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Diff :- It is that branch of chemistry in which we study about the spontaneous conversion of chemical energy in to electrical energy and also non-spontaneous electrical conversion of energy in to chemical energy.

Electrochemical charge :-

That (-) charge is called as electrochemical change in which due to chemical reaction. Electrical current flows or due to electrical (Redox reaction are going on) current chemical reaction take place.

Now, electrochemical change is of two types :-

(1). Electrolysis :- That phenomenon is called as electrolysis in which electrical energy non-spontaneous and the device used for electrolysis is called as electrolytic cell.

At cathode = $Na^+ + e \longrightarrow Na$

At anode   = $2Cl^- \longrightarrow Cl_2 + 2e$
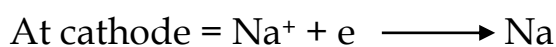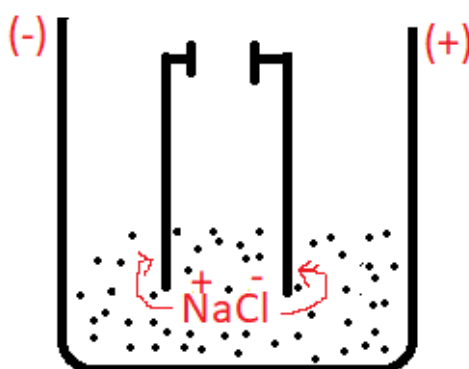
(2). Electrochemical reaction :- That phenomenon is called as electrochemical reaction in which chemical energy is converted in to electrical energy and spontaneous the device used for it is called as electrochemical cell. Electrochemical cell is also called as Galvanic cell or Voltaic cell.

Non – conductor :- Those substances are called as Non-conductor or insulator which do not conduct electricity through them.

Example :- Wood, Rubber, Plastic, Glucose, Sugar etc.

Conductor :- Those substances are called as conductors which conductor electricity through them.

Ex :- All metals, All strong electrolytes (ionic compounds), Acids and Bases.

Again these are two types of conductors.

- Metallic conductors :- Those conductors are called as metallic conductors in which electrical current is flow. Through electron but not through chemical reactions.

Ex :- All metals, Graphite.

(2). Electrolytic conduction :- Those conductors are called as electrolytic conductors in which electrical current flows through ions by chemical reactions.

Ex :- All electrolyte – ionic compounds. NaOH, HCl, H_2SO_4, NaCl etc.
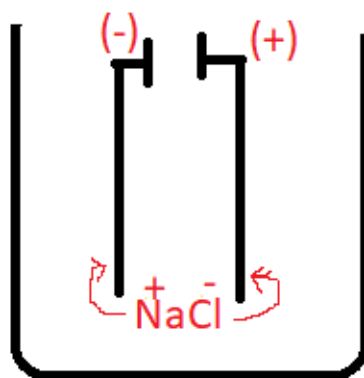
At cathode = $Na^+ + e \longrightarrow Na$

At anode   = $2Cl^- \longrightarrow Cl_2 + 2e$

Again electrolytes are of two types.

- Strong electrolytes :- Those electrolytes are called as strong electrolytes which dissociate about 100% in solution or in fused state.

Ex :- All strong acids and strong bases, salt (NaCl, $CaCl_2$, KCl).

(II). Weak electrolytes :- Those electrolytes are called as weak electrolytes which do not dissociated 100% in to water.

Ex :- All weak acid and weak bases [All organic acids are weak acids H_3PO_4, HCN, $Al(OH)_3$, $Zn(OH)_2$, $Fe(OH)_3$].

Difference Metallic Conductance and Electrolytic Conductance :-	
Metallic Conductance.	Electrolytic Conductance.
(1). It takes place in state.	(1). It takes place in liquid state it never conducts electricity in solid state.
(2). Here conductance takes place through electrons.	(2). Here conductance takes place through ions.
(3). There is no chemical change in metallic conductance.	(3). In electrolytic conductance there is chemical change.
(4). There is not any deposition of materials.	(4). In it there is deposition of material.
(5). Metallic conductance decreases with increase of temperature.	(5). Electrolytic conductance increases with increase of temperature.
(6). Factors on with metallic conductance depend.	(6). Factor on which electrolytic conductance depend.
(a). Number of valence electron per atom.	(a). Upon the nature of the electrolytes.
(b). On the density of metal.	(b). Size of the ion.
	(c). Upon nature of the solvent.
	(d). Upon concentration of the electrolytic.

