ELECTROCHEMISTRY

Electrochemistry is that branch of chemistry which deals with the relationship between electrical energy and chemical energy changes taking place in a redox reaction.

(1) Resistance: It measures the obstruction to the flow of current.

$$R \propto \frac{1}{a} \quad \text{or} \quad R = \rho \frac{1}{a}$$

Where ρ is the constant of proportionality and is called specific resistance or resistivity. The resistance depends upon the nature of the material. Units: The unit of resistance is ohm (Ω).

(2) Resistivity or specific resistance:

$$\because R = \rho \frac{1}{a} \; ; \quad \text{Now, if } 1 = 1 \text{ cm, } a = 1 \text{ cm}^2 \text{ then } R = \rho$$

Thus, resistivity is numerically equal to the resistance of a conductor of 1 cm length and having area of cross-section equal to 1 cm^2.

Units: The unit of resistivity is $\rho = R\frac{a}{1} = \text{Ohm}\frac{cm^2}{cm} = \text{Ohm.cm}$ (c.g.s unit). Its SI Unit is Ohm metre.

(3) Conductance: It measures the ease with which current flows through a conductor. It is an additive property. It is expressed as C. It is reciprocal of the resistance, i.e.

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

Units: The c.g.s. unit of conductance is (ohm^{-1}) or mho.

According to SI system, the units of electrical conductance is Siemens, S (i.e. $1S = \Omega^{-1}$).

(4) Conductivity(κ) : The inverse of resistivity is called conductivity (or specific conductance). It is represented by the symbol κ. It may be defined as, the conductance of a solution of 1 cm length and having 1 sq. cm as the area of cross-section.

$$\text{Thus, } \kappa = \frac{1}{\rho}$$

Units: The units of conductivity is $\kappa = \frac{1}{\text{Ohm.cm}} = \text{Ohm}^{-1}\text{cm}^{-1} \text{ or } \Omega^{-1}\text{cm}^{-1}$

Its SI unit is Sm^{-1}.

(5) Molar conductivity or molar conductance: Molar conductivity is defined as the conducting power of all the ions produced by dissolving one mole of an electrolyte in solution.

$$\Lambda = \frac{\kappa \times 1000}{M}$$

The c.g.s. unit of molar conductance is ohm^{-1} cm^2 mol^{-1}

The SI unit of molar conductance is Sm^2 mol^{-1}.

(6) Equivalent conductivity: It is defined as the conducting power of all the ions produced by dissolving one gram equivalent of an electrolyte in solution.

It is expressed as Λ_{eq} and

$\Lambda_{eq} = \kappa \times \frac{1000}{N}$, where, N = Normality of solution.

The units of equivalent conductance (a) Ohm^{-1} cm^2 (gm equiv)$^{-1}$ (in c.g.s. system) (b) Sm^2 equiv^{-1} (in S.I. system)

(7) Experimental measurement of conductance

 (i) The conductance of a solution is reciprocal of the resistance, therefore, the experimental determination of the conductance of a solution involves the measurement of its resistance.

(ii) Calculation of conductivity: We have seen that conductivity (κ) is reciprocal of resistivity (ρ), i.e.

$$\therefore \ \kappa = \frac{1}{R}\left(\frac{1}{a}\right) \text{ or } \kappa = C\left(\frac{1}{a}\right) \quad \text{Conductivity} = \text{Conductance} \times \text{Cell constant}$$

$$\Rightarrow \text{Cell consant} = l/a, \text{ unit of cell constant } (a) \text{ cm}^{-1} \text{ (c.g.s unit) } (b) \text{ m}^{-1} \text{ (S.I. unit)}$$

Factors affecting the electrolytic conductance

(1)   Nature of electrolyte

(2)   Concentration of the solution: The molar conductance of electrolytic solution varies with the concentration of the electrolyte. In general, the molar conductance of an electrolyte increases with decrease in concentration or increase indilution.

(3)   Temperature: The conductivity of an electrolyte depends upon the temperature. With increase in temperature, the conductivity of an electrolyte increase.

