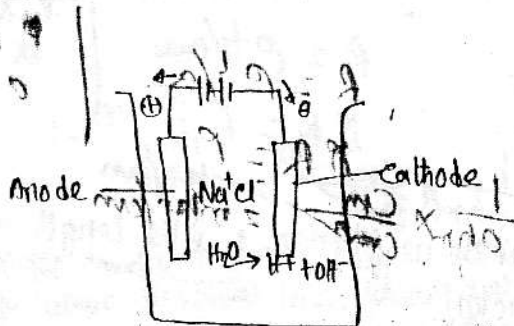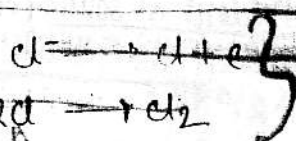# Electrochemistry

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031107
EEE, RUET

 # Electrolyte solution: The solution having free ions either in solution or in molten state are known as electrolyte solution.

Example: salts, mineral acids, or bases etc are electrolyte solution.

Cathodic reaction: $H + e \longrightarrow H$
$2H^+ \longrightarrow H_2$

Anodic reaction: $Cl \longrightarrow Cl + e$
$2Cl \longrightarrow Cl_2$

 # Electrolysis: When an electric current is passed through an electrolyte a chemical change will take place either at anode or cathode with liberation or deposition of mass. This dissociation of electrolyte by influence of current is known as electrolysis.

 # Conductance of electrolyte: From ohm's law

$$I = \frac{V}{R}$$

But $L = \frac{1}{R}$ ohm^{-1}, $L = \frac{1}{R}$ ohm^{-1}
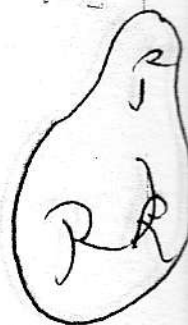
$$L = \frac{1}{R}$$

where, I is the flowing current through a metallic conductor, V is the potential difference at two ends, R is the resistance. L is the conductance of electrolyte. The resistance R of conductor is directly proportional to the length (l) and inversely proportional to the area of its cross section A i.e

$$R \propto \frac{l}{A}$$

[ρ is the resistivity or specific resistance]

$$\Rightarrow \frac{1}{L} = \rho \frac{l}{A}$$

$R \gtrless \frac{1}{R}$ $\therefore R = \frac{1}{L}$

$$\rightarrow L = \frac{1}{\rho} \cdot \frac{A}{\ell}$$

$$R = \rho \frac{L}{A}$$

$$\boxed{\therefore L = K \cdot \frac{A}{\ell}} \quad [K = \frac{1}{\rho} \text{ is the specific conductivity}]$$

 # Specific conductivity: The reciprocal of specific resistance is called specific conductance or specific conductivity.

Specific conductance,

$$K = \frac{1}{\rho} = \frac{1}{R} \times \frac{\ell}{A} \quad \frac{1}{ohm} \times \frac{cm}{cm^2} = mho/cm$$

$$R = \rho^{\ell}/a \quad | \quad \begin{array}{l} \ell = 1\,cm \\ a = 1\,cm^2 \end{array}$$

$$\text{or } R = \rho$$

Where ρ is specific resistance, R is the resistance, ℓ is the length and A is a the area of cross section of the conductor.

 # Equivalent conductance: Equivalent conductance may be defined by the conductance of a volume of solution containing equivalent of solute (electrolyte) dissolved in 1 litre of solvent, the solution being placed between two parallel electrodes 1 cm apart and 1 square cm in cross sectional area.

$$\Lambda = K \times V = \frac{1000 \times K}{C} \quad V = \frac{1000}{C}$$

It is denoted by Λ and is equal to the product of specific conductance K and and the volume V.

$$\Lambda = K V = \frac{1}{R} \times \frac{L}{A} \times V$$

$$C \rightarrow gm\,eq/Lit$$

$$\therefore \Lambda = K V$$

 # Faraday's law of electrolysis:

at the electrode

1st law: The amount of chemical decomposition is proportional to the quantity of the electricity which passes through an electrolytic solution.

