UNIT 4 CONDUCTOMETRY

Structure

4.1 INTRODUCTION

So far we have discussed potentiometric methods. In these methods we measure the emf of a galvanic cell which is operating near zero current. Because, this emf is a function of the ionic activities within the cell, it can be used to measure ionic concentrations in titration, water samples, biological samples and other industrial and environmental samples. We have also seen that both potentiometry and pH metry are most widely used electroanalytical technique. In this unit you will study another electroanalytical technique called the conductometry, which is one of the oldest and in many ways simplest among the other electroanalytical techniques. This technique is based on the measurement of electrolytic conductance.

An application of electrical potential across the solution of an electrolyte involves the transfer of mass and charge from one part of the solution to the other. Such transport processes enable an insight into the structure of such solution. A transport property of great significance, which can be easily measured, is the conductance. Since an electrolytic solution consists of ions and the nature of interaction existing in the medium could be better understood in terms of the conducting power of these ions, it is more convenient to speak of conductance rather than resistance. The conducting ability of electrolytic solutions provides a direct prove of the existence of ions in solutions. The experimental determinations of the conducting properties of electrolytic solutions are very important as they can be used to study quantitatively the behaviour of ions in solutions. They can also be used to determine the values of many physical quantities such as solubilities and solubility product of sparingly soluble salts, ionic product of self ionizing solvents, hydrolysis constant of salts, dissociation constants of weak acids and bases and to form the basis for conductometric titration methods.

Objectives

After studying this unit, you will be able to:

- define electrolytic conduction,
- distinguish between the electrolytes and non-electrolytes solutions; and strong and weak electrolytes,
- explain conductance of solutions, molar and equivalent conductivities,
- describe different factors effecting conductance, and

- discuss the method of operation of a coductometer to measurement of conductance.

4.2 ELECTROLYTIC CONDUCTANCE

An electrolytic solution contains free ions in addition to other kinetically identifiable species. When electrical potential is applied across the solution the macroscopic observations are, the flow of current through the solution and the chemical changes generally resulting in the liberation or dissolution of the electrode material at the points where the current enters or leaves the solution. This phenomenon of decomposition of the solutions by electrical current is termed as electrolysis.

Electrolytic conduction, in which charges carried by ions, will not occur unless the ions of the electrolyte are free to move. Hence, electrolytic conduction is exhibited principally by molten salts and by aqueous solutions of electrolytes. The principle of electrolytic conduction is best illustrated by reference to an electrolytic cell such as that shown in
Fig. 4.1 for the electrolysis of molten NaCl between inert electrodes. The entire assembly except that of the external battery of Fig.4.1 is known as the cell.

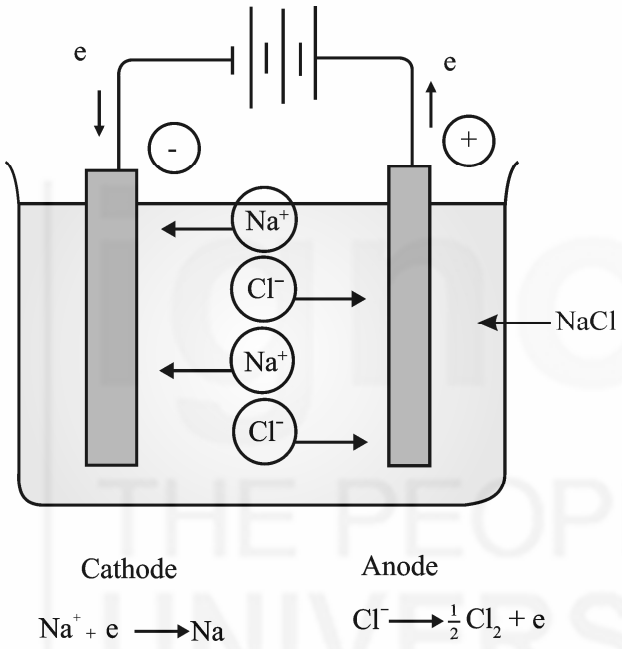


Fig. 4.1: Electrolysis of molten sodium chloride

The electrons are received from the negative end of the external battery by the negative electrode of the cell. These are used up in the reduction reaction at this electrode. The numbers of electrons received at the negative electrode are given back to the positive end of the external battery from the positive electrode of the cell where electrons are released as the result of oxidation reaction. Within the cell, current is carried by the movement of ions; cations moves towards negative electrode called the cathode and anions towards the positive electrode called anode. This movement of ions give rise to what is known as the electrolytic conduction. The latter, thus, depends on the mobility of ions and anything that inhibits the motion of ions causes resistance to current flow. Factors that influence the electrical conductivity of solutions of electrolytes include interionic attraction, solvation of ions, and viscosity of solvents. These factors depend on the attraction i.e. solute-solute, solute-solvent and solvent-solvent respectively. The average kinetic energy of the solute ions increases as the

temperature is raised and, therefore, the resistance of electrolytic conductors generally decreases, that is, conduction increases as the temperature is raised.

Electrolytes and non-electrolytes

The ionic compounds, which furnish ions in solution and conduct electric current, are electrolytes e.g. NaCl, KCl, etc. There are covalent compounds, which also conduct electric current in solutions. These include HCl, CH_3COOH, etc. All other substances which do not produce ions in solutions are called non-electrolytes, e.g. cane sugar, benzene, carbon tetrachloride, etc.

Sometimes electrolytes are also called as true electrolytes and potential electrolytes. In true electrolytes the cations and anions do exist even in the molten states, e.g. NaCl, KCl. They are true electrolytes because they exist as $Na^+ Cl^-$ and $K^+ Cl^-$ in their normal states and in the molten states. Also when they are dissolved in water they ionise and conduct current.

$$Na^+ Cl^- \longrightarrow Na^+(aqueous) + Cl^- (aqueous)$$

The potential electrolytes do not conduct electricity in the pure normal state rather they conduct electricity when dissolved in water, e.g. HCl, CH_3COOH and NH_3.

Strong and weak electrolytes

Electrolytes can be classified as strong or weak. This has nothing to do with their concentration but related to their extent of ionisation.

Strong electrolytes: The substances, which are completely ionized in aqueous solutions are called strong electrolytes, e.g. NaCl, NH_4Cl, KNO_3, HCl, HBr, etc.

Weak electrolytes: The substances which ionise only to a certain extent are called weak electrolytes, e.g. CH_3COOH, HCN, etc.

