Electrolysis

- It deals with chemical changes involving electricity
- Some chemical reactions require electric current and some chemical reactions produce electric current.

  Conductors : The substances which allow current to pass through them.
- Conductors are of 2 types.

  i) Electronic conductors : The substances which allow current to pass through them without undergoing any physical or chemical change are called electronic conductors.

  Ex. metals, gas carbon, petroleum coke, CdS and CuS etc.

  ii) Electrolytic conductors: Substances which conducts electricity in molten state or in aqueous solution because of some chemical change are called electrolytic conductors or electrolytes.

  Ex. – All salts, acids and bases.

Differences between electronic conductors and electrolytic conductors :

Electronic conductors	**Electrolytic conductors**
1. Flow of electrons.	1. Flow of ions.
2. No chemical change.	2. Chemical change occurs.
3. No transfer of mass.	3. Transfer of mass.
4. Increase in temperature conductance decreases with increase in temperature and resistance increase.	4. Conductance increases with increase of temperature due to decrease in resistance for mobility of ions.

Arrhenius theory of electrolytic dissociation:

- It explains the behaviour of weak electrolytes.
- Any electrolyte must ionise and should be in equilibrium with unionised, substance.

  $AB \rightleftharpoons A^+ + B^-$ $\alpha = \sqrt{\frac{ka}{c}}$

  α = degree of dissociation

  c = concentration

  ka = dissociation constant
- For strong electrolytes $\alpha \approx 1$.

  Ex : All strong acids and strong bases, solutions of all salts.
- For weak electrolytes $\alpha << 1$.

  Ex :All weak acids and weak bases.
- α of weak acids and bases depend on dielectric constant value of solvent.

- Property of solvent to increase the ionisation of solute is called as dielectric constant.
  Degree of ionisation α Dielectric constant.
- Cation $\rightarrow$ cathode (reduced)
- Anion $\rightarrow$Anode (oxidised)

Electrolysis : The decomposition of a chemical compound in the molten state or in the solution state into it's constituent elements under the influence of an applied emf is called electrolysis.

- It is a redox reaction and endo-energic reaction
- It is non – spontaneous.
- At infinite dilution for weak acids and weak bases. ⍰⍰≈⍰1.
- With increase in dilution interionic attractions decreases and so mobility of ions increases and conductance increases.

Electrodes are of two types.

- Inert electrodes : Which do not take part in electrolysis reaction. Ex: Graphite, pt.
- Active electrodes: Take part in electrolyte reaction.
  Metal present in same electrolyte acts as an active electrode.
  Ex: Cu rods in $CuSO_4$ sol., Ag rods in $AgNO_3$ sol.
- Nature of products of electrolysis : Depends on
  i) Nature of electrolyte.
  ii) Nature of electrodes.
- The ion (cation / anion) with low discharge potential is preferentially discharge first.
- Discharge potential: It is the amount of current required to discharge the ion.
- In case of cations, the cation with high reduction potential is discharged preferentially.
- In case of anions, the anion with higher oxidation potential is discharged preferentially.
- Less reactive cation / anion is readily discharged.

Cations	Anions
1) $Zn^{2+} < Cu^{2+}$	1) $F^- < Cl^- < Bi^- < I^-$
2) $Cu^{2+} < Ag^+$	2) $OH^- < Cl^-$
3) $Zn^{2+} < H^+$	3) $OH^- > SO_4^{2-}$
4) $Cu^{2+} > H^+$	4) $OH^- > NO_3^-$

- The products in the electrolysis will depend on nature of electrolyte, concentration of electrolyte and nature of electrode.

Electrolyte	Product at cathode	Product at anode
1) H_2O	H_2	O_2
2) dil.H_2SO_4	H_2	O_2
3) dil.NaOH	H_2	O_2
4) fused. NaCl	Na	Cl_2
5) aq.NaCl	H_2	Cl_2
6) very dil.NaCl	H_2	O_2
7) aq.NaCl [(Hg) cathode]	Na	Cl_2
8) 50% dil H_2SO_4	H_2	$H_2S_2O_8$
9) Na_2SO_4 sol.	H_2	O_2
10) $CuSO_4$ sol.	Cu	O_2
11) $CuSO_4$ (Cu electrode)	$Cu^{2+} \xrightarrow{2e^-} Cu$	$CU \rightarrow Cu^{2+} + 2e^-$
12) $AgNO_3$ sol.	Ag	O_2
13) $AgNO_3$ sol./ (Ag electrodes)	$Ag^+ \xrightarrow{e^-} Ag$	$Ag \rightarrow Ag^+ + e^-$
14) Stannous chloride (fused)	Sn	$SnCl_4$
15) Aq.K_2SO_4	H_2	O_2
16) Aq.KCl	H_2	Cl_2
17) Aq.$CuCl_2$	Cu	Cl_2
18) Fused NaOH	Na	O_2

Faradays laws of electrolysis : (Quantitative laws).

- **First law :** The amount of substance deposited or dissolved or evolved at an electrode in an electrolysis process is directly proportional to the amount of electricity passed through the electrolyte.

  $w \propto Q$

  $w \propto ct$

  $w = ect$

  $w \rightarrow$ wt in gms, $c \rightarrow$ current in amp, $t \rightarrow$ time in sec.

  $w = e$ (when $c = 1$ amp and $t = 1$ sec)

  $e \rightarrow$ electrochemical equivalent.

Electrochemical equivalent : Weight of the substance deposited or liberated or evolved at an electrode when 1 amp of current is passed in 1 sec through an electrolyte.

Units: gm / coulomb or gm/ ampere

Second law : When equal amount of electricity is passed through one or more electrolytes connected in series the weights of different substances deposited or liberated or dissolved at the electrodes are directly proportional to the chemical equivalents of the substances.

: $w \propto E$

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

Faraday : The amount of electricity which deposits one gram equivalent of the substance is called Faraday. One faraday = 96500 coulombs.

- **Gram equivalent weight :** Amount of substance deposited when one Faraday (96500C) of electricity is passed through an electrolyte.

$1\ F \rightarrow 1\ GEW$

$96500\ C \rightarrow E$

$1\ Coulomb \rightarrow E/F$

$e \rightarrow E/F$; $w = ect$; $= \frac{E}{F}ct$

$E = \frac{M}{Z}$ ($M \rightarrow$ at. wt , $Z \rightarrow$ valency)

$$\therefore w = \frac{MCt}{ZF}$$

Applications of Electrolysis :

- To determine the equivalent weights.
- To extract more electropositive metals like Na, K, Mg, Al etc,.
- To extract non – metals like F_2, Cl_2, H_2, O_2.
- To obtain compounds like NaOH, Na_2CO_3.
- In electroplating to prevent corrosion.