If w be mass of substance deposited on electrode by passing Q of coulombs of electricity then, $w \propto Q$ But $Q = I t$

$$\Rightarrow w \propto I t$$

$$\therefore w = Z I t$$

where Z is a constant which is called electrochemical equivalent.

$$\frac{1}{J} = \lambda \quad | \quad \frac{1}{\rho} \& Z \text{ electrochemical equivalent}$$

2nd law: when the same quantity of electricity is passed through different electrolysis, the amount of products obtained at the electrode is directly proportional to their electrochemical equivalents.

If w be the amount of products obtained at the electrode and its electrochemical equivalent is m then,

$$w \propto m$$

$$\therefore \frac{w_1}{m_1} = \frac{w_2}{m_2} = \cdots = \frac{w_n}{m_n} = \text{constant.}$$

 # Molar conductance: the conductance of all ions produced by one mole of an electrolyte when dissolved in a concentration certain volume V_m.

It is denoted by μ. Molar constant $\mu = K V_m$

EEE'03
ELC'99 # what is transport number? Describe moving boundary methode for determining transport number?

Transport number: During electrolysis the current is carried by the anions and the cations. The fraction of the total current carried by the cation or the anion is termed it's transport number.

If V_+ represents the speed of migration of the cation and V_- that of the anion, then the transport number of cation,

$$t_+ = \frac{V_+}{V_+ + V_-} \quad \text{—①}$$

and the transport number of the anion,

$$t_- = \frac{V_-}{V_+ + V_-} \quad \text{—②}$$

$Q \propto \mu_+$

$V = $ velocity of ions at of infinite dillution.

Dividing ① by ② we get, $\dfrac{t_+}{t_-} = \dfrac{V_+}{V_-}$ and

adding ① & ② we get, $t_+ + t_- = 1$

If the speed ratio $\left(\frac{v_+}{v_-}\right)$ be denoted by r, we have

$$r = \frac{t_+}{t_-} = \frac{t_+}{1-t_+} \qquad \left[\because t_+ + t_- = 1 \\ \therefore t_- = 1 - t_+\right]$$

and

$$t_- = \frac{1}{1+r}.$$

Moving boundary method for the determination of a transport number of an ion:

The apparatus used consist of a long vertical tube filled with two electrodes at two ends. The tube is filled with a solution of $CdCl_2$ at the lower end and N/y HCl at the upper end, and in a way that there is a sharp boundary between the two.

The Pt cathode dipped in HCl solution is inserted at the top and the anode is introduced at the bottom.

On passing electric current through the apparatus the H_2 gas is evolved at cathode and H^+ ions move toward the cathode. The H^+ ions are replaced by Cd^{2+} ions and hence the boundary line moves in the upward direction. By noting the length through which the boundary moves and the quantity of electricity passed through the cell, the transport number of H^+ ion can be calculated.
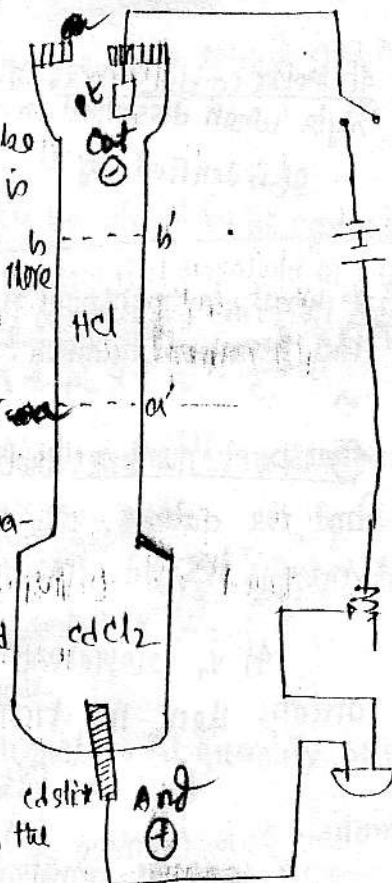
In general, if the transport number of a cation A^+ is to be determined, the electrolyte Ax solution is taken in the upper part of the apparatus and a layer of another electrolyte Bx is introduced in the lower part of the apparatus. The electrolyte Bx is selected so that the velocity of B^+ ion is less than that of A^+ ion. In such a case,

