Electrolytic conduction.

When a voltage is applied to the electrodes dipped into an electrolytic solution, ions of the electrolyte move and, therefore, electric current flows through the electrolytic solution. The power of the electrolytes to conduct electric current is termed conductance or conductivity.

(1) **Ohm's law:**This law states that the current flowing through a conductor is directly proportional to the potential difference across it, i.e.$\boxed{I \propto V}$

Where I is the current strength (In Amperes) and V is the potential difference applied across the conductor (In Volts)

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

WhereR is the constant of proportionality and is known as resistance of the conductor. It is expressed in Ohm's and is represented as Ω. the above equation is known as Ohm's law. Ohm's law may also be stated as:

"The strength of current flowing through a conductor is directly proportional to the potential difference applied across the conductor and inversely proportional to the resistance of the conductor."

(2) **Resistance**:**It measures the obstruction to the flow of current**.The resistance of any conductor is directly proportional to the length (l)and inversely proportional to the area of cross-section (a) so that

$$\boxed{R \propto \frac{l}{a} \quad \text{or} \quad R = \rho \frac{l}{a}}$$

Where ρ (rho) is the constant of proportionality and is called specific resistance or resistivity. The resistance depends upon the nature of the material.

Units: The unit of resistance is ohm (Ω). In terms of SI, base unit is equal to $(kgm^2)/(s^3 A^2)$.

(3) **Resistivity or specific resistance:**We know that resistance R is

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

Now, if $l = 1\,cm, a = 1\,cm^2$ then $R = \rho$

Thus, resistivity is defined as the resistance of a conductor of 1 cm length and having area of cross-section equal to $1\,cm^2$.

Units: The units of resistivity are $\rho = R.\frac{a}{l} = Ohm\,\frac{cm^2}{cm} = Ohm.cm$

Its SI units are Ohm meter $(\Omega\,m)$. but quite often Ohm centimeter $(\Omega\,cm)$ is also used.

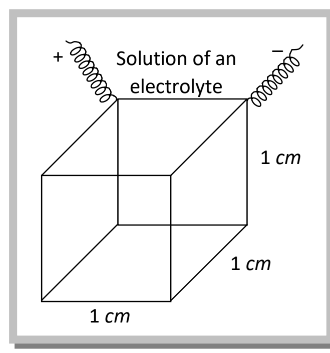
(4) **Conductance:** It is a measure of the ease with which current flows through a conductor. It is an additive property. It is expressed as G. It is reciprocal of the resistance, i.e.,

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

Units: The units of conductance are reciprocal Ohm (ohm^{-1}) or mho. Ohm is also abbreviated as Ω so that Ohm^{-1} may be written as Ω^{-1}.

According to SI system, the units of electrical conductance are Siemens, S (i.e. $1S = 1\,\Omega^{-1}$).

(5) **Conductivity:** The inverse of resistivity is called conductivity (or specific conductance). It is represented by the symbol, κ (Greek kappa). The IUPAC has recommended the use of term conductivity over specific conductance. It may be defined as, the conductance of a solution of 1 cm length and having 1 sq. cm as the area of cross-section. In other words, conductivity is the conductance of one centimeter cube of a solution of an electrolyte. Thus,



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

Units: The units of conductivity are $\kappa = \frac{1}{Ohm.cm} = Ohm^{-1}$ cm^{-1} or $\Omega^{-1}\,cm^{-1}$

In SI units, l is expressed in m area of cross-section in m^2 so that the units of conductivity are $S\,m^{-1}$.

(6) **Molar conductivity or molar conductance:** Molar conductivity is defined as the conducting power of all the ions produced by dissolving one mole of an electrolyte in solution.

It is denoted by Λ (lambda). Molar conductance is related to specific conductance (κ) as,

$$\boxed{\Lambda = \frac{\kappa}{M}}$$

Where, M is the molar concentration. If M is in the units of molarity i.e., moles per liter $(mol\,L^{-1})$, the Λ may be expressed as,

$$\boxed{\Lambda = \frac{\kappa \times 1000}{M}}$$

For the solution containing 1 gm mole of electrolyte placed between two parallel electrodes of 1 sq. cm area of cross-section and one cm apart,

$$\boxed{\text{Conductanc e}(G) = \text{Conductivi ty} = \text{Molar conductivi ty}(\Lambda)}$$

But if solution contains 1 gm mole of the electrolyte therefore, the measured conductance will be the molar conductivity. Thus,

$$\boxed{\text{Molar conductivi ty}(\Lambda) = 100 \times \text{Conductivi ty}}$$

In other words, $\boxed{(\Lambda) = \kappa \times V}$

Where V is the volume of the solution in cm^3 containing one gram mole of the electrolyte.