Current :- Flow of change in unit second through a conductor is called as current.

Thus,

$$I = \frac{Q}{t}$$

Here, I = Current, Q = Charge, t = Time.

Unit :- In SI system the unit of current is ampere.

Definition of ampere :- The flow of 1 coulomb charge per second through a conductor is called as one ampere current.

Potential difference :- The amount of work done to bring a coulomb charge from one point to another point in joule is called as 1 volt potential difference.

$$V = \frac{W \ (joule)}{q \ (coolumb)}$$

Or, $W = V \times q$

Ohm's law :- At constant temperature the current blowing through a conductor is directly proportional to the potential different between two points of the conductor.

$$I \propto v \text{ (at constant temperature)}$$

$$RI = V \quad , \quad R = \frac{v}{i}$$

Here, I = Current, R = Resistance (Proportionality constant).

Resistance :- In SI system the unit of resistance Ohm.

Definition of Ohm :- One Ohm is the resistance produced when one ampere current is ''Resistance is a parameter due to which a conductor ampere the flow of current'' flown between two points through a conductor having potential difference 1 volt.

$$R = \frac{v}{I} \quad \text{Where, V = 1 volt, I = 1 ampere.}$$

$$Ohm = \frac{volt}{1 ampear}$$

Resistance is directly proportional to the length of the conductor and inversely proportional to the cross sectional area of the conductor.

Thus,

$$R \propto l \longrightarrow (1)$$

$$R \propto \frac{l}{A} \longrightarrow (2)$$

From equation (1) and (2)

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

Here, l = length of conductor, A = Cross sectional area of conductor.

Or, $R = \rho \times \frac{l}{A}$ ------------- (3)

Here in equation (3)

ρ = Proportionality constant called specific resistance or resistivity.

Note :- IUPAC recommended the use of resistivity over specific resistance.

We know :-

$$R = \rho \frac{l}{A} \qquad , \quad \therefore \ \rho = \frac{R \times A}{l}$$

If A = m², l = m,

$$= R \times \frac{1m^2}{1m}$$

$$= R \ m \qquad \text{If A = l,} \quad l = 1$$

$$\therefore \ \rho \times R$$

Definition of resistivity :- Resistivity is defined as the resistance of conductor having unit length and unit cross sectional area.

Unit of resistivity :- The unit of resistivity is

$$Ohm \times m \qquad = 100 \ Ohm \times cm$$

Thus, the resistance of 1 cm³ volume or 1 cc volume of a conductor is called as resistivity.

Conductance :- The ease with which an electric current passes through a conductor is called as conductance of the conductor.

The conductance can be defined as below ''The reciprocal of resistance of a conductor is called as conductance of the conductor''.

Thus,

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

Here, C = conductance, R = resistance.

Unit of C :- C = = = Ohm⁻¹ = mho = Siemens (s) in SI.

Specific conductance (or conductivity) :-

IUPAC recommends conductivity over specific conductance conductivity can be defined as below.

''The reciprocal of resistivity is called as conductivity''

It is represented by kappa (K)

Thus,

$$K(cappa) = \frac{1}{\rho}$$

''Thus conductivity is defined as the conductance of 1 cm³ volume of a solution''.

Unit of conductivity :-

$$K = \frac{1}{\rho} \longrightarrow (1)$$

Now we know that.

$$R = \rho \times \frac{l}{a} \quad \text{or,} \quad \rho = \frac{Ra}{l} \longrightarrow (2)$$

After putting the value of from equation (2) to (1) we have.

$$K = \frac{1}{Ra} \times l = \frac{1}{R} \times \frac{l}{a} = C \times \frac{1}{l}$$

$$= \frac{Ohm^2 \, cm^{-1}}{siemens \, cm^{-1}} = \frac{Ohm^{-1}}{cm^{-1}/100} = \frac{100 \, Mhom^{-1}}{SI}$$

Nature of conductivity :-

(1) It depends on nature of the material.

(2) It depends on temperature and pressure of the environment.

Material are divided in to following Y types with respect to conductivity.

- Conductors :- Those materials are called as conductors whose conductivity is very high.

