Electrochemistry - Part 3

Objectives

After going through this lesson, the learners will be able to understand the following:

- Define resistivity, conductivity (κ), molar conductivity (m_0) of ionic solutions.
- Describe the method for measurement of conductivity of electrolytic solutions and calculate the molar conductivity.
- Justify the variation of conductivity and molar conductivity of solutions with change in their concentration and define m_0 (molar conductivity at zero concentration or infinite dilution)

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Introduction

Conductivity and pH are characteristic properties of aqueous solutions. Conductivity determines the ability of a liquid to conduct electric current. Liquids, particularly water, dissolve various substances, and on dissolving many substances, water conducts electric current more easily than before. Therefore, conductivity is a property of a solution that indicates the amount of substance dissolved in the liquid. For example, the liquid we are most familiar with, natural water which is found in sea as well as in the lakes and rivers, if checked for its conductivity will show varying conductivities. Sea water has high conductivity because it contains a large amount of salts dissolved in it. On the other hand, water in rivers, lakes and rain, in their original form contain very small amounts of dissolved substances, shows very low conductivity. Therefore, when water which has a low inherent conductivity is polluted, its conductivity increases. Hence, conductivity is widely used as an indicator of pollution in rain, river and lake water. From the environmental protection view point also, it is very important to monitor rainwater pollution levels. Acid rain is a major water polluting agent of modern times. Therefore, pH and conductivity are important factors to monitor rain water pollution. In practice, some types of pollution cause high conductivity without greatly affecting the pH. The conductivity of tap water (drinking water) and the water in swimming pools, which comes in direct contact with our bodies, needs to be regularly measured. In this module conductivity, the measurement of conductivity of an electrolytic solution and its application will be discussed.

Conductance of Electrolytic Solutions

It is necessary to define a few terms before taking up the subject of conductance of electricity through electrolytic solutions. The electrical resistance is represented by the symbol 'R' and it is measured in ohm (Ω) which in terms of SI base units is equal to (kg m^2)/(S^3A^2). It can be measured with the help of a Wheatstone bridge with which one is familiar with while studying physics. The electrical resistance of any object is directly proportional to its length, *l*, and inversely proportional to its area of cross section, A. That is,

$$R\frac{l}{A} \vee R = \rho\frac{l}{A}$$

The constant of proportionality, ρ (Greek, rho), is called resistivity (specific resistance). Its SI units are ohm meter (Ω m) and quite often its submultiple, ohm centimeter (Ω cm) is also used. IUPAC recommends the use of the term resistivity over specific resistance and hence in the rest of the module the term resistivity is in use. **Physically, the resistivity for a substance is its resistance when it is one meter long and its area of cross section is one m^2.** It can be seen that: 1 Ω m = 100 Ω cm or 1 Ω cm = 0.01 Ω m

The inverse of resistance R is called conductance, G, and we have the relation as follows:

$$G = \frac{1}{R} = \frac{A}{\rho l} = \kappa\frac{A}{l}$$

The SI unit of conductance is Siemen's, represented by the symbol 'S' and is equal to ohm^{-1} (also known as mho) or Ω^{-1}. The inverse of resistivity, called conductivity (specific conductance) is represented by the symbol, κ (Greek, kappa). IUPAC has recommended the use of term conductivity over specific conductance and hence the term conductivity is in use in the rest of the module. The SI unit of conductivity is S m^{-1} but quite often, κ is expressed in S cm^{-1}**. Conductivity of a material in S m^{-1} is its conductance when it is 1 m long and its area of cross section is 1 m^2.** It may be noted that 1 S cm^{-1} = 100 S m^{-1}.

It can be seen from Table 1 that the magnitude of conductivity varies a great deal and depends on the nature of the material. It also depends on the temperature and pressure at which the measurements are made. Materials are classified into conductors, insulators and semiconductors depending on the magnitude of their conductivity. Metals and their alloys have very large conductivity and are known as conductors. Certain non-metals like carbon-black, graphite and some organic polymers are also electronically conducting. Substances like glass, ceramics, etc., having very low conductivity are known as insulators. Substances like silicon, doped silicon and gallium arsenide having conductivity between conductors and insulators are called semiconductors and are important electronic materials. Certain materials called superconductors by definition have zero resistivity or infinite conductivity. Earlier, only metals and their alloys at very low temperatures (0 to 15 K) were known to behave as superconductors, but nowadays a number of ceramic materials and mixed oxides are also known to show superconductivity at temperatures as high as 150 K. Electrical conductance through metals is called metallic or electronic conductance and is due to the movement of electrons.