The terms strong and weak are relative. The behaviour of electrolytes also depends on the nature of solvents, e.g. NaCl behaves as strong electrolyte whereas acetic acid as a weak electrolyte in water. On the other hand, when dissolved in ammonia both NaCl and acetic acid show comparable behaviour towards electricity.

Conductance of solutions

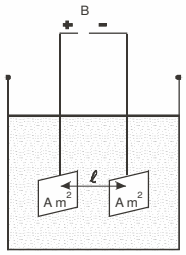
The ease of flow of electric current through a body is called its conductance. In metallic conductors it is caused by the movement of electrons, while in electrolytic solutions it is caused by ions of electrolyte. The electrolytic **conductance**, G, of a medium is equal to the reciprocal of its electrical resistance R in ohms:

$$G = \frac{1}{R} \qquad \ldots (4.1)$$

Ohm's Law states that the current I (amperes) flowing in a conductor is directly proportional to the applied electromotive force E (volts) and inversely proportional to the resistance, R (ohms) of the conductor:

$$I = \frac{E}{R} \quad \text{or} \quad I = EG \qquad \ldots (4.2)$$

Since a solution is a three-dimensional conductor, the exact resistance will depend on the spacing (l) and area (A) of the electrodes. The resistance of a solution in such situation is directly proportional to the distance between the electrodes and inversely proportional to the electrode surface area.



Consider the electrolytic cell shown above, its two electrodes are having a cross-sectional area of A m^2 and separated by l m. The resistance (R) of the electrolyte solution present between the two electrodes is:

$$R \propto l$$

$$R \propto \frac{1}{\mathrm{A}}$$

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

$$R = \rho \frac{l}{A} \qquad \ldots (4.3)$$

where ρ (rho) is proportionality constant is called resistivity (formerly called specific resistance). It is a characteristic property of the material and it is the resistance offered by a conductor of unit length and unit area of cross section.

$$\rho = R \frac{A}{l} \qquad \ldots (4.4)$$

In SI units, l and A are measured in meters and square meters respectively, and the resistance is expressed in ohm, Ω (omega). Therefore, the unit of ρ is ohm meters (Ω m). Formerly, resistivity measurements were made in terms of a centimetre cube of a substance, giving ρ the units Ω cm.

Substitute the value of R from Eq. (4.4) in Eq. (4.1). The expression for the conductance, G is

$$G = \frac{1}{R} = \frac{1}{\rho\,(A/l)} = \kappa \frac{A}{l} \qquad \ldots (4.5)$$

where K (kappa) is reciprocal of specific resistance called as **specific conductance** or **conductivity**. It is measured in Ω^{-1} m^{-1}. This quantity may be considered to be the conductance of a cubic material of edge length unity. However, in SI system, the unit for conductance is 'Siemens' and, given the symbol 'S'. Hence, the unit for conductivity will be S m^{-1} ($1S = 1\Omega^{-1}$) or S cm^{-1}. It may be remembered that S m^{-1} = 1/100 S cm^{-1}. However conductivity is customarily reported in smaller units as milli Siemens per meter (mS m^{-1}) and micro Siemens per cm (μS cm^{-1}).

Cell constant: For a given cell, l and A are constant, and the quantity (l/A) is called the cell constant (k).

$$K_{\text{cell}} = \frac{l}{A}$$

Substitute this value in Eq. (4.5)

$$\kappa = G K_{cell} \quad \ldots (4.6)$$

Conductivity = observed conductance × cell constant

To obtain the value of the cell constant, it is not necessary to determine l and A directly. Instead, it is measured by a solution of known conductivity. Potassium chloride solutions are invariably used for this purpose, since their conductances have been measured with sufficient accuracy in cells of known dimensions. A given solution of potassium chloride of conductivity κ' is placed in the cell and its resistance R' is measured. The cell constant is then equal to $\kappa' R'$. Therefore,

$$K_{cell} = \kappa' R'$$

Cell constant = conductivity KCl solution × measured resistance

Conductance is an additive property, e.g. in an aqueous solution containing several electrolytes, the total conductance is

$$G(\text{total}) = \Sigma G_i + G(\text{water}) \quad \ldots (4.7)$$

where the summation is to be carried over all the electrolytes present in the solution and G (water) is the conductance of water, which is utilized for making the solution. G (water) is often negligible in comparison to ΣG_i as repeatedly distilled water (known as conductivity water) of very low conductance is employed for making the solutions.

SAQ 1

The resistance of a conductivity cell containing 0.01 mol dm^{-3} KCl is 150 Ω. The same conductivity cell gives the resistance of 0.01 mol dm^{-3} HCl 51.4 Ω. The conductivity of the KCl solution is 1.41×10^{-3} Ω^{-1} cm^{-1}. Calculate the following values:

i) Cell constant, and

ii) Conductivity of the HCl solution.

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4.2.1 Molar Conductivity

In order to compare quantitatively the conductivities of electrolytes, a quantity called **molar conductivity** is frequently used. The molar conductivity, Λ_m (capital lambda) is the conductivity per unit molar concentration of a dissolved electrolyte. It is related to conductivity, κ by the relation:

$$\Lambda_m = \frac{\kappa}{c} \quad \ldots (4.8)$$

where c is the concentration in mol m^{-3}. The molar conductivity is usually expressed in S m^2 mol^{-1} or S cm^2 mol^{-1}. It may be remembered that S m^2 mol^{-1} = 10,000 s cm^2 mol^{-1}.

It is to be remembered that c in Eq. 4.8 is to be expressed in mol m^{-3} unit. If the concentration is given in terms of Molarity (mol dm^{-3}), then the following conversion is to be carried out

$$c\ (\text{mol m}^{-3}) = \text{Molarity} \times 1000 \quad \ldots (4.9)$$

Earlier equivalent conductivity (Λ_{eq}), which is given by the following expression, was in use

$$\Lambda_{eq} = \frac{1000 \times \kappa}{c} \quad \ldots (4.10)$$

where c is the concentration expressed in terms of normality of the solution. Unit of Λ_{eq} is $\Omega^{-1}\,cm^2\,eq^{-1}$. However, IUPAC recommends the use of molar conductivity only.

