ELECTROLYTIC CONDUCTANCE

Specific Conductance

The resistance (R) of a metallic conductor is directly proportional to its length (ℓ) and inversely proportional to its cross-section area (a), is

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

$$\Rightarrow R = \rho \cdot \frac{\ell}{a}$$

$$\Rightarrow \frac{1}{\rho} = \frac{1}{R} \cdot \frac{\ell}{a} \qquad \ldots(1)$$

Where is a constant depending upon the nature of the material and is called specific resistance of the material.

The reciprocal of the resistance is called conductance or conductivity and similarly, the reciprocal of specific resistance is called specific conductance,

Thus, from equation (1)

$$\text{Specific conductance} = \text{observed conductance} \times \frac{\ell}{a} \qquad \ldots(2)$$

When R = 1 cm and a = 1 cm^2

Specific conductance = observed conductance

Thus, specific conductance is the conductance of a conductor which is observed when it is 1 cm in length and 1 sq. cm in cross-sectional area. In other words, it is the conductance of 1 cc of the conductor.

The unit of resistance is ohm (Ω) so unit of conductance will be ohm^{-1} or Ω^{-1} and expression ℓ in cm and a in cm^2, the unit of specific conductance will be. Ohm^{-1} cm^{-1}, Ω^{-1} cm^{-1} or mho cm^{-1}. In sI system, the units of specific conductance are Sm^{-1} where S stands for Semen.

The equation (2) mentioned above is also applicable for solution an electrolyte i.e. electrolytic conductor. The specific conductance of an electrolytic solution is defined as the conductance that is observed when two electrodes each of 1 sq. cm in cross-sectional are dipped into solution at a distance of 1 cm apart. In other words, specific conductance is the conductance per c.c. solution of the electrolyte. It is denoted by the symbol (K (kappa). Sometimes K_v or K_c is also used, the subscript v or c standing for dilution or concentration, respecting, signifying that K is dilution or concentration dependent.

Equivalent Conductance

Equivalent conductance is the conducting power of all the ions produced by one g-equivalent i.e. one equivalent of an electrolyte in a given solution. The equivalent conductance my, therefore, be defined as the conductance which is observed when two sufficiently large electrodes are dipped into solution at such a distance so as to enclose in between them the entire volume of solution containing one equivalent of the electrolyte.

It is denoted by the symbol $\wedge$

Let one equivalent of an electrolyte is dissolved in v.c.c. solution. Then all the ions produced by 1 equivalent of the electrolyte will be present in the v.c.c. solution. So, the conductance of this v.c.c. solution will be the equivalent conductance of the electrolyte i.e.

$\wedge$ = Conductance of v.c.c. solution containing one equivalent of the dissolved electrolyte.

= Conductance of 1 c.c solution × v

= $K \times v$ …(3a)

Where v = volume of solution in c.c containing 1 equivalent of the electrolyte

If C be the normality of solution i.e. concentration of electrolytic solution in equivalent/L, then

$$V = \frac{1000}{C}$$

$$\therefore \wedge = \frac{1000K}{C} \quad \text{…(3b)}$$

Unit of $\wedge$: $\text{Ohm}^{-1}\ \text{cm}^{-1} \times \text{cm}^3$ i.e. $\text{Ohm}^{-1}\ \text{cm}^2$ or $\Omega^{-1}\text{cm}^2$

Molar Conductance

The recent trend is to describe electrolytic conductance in terms of molar conductance which is defined as the conductance of solution due to all the ions produced by one mole of the dissolved electrolyte in a given solution.

It is denoted by the symbol $\wedge_m$

$\wedge_m$ and K are inter-related are

$\wedge_m = K \times V$

$$\Rightarrow \wedge_m = \frac{1000K}{C} \quad \text{…(4)}$$

Where V = Volume of solution in c.c. containing one mole of the electrolyte and

C = Concentration of solution in mole L^{-1} i.e. molarity

The above inter-relationship may also be expressed as

$$\wedge_m = \frac{K}{C}$$

Where C is the concentration of the solution in moles per cubic metre.