Table 1: The values of conductivity of some selected materials at 298.15 K

Materials	**Conductivity, S m^{-1}**	**Materials**	**Conductivity, S m^{-1}**
Conductors		*Aqueous solutions*	
Sodium	2.1×10^3	Pure water	3.5×10^{-5}
Copper	5.9×10^3	0.1 M HCl	3.91
Silver	6.2×10^3	0.01 M KCl	0.14
Gold	4.5×10^3	0.01 M NaCl	0.12
Iron	1.0×10^3	0.1 M HAc	0.047
Graphite	1.2×10	0.01 M HAc	0.016
Insulators		*Semiconductor*	
Glass	1.0×10^{-16}	CuO	1.0×10^{-7}
Teflon	1.0×10^{-18}	Si	1.5×10^{-2}
		Ge	2.0

The electronic conductance depends on:

(i) the nature and structure of the metal

(ii) the number of valence electrons per atom

(iii) temperature (it decreases with increase of temperature).

As the electrons enter at one end and go out through the other end, the composition of the metallic conductor remains unchanged. The mechanism of conductance through semiconductors is more complex. It is a known fact that very pure water also has small amounts of hydrogen and hydroxyl ions (~10^{-7} M) which lend it very low conductivity (3.5×10^{-5} S m^{-1}). When electrolytes are dissolved in water, they furnish their own ions in the solution hence its conductivity also increases. The conductance of electricity by ions present in the solutions is called electrolytic or ionic conductance.

The conductivity of electrolytic (ionic) solutions depends on:

(i) the nature of the electrolyte added
(ii) size of the ions produced and their solvation
(iii) the nature of the solvent and its viscosity
(iv) concentration of the electrolyte
(v) temperature (it increases with the increase of temperature).

Passage of direct current through ionic solution over a prolonged period can lead to change in its composition due to electrochemical reactions.

Measurement of the Conductivity of Ionic Solutions

We know that accurate measurement of an unknown resistance can be performed on a Wheatstone bridge. However, for measuring the resistance of an ionic solution we face two problems. Firstly, passing direct current (DC) changes the composition of the solution. Secondly, a solution cannot be connected to the bridge like a metallic wire or other solid conductor. The first difficulty is resolved by using an alternating current (AC) source of power. The second problem is solved by using a specially designed vessel called conductivity cell. It is available in several designs and two simple ones are shown in Fig.1.

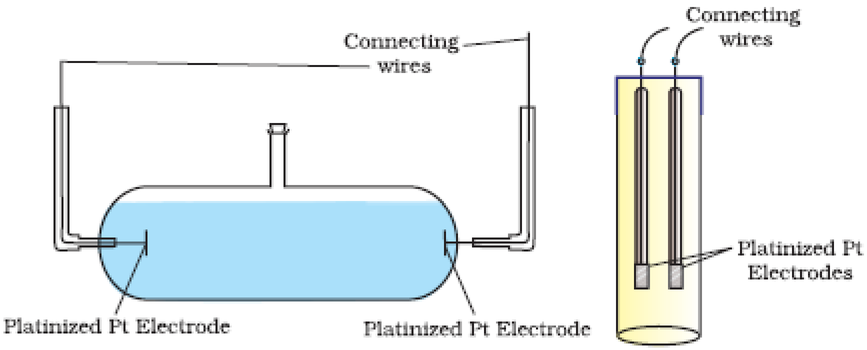

Fig. 1: Two different types of conductivity cells.