SAQ 2

Write the units of the following:

a) Conductivity

b) Equivalent conductivity

c) Cell constant

d) Molar conductivity

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SAQ 3

From the following data, calculate the molar conductivity of KCl in aqueous solution:
Conductivity of 5.0×10^{-4} mol dm^{-3} KCl = 7.44×10^{-3} S m^{-1}
Conductivity of the water = 0.06×10^{-3} S m^{-1}

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4.2.2 Variation of Conductance with Concentration

The conductivity of an ionic solution increases with increasing concentration. For strong electrolytes, the increase in conductivity with increase of concentration is sharp. However, for weak electrolytes, the increase in conductivity is more gradual. In both cases the increase in the conductivity with concentration is due to an increase in the number of ions per unit volume of the solution. For strong electrolytes, which are completely ionised, the increase in conductivity is almost proportional to the concentration. In weak electrolytes, however, the increase in specific conductance is not large due to the low ionisation of the electrolytes, and consequently the conductivity does not go up so rapidly as in the case of strong electrolytes. Table 4.1 shows the variation of molar conductivity of a number of electrolytes at various concentrations at 298 K.

Table 4.1: Molar conductivity ($10^4 \times$ S m^2 mol^{-1}) of electrolytes in aqueous solutions at 298 K

c/mol dm^{-3}	KCl	NaCl	HCl	$AgNO_3$	CH_3COOH	CH_3COONa
1.0	111.9	89.9	332.8	-	-	49.1
0.1	129.0	106.7	391.3	109.1	5.2	72.8
0.05	133.4	111.1	399.1	115.7	7.4	76.9
0.01	141.3	118.5	412.0	124.8	16.3	83.8
0.005	143.5	120.6	415.8	127.2	22.9	85.7
0.001	146.9	123.7	421.4	130.5	49.2	88.5
0.0005	147.8	124.5	422.7	131.4	67.7	89.2

It is observed that in contrast to the conductivity, the molar conductivity, Λ_m invariably increases with decreasing concentration for both weak and strong electrolytes. If we plot the molar conductivities of a large number of electrolytes against the square root of the concentrations we find that these fall into two distinct categories. In the case of strong electrolytes (for example KCl, NaCl or acids such as HCl, H_2SO_4, etc), there is a small increase in molar conductivities with the decrease in concentration. Since these electrolytes dissociate almost completely even in concentrated solution, the number of ions do not change much with concentration. The conductivity should not vary much since it is directly related to the number of ions present in solution. The minor changes observed are due to interionic interactions. In the case of weak electrolytes (for example CH_3COOH, ammonia, organic fatty acids, etc), the ionization will increase with dilution, and hence, the molar conductivity increases with dilution. Thus the conductivity is directly proportional to the degree of dissociation of a weak electrolyte.These above results are depicted in Fig.4.2 in which the molar conductivity, Λ_m, of two electrolytes (KCl and acetic acid) at a constant temperature is plotted against $\sqrt{c}$. It may be seen from the figure that two different types of behaviours are exhibited by these electrolytes. The strong electrolyte, KCl shows a linear plot (almost straight lines). On the other hand, the weak electrolyte, CH_3COOH seems to approach the dilute solution limit almost tangentially. It is, however, impossible to draw a sharp line of demarcation between the two categories as many substances are known to exhibit intermediate behaviour, e.g., nickel sulphate. Such electrolytes are sometimes called moderately strong electrolytes.

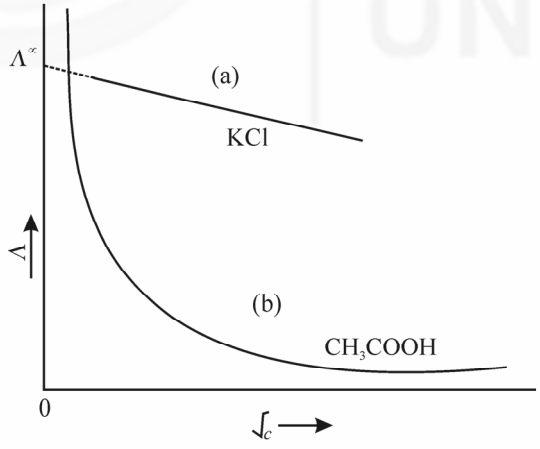


Fig. 4.2: Variation of molar conductivity on dilution (a) for aqueous solution of potassium chloride (strong electrolyte) (b) acetic acid (weak electrolyte)

The conductance of a solution depends on the number of ions and the speed with which the ions move in solution. In case of strong electrolytes, the number of ions is the same at all dilutions (since strong electrolytes are completely ionized) and the variation of equivalent conductance with dilution is therefore due to the change in the speed of the ions with dilution. In a concentrated solution of such electrolytes, the interionic attractions among the oppositely charged ions would be quite appreciable. The ions may also form some ion-pairs of the type A^+B^- that would not contribute to the conductance. These interionic forces considerably lower the speed of the ions and hence the conductivity of the solution. As the dilution is increased the interionic attractions decrease with the result that the ions will move more freely and independently of their co-ions and thus increasing the equivalent conductance with dilution. At infinite dilution, the ions are quite far apart, the interionic attractions are almost absent and each ion moves completely independent of its co-ions. The molar conductivity then approaches a limiting value at infinite dilution and represents the conducting power of 1 mole of the electrolyte when it is completely split up into ions. It is denoted by Λ^∞.

It can be concluded that in case of weak electrolytes, the increase in molar conductivity with dilution is mainly due to (a) an increase in the number of ions in the solution (degree of ionization increases with dilution), and (b) smaller interionic attractions at higher dilutions.

4.2.3 Limiting Molar Conductivity

An important relation can be obtained by extrapolating the curve for strong electrolytes (Fig.4.2) to $c \to 0$ where all interionic effects are absent. The limiting value obtained by this extrapolation is called the molar conductivity at infinite dilution.

Observing the linearity of Λ_m versus $\sqrt{c}$ for strong electrolytes in dilute solutions, Kohlrausch suggested the following empirical relation for the variation of equivalent conductance of strong electrolytes with dilution.

$$\Lambda_m = \Lambda^\infty - b\sqrt{c} \qquad \ldots (4.11)$$

where b is a constant for the given electrolyte and Λ^∞ is the molar conductivity of the electrolyte at infinite dilution. The validity of this equation may be seen from the plot for electrolytes like HCl, KCl, etc. To obtain Λ^∞ of such electrolytes the curve is extrapolated to $c \to 0$ and the intercept so obtained gives the value of Λ^∞. The same method cannot be used for obtaining Λ^∞ for weak electrolytes because of the steep increase in Λ at high dilutions. Λ^∞ may also be computed from the molar conductivities at infinite dilution of the respective ions, since at infinite dilution, the ions are independent of each other according to the law of independent migration of ions and each contribute its part to the total conductivity, therefore,

$$\Lambda^\infty = \Lambda_+^\infty + \Lambda_-^\infty \qquad \ldots (4.12)$$

where Λ_+^∞ and Λ_-^∞ are the ionic conductivities at infinite dilution of the cation and anion, respectively.

