Electrochemistry - I

* Substances which allow electricity to pass through them are known as conductors.
* Which do not allow electricity to pass through as insulators.

Conductors.
- without undergoing any decomposition → (1) Electronic Conductor
- undergo decomposition to pass current through them → (2) Electrolytic Conductors
  - eg. Solutions of acids, bases salts in water (fused salts also)

* In case of electrolytic conductors conduction is due to movement of ions.

Electrolytes
- (1) Strong electrolytes: HCl, HNO_3, H_2SO_4 / $NaOH$, KOH
- (2) Weak Electrolytes: CH_3COOH, HCN, H_2CO_3, H_3PO_4 / NH_4OH, $Ca(OH)_2$, $Al(OH)_3$

Non electrolytes. Do not conduct electricity like, Sugar Urea etc.

Factors Affecting Electrolytic conduction.

(1) Inter Ionic Interactions — Solute-solute Interaction
(2) Solvation of ions. — Solute-solvent Interaction.
(3) Viscosity of solvent. — Solvent-solvent Interaction

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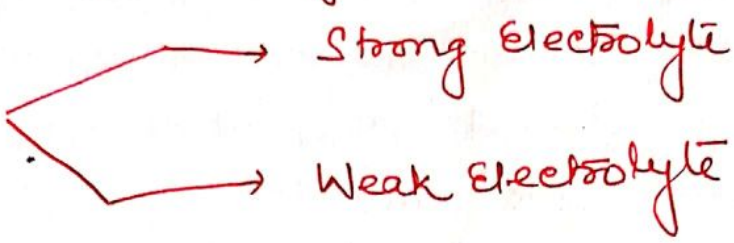
On the basis of ionic interactions Electrolytes are of two types.



① Nature of Electrolyte →

Strong Electrolyte – Ionise completely → conduct electricity up to a Large Extent

Weak Electrolyte – Ionise in small extent → Conduct electricity up to a lesser extent

② Nature of Solvent :

Electrolyte → Ionise more in polar solvents → hence Greater conduction

③ Concentration of solution :

Electrolyte → Higher concentration → Less conduction.

④ Temperature :

Electrolyte → Temperature Increases → dissociation Increases → Conduction Increases.

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Difference Between Metallic Conductors and Electrolytic conductors.

Metallic Conductors	Electrolytic Conductor
1- Flow electricity without decomposition of substance	1. Flow of electricity accomplished by the decomposition of substance
2. Flow of electricity is due to electrons only.	2. Flow of electricity is due to ion. it means flow of matter
3. Electrical conductance decreases with increase in temp. ↓ because. Kernels start vibrating which hinder the flow of electrons	3. Electrical conduction increases with increase in temperature ↓ because Increase in dissociation or Decrease in interionic attraction
4- The resistance offered by metal is also due to vibrating Kernels.	4- The resistance by an electrolyte solution due to factors like. interionic attractions viscosity of solvent.

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Electrical Resistance and conductance.

* Every substance offer resistance to the flow of electricity. upto a small or large extant.
* Ohm's Law provides the exact vallue of resistance.
* If the ~~two~~ ends of a conductor are applied a voltage 'V' and the current flow through it is i then the resistance can be calculated as.

$$R = \frac{V}{i} = \frac{\text{volts}}{\text{ampere}} = \Omega$$

* It is seen that like metallic conductors ~~as~~ electrolytic solutions also obey Ohm's law
* The substance which have a large resistance ~~ha~~, will have less electricity flow.

$$i \propto \frac{1}{R}$$

* The reciprocate of electrical resistance is called the conductance.

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

unit Ω^{-1} (mho).

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* If the volume of solution is V cm³, the specific conductivity of such a solution ~~of electrolyte~~ at this dilution V is written as K_v, Similarly at concentration C it is represented as K_c

Units-

Resistivity 'ρ' = $R\frac{a}{l}$

$= \text{ohm} \times \frac{(cm^2)}{cm}$

$= \text{ohm} \cdot cm$.

or $\Omega \cdot cm$.