Basically it consists of two platinum electrodes coated with platinum black (finely divided metallic Pt is deposited on the electrodes electrochemically). These have an area of cross section equal to 'A' and are separated by distance '*l*'. Therefore, the solution confined between these electrodes is a column of length l and area of cross section A. The resistance of such a column of solution is then given by the equation:

$$R = \rho\frac{l}{A} = \frac{l}{\kappa A}$$

The quantity l/A is called cell constant denoted by the symbol, G*. It depends on the distance between the electrodes and their area of cross-section and has the dimension of length^{-1} and can be calculated if we know l and A. Measurement of l and A is not only inconvenient but also unreliable. The cell constant is usually determined by measuring the resistance of the cell containing a solution whose conductivity is already known. For this purpose, we generally use KCl solutions whose conductivity is known accurately at various concentrations (Table 2) and at different temperatures. The cell constant, G*, is then given by the equation:

$$G = \frac{l}{A} = R$$

Table 2: Conductivity and Molar conductivity of KCl solutions at 298.15 K

Molarity/Concentration		Concentration Conductivity		Molar Conductivity	
mol L^{-1}	mol m^{-3}	S cm^{-1}	S m^{-1}	S cm^2 mol^{-1}	S cm^2 mol^{-1}
1000	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}

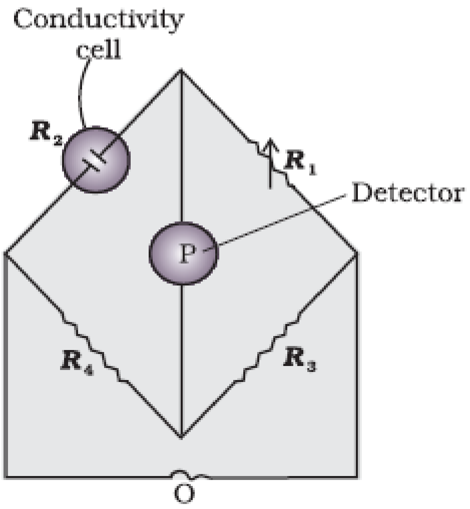

Fig. 2. Arrangement for measurement of resistance of a solution of an electrolyte

Once the cell constant is determined, we can use it for measuring the resistance or conductivity of any solution. The set up for the measurement of the resistance is shown in Fig. 2.

It consists of two resistances R_3 and R_4, a variable resistance R_1 and the conductivity cell having the unknown resistance R_2. The Wheatstone bridge is fed by an oscillator O (a source of a.c. power in the audio frequency range 550 to 5000 cycles per second). P is a suitable detector (a headphone or other electronic device) and the bridge is balanced when no current passes through the detector. Under these conditions:

	Unknown resistance $R_2 = \frac{R_1 R_4}{R_3}$

Cost effective, conductivity meters are available which can directly read the conductance or resistance of the solution in the conductivity cell. Once the cell constant and the resistance of the solution in the cell are determined, the conductivity of the solution is given by the equation:

$$\frac{cell\ constant}{R} = \frac{G}{R}$$

The conductivity of solutions of different electrolytes in the same solvent and at a given temperature differs due to charge and size of the ions in which they dissociate the concentration of ions or ease with which the ions move under a potential gradient. It therefore, becomes necessary to define a physically more meaningful quantity called ***molar conductivity*** denoted by the symbol Λ_m (Greek, lambda). It is related to the conductivity of the solution by the equation:

$$Molar\ Conductivity = \Lambda_m = \frac{\kappa}{C}$$

In the above equation, if κ is expressed in $S\ m^{-1}$ and the concentration, C in $mol\ m^{-3}$ then the units of Λ_m are $S\ m^2\ mol^{-1}$. Therefore,

$$\Lambda_m = \frac{k\left(S\,m^{-1}\right)}{1000\left(L\,m^{-3}\right) \times molarity\left(moles\ L^{-1}\right)}$$

[Here, $1\ mol\ m^{-3} = 1000\ (L\ m^{-3}) \times$ molarity $(mol\ L^{-1})$]

If $S\ cm^{-1}$ units are used for k and $mol\ cm^{-3}$ for concentration then the units of molar conductivity (Λ_m) would be $S\ cm^2\ mol^{-1}$. The molar conductivity can be calculated using the equation:

$$(\Lambda_m S\,cm^2 mol^{-1}) = \frac{k\left(S\,cm^{-1}\right) \times 1000\left(\frac{cm^3}{L}\right)}{molarity\left(\frac{moles}{L}\right)}$$

Both the types of units are in use in various books and are related to each other as below:

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

Problem 1: Resistance of a conductivity cell filled with $0.1\ mol\ L^{-1}$ KCl solution is 100 Ω. If the resistance of the same cell when filled with $0.02\ mol\ L^{-1}$ KCl solution is 520 Ω, calculate the conductivity and molar conductivity of $0.02\ mol\ L^{-1}$ KCl solution. The conductivity of $0.1\ mol\ L^{-1}$ KCl solution is 1.29 S/m.

