation (α) increases therefore conductance increases.

(ii) Effect of dilution on specific conductance :-

With dilution specific conductance decreases because with increase dilution number of ions in 1cm^3 solution decreases.

(iii) Effect of dilution on equivalent and molar conductance :-

The equivalent/molar conductance increases with dilution because normality or molarity decreases.

DETERMINATION OF MOLAR CONDUCTANCE OF ELECTROLYTES AT INFINITE DILUTION :

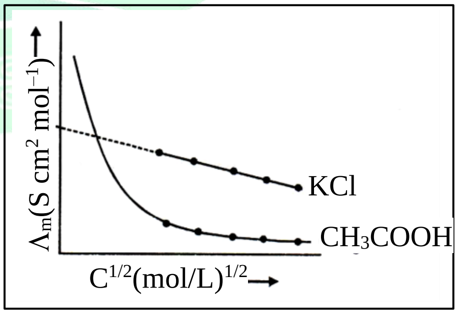
Debye Huckel Onsager equation :

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

where Λ_m = molar conductance at concentration C,

Λ_m^{∞} = molar conductance at ∞ dilution,

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



If a graph is plotted between Λ_m vs $\sqrt{C}$ a straight line is obtained for strong electrolyte. On extrapolation this line touches 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 can not 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 conductance of any electrolyte irrespective of the nature of other ion associated with it.
- ➢ This law states that the equivalent conductance of any electrolyte at infinite dilution (Λ_{eq}^{∞}) is the sum of equivalent ionic conductance of the cation and anion given by the electrolytes at infinite dilution.

$$\boxed{\Lambda_{eq}^{\infty} = \lambda_{eq(c)}^{\infty} + \lambda_{eq(a)}^{\infty}}$$

Where $\lambda_{eq(c)}^{\infty}$ = equivalent conductance of cation at infinite dilution.

$\lambda_{eq(a)}^{\infty}$ = equivalent conductance of anion at infinite dilution.

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

In terms of molar conductances of cation and anion

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

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.

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

Where x = Stoichiometric coefficient of cation

y = Stoichiometric coefficient of anion.

APPLICATIONS OF KOHLRAUSCH'S LAW :

(a) TO CALCULATE CONDUCTANCE OF WEAK ELECTROLYTE.

Λ_{m}^{∞} of CH_3COONa. = $\Lambda_{m\left(Na^{+1}\right)}^{\infty} + \Lambda_{m\left(CH_3COO^{-1}\right)}^{\infty}$

(b) TO CALCULATE DEGREE OF DISSOCIATION :

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

$$\boxed{\alpha = \frac{\Lambda_m}{\Lambda_m^{\infty}}}$$

(c) TO CALCULATE DISSOCIATION CONSTANT OF WEAK ELECTROLYTE

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

If $\alpha \le 5\%$ then $K_a = C\alpha^2$

(d) SOLUBILITY (S) AND K_{SP} OF ANY SPARINGLY SOLUBLE SALT.

- ➢ Sparingly soluble salt means salt with very less solubility
- ➢ Saturated solution of sparingly soluble salt can be considered as infinitely dilute solution.
- ➢ In a saturated solution of sparingly soluble salt. $\Lambda_m = \frac{\kappa \times 1000}{M}$

M = Solubility (S).

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

• TRANSPORT NUMBER/HITTORF'S NUMBER (t)

The current flowing through an electrolytic solution is carried by ions (cation and anion).

The fraction of total current carried by an ion is called its transport number.

transport number of cation (t_c) = $\dfrac{\lambda_c}{\lambda_c + \lambda_a} = \dfrac{u_c}{u_c + u_a}$

transport number of anion (t_a) = $\dfrac{\lambda_a}{\lambda_c + \lambda_a} = \dfrac{u_a}{u_c + u_a}$

and $\boxed{t_c + t_a = 1}$

if $u_c = u_a$ then $t_c = t_a = 0.5$.

IONIC CONDUCTANCE (λ) AND MOBILITY OF IONS (u)

In electrolyte solution the ionic conductance of any ion is directly proportional to their mobility or speed of ion.