Calculation:

Let,

c = original concentration of A^+ ions

l = distance through which boundary moves

S = area of cross-section of tube

Then the number of equivalents of A^+ moving upward = $S \times l \times c$

let, # n = the number of faradays current passed

The fraction of current carried by A^+ ions = $n \times t_{A^+}$

Hence, $n \times t_{A^+} = S \times l \times c$

$$\therefore t_{A^+} = \frac{S \times l \times c}{n} \quad \left(\text{where } n = \frac{Q}{F} \quad f = 96,500 \text{ coulombs}, \right.$$

$$\therefore t_{A^+} = \frac{S \times l \times c \times F}{Q} \quad \left. \& Q = \text{the quantity of current passed} \right)$$

EE'00,04# **Kohlrausch's Law:** Kohlrausch's law states that the equivalent conductance of an electrolyte at definite dillution is equal to the sum of the equivalent conductances of the component ions.

mathematically the law may be expressed as :-

$$\lambda_\alpha = \lambda_a + \lambda_c \qquad \Lambda_0 = \lambda \quad \lambda$$

where λ_a is the equivalent conductance of the anion and λ_c that of the cation.

λ_c = conductance at infinite dilution of ions.

we have,

$$t_+ = \frac{u_+}{u_+ + u_-}$$

$$t_- = \frac{u_-}{u_+ + u_-}$$

$\Big\lceil$ t = transport number

u = velocity of ions at infinite dilution

EEE'99 # Application of Kohlrauch's law:

(i) calculation of of equivalent conductance for weak electrolytes.

(ii) Calculation of absolute ionic mobilities.

(iii) calculation of the solubility of sparingly soluble salts.

(iv) calculation of the degree of dissociation or conductance ratio.

E.EE'99 # Quinhydrone electrode: It is a widely used secondary standard electrode. It involves the redox reaction between quinone (Q) and hydroquinone (QH_2).
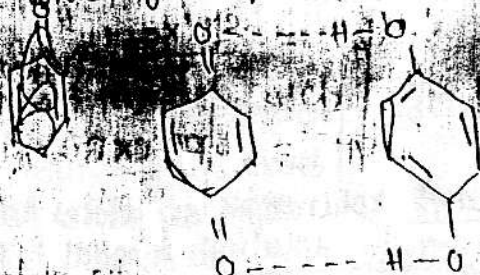

$$\text{Quinone} + 2H^+ + 2e \rightleftharpoons \text{Hydro quinone}$$

∴ simply,

$$Q + 2H^+ + 2e \rightleftharpoons QH_2$$
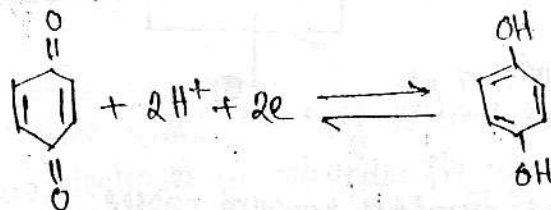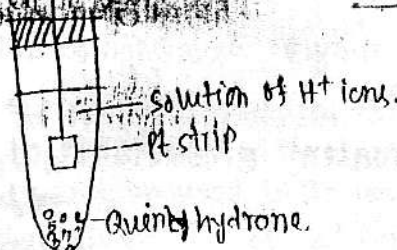
The hydro quinone half-cell consist of a platinum strip impressed in a saturated solution of quinhydrone at a definite H^+ ion concentration. Quinhydrone is a molecular compound which gives equimolar amounts of quinone and hydroquinone in solution.

$$O \cdots H - O$$

The electrode system may be represented as, $Pt \mid QH_2, Q, H^+$

- solution of H^+ ions.
- Pt strip
- Quinhydrone.