- Insulator :- Those material are called as insulators whose conductivities are very low.

  Ex :- Glass, Wood, Teflon etc.

- Semiconductor :- Those material are called as semiconductor whose conductivity is in between conductors and insulators.

  Ex:- CuO, Si, Ge, etc, As, Sb, Te, At electrical equipment are made up of semiconductors.

- Super conductor :- Those conductors are called as super conductors. Whose resistance is zero.

  Ex:- Metals and Alloy at 0.k to 15k are super conductors ceramic materials and mixed oxide at 150k are super conductors.

Equivalence conductance :-

For the metallic conductance we can take specific conductance or conductivity universally because conductivity of a metal is equal to the conductance of 1cm³ of the conductor. It will never change at particular temperature. But for solution the conductance of 1cm³ volume is not the same at all concentration. So,

Conductivity of the solution changes with change of concentration. That is why the concept of equivalence conductance has been taken.

Definition of equivalent conductance :- The conductance of 1gram equivalent of an electrolyte in solution is called as equivalent conductance of the electrolyte. It is represented by Λ (cape).

Relation between specific conductance and equivalent conductance :-

For this purpose let us take an electrolytic solution of 1gram equivalent having 1ml volume placed between two electrodes having cross sectional area 1cm².

For this solution,

Conductance (C) = Specific conductance = Equivalent conductance

Now, If the above solution is diluted to 1000 ml then

Λ = 1000 K(cappa)

Again if the above solution is diluted to 5000 ml, then

Λ = 5000 K

$\Lambda \longrightarrow$ cape.

Λ (cape), K (cappa).

Thus we can conclude that,

$\Lambda = K \times \phi$

Here, ϕ = Volume of the solution.

Now, Let us suppose.

Ce = Concentration of a solution in gram equivalent per litre.

∴ Ce gram equivalent is present in 1 litre of solution.

∴ 1 gram equivalent is present in $\frac{1}{ce}$ litre.

So,

$\Lambda = K$

$$\boxed{\Lambda = \frac{1000K}{ce}}$$

Unit of equivalent conductance :-

Λ = cm^3 Ohm^{-1} cm^{-1}

$$\boxed{\text{Ohm}^{-1}\text{ cm}^2}$$

Molar conductance (μ) :-

Molar conductance is defined as the conductance of 1 mole of a solute electrolyte.

Relation between molar conductance and specific conductance :-

For this purpose we can take a 1 molar solution having volume 1cm^3 placed between two electrodes having 1cm^2 cross sectional area.

Then,

Conductance (C) = Molar conductance = Specific conductance (K).

Now, if the above solution is diluted to 1000 ml.

M = 1000 K

In general,

M = K

Here, ϕ = Volume in ml.

Again,

If cm = Number of molar of solute present in one litre.

Then,

$\therefore$ cm molar are present in 1 litre.

$\therefore$ 1cm molar are present in $\frac{1}{cm}$ litre.

Now,

$$\boxed{M = \frac{K \times 1000}{cm}}$$

Relation between Λ amd M :-

$$\Lambda = \frac{1000 \times K}{ce}$$

$$M = \frac{1000K}{cm}$$

$$\Lambda = \mu$$

When Ce = Cm.

That is when equivalent weight is equal to the molecular weight of solute electrolyte.

For ex :- Equivalent conductance is equal to the molar conductance for electrolyte.

HCl, NaOH, NaCl.

But for electrolyte having different molecular weight and equivalent weight $\Lambda \neq \mu$.

For ex :- for H_2SO_4

$$\Lambda = \frac{1000\ K}{49}$$

$$\mu = \frac{1000\ K}{98}$$

$$\Lambda = \frac{1000\ K}{M \times V \cdot F}$$

$$\therefore\ \Lambda = \frac{\mu}{V \cdot F}$$

$$\boxed{M = \Lambda \times V \cdot F}$$

Note :- Here DC current cannot be used because it changes the composition of the solution. So, here AC current is used.

Measurement of electrical conductance :-

The measurement of electrical conductance of a solution in fact is to determine the electrical resistance of the solution because conductance is just the reciprocal of resistance. The wheat stone bridge method is generally employed for the purpose. A schematic diagram of the apparatus is shown as below.