$\lambda \propto u$

for a cation $\lambda_c \propto u_c$

or $\boxed{\lambda_c = Fu_c}$ where F = 96500 C

for an anion $\lambda_a \propto u_a$

or $\boxed{\lambda_a = Fu_a}$

Example: 12 The resistance of a 1N solution of salt is 50 Ω Calculate the equivalent conductance of the solution, it the two platinum electrodes in solution are 2.1 cm apart and each having an area of 4.2 cm^2.

(1) 8 ohm^{-1} cm^2 eq^{-1} (2) 9 ohm^{-1} cm^2 eq^{-1}

(3) 5 ohm^{-1} cm^2 eq^{-1} (4) 10 ohm^{-1} cm^2 eq^{-1}

Solution: **(4)**

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

Example: 13 Which of the following have maximum molar conductivity.

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

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

(1) (i) > (ii) (2) (ii) > (i) (3) (i) > (ii) (4) Not

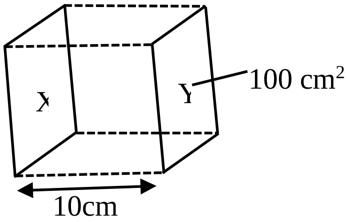
Solution: **(1)**

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

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

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

Example: 14 The conductance of a salt solution (AB) measured by two parallel electrodes of area 100 cm^2 separated by 10 cm was found to be 0.0001 Ω^{-1}. If volume enclosed between two electrodes contain 0.5 mol of salt. What is the molar conductivity ($Scm^2\ mol^{-1}$) of salt at same concentration.



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

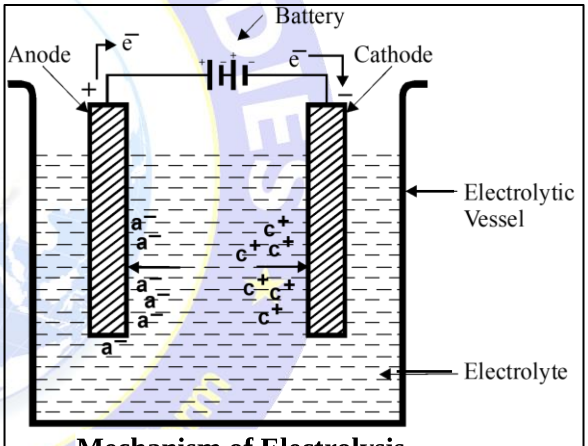
Solution: **(2)**

$$G^* = \frac{\ell}{A} = \frac{10}{100} = 0.1;\ G = 0.0001\ S;\ V = 100 \times 10 = 1000\ cm^3 = 1\ \text{litre}$$

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

$$\Lambda_m = \frac{k \times 1000}{M} = \frac{(0.1 \times 0.0001) \times 1000}{0.5} = 0.02\ S\ cm^2\ mol^{-1}$$

ELECTROLYSIS



Mechanism of Electrolysis

- The process of chemical 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 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 :

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

(i) NATURE OF ELECTROLYTE

(ii) NATURE OF ELECTRODES : The metal strip at which current enters is called anode; anode is positively charged in electrolytic cell. On the other hand, the electrode at which current leaves is called **cathode**. Cathodes are 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 that solution. Thus, such anodes get dissolved and their mass decreases.
- If electrodes 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 made up of unreactive elements like Pt, graphite etc.
- Such electrodes do not dissolve and their mass remain same.
- Among the two cations, first that cation is discharged at the cathode which has higher reduction potential.
- Among the two anions, that anion will be discharged first 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

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

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

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

(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

$Na^+_{(aq)} + e^- \longrightarrow Na_{(s)} \qquad E° = -2.71\ V$

$2H_2O_{(l)} + 2e^- \longrightarrow H_{2(g)} + 2OH^-_{(aq)} \qquad E° = -0.83\ V$

- Under the standard conditions, H_2O is to be reduced in preference to Na^+, Hydrogen is evolved at the cathode.
- The possible anode half-reactions are