$1\ \Omega m = 100\ \Omega cm$

Specific Conductivity 'K' $= \frac{1}{\rho}$

$= \frac{1}{\text{ohm} \cdot cm}$.

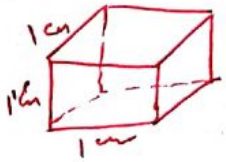
$= \text{ohm}^{-1} cm^{-1}$

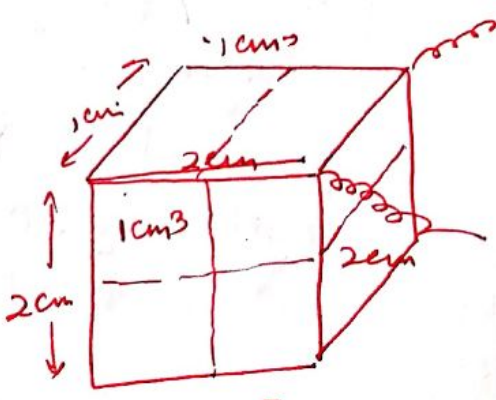
or $S\ cm^{-1}$ $1\ S\ m^{-1}$ SI Unit

S → Simens.

Equivalent Conductivity: Conducting power of all the ions produced by one gram equivalent of an electrolyte in a given solution of volume V is denoted by 'Λ' (lambda)

(when distance between electrodes is 1cm. and area is so large that whole solution is contained between them.)





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(I) Suppose 1 cm^3 of solution containing one gram equivalent of the electrolyte is taken in a vessel. the conductance of this solution will be then its specific conductivity.

If 1 cm^3 of the solution taken contains one gram equivalent of the electrolyte the conductance of solution will be its equivalent conductance.

⇒ Equivalent conductance is equal to specific conductivity when 1 cm^3 of solution containing 1 gram-equivalent of the electrolyte.

(II) Suppose 4 cm^3 of solution containing 1 gram equivalent of electrolyte is taken.

⇒ The conductance of the solution will be still equivalent conductance at this dilution.

⇒ But there are four cubes of volume 1 cm^3. The conductance of each 1 cm^3 of solution is specific conductance

⇒ So the total conductance of the solution (Equivalent conductivity) is four times of specific conductivity.

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If the volume of the solution containing one gram equivalent of the electrolyte is V cm^3.

Equivalent Conductivity = Specific Conductivity × V

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

If the solution has concentration of c gram equivalent per litre then

c gram eq. are present in 1000 cm^3

∴ 1 " " " " " $\frac{1000}{c}$ cm^3.

Hence we can write

$$\Lambda_{eq.} = K_c \times \frac{1000}{c}$$

or

$$\Lambda_{eq.} = K_c \times \frac{1000}{\text{Normality}}$$

M

Kohlrausch's Law

Electrolyte	Λ_m at 298K	Difference.
KCl	149.86	23.41
NaCl	126.45	
KBr	151.92	23.41
NaBr	128.51	
KNO_3	144.96	23.41
$NaNO_3$	121.55	
K-Br	151.92	2.06
KCl	149.86	
NaBr	128.51	2.06
NaCl	126.45	
LiBr	117.09	2.06
LiCl	115.03	

Λ°_m for each Pair of Na & K salts. having common ~~ion~~ anion was same.

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Ostwald's Dilution Law

According to Arrhenius theory of ionization,

$$AB \rightleftharpoons A^+ + B^-$$

Initial concentration	C moles/lit	0	0
	$1-\alpha$	α	α
Concentration at Equilibrium.	$C - C\alpha$	$C\alpha$	$C\alpha$ moles/lite
	$C(1-\alpha)$		

Applying Law of chemical equilibrium

$$K = \frac{[A^+][B^-]}{[AB]}$$

$$K = \frac{C\alpha \cdot C\alpha}{C(1-\alpha)} \qquad \frac{\alpha^2}{1-\alpha}$$

$$K = \frac{C\alpha^2}{C(1-\alpha)} \qquad \text{——— (1)}$$

Equilibrium constant K is known as ionisation constant (K_i) or dissociation constant (K_d).