AB is a uniform wire and a sliding contact point X-moves over it S represents the source of alternating current, fed in to circuit ''C'' is the conductivity cell containing the solution. Whose resistance is to be measured. R is the resistance box and T is a telephone head to detect the current.
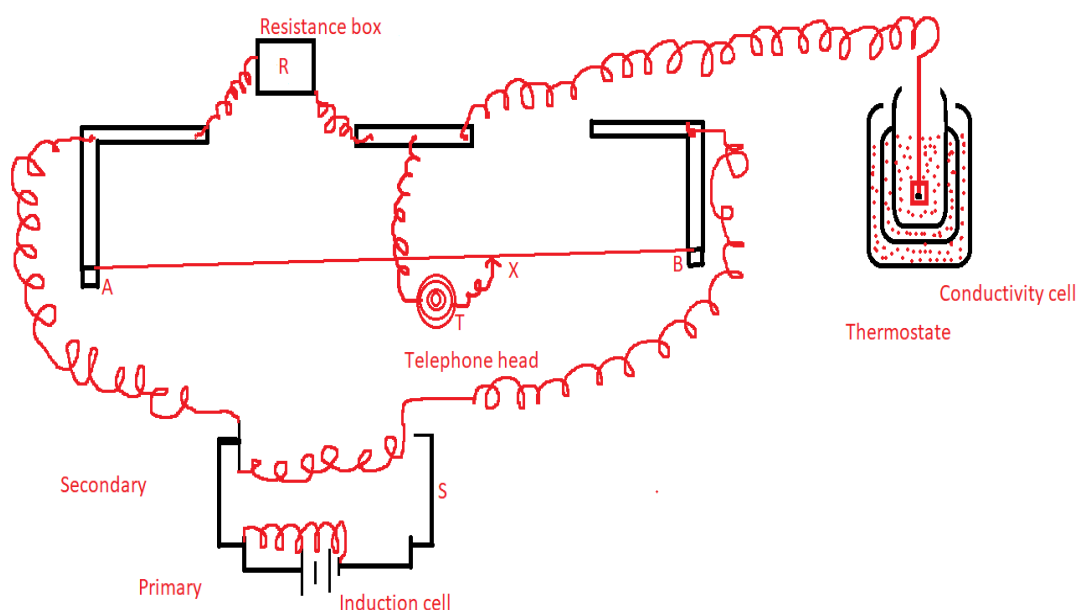
When current is flowing a known resistance ''R'' is introduced through the resistance box. The resistance should be of about the same or clear as that of the solution under examination in the cell. The sliding contact X is then moved along the wire AB until a point of minimum sound in the telephone is detected. At this stage,

$$\frac{\text{Resistance of the solution}}{\text{Resistance (R)}} = \frac{\text{Length} \times B}{\text{Length of} \times A}$$

Since R is known and length XA and XB can be read from the scale fixed below the wire AB, the resistance of the solution can be measured.

Reciprocal of the resistance gives the conductance of the solution.

Cell constant :-

Specific conductance is the conductance of one cm cube of the material. Therefore, the conductance measured as above coil be the specific conductance. Only if the electrons are exactly 1sq cm in area and 1cm a part. This is not usually the case. Thus cell constant can be defined as.

''The cell constant is a factor which when multiplied to conductance of a solution gives the value of specific conductance''.

We know that,

$$K = \frac{l}{a} \times \text{conductance.}$$

Evidently the conductance measured in a cell has to be multiplied by a factor l/a in order to get the specific conductance. It followers therefore, that the factor l/a is the cell constant. 'l' is the distance in cm between the electrodes and 'a' is the cross section area of the electrodes in cm^2.

Instead of determining cell constant from the dimension of the cell. It is more convenient to obtain the value by working first with a solution of known specific conductance at a given temperature.

Conductance	Specific conductance (Ohm^{-1}cm^{-1}).		
	0^{0}c	18^{0}c	25^{0}c
1.0 N	0.06543	0.09820	0.11173
0-1 N	0.007154	0.011192	0.012886
0.01 N	0.0007751	0.0012227	0.0014114

Specific conductance of KCl solution.

Now, for known solution.

K = cell constant conductance.

$$\text{Cell constant} = M = \frac{K}{\text{Conductance}}$$

Thus, specific conductance of a unknown solution can be measured by multiplying cell constant with its conductance. Measured in the experiment.