EEE'00 # Specific conductance increases but specific conductance decrease in dilution:

As the solution becomes dilute, the number of current carrying particles or ions present per ml of the solution becomes less and less. Since specific conductance is the conductance of the solution it is to be expected that its value will fall with dilution.

The value of equivalent and molar conductance will however increase with dilution as it is the product of k_v and the volume (v) of the solution and on dilution more and more of the electrolyte ionizes.

# Modern theory of electrolytic conduction (independent migration of ions)

Debye-Huckel theory: Debye-Huckel theory is discussed discussed below:-

(i) The strong electrolyte is completely ionized at all dilution.

(ii) Since oppositely charged ions attract each other, it suggests that anions and cations are not uniformly distributed in the solution of an electrolyte but that the cations tend to be found in the vicinity of anions and vice-versa.

(iii) Decrease in equivalent conductivity with increase in concentration is due to fall in mobilities of the ions due to greater inter-ionic effect and vice-versa.
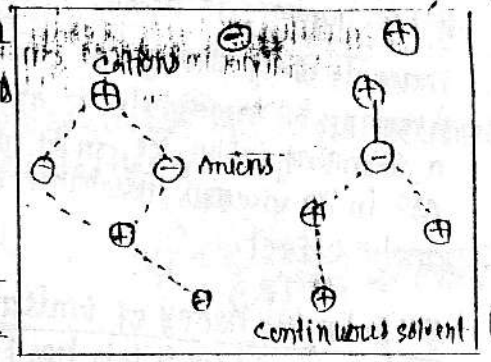
(iv) The ratio of $(\lambda_v/\lambda_\infty)$ does not correctly give the degree of dissociation (α) for strong electrolytes but only the conductivity ratio or conductivity constant f_c.

more and more

cations
anions
continuous solvent

Relaxation effect: Imagine a central negative ion. This is surrounded by a number number of positively charged ions which forms up its ionic atmosphere. This atmosphere is symmetrically situated in the absence of any electrical field. When an electrical field is applied, the negative ions moves towards the anode and the positive ionic atmosphere towards the cathode. And the atmosphere about the central negative ion is destroyed. Where the initially force of attraction exerted by the atmosphere of the central atom ion was uniform, it becomes greater now behind a force which tends

executed

cat and
   ⊖   ℗
cathode
anode
+ → or cation
- → anion
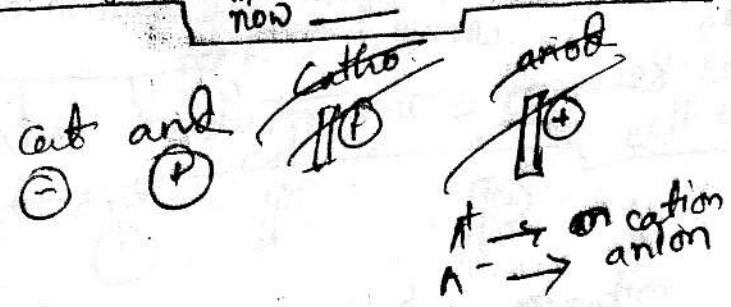
assymetry effect

to drag it backwards and this shows down in movement in the forward direction. This behaviour is known as assymetry effect. It may be said that the negative ion which leaves the ionic atmosphere of positive ions behind to die away, would build a new ionic atmosphere. The formation of it does not takes place at the same rate at which the old one decays latter and its latter lags behind or __takes more__ __time__ known as __relaxation time__. During this interval, there is a __pre-pond-__ __erance__ of positive ions to the left of the central negative ions which is under move and there tends to drag it back. For this reason assymetry effect is called "relaxation effect."
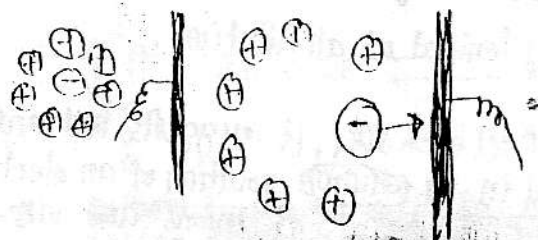

= Electrophoretic effect : The central negative ion moving towards the anode has to make its way through the ionic atmosphere with its associated solvent molecules which is moving to towards in the opposite direction that means towards the cathode. This cases a retarding influence on the movement of the ion the effect of which is equal to the increase in the viscous resistance of the solvent. By analogy, the effect is called electrophoretic effect.