$2Cl^-_{(aq)} \longrightarrow Cl_{2(g)} + 2e^- \qquad E° = -1.36\ V$

$2H_2O_{(l)} \longrightarrow O_{2(g)} + 4H^+_{(aq)} + 4e^- \qquad E° = -1.23\ V$

- 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 reduced 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 :

$2H_2O_{(l)} + 2e^- \longrightarrow H_{2(g)} + 2OH^-_{(aq)} \qquad$ (cathode)

$2Cl^-_{(aq)} \longrightarrow Cl_{2(g)} + 2e^- \qquad$ (anode)

$2H_2O_{(l)} + 2Cl^-_{(aq)} \longrightarrow H_{2(g)} + Cl_{2(g)} + 2OH^-_{(aq)}$

- 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) : $Pb^{2+} + 2e^- \rightarrow Pb(s) \qquad E° = -0.126\ V$

Anode (oxidation) : $2Br^- \rightarrow Br_2(g) + 2e^- \qquad E° = -1.08\ V$

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

$E_{cell} = -0.126 - 1.08 = -1.206\ V$

$E_{ext} > 1.206\ V$

(d) ELECTROLYSIS OF AQ. $CuSO_4$ USING INERT (Pt / GRAPHITE) ELECTRODE

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

$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$ $E° = -0.83$ 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: $Cu^{2+} + 2e^- \rightarrow Cu(s)$

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

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

After electrolysis solution will become acidic (pH < 7)

(e) ELECTROLYSIS OF aq. $CuSO_4$ USING Cu ELECTRODE

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

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

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

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

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

$Cu(s) \rightarrow Cu^{2+} + 2e^-$ $E° = -0.34$ 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 :

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

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

$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-$ $E° = -0.83$ 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 persulphate ion ($S_2O_8^{-2}$) takes place.

Example: 15 An acidic solution of Cu^{+2} salt containing 0.4 g of Cu^{+2} is electrolysed until all the Cu is deposited. The electrolysis is continued for seven more minutes with the volume of solution kept at 100 m; and the current at 1.2 ampere. calculate volume of gases evolved at N.T.P. during entire electrolysis. at. wt of Cu = 63.6

(1) 58.46 ml, 99.68 ml
(2) 55.45 ml, 95.68 ml
(3) 52.46 ml, 90.68 ml
(4) 57.46 ml, 92.68 ml

Solution: **For I part of electrolysis**

Anode :

$$2H_2O \longrightarrow 4H^+ + O_2 + 4e$$

Cathode :

$$Cu^{+2} + 2e \longrightarrow Cu$$

$\therefore$ Eq. of O_2 formed = Eq. of Cu = $\frac{0.4\times2}{63.6}$ = 12.58×10^{-3}

For II part of electrolysis : Since Cu^{2+} ions are discharged completely and thus further passage of current through solution will lead the following changes.

Anode :

$$2H_2O \longrightarrow 4H^+ + O_2 + 4e$$

Cathode :

$$2H_2O + 2e \longrightarrow H_2 + 2OH^-$$

$\therefore$ Eq. of H_2 = Eq. of O_2 = $\frac{i.t}{96500}\ \frac{1.2\times7\times60}{96500}$ = 5.22×10^{-3}

$\therefore$ Total Eq. of O_2 = $5.22 \times 10^{-3} + 12.58 \times 10^{-3} = 17.8 \times 10^{-3}$

$\because$ 2 Eq. of H_2 at NTP = 22.4 litre

or 4 eq. O_2 at NTP = 22.4 litre

$\therefore$ 5.22×10^{-3} Eq. H_2 at NTP = $\frac{22.4\times17.8\times10^{-3}}{4}$ = 58.46 ml

and 17.8×10^{-3} Eq. O_2 at NTP = $\frac{22.4\times17.8\times10^{-3}}{4}$ = 99.68 ml

Note : If salt is $CuCl_2$ than in II part of electrolysis Cl_2 gas will liberate.

PRODUCTS OF ELECTROLYSIS OF SOME ELECTROLYTES

S.NO.	Electrolyte	Electrode at anode	Product obtained	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)	Dilute 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 or 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 electrolytic cell D.C. current is used.