Kohlrausch's Law

Kohlrausch's law states that "Equivalent conductivity of any electrolyte at infinite dilution is the sum of the equivalent conductivities of the cations and the anions" i.e. $\wedge_m^0$ for $A_xB_y = x \times \lambda^0_{A^{y+}} + y\lambda^0_{B^{x-}}$

Application of Kohlrausch's law: Some typical applications of the Kohlrausch's law are described below,

(i)   In the determination of Λ_M^∞ for weak electrolyte:
(ii)   In the determination of the degree of ionisation of an weak electrolyte
(iii)   In the determination of the ionisation constant of a weak electrolyte
(iv)   In the determination of the solubility of a sparingly soluble salt

Transport number or Transference number

Definition : "The fraction of the total current carried by on ion is known as transport number, transference number or Hittorf number may be denoted by sets symbols like t_+ and t_- or t_c and t_a or n_c and n_a".
From this definition

$$t_a = \frac{\text{Current carried by an anion}}{\text{Total current passed through the solution}} \text{ and } t_c = \frac{\text{Current carried by an cation}}{\text{Total current passed through the solution}}$$

evidently, $t_a + t_c = 1$

Determination of transport number: Transport number can be determined by Hittorf's method, moving boundary method, emf method and from ionic mobility.

(a) Primary cells are those which cannot be recharged e.g. dry cell and mercury cell.

(b) Secondary cells are those which can be recharged e.g. lead storage battery and Ni-Cd cell.

(c) Fuel cells are those in which energy produced from the combustion of fuels can be converted into electrical energy e.g. H_2–O_2 fuel cell.
Main features of different cells.

	Nature of cell/Battery	Anode	Cathode	Electrolyte
(i)	Dry cell	Zinc	Graphite	MnO_2 + C (touching cathode) NH_4Cl + $ZnCl_2$ touching anode
(ii)	Mercury cell	Zinc	Grpahite	HgO + KOH (moist)
(iii)	Lead storage battery	Lead	Lead dioxde	H_2SO_4 (38%)
(iv)	Ni-Cd cell	Cadmium	Nickel dioxide	KOH (sol.)

Conductors and Insulators

Those which allow the passage of current are known as conductors. The others which do not allow electric current to pass through are insulators.

Types of conductors

Difference between Electronic/Metallic conductors and Electrolyte conductors

	Electronic conductors		Electrolytic Conductors
(i)	Flow of electricity is due to flow of electrons	(i)	Flow of electricity is due to flow of ions.
(ii)	Flow takes place without decomposition of the substance.	(ii)	Flow is accompanied by decomposition of the substance
(iii)	Conduction decreases with temperature because kernels start vibrating which interfere in the flow of electrons.	(iii)	Conduction increases with temperature because dissociation increases.

Electrolyte: An electrolyte is defined as the substance that, in solution or in the molten state, conducts electric current and is simultaneously decomposed by it.

Electrode: An electronic conductor in contact with an electrolytic conductor is known as an electrode or a half cell.

Electrode potential: The potential difference set up across the surface of separation of an electronic and electrolytic conductor in contact with each other is known as electrode potential or half cell e.m.f.

Cell: An assembly of two half cells.

ELECTROLYSIS

The phenomenon in which passage of current through an electrolyte (molten or solution) brings in chemical changes involving electronation (reduction) as well as oxidation (de-electronation) of ions is known as electrolysis.

1.   The cations migrate towards cathode, where they gain electrons and show reduction.

   At cathode: $M^{n+} + ne \longrightarrow M$ (reduction)
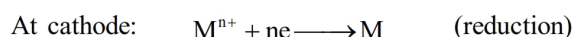
2.   The anions migrate towards anode, where they lose electrons and show oxidation

   At anode: $A^{n-} \longrightarrow A + ne$ (oxidation)
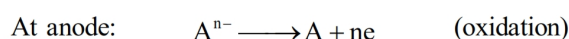
The Products formed During Electrolysis Depends Upon

1.   Nature of electrodes (attackable or non-attackable electrodes)

2.   Nature of electrolyte (Motlen or aqueous solution)

3.   Charge density flown during the process

4.   Concentration of solution used

e.g.

Electrolyte	Electrode	Cathodic Reaction	Anodic Reaction
NaCl (fused)	Pt	$Na^+ + e \longrightarrow Na$	$Cl^- \longrightarrow \frac{1}{2}Cl_2 + e$
NaCl (aq, very dilute)	Pt	$H^+ + e \longrightarrow \frac{1}{2}H_2$	$2OH^- \longrightarrow H_2O + \frac{1}{2}O_2 + 2e$
NaCl (aq.)	Hg	$Na^+ + e \longrightarrow Na$	$Cl^- \longrightarrow \frac{1}{2}Cl_2 + e$
HCl (aq.)	Pt	$H^+ + e \longrightarrow \frac{1}{2}H_2$	$Cl^- \longrightarrow \frac{1}{2}Cl_2 + e$