Because cell constant of the unknown solution will be equal to the cell constant of the known solution.

Variation of equivalent conductance or molar conductance of electrolyte with dilution :-

The conductivity of solution depends upon the number of ions present in it.

That is to say the larger is the number of ions greater is the conductivity and vice - versa. Again we know that larger the dilution of an electrolyte greater is the degree of dissociation the electrolyte.

''The degree of dissociation is defined as the fraction of total electrolyte in the solution. Which exists in the form of ions''.

Thus, degree of dissociation (α).

$\alpha = \dfrac{\text{Total number of ionised or dissociation molecules.}}{\text{Total number of molecule taken.}}$

Generally the value of degree of dissociation is less than one and its maximum value is one. As the dilution of an electrolytic solution increases the value of (α) degree of dissociation also increases and hence the number of ions in the solution also increases.

That is why equivalent conductance or molar conductance of electrolyte increase with dilution. The value of equivalent conductance (Λ) is maximum at infinite dilution.

The infinite dilution is that dilution on which concentration of solution is very-very small.

Infinite dilution on which there is complete ionization of electrolyte and hence $\alpha = 1$.

After infinite dilution there is no effect of dilution on ionization or degree of dissociation or electrical conductivity.

The increase in the equivalent conductance or molar conductance with the increase of in dilution of strong electrolyte (HNO_3, HCl, KCl, etc) is not. So, large as in the case of weak electrolyte (CH_3COOH, NH_4OH, HCN, etc).

Variation of specific conductance with dilution :-

The specific conductance of the solution decreases with dilution. The reason is that although degree of dissociation increases but, the number of ions in one cc of the solution decreases with dilution.

The reason is that equivalent conductance is given by.

$$\Lambda = K \times \phi$$

Here, K = Conductivity.

ϕ = Increases in the value of solution.

Λ = Equivalent conductance.

Since the decrease in the value of K after dilution is much less than the increase in the value of of the solution. Hence the product of the two becomes greater after dilution. Thus equivalent conductance increases with dilution
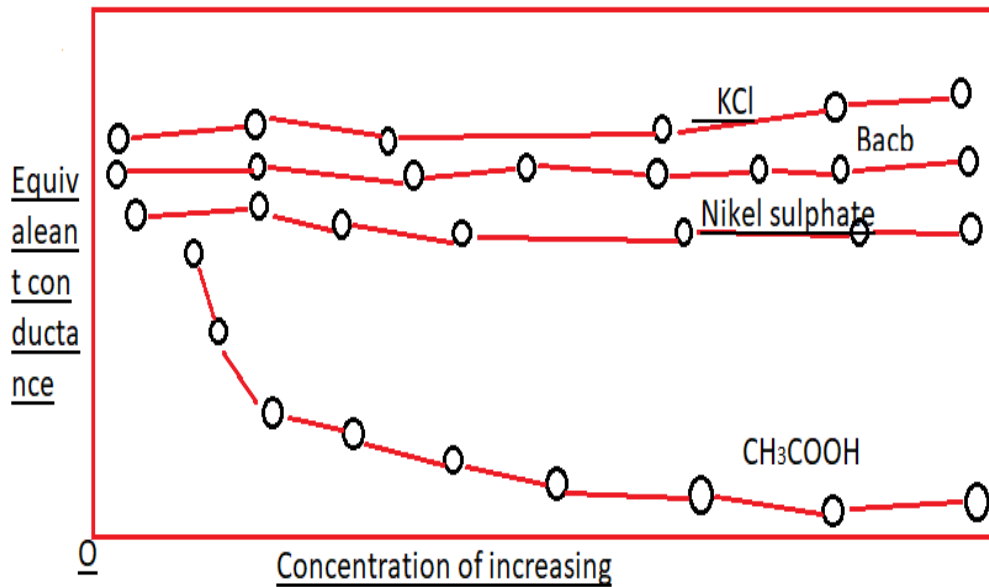
Variation of equivalent conductance with dilution.

Relationship between equivalent conductance and degree of dissociation :-

$$\alpha = \frac{\Lambda c}{\Lambda o}$$

Here, = Degree of dissociation.

Λc = Equivalent conductance at concentration 'C'.

