Conductivity

Electrolyte: – A substance, which dissolve in water and dissociates into ions are called electrolyte.

Ohm's Law: – At constant temperature the potential difference developed on the ends of conductor is proportional to the amount of current passing through it.

$$V = CR \quad \begin{cases} V = \text{Potential difference, Unit is volt} \\ C \text{ or } i = \text{Current, Unit} \rightarrow \text{Ampere} \\ R = \text{Resistance, Unit} \rightarrow \text{Ohm} \end{cases}$$

Resistance: – Resistance R is proportional to length l and inversely proportional to area of cross-section 'a' of conductor.

$$R \propto l$$
$$R \propto \frac{1}{a}$$
$$R \propto \frac{l}{a}$$
$$R = \rho \cdot \frac{l}{a} \quad (\text{where } \rho \text{ is a constant})$$

The constant ρ is known as specific resistance.

Thus specific resistance is defined as the resistance of a specimen 1 metre in length and $1m^2$ cross-section. In other words the resistance of one metre cube of a material is called specific resistance.

Conductance: – The reciprocal of Resistance is called Conductance, $\Lambda \propto \frac{1}{R}$

Any substance that allows an electric current to flow through it self is called conductor.

The conductor which offers a little resistance to the flow of electricity and allow more current to pass through it.

The capacity to conduct electricity is known as conductivity or conductance of a conductor.

$$\text{Conductance } \Lambda \propto \frac{1}{R}$$

Unit of conductance Ohm^{-1} or Mho.
It's SI unit is Siemen (S)

Specific Conductance: –

The reciprocal of specific resistance is called specific conductance.

Specific conductance is the conductivity of a conductor having unit length and unit area of cross-section i.e conductance of a unit cube of a conductor.

For electrolyte solution the conductance of ($1m^3$) one metre cube of the solution is called specific conductance.

Specific conductance is denoted by K (cuppa)

We know that,
$$R \propto l/a$$
$$R = \rho \times \frac{l}{a}$$
$$\text{or } \frac{1}{\rho} = \frac{1}{R} \times \frac{l}{a}$$
$$\text{or } \frac{1}{\text{Specific Resistance}} = \frac{1}{\text{Resistance}} \times \frac{l}{a}$$
$$\text{or Specific Conductance} = \text{Conductance} \times \frac{l}{a}$$

or Specific Conductivity = Conductivity × Cell Constant

[$\because \frac{l}{a}$ = Cell Constant] where; l = length and a = area of cross-section

Unit of Sepecific Conductivity K

$$K = \Pi \times \frac{l}{a}$$

$$K = \text{Ohm}^{-1} \times \frac{\text{metre}}{\text{metre}^2}$$

$$= \text{Ohm}^{-1}\ \text{metre}^{-1}$$

$$\text{In S.I unit} = S\ m^{-1}$$

Equivalent Conductan or Equivalent Conductivity

When $1\ m^3$ of the solution contains 1 gram equivalent of the electrolyte dissolved in it then the conductance of the solution is said to be equivalent conductance or equivalent conductivity and denoted by symbol (λ) Lemda. It is defined as the conductivity of V cubic metre of solution containing one gram equivalent of an electrolyte. So the product of sp. conductivity and the volume of solution V give equivalent conductivity λ.

$$\therefore \lambda = K \cdot V$$

$\because$ 1 gram equivalent is present in 1000 c.metre of the solu

$$\therefore \lambda = 1000 \times K$$

$$\text{i.e. } \lambda = K \times V$$

Where V is the volume of solu in cubic metre containing 1 gr. equivalent of electrolyte.

$$\lambda = S\ m^{-1} \times m^3$$

$$= S\ m^2$$

So, unit of equivalent conductance is Sm^2.

Molecular Conductivity: —

It is defined as the conducting power of all the ions produced by one mole of electrolyte in a given solution. It is denoted by μ.

Let us consider a solution containing 'c' moles of an electrolyte in a given one cubic metre of the solution. The volume of the solution containing 1 mole of the electrolyte would be 1/c cubic metre.

μ = Conductance of $1\ m^3$ of the solution × Volume of the Solution Containing 1 mole of electrolyte

$$= \text{specific conductance} \times \frac{1}{c}$$

$$= K/c = \frac{S\ m^{-1}}{mol\ m^{-3}}$$

$$\text{unit of } \mu = S\ m^2\ mol^{-1}.$$

Cell Constant

We know Resistance R is given by $\left[\begin{array}{l} l = \text{length} \\ a = \text{area of crossection} \end{array}\right]$

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

$$R = \rho \cdot \frac{l}{a}$$

$$\frac{1}{\rho} = \frac{1}{R} \cdot \frac{l}{a}$$

[Where R is Resistance
[ρ is specific Resistance

$$\kappa = \pi \cdot \frac{l}{a}$$

i.e. Specific conductivity = conductivity × Cell Constant.

or Cell constant = $\frac{\text{Specific Conductivity}}{\text{Obs. conductivity}}$

$\because \frac{l}{a}$ = Cell const, so, Unit of Cell constant = m^{-1}

Effect of dilution On Conductivity:-

We know that the conductivity or specific Conductivity (κ) of an electrolytic solution depends on the number of ions present per m^3 of the solⁿ. Through the degree of dissociation increases on dilution but the number of ions per m^3 decreases so specific conductance decrease on dilution.

The equivalent Conductivity is the product of specific Conductivity and volume of the solution Containing one gr. equivalent of the electrolyte.

$$\lambda = \kappa \times V$$

As the decreasing κ value, is more than compensated by the increasing V value, hence λ increases on dilution

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Kohlrausch Law of Independent Migration of ions.