Solution: The cell constant is given by the equation:

Cell constant = G^* = conductivity × resistance

$= 1.29\ \mathrm{S\ m^{-1}} \times 100\ \Omega$

$= 129\ \mathrm{m^{-1}}$ or $= 1.29\ \mathrm{cm^{-1}}$

Conductivity of 0.02 mol $\mathrm{L^{-1}}$ KCl solution = cell constant/resistance

$$\frac{G}{R} = \frac{129\, m^{-1}}{520\ \Omega} = 0.248 S\, m^{-1}$$

Concentration = 0.02 mol $\mathrm{L^{-1}}$

$= 1000 \times 0.02\ \mathrm{mol\ m^{-3}}$

$= 20\ \mathrm{mol\ m^{-3}}$

Molar conductivity $\Lambda_m = \frac{k}{c}$

$$= \frac{24810^{-3} S\, m^{-1}}{20\, mol\, m^{-3}}$$

$= 124 \times 10^{-4}\ \mathrm{S\ m^2\ mol^{-1}}$

Alternatively, $\kappa = \frac{1.29\ cm^{-1}}{520\ \Omega} = 0.248 \times 10^{-2}\ \mathrm{S\ cm^{-1}}$ and

$\Lambda_m = \kappa \times 1000\ \mathrm{cm^3\ L^{-1}}$ molarity

$= (0.248 \times 10^{-2}\ \mathrm{S\ cm^{-1}} \times 1000\ \mathrm{cm^3\ L^{-1}}) / (0.02\ \mathrm{mol\ L^{-1}})$

$= 124\ \mathrm{S\ cm^2\ mol^{-1}}$

Problem 2: The electrical resistance of a column of 0.05 mol $\mathrm{L^{-1}}$ NaOH solution of diameter 1 cm and length 50 cm is 5.55×10^3 ohm. Calculate its resistivity, conductivity and molar conductivity.

Solution: $A = \pi r^2 = 3.14 \times 0.5^2\ \mathrm{cm^2} = 0.785\ \mathrm{cm^2} = 0.785 \times 10^{-4}\ \mathrm{m^2}$

$l = 50\ \mathrm{cm} = 0.5\ \mathrm{m}$

$R = \frac{l}{A}$ or $\frac{RA}{l} = \frac{5.55 \times 10^3 X\, 0.785\ cm^2}{50\ cm} = 87.135\ \Omega\ \mathrm{cm}$ or

$= 87.135 \times 10^{-2}\ \Omega\ \mathrm{m}$

Conductivity $= \kappa = \frac{1}{\rho} = (\frac{1}{87.135})\ \mathrm{S\ cm^{-1}} = 0.01148\ \mathrm{S\ cm^{-1}}$

Molar conductivity, $\Lambda_m = \frac{k \times 1000}{c}\ \mathrm{cm^3\ L^{-1}}$

$$= \frac{0.01148\ S\ cm^{-1} \times 1000\ cm^3\ L^{-1}}{0.05\ mol\ L^{-1}}$$

$= 229.6\ \mathrm{S\ cm^2\ mol^{-1}}$ or $229.6 \times 10^{-4}\ \mathrm{S\ m^2\ mol^{-1}}$

Variation of Conductivity and Molar Conductivity with Concentration

Both conductivity and molar conductivity change with the concentration of the electrolyte. Conductivity always decreases with decrease in concentration both, for weak and strong electrolytes. This can be explained by the fact that the number of ions per unit volume that carry the current in a solution decreases on dilution. The conductivity of a solution at any given concentration is the conductance of one unit volume of solution kept between two platinum electrodes with unit area of cross section and at a distance of unit length. This is clear from the equation:

$G = \frac{kA}{l} = k$ (both A and l are unity in their appropriate units in m or cm)

Molar conductivity of a solution at a given concentration is the conductance of the volume V of solution containing one mole of electrolyte kept between two electrodes with area of cross section A and distance of unit length. Therefore,