Unit of K_d = Concentration unit used in eq.

For a weak electrolyte α is very very small so it can be neglected with respect to one.

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So.

$$K_d = C\alpha^2$$

or $$\alpha^2 = \frac{K_d}{C}$$

$$\boxed{\alpha = \sqrt{\frac{K_d}{C}}} \quad \text{——} \quad (2)$$

or $$\boxed{\alpha \propto \frac{1}{\sqrt{C}}}$$

For a weak electrolyte degree of dissociation is inversly proportional to square root of molar concentration.

For concentration terms.

$$C = \frac{\text{no. of moles}}{\text{volume}} = \frac{1}{V} \rightarrow \text{For one mole}$$

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

$$V = \frac{1}{C}.$$

from eqn (1) we can write

$$K_d = \frac{\alpha^2}{(1-\alpha)V}$$

$$\boxed{\alpha = \sqrt{K_d V}}$$

For a weak electrolyte, degree of dissociation is directly proportional to the square root of volume in litres containing one mole of electrolyte

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Debye Huckel-Onsager Equation

$$\Lambda^c_{eq} = \Lambda^0_{eq} - \left[\frac{82.4}{(DT)^{1/2}\eta} + \frac{8.20 \times 10^5}{(DT)^{3/2}} \Lambda^0_{eq}\right]\sqrt{C} \quad \text{—(1)}$$

Λ^c_{eq} = Equivalent conductance at conc. C

Λ^0_{eq} = Equivalent conductance at conc. 0
or
infinite dilution.

D = Dielectric constant of medium.

η = coefficient of viscosity of the medium

T = Temprature of solution in K

C = concentration of solution in moles/litre.

D = constant
η = constant } for a solvent so at constant temprature, the above equation can be written in this form.

$$\Lambda^c_{eq} = \Lambda^0_{eq} - (A + B\Lambda^0_{eq})\sqrt{C}. \quad \text{—(2)}$$

A & B are constants for particular solvent at particular temprature

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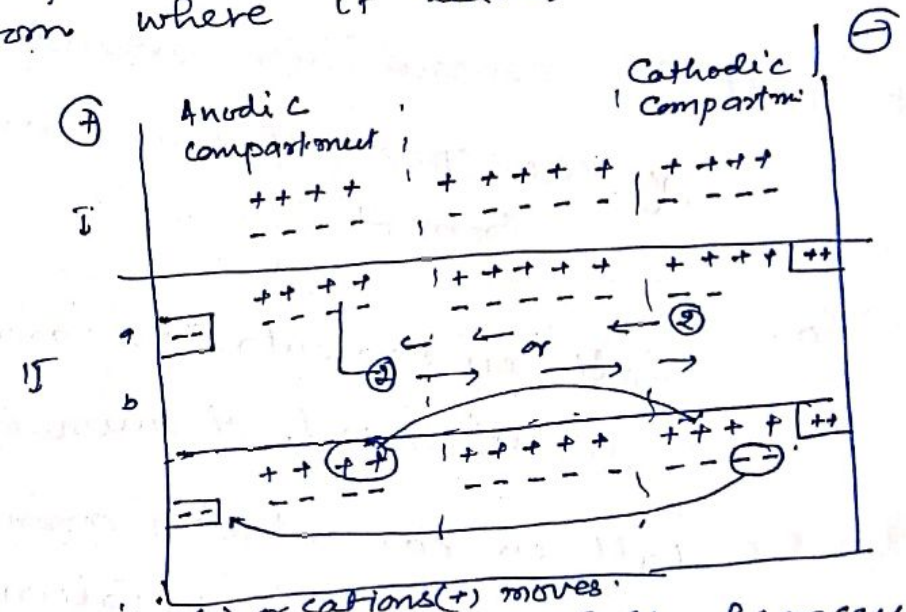
Migration velocity of ions and change in Concentration :- Hittorf's Theoretical method.