The molar conductivity of the ionic species is a measure of the amount of current carried by ions in question. Comparison of the molar conductivities of ions is, therefore, more meaningful when related to per unit charge, for example when $\Lambda^\infty(Na^+)$ is compared with $\frac{1}{2}\Lambda_-^\infty(Mg^{2+})$ rather than $\Lambda_-^\infty(Mg^{2+})$ or in terms

equivalent conductivities. The value of the limiting ionic molar and equivalent conductivities for some ions in water at 25°C are given in Table 4.2.

Table 4.2: Limiting ionic molar conductivities and limiting ionic equivalent conductivities of selected ions in water at 25o C

Cation	Λ^∞ /(S cm^2 mol^{-1})	Λ^∞ /(S cm^2 eq^{-1})	Anion	Λ^∞ /(S cm^2 mol^{-1})	Λ^∞ /(S cm^2 eq^{-1})
H^+	349.8	349.8	OH^-	198.3	198.3
Li^+	38.7	38.7	F^-	55.4	55.4
Na^+	50.1	50.1	Cl^-	76.3	76.3
K^+	73.5	73.5	Br^-	78.1	78.1
Be^{+2}	90.0	45.0	I^-	76.8	76.8
Mg^{2+}	106.2	53.1	NO_3^-	71.5	71.5
Ca^{2+}	119.0	59.5	SO_4^{2-}	160.0	80.0
Ba^{2+}	127.2	63.6	CH_3COO^-	40.9	40.9
Al^{3+}	183.0	61.0	$C_6H_5CO^-$	32.4	32.4
Cu^{2+}	107.2	53.6	HCO_3^-	44.5	44.5
Ag^+	61.9	61.9	CO_3^{2-}	138.6	69.3
Zn^{2+}	105.6	52.8	$Fe(CN)_6^{3-}$	302.7	100.9
Ce^{3+}	209.4	69.8	$Fe(CN)_6^{4-}$	442.0	110.5

Ionic Mobilities and Transport Number

The next question which arises in connection to the values of conductivity, given in Table 4.2, is why should there be a difference between the values of limiting molar conductivities of similarly charged ions, if these ions are just acting as carriers of electric charges only?

The answer lies in the fact that different ions have different mobilities in solution. The mobility of an ion in solution is mainly dependent upon the size of the hydrated ion. The ionic mobility is defined as the velocity with which an ion would move under a potential gradient of 1 V m^{-1} in a solution. It provides a link between theoretical and measurable quantities. For instance, ionic mobility, (u), is related to limiting molar ionic conductivity (Λ^∞) by the following equations:

$$\Lambda_+^\infty = z_+ u_+ F \text{ and } \Lambda_+^\infty = z_- u_- F \quad \ldots (4.13)$$

where z_+ and z_- are the valency of the ions, u_+ and u_- represent the ionic mobilities and F is the Faraday constant. In the above equation, if one of the two quantities, Λ^∞ or u, is known, the other can be calculated.

To find the values of Λ_+^∞ or Λ_+^∞, we define yet another quantity, called *transport* or *transference number* of an ion indicated by the symbol t_+ or t_-. It is defined as the fraction of the total current carried by an ionic species and can be expressed mathematically as,

$$t_+ = \Lambda_+^\infty / \Lambda_m \quad \text{and} \quad t_- = \Lambda_-^\infty / \Lambda_m \quad \ldots (4.14)$$

The transport number and the limiting molar conductivity are measurable quantities. Hence, the molar ionic conductivity value can be calculated from Eq. (4.14). The

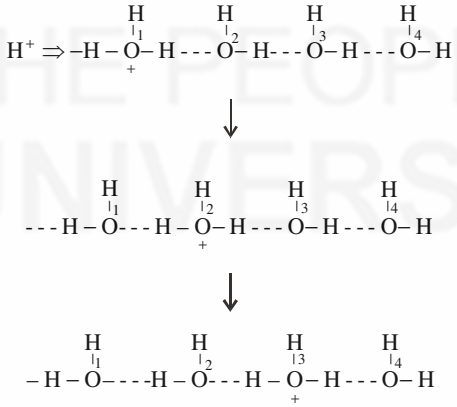
limiting molar conductivities of some common ions are given in Table 4.2. These values are important in predicting the molar conductivity of electrolytes and course of conductometric titrations. Finally, once the molar ionic conductivity value is obtained, we can then make use of Eq. (4.13) to calculate the ionic mobility. Some typical values of ionic mobility (in infinite dilute solutions) are listed in Table 4.3.

Table 4.3: Limiting ionic mobilities in water at 298 K

Cation	$10^8 u_+$ / $m^2 v^{-1} s^{-1}$
H^+	36.24
Li^+	4.01
Na^+	5.19
K^+	7.62
Ag^+	6.42

Anions	$10^8 u_-$ / $m^2 v^{-1} s^{-1}$
OH^-	20.58
Cl^-	5.74
Br^-	7.92
I^-	8.09
NO_3^-	7.41

It is interesting to look at Table 4.2 in more detail. You will see the Li^+ ion, because of its larger hydration shell, has a lower mobility than the potassium ion. Similar argument can be applied to the F^- & Br^- ions. Exceptional mobilities are observed for the H^+ and OH^- ions. This is because, in these case charge is transported through proton jump mechanism along with general migrations mechanism, consider he case of H^+ ion.



You can see how hydrogen ion jumps from O_1 to O_2, O_2 to O_3, ..., this result is equivalent to as the migration of charge from left to right. This conduction mechanism is more like a charge than ion movement. Such conduction is possible because of the peculiar structure of water and therefore only found in hydrogen-bonded solvents.

4.2.4 Effect of other Factors on Conductivity

Beside concentration, there are some more factors which affect the conductivity of the electrolyte solution.

a) *Effect of temperature and pressure:* The conductivity of all electrolytes increases with increasing temperature. The variation of molar conductivity at infinite dilution with temperature is given by an empirical equation.

$$\Lambda^{\infty}(t) = \Lambda^{\infty}\ (25)[1+ x(t - 25)] \quad \ldots (4.15)$$

where Λ^{∞} (t) and Λ^{∞} (25) are the value of molar conductivities at t and 25°C respectively, and x is a constant for each electrolyte. For salts x is about 0.022 to 0.025 and for acids and bases it is usually 0.016 to 0.019. It means that molar conductivity increases approximately by 2% for every one degree rise in temperature. For strong electrolytes, even at appreciable concentration, Eq. (4.15) holds well, whereas in case of weak electrolytes, the variation of Λ with temperature is not so regular. The rise in conductance with temperature is due to the decrease in the viscosity of the solution, increase in the speed of the ions and an increase in the degree of ionization in cases of weak electrolytes.