$\Lambda_m = \frac{kA}{l} = \mathrm{k}$ since $l = 1$ and A=V (volume containing 1 mole of electrolyte)

$\Lambda_m = \kappa\, \mathrm{V}$

Molar conductivity increases with decrease in concentration. This is because the total volume, V, of solution containing one mole of electrolyte also increases. It has been found that decrease in κ on dilution of a solution is more than compensated by increase in its volume. Physically, it means that at a given concentration, Λ_m can be defined as the conductance of the electrolytic solution kept between the electrodes of a conductivity cell at unit distance but having an area of cross section large enough to accommodate sufficient volume of solution that contains one mole of the electrolyte. When concentration approaches zero, the molar conductivity is known as **limiting molar conductivity** and is represented by the symbol Λ^0_m. The variation in Λ_m with concentration is different (Fig. 3) for strong and weak electrolytes.

Strong Electrolytes

For strong electrolytes, Λ_m increases slowly with dilution and can be represented by the equation:

$$\Lambda_m = \Lambda_m^0 - Ac^{\frac{1}{2}}$$

It can be seen that if we plot (Fig.3.) Λ_m against $c^{1/2}$, we obtain a straight line with an intercept equal to Λ^0_m and slope equal to '$-A$'. The value of the constant 'A' for a given solvent and temperature depends on the type of electrolyte i.e., the charges on the cation and anion produced on the dissociation of the electrolyte in the solution. Thus, NaCl, $CaCl_2$, $MgSO_4$ are known as 1-1, 2-1 and 2-2 electrolytes respectively. All electrolytes of a particular type have the same value for 'A'.

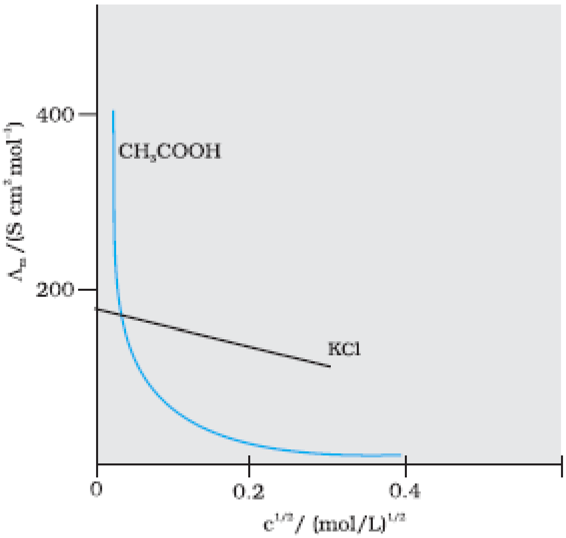

Fig.3. Molar conductivity Vs c1/2 for weak electrolyte (acetic acid) and strong electrolyte (KCl) in aueous solutions.

Problem 3: The molar conductivity of KCl solutions at different concentrations at 298 K is given below:

c/mol L^{-1}	Λ_m / S cm^2 mol^{-1}
0.000198	148.61
0.000309	148.29
0.000521	147.81
0.000989	147.09

Show that a plot between Λ_m and $c^{1/2}$ is a straight line. Determine the values of Λ^0_m and A for KCl.

Solution: Taking the square root of concentration we obtain:

$c^{1/2}$/ (mol L^{-1})$^{1/2}$	Λ_m/ S cm^2 mol^{-1}
0.01407	148.61
0.01758	148.29
0.02283	147.81
0.03145	147.09

A plot of Λ_m (y-axis) and $c^{1/2}$ (x-axis) is shown below (Fig. 4). It can be seen that it is nearly a straight line. From the intercept ($c^{1/2} = 0$), we find that $\Lambda^0_m = 150.0$ S cm^2 mol^{-1} and

$A = -\text{ slope} = 87.46\ \text{S cm}^2\ \text{mol}^{-1}/(\text{mol/L}^{-1})^{1/2}$.