Unit of $\wedge_m$: $\Omega^{-1}cm^2mol^{-1}$

In SI system it is S m^2 mol^{-1}

Relation between $\wedge$ and $\wedge_m$

$\wedge_m = n\wedge$

Where n = n-factor of the electrolyte = total charge carried by either ion = $\frac{M}{E}$

Variation of Conductance with Dilution

Upon dilution i.e. lowering concentration, specific conductance decrease while equivalent and molar conductances increase. At infinite or almost zero concentration equivalent conductance and molar conductance attain their respective limiting values called equivalent conductance at infinite dilution ($\wedge_\infty$) or zero concentration ($\wedge_0$) and molar conductance at infinite dilution $\left(\wedge_m^\infty\right)$ or zero concentration ($\left(\wedge_m^0\right)$, respectively. The increase of $\wedge$ or $\wedge_m$ with dilution of a weak electrolyte is attributable to increase of degree of dissociation with dilution resulting into more number of ions in solution. Note that ions are carriers of electricity. The increase of $\wedge$ and $\wedge_m$ of a strong electrolyte which remains completely ionised at all dilutions, is attributed to increase in the ionic mobilities of ions due decrease in inter-ionic attraction. As dilution approaches unity, the member of ions becomes maximum and hence $\wedge$ as well as $\wedge_m$ approach their respective maximum value. In the case of strong electrolyte, however, the maximum value of $\wedge$ or $\wedge_m$ is attained due to the maximum ionic mobilities of the ions since at infinite dilution the dissociation of strong electrolyte is complete and inter-ionic attraction cases to exist completely.

The decrease in K may also be explained in the following way. Upon dilution the number of ions, in the case of weak electrolyte, increase but volume of solution also increases. The increase of volume is in greater proportion than the increase of number of ions resulting into decrease in number of ions per c.c. solution. The specific conductivity being the conductivity of 1 c.c. solution, should obviously decrease.

The variation of molar conductance of a strong electrolyte with concentration is theoretically give by Debye-Hückel-Onsager equation

$$\wedge_m = \wedge_m^0 - \left(A + B\wedge_m^0\right)\sqrt{C}$$

Where A and B are the Debye-Hückel constants depending upon nature of the solvent and temperature and C is the molar concentration of solution. For aqueous medium at 25°C:

$$\wedge_m = \wedge_m^0 - \left(60.2 - 0.299\wedge_m^0\right)\sqrt{C}$$

According to this equation a plot of $\wedge_m$ vs $\sqrt{C}$ should be a straight line having the slope equal to 60.2 + 0.229 $\wedge_m^0$ and intercept equal to $\wedge_m^0$. This has been checked in the case of a number of uni-univalent e4lectrolytes and found to be true for $C \leq 0.02$ M.

At higher concentration, the observed deviation from linearity is attributable to large inter-ionic attraction.

Determination of Conductance (k, $\wedge$ and $\wedge_m$)

As already mentioned above

K = Ohs conductivity × $\frac{\boxtimes}{a}$

For a given conductivity cell in a given experiment: $\frac{\boxtimes}{a}$ = constant called cell constant (x). Thus,

K = Ohs conductance × x = $\frac{1}{\text{Ohs. resistance}} \times x$

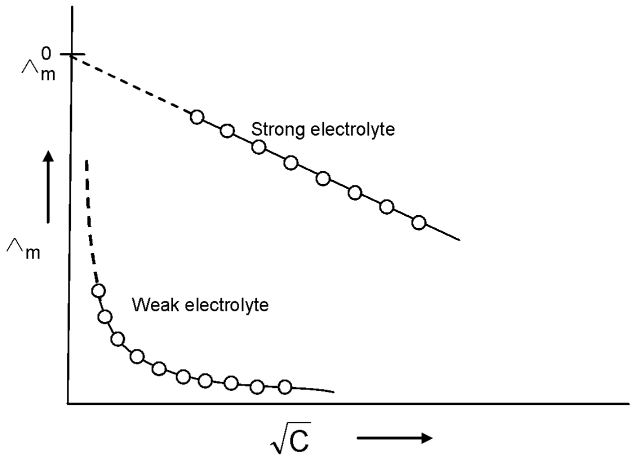
The resistance of a solution is determined by Wheatstone bridge method using a meter bridge the conductivity dipped in the test solution. The current used is AC.

The specific conductance of 0.1M KCl solution is known. The resistance of 0.1M KCl solution is first determined experimentally from the cell, it is washed with conductivity water and then filled with test solution. The resistance of the test solution is measured and since cell constant is already known so specific conductance of the test solution can be calculated.

From specific conductance, we determine $\wedge$ and $\wedge_m$ using the equation (3) and equation (4) respectively.

Determination of $\wedge_m^0$ or $\wedge^0$

A plot of Λ_m vs $\sqrt{C}$ as found experimentally is as shown below graphically.



The Λ_m vs $\sqrt{C}$ plot of strong electrolyte being linear it can be extrapolated to zero concentration. Thus, Λ_m values of the solution of the test electrolyte are determined at various concentrations the concentrations should be as low as good.