The conductivity increases slightly with increase in pressure. The effect is mainly through changes in the viscosity of the medium, which decrease by an increase in pressure. Consequently, the equivalent conductance of the solution will increase with rise in pressure.

b) *Effect of solvent:* In solvents of low dielectric constants, having small ionizing effect on the electrolytes, the electrostatic forces between oppositely charged ions would be appreciable and equivalent conductance will have small value. However, solvents with high dielectric constants yield more conducting solutions.

c) *Viscosity of the medium:* The dependence of conductance on viscosity of the medium is given by Walden's rule, according to which the equivalent conductance of an electrolyte is inversely proportional to the viscosity of the medium, i.e.

$$\Lambda^{\infty}\ \eta_0 = \text{constant} \quad \ldots (4.16)$$

where Λ_0 is the equivalent conductance at infinite dilution and η_o is coefficient of viscosity of the solvent. If ions are not solvated, i.e., they have the same size in all the solvents, then it follows from Walden rule that $\Lambda^{\infty}\ \eta_0$ should be constant and independent of the nature of the solvent. This is true only for ions like tetra-alkyl ammonium cations, which are not solvated. Ions where extensive solvation occurs, effective radii of the ions will not be constant and Walden rule will not be obeyed.

SAQ 4

List the factors which are affecting the conductivity of the solution.

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4.3 MEASUREMENT OF ELECTROLYTIC CONDUCTANCE

The conductance of a solution can be determined by measuring the resistance offered by solution contained within the two electrodes of a conductivity cell. For measuring

resistance, the Wheatstone bridge principle is employed. Therefore, before taking up the measurement of conductance of solution, let us study the principle of Wheatstone Bridge.

4.3.1 The Wheatstone Bridge Principle

A Wheatstone bridge (Fig. 4.3) is employed to measure the resistance of an electronic conductor. It works on the principle of obtaining balance between two arms with the help of a balance indicator (e.g. a galvanometer) at the condition of potential being equal.

Let R_x be an unknown resistor, R_1 and R_2 two standard resistors, R_3 an adjustable resistor and G a galvanometer. The bridge is connected to a source of power S, a battery, and a tapping key K is placed in the path to control the connections.

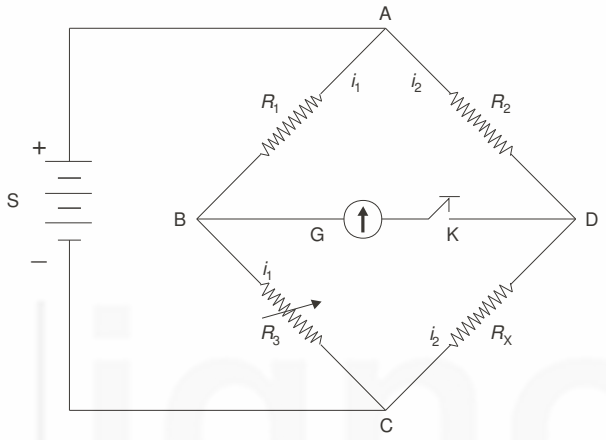

Fig. 4.3: A DC Wheatstone bridge circuit

To measure the resistance R_x, the tapping key K is held down momentarily and the bridge is balanced by adjusting R_3 to get no deflection in galvanometer under these conditions.

In the bridge the total current is divided into two paths: i_1 through R_1 and R_3, and i_2 through R_2 and R_x. Under the balancing conditions, the potential at points B and D must be the same, i.e. the ohmic voltage drop through the resistors R_1 and R_2 must be the same. Hence, the potential at B (E_B) must be equal to potential at D (E_D).

$$E_B = E_D \quad \ldots (4.17)$$

$$\text{Or } i_1 R_1 = i_2 R_2 \quad \ldots (4.18)$$

$$\text{Similarly, } i_1 R_3 = i_2 R_x \quad \ldots (4.19)$$

Dividing Eq. (4.18) by Eq. (4.19), we get

$$\frac{R_1}{R_3} = \frac{R_2}{R_X}$$

$$\text{and } R_x = \frac{R_2 R_3}{R_1} \quad \ldots (4.20)$$

Thus, we can calculate R_x as R_1, R_2 and R_3 are all known. Conductance G, being the reciprocal of resistance will be,

$$G = \frac{R_1}{R_2 R_3} \quad \ldots (4.21)$$

Alternatively, the conductometric cell can be incorporated into operational amplifier control circuit, as shown in Fig. 4.4. The amplifier balances the potential of two inputs. The current from the input potential, E_i, is balanced by the current from amplifier output which passes through a feedback resistor (R_f). The output potential, E_0 is in terms of resistance:

$$E_0 = E_i (R_f/R_x + 1)$$

where R_x is the resistance of conductometric cell.

With respect to the solution conductance,G, above equation becomes

$$E_0 = E_i(R_f G + 1)$$

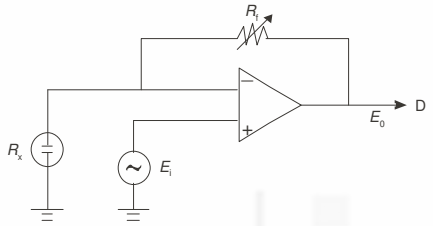

Fig. 4.4: An operational amplifier control circuit for conductometric measurement.

R_x is the solution resistance and R_f is the feedback resistance

4.3.2 Measurement of Conductance of a Solution

The Principle of the Wheatstone bridge discussed above can be used to measure the conductance of solutions. However, the following considerations must also be kept in mind:

i) Since a direct current would polarize the electrodes in the conductivity cell by electrolyzing the solution to avoid polarization an alternating current (ac) source of power must be used in place of a dc source (battery) usually ac voltages of 3-6 volts with frequency of 50 Hz or 1000 Hz used across points A and C of Fig. 4.5.

ii) A suitable conductivity cell (with electrodes dipped in the solution) is located between points C and D. Thus, R_x represents the resistance of the conductivity cell.

iii) Since, the cell also acts like a small capacitor (C_x), and to balance its capacitive resistance a variable capacitor, C_B, must be inserted into the bridge.

iv) The balance indictor (BI) may be an ac galvanometer, but some other devices are also be used:

- An earphone can act as a balance indicator if the frequency of the ac source is in audio-range.