Kohlrausch's Law: - The equivalent conductivity of an electrolyte at infinite dilution (λ_α) is the sum of ionic conductivity of anion and Cation.

i.e. $\lambda_\alpha = \lambda_a + \lambda_c$

The above statement is known as Kohlrausch's law.

Ionic Mobality

The ionic conductance is proportional to the ionic mobality.

Thus, $\lambda_a \propto u_a$

$$\lambda_a = K u_a$$

Similarly, $\lambda_c \propto u_c$

$$\lambda_c = K u_c$$

If u_+ is the ionic mobality of cation and u_- the ionic mobility of anion,

then $t_+ = \dfrac{\text{Current carried by Cation}}{\text{Total Current}} = \dfrac{u_+}{u_+ + u_-}$

Where t_+ is transport number of Cation

or

transport no of anion $t_- = \dfrac{\text{Current Carried by anion}}{\text{Total current}}$

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

The above facts of mobality on ions is based on Faraday's First law of electrolysis, the number of ions discharged at an electrode is proportional to the total quantity of electricity passed through the solution, hence it follows that

Total quantity of electricity that passes through the solution $\propto$ Sum of the mobalities of the ions

The quantity of electricity carried by a particular ion $\propto$ the mobality of that particular ion

Application of Kohlrausch's Law

Some application of Kohlrausch's Law is given below,

(1) Calculation of equivalent conductivity at infinite dilution for weak electrolyte (i.e. calculation of λ_α for weak electrolyte) :—

Kohlrausch's law is applicable in calculating the equivalent conductance at infinite dilution (λ_α) in case of weak electrolytes.

The ionic conductance are proportional to their ionic speed as follows,

$$\lambda_a = K\, u_a \quad \text{—— (1)}$$

$$\lambda_c = K\, u_c \quad \text{—— (2)}$$

Adding eqn (1) and (2), we have

$$\lambda_a + \lambda_c = K\,(u_a + u_c) \quad \text{—— (3)}$$

But from Kohlrausch's law

$$\lambda_\alpha = \lambda_a + \lambda_c \quad \text{—— (4)}$$

Now from Equation (3) and (4) we have.

$$\lambda_\alpha = K\,(u_a + u_c) \quad \text{—— (5)}$$

On dividing equation (1) by equation (5), we get

$$\frac{\lambda_a}{\lambda_\alpha} = \frac{K\,u_a}{K(u_a + u_c)} = n_a \text{ or } t_-$$

$$\therefore \quad \frac{u_a}{u_a + u_c} = n_a = \frac{\lambda_a}{\lambda_\alpha}$$

$$\text{and} \quad \frac{u_c}{u_a + u_c} = n_c = \frac{\lambda_c}{\lambda_\alpha} \quad \text{— (7)}$$

Where n_a and n_c are Transport number's of anion and cation respectively.

Or, Alternate method

To Determination of Equivalent Conductance at Infinite dilution of an electrolyte: —

Weak electrolytes are not Completely dissociated even at high dilution and as such their λ_∞ value Can not be measure by specific conductivity measurement.

For weak electrolytes the value of λ_∞ Can be measured indirectly by applying Kohlrausch's Law.

If we have to Calculate the value of λ_∞ for CH_3COOH (acetic acid a weak acid) then the λ_∞ Values of HCl, $NaCl$ and CH_3COONa, all are strong electrolytes are measured experimentally.

Let $$\lambda_\infty HCl = \lambda H^+ + \lambda Cl^- \quad \text{— (a)}$$

$$\lambda_\infty NaCl = \lambda Na^+ + \lambda Cl^- \quad \text{— (b)}$$

$$\lambda_\infty CH_3COONa = \lambda Na^+ + \lambda CH_3COO^- \quad \text{— (c)}$$

$$\therefore \lambda_\infty CH_3COOH = a + c - b$$

i.e. $$\lambda_\infty CH_3COOH = \lambda_\infty HCl + \lambda_\infty CH_3COONa - \lambda_\infty NaCl$$

$$\therefore \lambda_\infty CH_3COOH = \lambda H^+ + \lambda Cl^- + \lambda Na^+ + \lambda CH_3COO^- - \lambda Na^+ - \lambda Cl^-$$

Box is (To understand only, not to note)

$$\lambda_\infty CH_3COOH = \lambda H^+ + \lambda CH_3COO^-$$

If we experimentally know the values $\lambda_\infty HCl$ and adding the value of $\lambda_\infty CH_3COONa$ and Substracting the value of $\lambda_\infty NaCl$ we get the value of $\lambda_\infty CH_3COOH$.

Similarly, $$\lambda_\infty NH_4OH = \lambda_\infty NH_4Cl + \lambda_\infty NaOH - \lambda_\infty NaCl$$

(2) Calculation of Absolute ionic mobality

(a) It is shown that under the Potential gradient of One volt per cm the ionic Conductivity λa and λc are the the charge on the one g. equivalent (i.e. 96500 Coulombs)

$$\lambda a = U_a \times 96500$$

(b) Direct method for Calculating ionic mobality (By moving boundary Method like transport Number)

If KCl is taken as principal electrolyte and CdCl (Cadmium chloride) is taken as Indicator electrolyte-

If the boundary moves through a distance of x metre in t Seconds when the fall of Potential in the electric field i.e say z volt per metre,

then,

$$\text{The Mobality of the } K^{+} \text{ ion} = \frac{\text{Speed of ion}}{\text{Potential gradient}}$$

$$= \frac{\left(\frac{x}{t}\right) \text{ metre Second}^{-1}}{z\,V\,m^{-1}}$$

$$= \left(\frac{x}{tz}\right) m^{2} s^{-1} V^{-1}$$

Continued...