Λ_m values are then plotted against $\sqrt{C}$ when a straight line is obtained. This is the extrapolated to zero concentration. The point where the straight line intersects Λ_m axis is Λ_m^0 of the strong electrolyte.

However, the plot in the case of weak electrolyte being non linear shooting up suddenly at some low concentration and assuming the shape of a straight line to Λ_m axis. Hence extrapolation in the case is not possible. Thus, Λ_0 of a weak electrolyte cannot be determined experimentally. It can, however, be done with the help of Kohlransch's law to be discussed later.

Kohlransch's Law of Independent Migration of Ions

Kohlransch determined Λ_0 values of pairs of some strong electrolytes containing same cation say KF and KCl, NaF and NaCl etc., and found that the difference in Λ_0 values in each remains the same.

$$\Lambda_m^0\,(\mathrm{KCl}) - \Lambda_m^0(\mathrm{KF}) = \Lambda_m^0(\mathrm{NaCl}) - \Lambda_m^0(\mathrm{NaCl}) - \Lambda_m^0(\mathrm{NaF})$$

He also determined Λ_0 values of pairs of strong electrolytes containing same anion say KF and NaF, KCl and NaCl etc. and found that the difference in Λ_0 values in each case remains the same.

$$\wedge_m^0(KF) - \wedge_m^0(NaF) = \wedge_m^0(KCl) - \wedge_m^0(NaCl)$$

This experimental data led him to formulate the following law called Kohlransch's law of independent migration.

At infinite dilution when dissociation is complete, every ion makes some definite contribution towards molar conductance of the electrolyte irrespective of the nature of the other ion which with it is associated and that the molar conductance at infinite dilution for any electrolyte is given by the sum of the contribution of the two ions. Thus

$$\wedge_m^0 = \lambda_+^0 + \lambda_-^0 \qquad \ldots(5)$$

Where λ_+^0 is the contribution of the cation and λ_-^0 is the contribution of the anion towards the molar conductance at infinite dilution. There contributions are called molar ionic conductance at infinite dilution. Thus, λ_+^0 is the molar ionic conductance of cation and λ_-^0 is the molar ionic conductance of anion, at infinite dilution. The above equation (5) is however, correct only for binary electrolyte like NaCl, $MgSO_4$ etc.

For an electrolyte of the type of A_xB_y, we have

$$\wedge_m^0 = x\lambda_+^0 + y\lambda_-^0$$

Application of Kohlransch's Law

i) Determination of λ_m^0 of a weak electrolyte

In order to calculate $\wedge_m^0$ of a weak electrolyte say cH_3COOH, we determine experimentally $\wedge_m^0$ values of the following three strong electrolysis:

a) A strong electrolyte containing same cation as in the last electrolyte, say HCl

b) A strong electrolyte containing same anion as in the test electrolyte, say CH_3COONa

c) A strong electrolyte containing same anion of (a) and cation of (b) i.e. NaCl.

$\wedge_m^0$ of CH_3COOH is the given as

$$\wedge_m^0(CH_3COOH) = \wedge_m^0(HCl) + \wedge_m^0(CH_3COONa) - \wedge_m^0(NaCl)$$

Prof:

$$\wedge_m^0(HCl) = \lambda_H^0 + \lambda_{Cl^-} \qquad \ldots I$$

$$\wedge_m^0\ (CH_3COONa) = \lambda^0_{CH_3COO^-} + \lambda_{Na^+} \qquad \text{...II}$$

$$\wedge_m^0\ (NaCl) = \lambda^0_{Na^+} + \lambda^0_{Cl^-} \qquad \text{...III}$$

Adding equation (I) and equation (II) and substracting(III) from them

$$\wedge^0_{(HCl} + \wedge^0_{(CH_3COONa)} - \wedge^0_{(NaCl)} = \lambda^0_{H^+} + \lambda^0_{(CH_3COO^0)} = \wedge_{0(CH_3COOH)}$$

ii) **Determination of degree of dissociation (α)**

$$\alpha = \frac{\text{No.. of moleculars ionised}}{\text{total number of molecules dissolved}} = \frac{\wedge_m}{\wedge_m^0}$$

iii) Determination of solubility of sparingly soluble salt

The specific conductivity of a saturated solution of the test electrolyte (sparingly soluble) made in conductivity water is determined by the method as described above. From this the specific conductance of the saturated solution is taken to be equal to $\wedge_m^0$ as the saturated solution of a sparingly soluble is extremely dilute. Hence from equation (4).

$$\wedge_m^0 = \frac{1000K}{C}$$

Where C is the molarity of solution and hence the solubility.