(B) QUANTITATIVE ASPECTS OF ELECTROLYSIS :

1 mole electron = N_A electron = 96500 coulomb = 1 Faraday

$$\underset{1mol}{Na^+} + \underset{1\,F}{e^-} \rightarrow \underset{1\,mol}{Na}$$

$$\underset{1\text{mol}}{Cu^{2+}} + \underset{2F}{2e^-} \rightarrow \underset{1\text{ mol}}{Cu}$$

$$\underset{1\text{mol}}{M^{+n}} + \underset{nF}{ne^-} \rightarrow \underset{1\text{ mol}}{M}$$

Therefore

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

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

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

Hence $\boxed{1\text{ mole } e^- = 1F = 1g \text{ equivalent}}$

• FARADAY'S LAWS 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 by 1 coulomb charge is called **electrochemical equivalent**.

Let 1 ampere current is passed till 't' seconds.

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

1 Faraday = 96500 coulomb = Charge of 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 coulombs.

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

By definition, $Z = \frac{E}{96500}$ $\therefore W = \frac{EIt}{96500}$ $\boxed{\frac{W}{E} = \frac{1}{96500} = \text{number of g eq} = \text{number of faraday}}$

(b) SECOND LAW OF ELECTROLYSIS :

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

Example: 16 An electric current is passed through three cells connected in series containing $ZnSO_4$, acidified water and $CuSO_4$ respectively. What amount of Zn and H_2 are liberated when 6.25g of Cu is deposited? Eq.wt. of Cu and Zn are 31.70 and 32.6 respectively.

(1) 0.192 g (2) 0.197 g (3) 0.195 g (4) 0.205 g

Solution: Eq. of Cu = Eq. of Zn = Eq. of H_2

$= \frac{6.25}{31.70} = \frac{w_{Zn}}{32.6} = \frac{W_{H_2}}{1}$

$\therefore W_{Zn} = 6.43$ g and $W_{H_2} = 0.197$ g

Example: 17 If 3 Faradays of Charge are passed through a solution of ferrous bromide, how many grams of iron will be deposited if its atomic weight is 56 ?

(1) 84 g (2) 82 g (3) 86 g (4) 88 g

Solution: Since $2e^-$ are involved in the deposition of Fe ($Fe^{2+} + 2e^- \rightarrow Fe$), the g, eq.wt. of Fe in Fe^{2+} = 28g. or 1F of electricity deposits 28 g of Fe

∴ 3F of charge will deposit = 84 g of Fe

Example: 18 The electrochemical equivalent of copper is 0.0003296 g per coulomb^{-1}. Calculate the amount of copper deposited by a current of 0.5 ampere flowing through copper solution for 50 minutes.

(1) 0.4944 g (2) 0.4542 g (3) 0.4345 g (4) 0.4348 g

Solution: According to Faraday's first law,

$W = I \times t \times z$

$W = 0.5 \times 50 \times 60 \times 0.003296 = 0.4944$ g

Example: 19 5600 mL of oxygen at STP is liberated at the anode when 96500 coulombs of Charge is passed through acidified water. Calculate the charge on an electron.

(1) 1.603×10^{-19}C (2) 1.401×10^{-19}C (3) 1.502×10^{-19}C (4) 1.203×10^{-19}C

Solution: 96500 C of electricity liberates 5600 mL of O_2 at STP i.e., eq. of O_2 or 6.023×10^{23} electrons.

∴ 6.023×10^{23} electrons carry 96500 C.

$$\therefore \quad 1 \text{ electron carries} = \frac{96500\text{C}}{6.023 \times 10^{23}} = 1.603 \times 10^{-19}\,\text{C}$$

Example: 20 The charge required for the reduction of 1 mol of MnO_4^- to MnO_2 is :

(1) 1F (2) 3F (3) 5F (4) 7F

Sol: **(2)**

$$MnO_4^- + 4H^+ + 3e^- \longrightarrow MnO_2 + 2H_2O$$

Oxidation No. of Mn in MnO_4^- = + 7

Oxidation No. of Mn in MnO_2 = + 4

3F of charge will be required to reduce 1 mole of MnO_4.