* Velocity of an ion is proportional to the fall of concentration of chamber from where it leaves.



when only anions (-) or cations (+) moves.
In case I there will be a fall of concentration by two molecules in corresponding chamber

In case I. when cation (+) and anions (-) both move at the same rate

There is fall in concentration of 2 molecules in each compartment but the no. of ions liberated at both the electrodes is same.

In Case II when cations (+) move at double the speed of anions (-)

In same-time period. we will observe

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that the fall in concentration in anodic and cathodic compartments are 2 : 1.
no. of ions discharge is again the same.

From above we can say

(i)* Fall in concentration around any electrode $\propto$ the speed of ions moving away from it

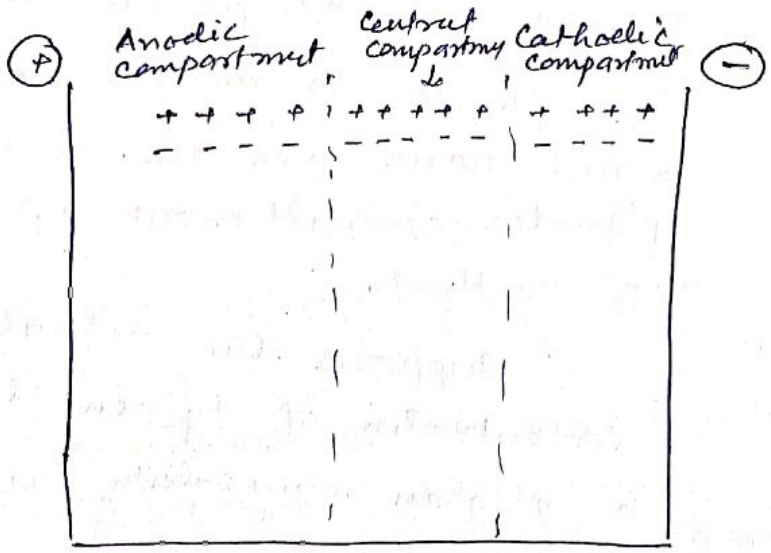
So. fall in concentration around cathode $\propto$ speed of anion (U_a)

& fall in concentration around anode $\propto$ speed of cation (U_c)

ie $$\frac{\text{Fall in concentration around anode}}{\text{Fall in concentration around cathode}} = \frac{\text{Speed of cation}}{\text{Speed of anion}}$$

(ii)* Irrespective of the speed of the ions. the number of ions liberated on both the electrods is equal.

So. instead of no. of ions we can say no. of gram equivalents of ions deposited on the electrods., depending upon the no of faraday's of electricity passed



When the electrods are attackable

~~On~~ The above relationship has been derived on the assumption that the ions do not react with the electrode.

But If the Electrode is attackable like in a silver voltameter containing $AgNO_3$ solution and having silver electrodes

In each this when silver ion reaches at cathodic compartment it dipossited at cathode

But when NO_3^- ion reaches to anodic compartment it reacts with silver and form silver nitrate solution which increases the concentration of Anodic compartment.

But meanwhile Ag^+ ions migrate from anodic chamber to cathodic chamber

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Suppose in x gm equivalent of Ag^+ deposited to cathode it means x gm equivalents would have been the decrease in concentration of anodic compartment if Ag^+ migrates to cathod.

Suppose the actual increase in the concentration of Ag in the anodic compartment is y gram equivalent

Fall in concentration in anodic compartment due to migration of Ag^+ ions = $(x-y)$ gram equiv.

Fall in conc. around cathode = Increase in conc around anode.

= y gram equivalent

Thus the speed ratio may be given by.

$$\frac{\text{Speed of } Ag^+ \text{ ions}}{\text{Speed of } NO_3^- \text{ ions}} = \frac{x-y}{y}$$

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Transport Number

The fraction of total current carried by an ion is called its transport number or Transference number or Hittorf's Number.

Greater the speed of the ion, greater the amount of current it will carry with it and hence greater will be its transport number.