iv) Determination of ionic product of water

From Kohlransch's law, we determine $\wedge_m^0$ of H_2O where $\wedge_m^0$ is the molar conductance of water at infinite dilution when one mole of water is completely ionised to give one mole of H^+ and one mole of OH^- ions i.e.

$$\wedge_m^0\ (H_2O) = \lambda^0_{H^+} + \lambda^0_{OH^-}$$

Again using the following

$\wedge_m = \frac{k \times 1000}{C}$, when C = molar concentration i.e. mol L^{-1} or mol dm^{-3}

$\Rightarrow \wedge_m = \frac{k}{C}$, when C = concentration in mol m^3

Assuming that $\wedge_m$ diggers very little from $\wedge_m^0$ very little from $\wedge_m^0$,

$$\wedge_m^0 = \frac{k}{C}$$

$$\Rightarrow C = \frac{k}{\wedge_m^0}$$

Specific conductance (k) of pure water is determined experimentally. Therefore, molar concentration of dissociated water is determined using the above equation.

K_w is then calculated as

$K_w = C^2$

Answers to Exercise

Exercise 1: 62 Ω^{-1} cm^2 $equiv^{-1}$ mol^{-1}
And 1.26×10^2 Ω^{-1} cm^2 mol^{-1}

Exercise 2: x = 1.166 cm^{-1}
$\wedge$ = 66.66 ohm^{-1} cm^2

Exercise 3: 523.2×10^{-4} S m^2 mol^{-1}

Exercise 4: 1.80×10^{-3} gdm^{-3}

Solved Problems

Objective

Problem 1: ***Equivalent conductance of 1M HCOOH is 12 ohm^{-1} cm^2 equiv^{-1} and that at infinite dilution is 240 ohm^{-1} cm^2 equiv^{-1}. Hence % ionisation of CH_3COOH is***

(A) 4 ***(B) 5***

(C) 2 ***(D) 1***

Solution: $\propto = \frac{\wedge_C}{\wedge_\infty} = \frac{12}{240}$, % ionisation = $100\propto = 5$

∴ (B)

Problem 2: ***Specific conductance of 0.01 M KCl solution is x ohm^{-1} cm^{-1}. When conductivity cell is filled with 0.01 M KCl the conductance is y ohm^{-1}. When the same cell is filled with 0.01 M H_2SO_4, the observed conductance was Z ohm^{-1} cm^{-1}. Hence specific conductance of 0.01 M H_2SO_4 is***

(A) xz ***(B)*** $\frac{z}{xy}$

(C) $\frac{xy}{y}$ ***(D)*** $\frac{xy}{z}$

Solution: Cell constant = $\frac{\text{Specific conduc tance}}{\text{Observed Conduc tance}} = \frac{x}{y}\text{cm}^{-1}$

Specific conductance of 0.01 M H_2SO_4

= Observed conductance × Cell constant = $z \times \frac{x}{y}$ ohm^{-1} cm^{-1}

∴ (C)

Problem 3: ***Among the cation H^+, Li^+, Na^+ and K^+, the one with highest ionic mobility and another with lowest ionic mobility respectively are:***

(A) [H^+, K^+] ***(B) [K^+, H^+]***

(C) [LI^+, Na^+] ***(D) [H^+, Li^+]***

Solution: H^+ ion has the maximum ionic mobility which is explainable by Grothus mechanics, Li^+ having the maximum charge density, is the most hydrated ion among the lot and hence the lowest ionic mobility.

∴ (D)

Problem 4: ***The specific conductance has the unit***

(A) ohm^{-1} cm^{-1} ***(B) ohm.cm***

(C) ohm cm^{-1} ***(D) ohm^{-1}.cm***

Solution: Specific conductance = Observed conductance × $\frac{\ell}{a}$

$= \text{ohm}^{-1} \times \frac{\text{cm}}{\text{cm}^2} = \text{ohm}^{-1} \cdot \text{cm}^{-1}.$

∴ (A)

Problem 5: ***The specific conductivity of solution depends upon***

(A) Number of ions as well as mobility of ions

(B) Number of ions per c.c solutin

(C) Number of ions per cc as well as mobilities of ions

(D) Mobilities of ions only

Solution: Specific conductance is the conductance per c.c. solution

∴ (C)

Assignment

Subjective

1. The specific conductance of a 0.01 M solution of acetic acid was found to be 1.63 × 10^{-4} S m^{-1} at 25°C. The molar ionic conductance of H^+ and CH_3COO^- ions at infinite dilution are 349.8 × 10^{-4} and 40.9 × 10^{-4} S m^2 mol^{-1}, respectively, at the same temperature. Calculate dissociation constant of acetic acid.