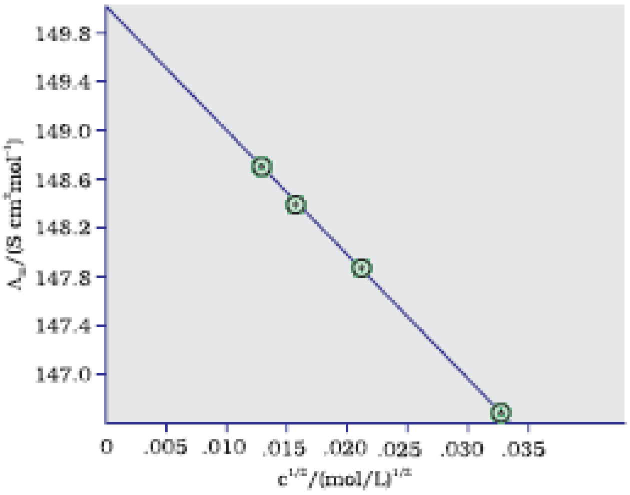

Fig. 4 A plot of Λ_m and $c^{1/2}$

Kohlrausch Law

Kohlrausch examined Λ^0_m values for a number of strong electrolytes and observed certain regularities. He noted that the difference in Λ^0_m of the electrolytes NaX and KX for any X is nearly constant at 298 K. For example:

$\Lambda^0_{m\,(\text{KCl})} - \Lambda^0_{m\,(\text{NaCl})} = \Lambda^0_{m\,(\text{KBr})} - \Lambda^0_{m\,(\text{NaBr})} = \Lambda^0_{m\,(\text{KI})} - \Lambda^0_{m\,(\text{NaI})} = 23.4\ \text{S cm}^2\,\text{mol}^{-1}$

and similarly it was found that:

$\Lambda^0_{m\,(\text{NaBr})} - \Lambda^0_{m\,(\text{NaCl})} = \Lambda^0_{m\,(\text{KBr})} - \Lambda^0_{m\,(\text{KCl})} = 1.8\ \text{S cm}^2\ \text{mol}^{-1}$

On the basis of the above observations he enunciated **Kohlrausch law of independent migration of ions**. The law states that *limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolyte. Thus, if* λ°_{Na+} *and* $\lambda^\circ_{Cl^-}$ *are limiting molar conductivity* of the sodium and chloride ions respectively, then the limiting molar conductivity for sodium chloride is given by the equation:

$\Lambda^0_{m(\text{NaCl})} = \lambda^0_{\ \text{Na+}} + \lambda^0_{\ \text{Cl}-}$

In general, if an electrolyte on dissociation gives v_+ cations and v_- anions then its limiting molar conductivity is given by:

$\Lambda^0_m\ = \nu_+\lambda^0_{\ +} + \nu_-\lambda^0_-$

Here, $\lambda^{\ 0}_+$ and $\lambda^{\ 0}_-$ are the limiting molar conductivities of the cation and anion respectively. The values of λ^0 for some cations and anions at 298 K are given in Table 3.

Table 3: Limiting molar conductivity for some ions in water at 298 K

Ion	λ^0 (S cm^2 mol^{-1})	Ion	λ^0 (S cm^2 mol^{-1})
H^+	349.6	OH^-	199.1
Na^+	50.1	Cl^-	76.3
K^+	73.5	Br^-	78.1
Ca^{2+}	119.0	$CH3COO^-$	40.9
Mg^{2+}	106.0	SO_4^{2-}	160.0

Weak Electrolytes

Weak electrolytes like acetic acid have lower degree of dissociation at higher concentrations and hence for such electrolytes, the change in Λ_m with dilution is due to increase in the degree of dissociation and consequently the number of ions in total volume of solution that contains 1 mol of electrolyte. In such cases Λ_m increases steeply on dilution, especially near lower concentrations. Therefore, Λ^0_m cannot be obtained by extrapolation of Λ_m to zero concentration. At infinite dilution (i.e., concentration c → zero) electrolyte dissociates completely (α =1), but at such low concentration the conductivity of the solution is so low that it cannot be measured accurately. Therefore, Λ^0_m for weak electrolytes is obtained by using Kohlrausch law of independent migration of ions. At any concentration c, if α is the degree of dissociation then it can be approximated to the ratio of molar conductivity Λ_m at the concentration c to limiting molar conductivity, Λ^0_m. Thus we have:

$$\alpha = \frac{\Lambda_m}{\Lambda_m^0}$$

But we know that for a weak electrolyte like acetic acid:

$$K_a = \frac{c\alpha^2}{(1-\alpha)} = \frac{c\Lambda_m^2}{\Lambda_m^{o2}\left(1-\frac{\Lambda_m}{\Lambda_m^0}\right)} = \frac{c\Lambda_m^2}{\Lambda_m^0\left(\Lambda_m^0-\Lambda_m\right)}$$