Λo = Equivalent conductance at infinite dilution (O concentration).

Kohlrausch's Law :-

According to this law---

''At infinite dilution, when dissociation is completed each ion makes a definite contribution towards equivalent conductance of the electrolyte irrespective of the nature of other ion with which it is associated and that the value of the equivalent conductance at infinite dilution for any electrolyte is given by the sum of the contributions of the two ions''.

Thus,

$$\Lambda o = \lambda^{o}_{c} + \lambda^{o}_{a}$$

Here, Λo = Equivalent conductance at infinite dilution.

λ^o_c = Contribution of cation in equivalent conductance at infinite dilution.

λ^o_a = Contribution of anion in equivalent conductance of infinite dilution.

Example :-

(With same anion)			(With same cation)		
Electrolyte		Difference	Electrolyte		Difference
NaF	90.1	22.1	KCl	130.0	17.8
KF	112.2		KF	112.2	
KCl	130.0	22.1	NaCl	107.9	17.8
NaCl	107.9		NaF	90.1	

It is quite dear from the above table that the difference in the conductance of any two cations appears to be about the same irrespective of the nature of the anion with which they are associated.

It may be emphasize that ionic conductance is not the same thing as the ionic mobility.

These are proportional to each other.

Thus for infinite dilution.

$\lambda^o_c \propto U^o_c$

Or, $\lambda^o_c = KU^o_c$

And, $\lambda^o_a \propto U^o_a$

Or, $\lambda^o_a = KU^o_a$

Here, U^o_c = Mobility of cation infinite dilution.

U^o_a = Mobility of anion at infinite dilution.

In general, $\lambda^o = k \times v^o$

$$\text{Or, } U^o = \frac{\lambda^o}{K} = \frac{\lambda^o}{96500}$$

Here, K = 96500 coulomb = 1 Faraday.
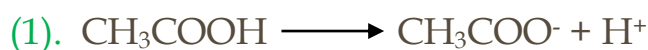
Application of Kohlrausch's Law :-

(I). Calculation of equivalent conductance for weak electrolyte :-

Equivalent conductance of strong electrolyte at infinite dilution one be obtained graphically be electroplating the graph drawn concentration vs equivalent conductance.

But this method is not applicable for weak electrolytes, because they are very feebly dissociated or ionized. The application of Kohlrausch's law enable indirect calculation in such cases.
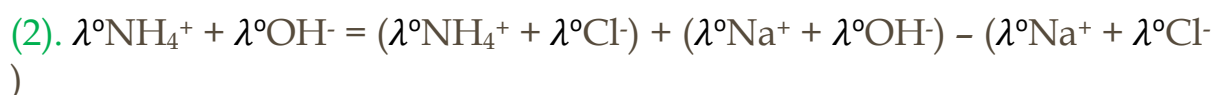
For instance the equivalent conductance of acetic acid at infinite dilution can be obtained from the knowledge of equivalent conductance at infinite dilution of same strong electrolytes that HCl, CH_3COONa, $NaCl$ as given below.

Example :-

(1). $CH_3COOH \longrightarrow CH_3COO^- + H^+$

$\lambda^o CH_3COO^- + \lambda^o H^+ = (\lambda^o H^+ + \lambda^o Cl^-) + (\lambda^o CH_3COO^- + \lambda^o Na^+) - (\lambda^o Na^+ + \lambda^o Cl^-)$

$$\boxed{\Lambda^o\ CH3COOH = \Lambda_o(HCl) + \Lambda^o\ CH_3COONa - \Lambda^o\ (NaCl)}$$

(2). $\lambda^o NH_4^+ + \lambda^o OH^- = (\lambda^o NH_4^+ + \lambda^o Cl^-) + (\lambda^o Na^+ + \lambda^o OH^-) - (\lambda^o Na^+ + \lambda^o Cl^-)$

$$\boxed{\therefore \Lambda^o\ (NH_4OH) = \Lambda^o\ (NH_4Cl) + \Lambda^o\ (NaOH) - \Lambda^o\ (NaCl)}$$

Conductance of electrolytes :-

The power of electrolytes to conduct electric current is termed conductivity or conductance.

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

Specific conductance :-

The conductance of 1cm cube (cc) of a solution of an electrolyte.