- A magic eye, which gives a green fluorescence as a result of electrons striking a phosphor coating inside the glass tube, is used in several commercial instruments.
- For much precise conductance measurements a cathode ray oscilloscope is used as the balance indicator.

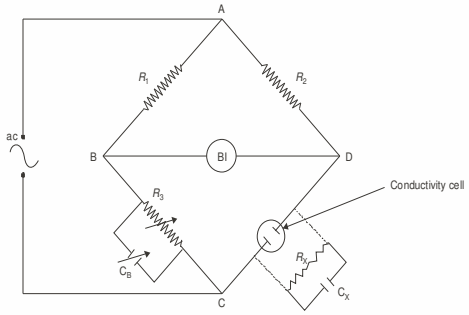

Fig. 4.5: A conductivity bridge circuit

v) Conductance (G=1/R_x) can be read directly on commercially available instruments as a panel mounted meter. Now several digital instruments are also available, such instruments give the conductance directly as the numerical value.

Conductometer

From above discussion we can conclude that conductance is reciprocal of resistance and the resistance of a cell can be measured by placing it in an arm of a Wheatstone bridge. The inverse of the resistance gives the conductance and can be directly read on a conductivity measuring instrument, known as "Conductometer".

A typical conductometer, consists of an ac source, a Wheatstone bridge circuit, a null detector or direct reading display and a conductivity cell.

To avoid the effects of polarization, i.e. the change is composition of the measuring cell, alternating current (ac) is used. The instrument has an arrangement to convert the supply of 50 Hz to higher frequency, say 1000 Hz. For measuring low conductance solutions, the lower frequency is preferable and for high conductive solutions higher frequencies are preferably used.

Several inexpensive conductometers are commercially available. The instruments come as a line-operated unit with and without digital readout. Fig. 4.6 gives the view of a typical conductometer, which can be operated as with given instructions.

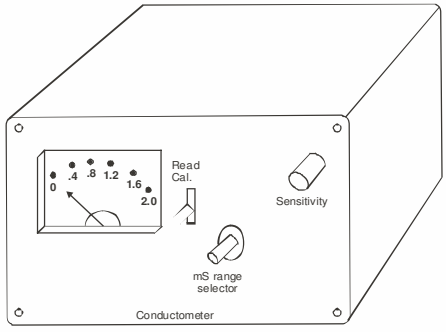

Fig. 4.6: Conductometer

Cells

Various types of cells have been designed and are in use for the measurement of conductance of a solution. These are made of Pyrex glass fitted with electrodes of platinum or gold. To overcome the imperfections in the current and the other effects at the electrodes, these are coated with a layer of finely divided platinum black. This is achieved by electrolyzing a 3% solution of chloroplatinic acid containing a little of lead acetate. The distance between the electrodes is determined by the conductance of the solution to be measured. For highly conducting solution, the electrodes are widely spaced whereas for low conducting solutions the electrodes are mounted near each other. A cell suitable for conductometric titration is depicted in Fig. 4.7 (a, b and c); the electrodes are firmly fixed in the Perspex lid which is provided with opening for the stirrer and the jet of the burette. A magnetic stirrer can be used in place of mechanical stirrer.

For most purposes a special cell is not required and good results are obtained by clamping a commercially available dip cell [shown diagrammatically in Fig. 4.7 (b)] inside a beaker which is placed on a magnetic stirrer. With this arrangement, the dipping cell should be lifted clear of the solution after each addition from the burette to ensure that the liquid between the electrodes becomes thoroughly mixed. Since absolute conductivity values are not required it is not necessary to know the cell constant.

For spot checking on a process stream or tank, a dip-type of conductivity cell is used. In some titrations on open beaker with fixed electrodes is sufficient. However, for fairly dilute solutions an open beaker would not be satisfactory because atmospheric CO_2 may alter the conductance.

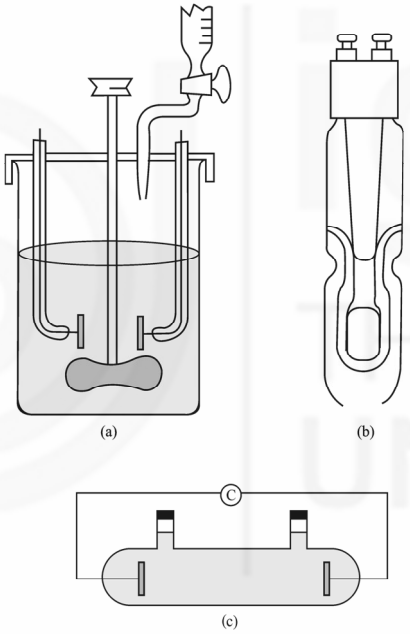

Fig. 4.7: Typical designs of conductivity cells

Procedure

1. Plug the instrument to an ac supply.

2. Put the frequency selector switch to required frequency (say 1000 Hz).

3. Set the mode selector on CAL and set the range selector on the desired setting e.g., 2, 20 or 200. These figures refer to the full scale meter value in milli Siemens (mS). With the help of sensitivity knob keep the pointer roughly midway between the lowest and highest sensitivity say at 1 position.

4. Connect the conductivity cell electrodes to the appropriate terminals of the instrument. Clean the conductivity cell with distilled water (Conductivity water).

5. Take the standard KCl solution (say 0.1M) in a clean beaker. Introduce a stirring rod (to be used for magnetic stirring) in the solution and put the solution beaker on a magnetic stirrer plate.

6. Insert the conductivity cell in the solution. Ensure that the platinum plate electrodes are completely immersed in the solution and they do not touch the stirring rod or the sides or the bottom of the beaker.

7. Switch on the instrument and allow it to warm up for 2-5 minutes.

8. Measure the conductance, G_s, of the standard KCl solution by putting meter switch to READ position.

9. Remove the KCl solution from the beaker, wash the conductivity cell properly with distilled water. Take the unknown solution in the beaker and measure its conductance, G_u, in the manner as for standard KCl solution.

10. Calculate the cell constant, from the conductance and conductivity values of the standard,

$$K_{cell} = \frac{\text{Conductivity (specific conduc tan ce)}}{\text{Observed conduc tan ce of the s tan dard}}$$

$$= \frac{\kappa_s}{G_s} \text{cm}^{-1}$$

11. Calculate the conductivity (specific conductance) of the unknown solution = cell constant × observed conductance

$$\kappa_u = K_{cell} G_u$$

12. For titration work, the value of cell constant, K_{cell} is not required to be calculated, since the cell constant will remain unchanged during the course of any given titration.