Application of Kohlrausch Law

Using Kohlrausch law of independent migration of ions, it is possible to calculate Λ^0_m for any electrolyte from the λ^0 values of individual ions. Moreover, for weak electrolytes like acetic acid it is possible to determine the value of its dissociation constant once we know the $\Lambda^0{}_m$ and Λ_m at a given concentration c.

Problem 4: Calculate $\Lambda^0{}_m$ for $CaCl_2$ and $MgSO_4$ from the data given in Table 3.

Solution: We know from Kohlrausch law that

$$\Lambda^0_{m(CaCl_2)} = \lambda_{Ca\ +2\lambda_{Cl}}$$

$$119.0 S\ cm^2 mol^{-1} + 2(76.3) S\ cm^2 mol^{-1}$$

$$= (119.0 + 152.6)\ S\ cm^2\ mol^{-1}$$

$$= 271.6\ S\ cm^2\ mol^{-1}$$

Similarly for $MgSO_4$

$$\Lambda^0_{m(MgSO_4)} = \lambda_{Mg\ +2\lambda^0_{SO_4}}$$

$$=106.0 S\ cm^2 mol^{-1} + 160.0 S\ cm^2 mol^{-1}$$

$$= 266\ S\ cm^2\ mol^{-1}$$

Problem 5: $\Lambda^0{}_m$ for NaCl, HCl and NaAc are 126.4, 425.9 and 91.0 S cm^2 mol^{-1} respectively. Calculate Λ^0 for HAc.

Solution: $\Lambda^0_{m(HAc)} = \lambda_{H\ +\lambda_{Ac\ =\lambda_{H\ +\lambda_{Cl\ +\lambda_{Na\ +\lambda_{Ac\ -\lambda_{Na\ -\lambda_{Cl}}}}}}}}$

$$= \Lambda^0_{m(HCl)} + \Lambda^0_{m(NaAc)} - \Lambda^0_{m(NaCl)}$$

$$= (425.9 + 91.0 - 126.4)\ S\ cm^2\ mol^{-1}$$

$$= 390.5\ S\ cm^2\ mol^{-1}$$

Problem 6: The conductivity of 0.001028 mol L^{-1} acetic acid is 4.95×10^{-5} S cm^{-1}. Calculate its dissociation constant if $\Lambda^0{}_m$ for acetic acid is 390.5 S cm^2 mol^{-1}.

Solution: $\Lambda_m = \frac{}{c} = \frac{4.95X10^{-5} S\ cm^{-1}}{0.001028\ mol\ L^{-1}} \times \frac{1000\ cm^3}{L} = 48.15\ Scm^2 mol^{-1}$

$$\alpha = \frac{\Lambda_m}{\Lambda^{\circ}_m} = \frac{48.15 S\ cm^2 mol^{-1}}{390.5\ S\ cm^2 mol^{-1}} = 0.1233$$

$$K_a = \frac{c\alpha^2}{(1-\alpha)} = \frac{0.001028\ mol\ L^{-1} \times (0.1233)^2}{1-0.1233} = 1.78 \times 10^{-5} mol\ L^{-1}$$

Summary

The conductivity, κ, of an electrolytic solution depends on the concentration of the electrolyte, nature of solvent and temperature. **Molar conductivity**, Λ_m, is defined by = κ /c where c is the concentration. Conductivity decreases but molar conductivity increases with decrease in concentration. It increases slowly with decrease in concentration for strong electrolytes while the increase is very steep for weak electrolytes in very dilute solutions. Kohlrausch found that molar conductivity at infinite dilution, for an electrolyte, is the sum of the contribution of the molar conductivity of the ions in which it dissociates. It is known as the law **of independent migration of ions** and has many applications. Ions conduct electricity through the solution but oxidation and reduction of the ions take place at the electrodes in an electrochemical cell.