If M is the concentration of the solution in mole per liter, then

M mole of electrolyte is present in $1000\ cm^3$

1 mole of electrolyte is present in $= \frac{1000}{M} cm^3$ of solution

Thus, $\Lambda = \kappa \times \text{Volume in } cm^3$ containing 1 mole of electrolyte.

or $\boxed{\Lambda = \frac{\kappa \times 1000}{M}}$

Units of Molar Conductance: The units of molar conductance can be derived from the formula,

$$\Lambda = \frac{\kappa \times 1000}{M}$$

The units of κ are Scm^{-1} and units of Λ are, $\Lambda = S\ cm^{-1} \times \frac{cm^3}{mol} = S\ cm^2\ mol^{-1} = S\ cm^2 mol^{-1}$

According to SI system, molar conductance is expressed as $S\ m^2 mol^{-1}$, if concentration is expressed as $mol\ m^{-3}$. This is because

$$mol\ m^{-3} = 1000\left(\frac{L}{m^3}\right) \times molarity\left(\frac{mol}{L}\right)$$

Now, $$\Lambda = \frac{\kappa}{M} = \frac{\kappa(Sm^{-1})}{(1000\ Lm^{-3}) \times (Molarity\, mol\ L^{-1})} = S\ m^2\ mol^{-1}$$

Thus, the units of molar conductivity are $S\ m^2\ mol^{-1}$ (SI) and $S\ cm^2 mol^{-1}$. both types of units are used in literature and are related to each other as

$$1S\ m^2 mol^{-1} = 10^4\ S\ cm^2 mol^{-1} \text{ or } 1S\ cm^2 mol^{-1} = 10^{-4}\ S\ m^2 mol^{-1}$$

(7) **Equivalent conductivity:** It is defined as the conducting power of all the ions produced by dissolving one gram equivalent of an electrolyte in solution.

It is expressed as Λ_e and is related to specific conductance as

$$\boxed{\Lambda_e = \frac{\kappa \times 1000}{C} = \kappa \times \frac{1000}{M}}$$ (M is Molarity of the solution)

Where C is the concentration in gram equivalent per liter (or Normality). This term has earlier been quite frequently used. Now it is replaced by molar conductance. The units of equivalent conductance are $Ohm^{-1}\ cm^2 (gm\ equiv)^{-1}$.

(8) **Experimental measurement of conductance**

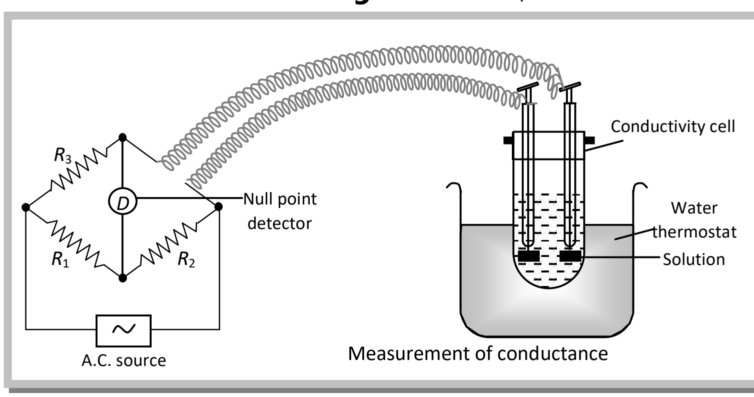
(i) The conductance of a solution is reciprocal of the resistance, therefore, the experimental determination of the conductance of a solution involves the measurement of its resistance.

We know that unknown resistance can be measured on a **Wheatstone bridge**. However, for measuring the resistance of an ionic solution, we face following two main difficulties,

(a) Direct current (DC) cannot be passed because it may change the composition of the solution by electrolysis and polarization.

(b) A solution of unknown resistance cannot be connected to the bridge like a metallic wire or other solid conductor.

First difficulty can be solved by passing an alternating current (AC) from ac source of power.



Measurement of conductance

The second difficulty can be solved by using a specially designed vessels called **conductivity cell**.

(ii) **Calculation of conductivity:** We have seen that conductivity (κ) is reciprocal of resistivity (ρ), i.e.,

$\kappa = \frac{1}{\rho}$ and $\rho = R\frac{a}{l}$ $\therefore$ $\boxed{\kappa = \frac{1}{R}\left(\frac{l}{a}\right) \text{ or } \kappa = G\left(\frac{l}{a}\right)}$

where G is the conductance of the cell, l is the distance of separation of two electrodes having cross section area $a\,cm^2$. The quantity $\left(\frac{l}{a}\right)$ is called cell constant and is expressed in cm^{-1}. Knowing the value of cell constant and conductance of the solution, the specific conductance can be calculated as,

$\kappa = G \times \text{Cell constant}$ i.e. $\boxed{\text{Conductivity} = \text{Conductance} \times \text{Cell constant}}$

(iii) **Determination of cell constant:** The cell constant is generally not calculated from the values of l and a because these are difficult to measure for a given cell. However, it is usually determined accurately by measuring the conductance of a standard solution whose conductivity is known. For this purpose, a standard solution of KCl is used whose conductivity is known at different concentrations and temperatures. The conductivities of different KCl solutions at 298 K are given in table.

Conductivity and molar conductivity of KCl solutions at 298.15 K

Molarity	**Concentration**	**Conductivity**		**Molar conductivity**	
(mol L^{-1})	**(mol m^{-3})**	**S cm^{-1}**	**S m^{-1}**	**S cm^2 mol^{-1}**	**S m^2 mol^{-1}**
1.000	1000	0.1113	11.13	111.3	111.3×10^{-4}
0.100	100.0	0.0129	1.29	129.0	129.0×10^{-4}
0.010	10.00	0.00141	0.141	141.0	141.0×10^{-4}