Notes

i) When the range selector is switched to a new position, it is essential to check the calibration again. Set the meter again to read one with the sensitivity control, if any deviation is observed.

ii) The conductivity cell, when not in use, should be kept in distilled water to prevent drying the platinum electrodes.

iii) In case of fouling the conductivity cell electrode plates, clean them by keeping in dilute $K_2Cr_2O_7$ containing H_2SO_4 solution (i.e. dilute chromic acid) for 24 hours and then washing with running water followed by rinsing with distilled water.

4.4 APPLICATIONS OF CONDUCTOMETRY

The high sensitivity of the conductometric measurements makes it an important analytical tool for environmental analysis and certain other applications. A continuous or spot check measurement of conductance is employed, usually, with a dip electrode cell and meter. In certain cases continuous recording of conductance is also employed. Since conductance depends on ionic concentrations, the purity of steam distillate, demineralized water, and the ionic contents of raw water can be checked with

measuring conductance directly. Metal industries, electroplating baths and rinse baths are monitored by conductance methods.

Perhaps the most common application of direct condutometry has been for estimating the purity of distilled water. Kohlrausch with a painstaking work after 42 successive distillations of water in vocuo obtained a conductivity water with specific conductance, $\kappa = 4.3 \times 10^{-8}$ S cm^{-1} at 18 °C. Traces of an ionic impurity will increase the conductance appreciably. Ordinary distilled water in equilibrium with the carbon dioxide of the air has a conductivity of about 7.0×10^{-7} S cm^{-1}. The sea water has much higher value of conductivity and the conductometric measurements are widely used to check the salinity of water in oceanography.

Measuring conductance of soil helps in finding the moisture content of soils at various places with portable instruments. All soils contain varying amount of water soluble salts upto 0.1% or even more. These salts are usually present as sulphate, chloride, carbonate or bicarbonate of sodium, potassium, calcium and magnesium and contribute to the conductance of the soil. The soil may be classed as saline and non-saline depending on the nature and quantity of the salts present. Conductivity of a saturated extract with water of saline soil at 25 °C has a conductivity greater than 4 mS cm^{-1}.

Based upon the relative change in the conductance/resistance of a solution with the addition of an other electrolyte, methods have been developed for the titration of a strong acid with a strong base, weak acid versus strong base or a weak base and a mixture of a strong acid and weak acid versus a strong base. Other types of titrations which can be performed conductometrically include displacement titrations: a salt of a weak acid (sodium acetate) versus a strong acid like HCl or a salt of weak base (ammonium chloride) versus sodium hydroxide; precipitation titrations: silver nitrate versus KCl; complexometric titrations: mercuric nitrate versus KCN or EDTA versus metallic ions and oxidation – reduction
(redox) titrations like the titration of Fe(II) versus $KMnO_4$.

Conductometric methods based upon precipitation or complex formation reactions are not as useful as those involving neutralization processes. Conductance changes during these titrations are seldom as large as those observed with acid-base reactions because no other reagent approaches the great ionic conductance of either hydronium or hydroxide ion.
The main advantage to the conductometric end point is its applicability to very dilute solutions and to systems that involve relatively incomplete reactions. For example, while neither a potentiometric nor indicator method can be used for the neutralization titration of phenol ($K_a = 10^{-10}$) a conductometric end point can be successfully applied.

Direct measurement of conductivity is potentially a very sensitive procedure for the determination of various parameters like the degree of dissociation of a weak electrolyte and its dissociation constant, ionic product of water, solubility and solubility product and hydrolysis constant of a salt

SAQ 5

At 298 K, the resistance of 2.00×10^{-2} M KCl is 195.96 Ω and that of 2.50×10^{-3} M K_2SO_4 is 775.19 Ω. The conductivity (κ) of 2.00×10^{-2} M KCl at 298 K is 0.2768 S m^{-1}. Calculate molar conductivity of K_2SO_4 solution.

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4.5 SUMMARY

In this unit, various parameters like resistance (R), conductance (G), resistivity (ρ), conductivity(κ), equivalent conductivity(Λ_{eq}), molar conductivity(Λ_m), molar conductivity at infinite solution(Λ_o) and cell constant have been defined in detail along with their units for measurements. The relationships among these parameters have also been worked out. Various factors affecting the conductance of solution are also given. At the end detailed procedure for the measurement of conductance is given.

4.6 TERMINAL QUESTIONS

1. What are electrolytes? How are they classified?
2. Define molar conductivity and equivalent conductivity of an electrolyte. How are they related to each other?
3. Write expression for a cell constant and conductivity of an electrolyte.
4. Why are platinum electrodes in conductometric cell are coated with Pt black?
5. What are the various factors affecting the conductance of solution?
6. How will you measure electrolytic conductance of a solution?
7. Explain the necessity of maintaining a constant temperature in conductometric measurements.
8. The conductivity of 0.1 M HCl is 0.0394 Ω^{-1} cm^{-1}. What is the molar conductivity of the solution?
9. The resistance of 0.1 M solution of a salt occupying a volume between two platinum electrodes 1.80 cm apart and 5.4 cm^2 in area was found to be 32 ohms. Calculate the molar conductivity of the solution.
10. A certain conductance cell was filled with 0.0100 M solution of KCl, whose conductivity is 0.001409 Ω^{-1} cm^{-1} (S cm^{-1}) at 25 °C, it had a resistance of 161.8 Ω, and when filled with 0.0050 M NaOH, it had a resistance of 190 Ω. Calculate the cell constant, conductivity and molar conductivity of NaOH solution.
11. A conductivity cell shows a resistance of 3950 Ω at 25 °C when filled with the experimental solution and 4864 Ω at the same temperature when filled with 0.02 M KCl solution. If the conductivity of the solution is 2.767×10^{-3} S cm^{-1}, calculate the conductivity of the experimental solution.
12. The resistance of a conductivity cell was 702 ohms when filled with 0.1 M KCl when filled with 0.1 M KCl solution (K = 0.14807 ohm^{-1} m^{-1}) and 6920 ohm when filled with 0.01M acetic acid solution. Calculate the cell constant and molar conductance for the acid solution.