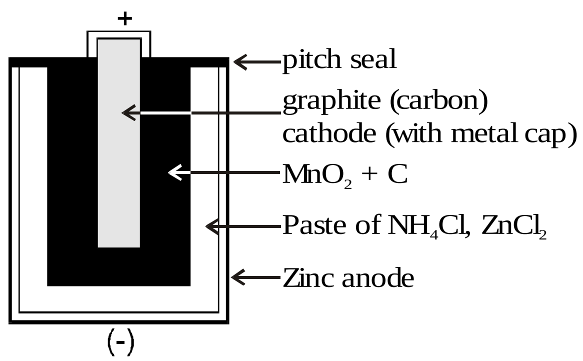
SOME COMMERCIAL BATTERIES

- 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 right and compact and its voltage should not vary appreciably during the use. There are mainly two types of cells :

  (i) primary cells

  (ii) secondary cells.
- 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



Dry Cell

- ➢ 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 : $Zn(s) \longrightarrow Zn^{+2} + 2e^-$

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

- ➢ In the cathode reaction, manganese is reduced from the + 4 oxidation state to the +3 oxidation 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 indefinite life as acidic NH_4Cl corrodes the zinc container even when not in use.
- ➢ **Dry cells have a potential of approximately 1.25 to 1.5 V.**
- ➢ A new type of dry cell which has found use in small electrical circuits (such as hearing aids, watches and camera) is the mercury cell.
- ➢ Here zinc-mercury amalgam is the anode; a paste of HgO and carbon is the cathode. The electrolyte is a paste of KOH and ZnO.
- ➢ The reaction of the cell is as follows :

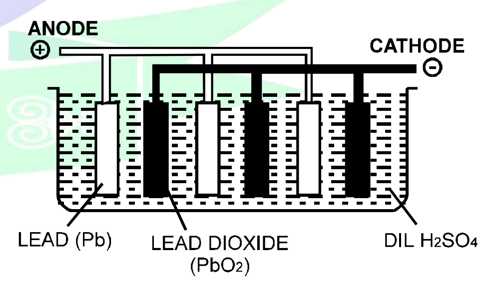
Anode $Zn(Hg) + 2OH^- \longrightarrow ZnO(s) + H_2O + 2e^-$

Cathode $HgO(s) + H_2O + 2e^- \longrightarrow Hg(I) + 2OH^-$

Overall reaction: $Zn(Hg) + HgO(s) \longrightarrow ZnO(s) + Hg(I)$

- ➢ Since the overall cell reaction does not involve any ion in solution whose concentration can change, the cell shows a constancy in potential throughout its life.
- ➢ **The cell potential is approximately 1.35 V.**

• 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 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.

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

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

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

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

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

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

Overall cell reaction → add equation (i), (ii), (iii) & (iv)

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

E_{cell} is 2.041 volt

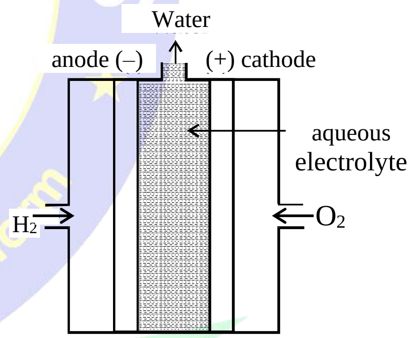
(A 12 V lead storage battery is generally used which consist of 6 cells each producing 2 volt)

- 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 :

  $$2PbSO_4(s) + 2H_2O \longrightarrow Pb(s) + PbO_2(s) + 2H_2SO_4$$
- 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. We shall not go into details of these cells here.

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 program.
- 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 :



Fuel Cell

Anode $2[H_2(g) + 2OH^-(aq) \longrightarrow 2H_2O(\ell) + 2e^-]$

Cathode $O_2(g) + 2H_2O(\ell) + 4e^- \longrightarrow 4OH^-(aq)$

Overall reaction : $2H_2(g) + O_2(g) \longrightarrow 2H_2O(\ell)$

- 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 fuel cell $\boxed{\eta = \frac{|\Delta G|}{|\Delta H|} \times 100}$

IMPORTANT POINTS

1. Electrolytes also conduct electricity in fused state and undergoes decomposition by the passage of electric current.

2. The theory of ionisation was proposed by Arrhenius.

3. Galvanic cells are used to convert chemical energy to electrical energy.

4. The amount of current which produce one gm equivalent of any substance is called faraday.

5. Mg can liberate H_2 gas from HCl

6. When zinc piece is added to $CuSO_4$ solution, copper gets precipitated because standard reduction potential of zinc is less than that of copper.