Electrolyte	Electrode	Cathode	Anode
$NaNO_3$ (aq) or Na_2SO_4 (aq)	Pt	$2H^+ + 2e \longrightarrow H_2$	$2OH^- \longrightarrow H_2O + \frac{1}{2}O_2 + 2e$
$CuSO_4$ (aq)	Pt	$Cu^{2+} + 2e \longrightarrow Cu$	$2OH^- \longrightarrow H_2O + \frac{1}{2}O_2 + 2e$
$AgNO_3$ (aq)	Pt	$Ag^+ + e \longrightarrow Ag$	$2OH^- \longrightarrow H_2O + \frac{1}{2}O_2 + 2e$
H_2SO_4 (at normal current density)	Pt	$2H^+ + 2e \longrightarrow H_2$	$2OH^- \longrightarrow H_2O + \frac{1}{2}O_2 + 2e$
H_2SO_4 (at high current density)	Pt	$2H^+ + 2e \longrightarrow H_2$	$2HSO_4^- \longrightarrow H_2S_2O_8 + 2e$

Note: 1. The phenomenon of electrolysis occurs only at the electrodes. Oxidation occurs at anode, reduction occurs at cathode.

2. In case of two or more similar ions to be discharged, the more is discharge potential of an ion, lesser is its tendency to get itself discharged at the electrodes.

3. The discharge of ions at the different electrodes takes place only during the passage of charge.

FARADAY'S LAWS OF ELECTROLYSIS

1st Law: The amount (W) of substance deposited on electrode is directly proportional the charge passed into the fused state or in aqueous solution of electrolyte.

i.e. $W \propto Q \quad (\because Q = it)$

$W \propto it$

$\therefore \quad W = z \cdot i \cdot t \quad ...(i)$

$\frac{W_1}{W_2} = \frac{z_1 i_1 t_1}{z_2 i_2 t_2}$, when $i_1 t_1 = i_2 t_2$ then $\frac{W_1}{W_2} = \frac{z_1}{z_2}$

i.e $w \propto z$ at constant Q.

IInd Law : By passing the same charge into different electrolytes, the amount of substances deposited on electrode are directly proportional to their no of equivalent .

i.e $w \propto E$ when Q is constant

or $\frac{w_1}{w_2} = \frac{E_1}{E_2}$ when Q is constant.

Note : (i) By passing 1 coulomb of charge, Z gm of substance is deposited on electrode.

(ii) By passing 1 F of charge, E gram of substance is deposited on electrode.

(iii) $W_{gm} = ZCt = \frac{E}{F} \times C \times t = \frac{A}{V} \times \frac{C_{amp} \times t_{sec}}{F}$

APPLICATIONS OF ELECTROLYSIS

1. In extracton of metals
2. Preparation of Chemicals
3. Preparation of Organic Compounds
4. Corrosion and its Prevention
5. In purification of metals

<u>Types of Cells</u>

Electrolytic Cells	Electrochemical Cells
1. Passage of current brings in chemical changes	A chemical change brings in passage of current.
2. Electrical energy is converted into chemical energy	Chemical energy is converted into electrical energy.

ELECTROCHEMICAL CELLS

Sl. No.	Chemical Cells	Concentration Cells
1.	A net chemical change inside the cell occurs, e.g., Daniel Cell $Zn \mid ZnSO_4 \parallel CuSO_4 \mid Cu$ Anode: $Zn \longrightarrow Zn^{2+} + 2e$ Cathode: $Cu^{2+} + 2e \longrightarrow Cu$	No net chemical change occurs. e.g., $M \mid M_{C_1}^+ \parallel M_{C_2}^+ \mid M$ $M \longrightarrow M_{C_1}^+ + e$ $M_{C_2}^+ + e \longrightarrow M$
	Redox change, $Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$	Net change, $M_{C_2}^+ \longrightarrow M_{C_1}^+$ where C_1 and C_2 are conc. of the electrolyte of the same metal whose two electrodes are used. The cell will work only when $C_2 > C_1$
2.	A decrease in free energy during the redox change brings in an equivalent amount of electrical work done.	A decrease in free energy during the transfer of concentration from C_2 to C_1 brings in an equivalent amount of electrical work done.
3.	The electrode having high standard oxidation potential works as anode, i.e., negative electrode.	The electrode having more dilute solution surrounding, works as anode.