4.7 ANSWERS

Self Assessment Questions

1. i) $K_{cell} = \kappa_{KCl} / G_{obs.}$ or $= \kappa_{KCl} \times R_{obs.}$
   $= 1.41 \times 10^{-3}\ \Omega^{-1}\ cm^{-1} \times 150\ \Omega = 0.2115\ cm^{-1}$

ii) $\kappa = K_{cell}\, G_{obs.} = K_{cell}/R_{obs.} = 0.2115\ cm^{-1}/51.5\ \Omega = 4.11 \times 10^{-3}\ \Omega^{-1}\ cm^{-1}$ or $(S\ cm^{-1})$

2. a) conductivity: $S\ m^{-1}$ or $\Omega^{-1}\ m^{-1}$

   b) Equivalent conductivity: $\Omega^{-1}\ cm^{-1}\ eq^{-1}$

   c) Cell constant : m^{-1} or cm^{-1}

   d) Molar conductivity: $S\ m^2\ mol^{-1}$ or $S\ cm^2\ mol^{-1}$

3. $\kappa_{KCl} = \kappa_{sol.} - \kappa_{water}$

   $(7.44–0.06) \times 10^{-3} = 7.38 \times 10^{-3}\ S\ m^{-1}$

$$\Lambda_m = K/c = \frac{7.38\times10^{-3}\ S\ m^{-1}}{5.0 \times 10^{-4} \times 10^{3}\ mol\ m^{-1}} = 1.476 \times 10^{-2}\ S\ m^2\ mol^{-1}$$

4. Concentration ionic mobility, temperature and pressure, nature of solvent, viscosity of medium, etc.

5. Consider following equation:

   $K_{cell} = \kappa \times R$

   $= 0.2768\ S\ m^{-1} \times 195.96\ \Omega = 54.24\ m^{-1}$.

   Conductivity of K_2SO_4 solution can be given by,

$$\kappa = \frac{K_{cell}}{R} = \frac{54.24\,m^{-1}}{775.19\,\Omega} = 0.06997\ S\ m^{-1}.$$

   Concentration of K_2SO_4 in $mol\ m^{-3}$ unit:

   $c = 1000 \times 2.50 \times 10^{-3}\ mol\ m^{-3}$

   $= 2.50\ mol\ m^{-3}$

   Molar conductivity of K_2SO_4 can be expressed as

$$\Lambda_m = \frac{\kappa}{c} = \frac{0.06997}{2.50} S m^2 mol^{-1}$$

$$= 0.028\ S\ m^2\ mol^{-1}$$

Terminal Questions

1. The ionic compounds which form ions in solution and conduct electric current are called electrolyte e.g. NaCl, KCl, etc. They can be classified strong and weak electrolyte, on the basis of their degree of ionisations.

2. Molar conductivity: It is the conductivity for unit molar concentration of a dissolved electrolyte.

$$\Lambda_m = \frac{\kappa}{c} = \frac{\kappa}{M \times 1000} S\,m^2\ mol^{-1} = \frac{1000\,\kappa}{M} S\,cm^2\ mol^{-1}$$

   Equivalent Conductivity: It is the conductivity of 1 g equivalent of an electrolyte when present in V cm^3 of solution

$$\Lambda_{eq} = \kappa V$$

   If c is the concentration of the solution in g equivalent per dm^3, then

$$\Lambda_{eq} = \frac{1000\,\kappa}{c}$$

   Its unit is $S\ cm^2\ eq^{-1}$

Relationship

$$\Lambda_{eq} = \frac{\text{Molar Conductivity (S cm}^2\text{ mol}^{-1})}{n}$$

where n = charge unit

3. Cell constant: The quantity (l/A) is called the cell constant.
Conductivity: It is the reciprocal of specific resistance. Conductivity of an electrolyte in a cell can be expressed as:

conductivity = observed conductance × cell constant

4. To overcame the imperfection in the current and the other effects at the electrode.

5. Concentration, ionic mobilities, temperature, solvent and viscosity of medium: for further details, please go through the section 4.2.2, 4.2.3 and 4.2.4.

6. Detailed procedure is given in the Sub Section 4.3.2.

7. Because conductivity of all electrolytes increases with increasing temperature.

8. $\Lambda_m = K/c$, therefore,
$\Lambda_m = 0.0394$ (Ω^{-1} cm^{-1})/ 0.1 M =0.0394 (Ω^{-1} cm^{-1})/0.1 × 10^{-3} mol cm^{-3}
= 394 Ω^{-1} cm^2 mol^{-1}

9. Cell constant = l/A, 1.8/5.4 = 1/3 cm^{-1}
Observed conductance = 1/32 Ω^{-1}
K = Cell constant × conductance=1/3 × 1/32 = 1/96 $\Omega^{-1}cm^{-1}$
$\Lambda_m = K/c$ = 1/96 (Ω^{-1} cm^{-1}) × 1/0.1 M
=1/96 (Ω^{-1} cm^{-1}) × 1/0.1 × 10^{-3} (mole cm^{-3}) =104.16 Ω^{-1} cm^2 mol^{-1}

10. Cell constant = KR = 0.001409 Ω^{-1} cm^{-1}× 161.8 Ω = 0.228 cm^{-1}
κ_{NaOH}= Cell constant/R = 0.228 cm^{-1}/190 Ω = 1.2 × 10^{-3} Ω^{-1} cm^{-1}
$\Lambda_m = K/c$ = 1.2 × 10^{-3} Ω^{-1} cm^{-1}/ 0.0050 × 10^{-3} mol cm^{-3} = 240 Ω^{-1} cm^2 mol^{-1}

11. Cell constant = KR = 2.767 × 10^{-3} (S cm^{-1}) × 4864 (Ω)
Conductivity of the experimental solution = K= Cell constant/R
= 2.767 × 10^{-3} × 4864 (cm^{-1})/3950(Ω) = 3.407 × 10^{-3} S cm^{-1}

12. Cell constant = KR = (0.14807 ×702) (ohm^{-1} m^{-1}) (ohm) =103.94 m^{-1} = 1.039 cm^{-1}
Conductivity of acetic acid K = (1/R) (l/A)
= (1 / 6920 Ω) (1.039) cm^{-1}
= 1.501 × 10^{-4} Ω^{-1} cm^{-1}
= 1.501 × 10^{-2} Ω^{-1} m^{-1}
Concentration = 0.01 M = 0.01 mol dm^3 = 0.01 × 10^3 mol m^{-3}
$\Lambda_m = K/c$ = 1.501×10^{-2} Ω^{-1} m^{-1}/ 0.01×10^3 mol m^{-3}
= 1.501 × 10^{-3} mol^{-1} Ω^{-1} m^2