If Speed of anion = u_a

" " cation = u_c

Current carried out by anion $\propto u_a = k u_a$.

" " " " cation $\propto u_c = k u_c$.

Since current is carried out by ions hence:

Total current carried = Current carried by anion + Current carried by cation

$$= k u_a + k u_c$$

$$= k (u_a + u_c)$$

Transport no. of anion.

$$n_a = \frac{k u_a}{k (u_a + u_c)}$$

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$$\boxed{n_a = \frac{u_a}{u_a + u_c}}$$

Transport no. of cation.

$$n_c = \frac{K u_c}{K u_a + K u_c}$$

$$n_c = \frac{K u_c}{K(u_a + u_c)}$$

$$\boxed{n_c = \frac{u_c}{u_a + u_c}}$$

* $$n_a + n_c = \frac{u_a}{u_a + u_c} + \frac{u_c}{u_a + u_c} = \frac{u_a + u_c}{u_a + u_c}$$

$$= 1$$

$$\boxed{n_a + n_c = 1}$$

*
$$n_a = \frac{u_a}{u_a + u_c}$$

on dividing both numerator and denominator

$$n_a = \frac{u_a / u_a}{(u_a + u_c / u_a)} = \frac{1}{1 + \frac{u_c}{u_a}} = \frac{1}{1 + r}$$

$$\boxed{r = \frac{u_c}{u_a}}$$ Speed ratio of cation to anion

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Similarly

$$n_c = \frac{u_c}{u_a + u_c}$$

~~deviding~~ deviding both side ~~by~~ (Numerator & denominator) by u_a.

$$n_c = \frac{u_c/u_a}{(u_a + u_c)/u_a}$$

$$\boxed{n_c = \frac{r}{1+r}}$$

Determination of Transport Numbers

1. Hittorf's Method.

+ Method is based upon the principle

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When Electrodes are non attackable :

After Electrolysis :

Suppose wt. of anodic solution taken out = W_1 gm.

wt of $AgNO_3$ present (By titration) = W_2 gm

$\therefore$ wt. of water present = $(W_1 - W_2)$ gm.

$(W_1 - W_2)$ gm. of water contains. W_2 gm of $AgNO_3$

W_2 gm of $AgNO_3$

will have $\frac{W_2}{170}$ gm. eq. of $AgNO_3$.

will have Ag = x gm eq (suppose).

Hence we can say after electrolysis

$(W_1 - W_2)$ gm of water contain x gm eq of Ag

Before Electrolysis :

Suppose W_3 gm of solution contain W_4 gm of $AgNO_3$

$\therefore$ wt of water = $(W_3 - W_4)$ gm.

Thus $(W_3 - W_4)$ gm of water contain W_4 gm of $AgNO_3$

$\therefore$ $(W_1 - W_2)$ gm of water will contain

$$= \frac{W_4}{(W_3 - W_4)} \times (W_1 - W_2) \text{ gm of } AgNO_3$$

$$= \frac{W_4}{(W_3 - W_4)} \times \frac{(W_1 - W_2)}{170} \text{ gm eq. of } AgNO_3$$

$$= \frac{W_4}{(W_3 - W_4)} \times \frac{W_1 - W_2}{170} \text{ gm. eq. of Ag}$$

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When electrodes are not attacked

$$x < y$$

∴ Fall in the concentration of anodic compartment

$$= (y - x) \text{ gm. eq. of Ag.}$$

Suppose the wt of silver deposited in the silver voltameter

$$= W \text{ gm} = \frac{W}{108} \text{ gm. eq. of Ag}$$

$$= z \text{ gm eq (say/suppose).}$$

∴ Transport No. of Ag^+ ion (n_{Ag^+})

$$= \frac{\text{Fall in concentration around anode in gm eq.}}{\text{Amount of Ag deposited in voltameter in gm eq}}$$

$$= \frac{y - x}{z}$$

Transport No. of NO_3^- ion ($n_{NO_3^-}$) $= 1 - n_{Ag^+}$

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