Chemical Cells: These are also known as redox cells or galvanic cells or voltaic cells. The simplest example of this category is Daniel cell. The cell is represented as,

$$Zn \mid Zn^{2+} \parallel Cu^{2+} \mid Cu$$
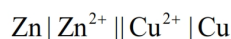
Characteristics of Daniel Cell

i) Oxidation and reduction occur simultaneously.

ii) oxidation occurs at one electrode (i.e, anode) whereas reduction occurs at other electrode (i.e., cathode)

iii) The number of electrons released at anode = No. of electrons consumed at cathode.

iv) The electrons released at anode flow through external wire towards cathode where they are used up.

Nernst Equation for Electrode Potential

Nernst gave an expression to express electrode potential for a change.

Metal:
$$\underset{\substack{\text{Reduced} \\ \text{State (R.S.)}}}{M} \rightleftharpoons \underset{\substack{\text{Oxidised} \\ \text{state(O.S.)}}}{M^{n+}} + ne$$

$$E_{OP} = E_{OP}^0 - \frac{RT}{nF} \ln \frac{a_{O.S.}}{a_{RS.}} = E_{OP}^0 - \frac{0.0591}{n} \log \frac{a_{O.S.}}{a_{RS.}} \, (\text{at } 25^0 C)$$

Non-metal:
$$\underset{O.S.}{A} + ne \rightleftharpoons \underset{R.S.}{A^{n-}}$$
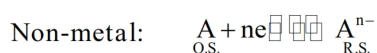
$$E_{RP} = E_{RP}^0 - \frac{RT}{nF} \ln \frac{a_{R.S.}}{a_{OS.}} = E_{RP}^0 - \frac{0.0591}{n} \log \frac{a_{RS.}}{a_{OS.}} \, (\text{at } 25^0 C)$$

Factors influencing electrode potential

1. Nature of electrode (i.e., E^0)
2. Concentration of ion in solution, i.e., [O.S.] and [R.S.]
3. Temperature: The temperature dependence of electrode potential has been discussed in application (iii) of Nernst equation under heading heat of reaction.

Some applications of Nernst equation

(i) In computation of the e.m.f. of cell

$$E_{cell}^0 = E_{OP}^0 + E_{RP}^0$$

$$E_{cell} = E_{OP} + E_{RP}$$

(ii) e.m.f. of Cell and equilibrium constant:

$$\Delta G = \Delta G^0 + RT\ lnQ$$

At equilibrium $\Delta G = 0$

$$\therefore \Delta G^0 = -RT\ K_{eq} = -2.303\ RT\ \log K_{eq}$$

$$\therefore \qquad E^0 = \frac{2.303}{nF} RT \log K_{eq}\ = \frac{0.0591}{n} \log K_{eq}\ \text{at } 25°C$$

(iii) Heat of reaction for cell reaction:

$$\Delta H = nF\left[T\left(\frac{\delta E}{\delta T}\right)_P - E \right]$$

where $\left(\dfrac{\delta E}{\delta T}\right)_P$ is called as temperature coefficient of e.m.f., i.e., rate of change of e.m.f. (E) with temperature at constant pressure.

(iv) To decide spontaneity of cell reaction:

(v) To evaluate solubility product

(vi) To evaluate pH of solution.

Reversible and Irreversible Cells

In order to find out if a given cell is reversible or not, it is connected to an external source of E.M.F. and if,

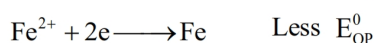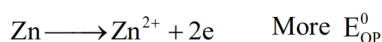1. the e.m.f. of test cell is slightly greater than the e.m.f. of external cell, the current flows from the test cell to external cell and cell reacton takes place.
2. the e.m.f. of test cell is slightly lesser than the external e.m.f. the current flows from external cell to test cell and reaction is reversed.
3. the e.m.f. of test cell is equal to external e.m.f., then no current is given out by the cell and no chemical reaction takes place in the cell.
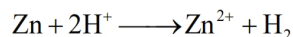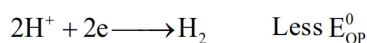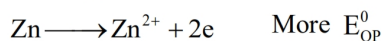
Electrochemical Series

1. An electrochemical series is one in which elements are placed in order of their decreasing tendency to lose electrons or decreasing tendency to get oxidised, measured interms of E_{OP}^0 (decreasing trend) or increasing tendency to gain electrons or increasing tendency to get reduced, measured in terms of E_{RP}^0 (increasing trend).