7. In a galvanic cell cathode acts as positive electrode and anode as negative electrode.

8. In electrolytic cell cathode acts as negative electrode and anode as positive electrode.

9. More negative the standard reduction potential of a metal, the greater is its ability to displace hydrogen from acids.

10. More the reduction potential less is the reducing power.

11. Cell voltage is independent of the size of cell or electrodes.

12. Standard potential is the potential measured at 25°C, 1 atm. pressure and one molar concentration of the ions.

QUICK FOLLOW

Electrochemistry

Basic Terms Used

RESISTANCE (R) :-

$\boxed{R = \frac{V}{I}}$ Unit: ohm.

Conductance (C) :

$$C = \frac{1}{R}$$

Unit: ohm^{-1} or Siemens

Conductivity (k) :

$$k = \frac{1}{\rho} = \frac{1}{R} \cdot \frac{\ell}{A}$$

Unit: $ohm^{-1}cm^{-1}$ or Scm^{-1}

Equivalent Conductivity (Λ_{eq}):

$$\Lambda_{eq} = \frac{k}{N} \times 1000$$

where

k = specific conductance

Unit: $cm^2\ ohm^{-1}\ g^{-1}eq^{-1}$

Molar Conductivity (Λ_m):

$$\Lambda_m = \frac{k}{M} \times 1000$$

where

k = specific conductance

~~**Unit:** $S\ cm^{-1}\ mol^{-1}$~~

Nernst Equation

➢ **Nernst Equation:** For the reaction:

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

$$E = E^0 - \frac{RT}{nF} \ln \frac{M}{[M^{n+}]} \text{ or}$$

$$E = E^0 - \frac{0.0591}{n} \log \frac{1}{[M^{n+}]}$$

at 298 K

➢ **For concentration cell:**

$$E_{cell} = \frac{0.0591}{n} \log \frac{C_2}{C_1}$$

E_{cell} =+ve if $C_2 > C_1$

➢ **At equilibrium:** $E_{cell} = 0$

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

➢ **Gibbs free energy:**

$\Delta G = -nFE_{cell}$ or $\Delta G^0 = -nFE^0_{cell}$

Types of Cells

Electrochemical Cells: These are the cells in which electrical energy is produced by virtue of redox reactions.

H_2–O_2 fuel Cell

Anode:

$2H_2(g) + 4HO^-(aq) \rightarrow 4H_2O(\ell) + 4e^-$

Cathode:

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

Net reaction:

$2H_2(g) + O_2(g) \rightarrow 2H_2O(\ell)$

Type	Energy change	Anode	Cathode
Electrolytic cell	Electrical energy → Chemical energy	+	–
Galvanic (Voltaic cell)	Chemical energy → Electrical energy	–	+

Lead Storage Cells

Cell reaction during use of battery:

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

Cathode:

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

Laws

➢ **Faraday's first law:**

W = ZIt

➢ **Faraday's second law:**

$$\frac{w_1}{w_2} = \frac{E_1}{E_2}$$

➢ **Kohlrausch law:** For an electrolyte A_xB_y,

$$\Lambda^0_m = x\lambda^0_{m(c)} + y\lambda^0_{M(A)} \text{ or}$$

$$\Lambda^0_{eq} = \lambda^0_{eq(c)} + \lambda^0_{eq(A)}$$

Potentials

Electrode Potential : It is defined as the tendency of an electrode i.e., tendency to get either oxidised or reduced when it is in contact with a solution of its own ions is known as electrode potential.

Cell Potential: The difference between potentials of two half cells I called potential or cell voltage or electromotive force (EMF) of the cell.