Arrhenius theory of ionisation : when dissolved in water, neutral electrolyte molecules are split up into two types of charged particles, thus—
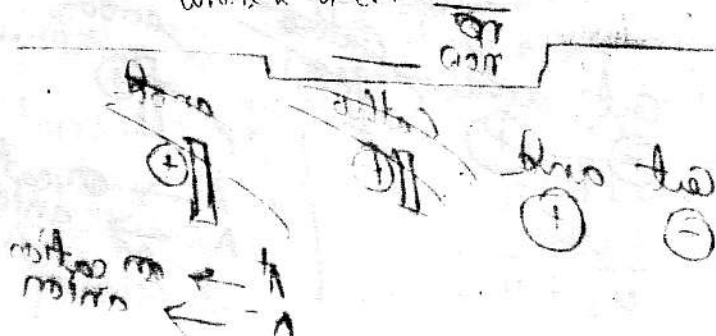
$$A^+ B^- \longrightarrow A^+ + B^-$$

(II) The ions present in solution constantly reunite to form neutral molecules.

consider, $A^+B^- \; AB \rightleftharpoons A^+ + B^-$
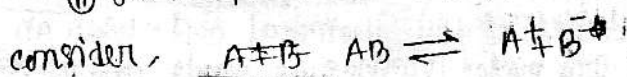
Therefore, according to the law of mass action,

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

where K is called dissociation constant.

(iii) The charged ions are free to move through the solution to the oppositely charged electrode.

(iv) The electrical conductivity of an electrolyte solution depends on the number of ions present in solution.

EEE'00# differences between strong and weak electrolytes:

strong electrolytes	weak electrolytes
1. A strong electrolyte is a substance that gives a solution in which almost all the molecules are ionised. such a solution is called a strong electrolyte solution.	1. A weak electrolyte is a substance that gives a solution in which almost only a small proportion of the solute molecules are ionised, such a solution is called strong electrolyte solution.
2. Have a high value of equivalent conductance.	2. Have a low value of equivalent conductance.
3. HCl, H_2SO_4, HNO_3, $NaOH$, KOH, $NaCl$ etc are strong electrolytes.	3. CH_3COOH, $C_2H_5NH_2$, $HgCl_2$ etc are weak electrolytes.

EEE'00# **cell constant:** The ratio of distance between electrodes and cross-sectional area of electrode is known as cell constant it is represented by x.

$$\therefore x = \frac{\text{distance between electrodes} (l)}{\text{area of electrode} (A)}$$

$$x = \frac{l}{\text{cross section area}}$$

EEE'00# **Determination of cell constant:** the actual value of distance between electrodes and cross-sectional area of electrodes is very difficult to measure. So another method is used as follows:

we know, specific conductance $K = \left(\frac{1}{R}\right) \times \frac{l}{A}$ = observed conductance × cell constant.

$$\therefore \text{cell constant} = \frac{\text{specific conductance}}{\text{observed conductance}}$$

$$\boxed{K = \frac{1}{\rho}}$$

$$\text{Specific conductance} = \frac{\text{observed conductance}}{\text{cell const}}$$

(Electrolytes are electrovalent substances that form ions in solution which conduct an electric current.)

NaCl, copper(II) sulphate and potassium nitrate are examples of electrolytes

$$\lambda_v = \lambda_\alpha - (A + B\lambda_\alpha)\sqrt{C}$$

※ D = Dielectric const η = co-efficient of velocity of the medium respectively at the absolute temp. T

A = electrophoretic effect
B = asymetry effect.

$\omega = \frac{\text{}}{965}$

$$\boxed{K = \frac{1}{R}}$$

specific cond⋅tivity = observed conductivity × cell constant