2. More or +ve is E_{OP}^0, more is the tendency to get oxidised

3. Stronger is oxidant, weaker is its conjugate reductant in a redox pair and vice versa.

4. The reducing power of metals decreases down the series.

5. The oxidsing power of metal ions increases down the series.

6. The activity of metals decreases down the series

7. The metal placed above in series replaces the other from its electrolyte solution placed below in series.

$$Zn \longrightarrow Zn^{2+} + 2e \qquad \text{More } E_{OP}^0$$
$$Fe^{2+} + 2e \longrightarrow Fe \qquad \text{Less } E_{OP}^0$$
$$Zn + Fe^{2+} \longrightarrow Zn^{2+} + Fe$$

8. The metals placed above H in series produce $H_2(g)$ on reaction with dilute acids.

$$Zn \longrightarrow Zn^{2+} + 2e \qquad \text{More } E_{OP}^0$$
$$2H^+ + 2e \longrightarrow H_2 \qquad \text{Less } E_{OP}^0$$
$$Zn + 2H^+ \longrightarrow Zn^{2+} + H_2$$

9. The reducing power of halide ion decreases down the series HI > HBr > HCl > HF

or $I^- > Br^- > Cl^- > F^-$ $\qquad (\because E_{OP}^0 \text{ decreases})$
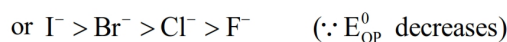
10. The oxidising power of halogens increases down the series.

$I_2 < Br_2 < Cl_2 < F_2$ $\qquad (\because E_{OP}^0 \text{ decreases})$
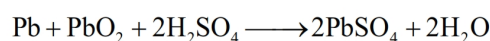
IMPORTANT INFORMATIONS

1. Reactions occurring in lead storage battery (a) Reactions occurring during discharge.

At anode : $\qquad Pb + SO_4^{2-} \longrightarrow PbSO_4 + 2e^-$

At cathode : $\qquad PbO_2 + SO_4^{2-} + 2e^- \longrightarrow PbSO_4 + 2H_2O$
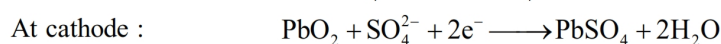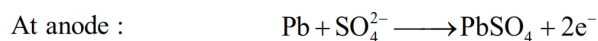
The complete reaction may be written as

$$Pb + PbO_2 + 2H_2SO_4 \longrightarrow 2PbSO_4 + 2H_2O$$

As H_2SO_4 is consumed, the consumed, the voltage of the battery drops.
(b) Reactions occurring during charging are the reverse of the above reactions.

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

3. Factors which enhance corrosion are
   (i) Presence of impurities in the metal (pure metal do not corrode)
   (ii) Presence of moisture (e.g. in rainy season)
   (iii) Presence of electrolytes (.e.g saline water)

4. Corrsion can be prevented by the following methods :
   (i) Barrier protection by oil/grease layer, paints or electroplating
   (ii) Sacrificial protection by coating the metal with more electropositive metal (e.g. Zn called galvanisation).
   (iii) Electrical protection by connecting the iron pipe to a more electropositive metal with a wire.

5. Effect of concentration and temperature on Transport number. With increase in concentration, transport number decreases. Further, for 1 : 1 electrolyte. if transport number of an ion is greater than 0.5 it decreases

with increase of temperature but if it is less than 0.5, it increases with increase in temperature till it approaches a value of 0.5.

- Loss of electron is oxidation whereas gain of electron is reduction.
- Increase in oxidation no. is said to be oxidation whereas decrease in oxidation number is said to be reduction
- Oxidised substance is said to be reducing agent whereas reduced substance is said to be oxidising agent.

- Equivalent mas of oxidising agent $= \dfrac{\text{Formula mass of O.A.}}{\substack{\text{No.of electrons gained} \\ \text{by one molecule of O.A.}}} = \dfrac{\text{Formula mass of O.A.}}{\substack{\text{Decrease in oxidation no.of active} \\ \text{element / s present in one molecule of O.A.}}}$

- Equivalent mass of Reducing agent $= \dfrac{\text{Formula mass of R.A.}}{\substack{\text{No.of electrons lost} \\ \text{by one molecule of R.A.}}} = \dfrac{\text{Formula mass of R.A.}}{\substack{\text{Decrease in oxidation no.of active} \\ \text{element / s present in one molecule of R.A.}}}$

- Types of redox reaction

    (a)   Inter molecular redox reaction $Zn + 2HCl \rightarrow ZnCl_2 + H_2$

    (b)   Intra molecular redox reaction $2KClO_3 \rightarrow 2KCl + 3O_2$

    (c)   Disproportion reaction $2Cu^+ \rightarrow Cu^{2+} + Cu$