The specific conductance is denoted by the symbol K (cappa).

Thus, $K = \frac{1}{P} = \frac{1}{R} \times \frac{l}{A}$

Unit of specific conductance :-

Specific conductance is generally expressed in reciprocal Ohms or mhos or Ohm^{-1}. It unit can be derived as follow.

$K = \frac{1}{A} \times \frac{l}{R} = \frac{1}{Ohm} \times \frac{cm}{cm^2} = Ohm^{-1}cm^{-1}$

The internationally recommended unit for Ohm^{-1} (or mho) is siemens, S.

Equivalent conductance :-

It is defined as the conductance of an electrolyte obtained by dissolving one gram – equivalent of it in V cc of water.

The equivalent conductance is denoted by A. It is equal to the product of the specific conductance, K and the volume V in cc. Containing one gram – equivalent of the electrolyte at the dilution V. Thus,

$$\Lambda = \frac{K \times 1000}{N}$$

Unit of equivalent conductance :-

The unit of equivalent conductance may be deduced as follow.

$$\Lambda = K \times V$$

$$= \frac{1}{R} \times \frac{l}{A} \times V$$

$$= \frac{1}{Ohm} \times \frac{cm}{cm^2} \times \frac{cm^3}{eqvt} = Ohm^{-1}cm^{-1} \ eqvt^{-1}$$

Variation of equivalent conductance with concentration (or dilution) :-

The equivalent conductance of a solution does not very linearly with concentration. The effect of concentration on equivalent conductance can be studied by plotting (Λ) values against the square root of the concentration. It has been found that variation of equivalent conductance with $\sqrt{C}$ depends upon the nature of electrolyte.

For strong electrolyte :-

Strong electrolytes are completely ionized at all concentration (or dilution). The increase in the number of current carrying species. This is in fact, due to the decrease in force of attraction between the ions of opposite charges with the decrease in concentration (or increase in dilution). At higher concentration, the forces of attraction between the opposite ions increase (F q_1q_2/r^2). It affects the speed of the ions. As the solution becomes more and more dilute, the equivalent conductance increases, till it reaches a limitary value. This value is known as equivalent conductance at infinite dilution (zero concentration) and is denoted by A.
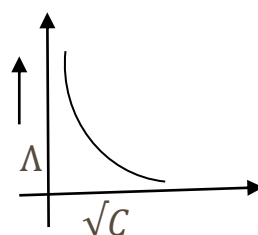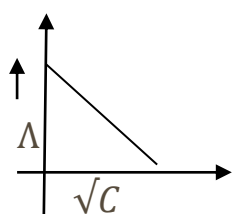
For strong electrolyte   For weak electrolyte

Weak electrolyte have low ionic concentration and hence interionic force are negligible. Ionic speeds are not effected with decrease in concentration (or increase in dilution). The increase in the number of current – carrier species. In other word the degree of ionization (α) increase. Thus, increase in equivalent conductance (Λ) in case of a weak electrolyte is due to the increase in the number of ions.

In case of a weak electrolyte A is the equivalent conductance when ionization is complete. So, the conductance ratio $\Lambda/\Lambda\alpha$ is the degree of ionization. That is,

$$\alpha = \frac{\Lambda}{\Lambda\alpha}$$

Molar concentration :-

The conductance of all ions produced by the mole (1 gram – molecular weight) of an electrolyte when dissolved in a certain volume V cc molar conductance is denoted by it. Its value is obtained by multiplying the specific conductance by the volume in cc containing one mole of the electrolyte.

Molar conductance, $\mu = K \times V$ where V is the volume of the solution in cc containing one mole of electrolyte.

Unit of molar concentration :-

Since, K = $\frac{1}{R} \times \frac{l}{A}$

$$\mu = \frac{1}{R} \times \frac{l}{A} \times V$$

$$= \frac{1}{Ohm} \times \frac{cm}{cm^2} \times \frac{cm^3}{mol} = Ohm^{-1}\, cm^2\, mol^{-1}$$

Calculation of molar conductance.

∴ Molar conductance and the calculated by using the relation :-

$$\mu = \frac{K \times 1000}{M}$$

Where M is the number of molecule of the electrolyte present in 1000cc of solution.

Upon dilution :-

Specific conductance decrease, while equivalent conductance and molar conductance increase.