2. At 25°C, the specific conductance a saturated solution of AgCl is 2.68 × 10^{-4} S m^{-1} and that of water in which the solution was made is 0.86 × 10^{-4} S m^{-1}. If molar conductances at infinite dilution of $AgNO_3$, HNO_3 and HCl are 133.0 × 10^{-4}, 421 × 10^{-4} and 426.0 × 0 × 10^{-4} S m^2 mol^{-2}, respectively. Calculate the solubility of AgCl in gram per dm^3 in water at the given temperature.

3. At 25°C, $\lambda^0(H^+)$ = 3.448 × 10^{-2} and $\lambda^0_{OH^-}$ = 1.98 × 10^{-2} S m^2 mol^{-1}. Given for water K = 5.7 × 10^{-6} S m^{-1}, calculate K_w.

4. The resistance of a conductivity cell containing 0.1M aqueous solution of KCl at room temperature was 24.96 Ω. Assume that conductivity water with specific conductance K = 7.5 × 10^{-6} S m^{-1} was used to prepare KCl solution whose K is 1.1639 S m^{-1}. When the cell is filled with 0.01 M aqueous solution of acetic acid, the all resistance was 1982 Ω. Calculate $\wedge_m$ of acetic acid.

5. The molar conductance of a 0.01 M solution of acetic acid was found to be 16.30 × 10^{-4} S m^2 mol^{-1} at 25°C. The molar ionic conductance of $H^=$ and CH_3COO^- ions at infinite dilution are 349.8 × 10^{-4} and 40.9 × 10^{-4} S m^2 mol^{-1}, respectively, at the same temperature. What percentage of acetic acid is dissociated at this concentration.

Objective

1. Equivalence conductance of 1.0 M HA is 8 ohm^{-1} cm^2 equiv^2 and that at infinite dilution is 160 ohm^{-1} cm^2 equiv^{-1}. Hence pH of 1.0 M HA is

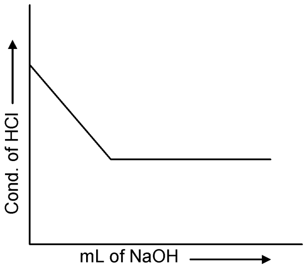
(A) 2.3	(B) 1.3
(C) 1.7	(D) 4.3

2. Equivalence conductance at infinite dilution of $BaCl_2$, H_2SO_4 and HCl solutions in water are x, y and z respectively. Equivalent conductance of $BaSO_4$ solution is

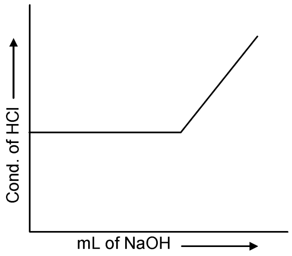
(A) x – y + z	(B) x + y – 2z
(C) x + 2y + z	(D) x – y + 2z

3. The kind

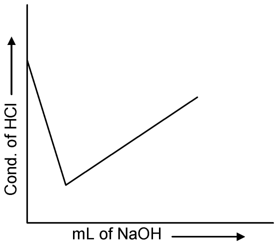
(A)



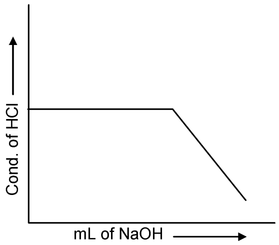
(B)



(C)



(D)



4. Molar conductance of saturated solution of $BaSO_4$ ohm^{-1} cm^{2}mole^{-1} and specific conductance is 8 × 10^{-5} ohm^{-1} cm^{-1}. Hence K_{sp} of $BaSO_4$ is:

(A) 4×10^{-8}M^2	(B) 1×10^{-8} M^2
(C) 2×10^{-4} M^2	(D) 1×10^{-4} M^2

5. In aqueous solution the ionic conductance or ionic mobility of any ion depends upon:

(A) Size of the bare ion	(B) Size of the hydrated ion
(C) Inter ionic space	(D) None of these

6. The ionic mobilities of Li^+, Na^+, K^+, Rb^+ and Cs^+ increase in the order

(A) Li^+, Na^+, K^+, Rb^+ and Cs^+	(B) Cs^+, Rb^+, K^+, and Li^+
(C) Na^+, Li^+, Rb^+, $Cs^+$and $K^=$	(D) None of these

7. The specific conductance of 1.0M solution a weak monobasic acid is 0.005 ohm^{-1} cm^{-1} while ionic conductances of its cation and anion are 120 and 130 ohm^{-1} cm^2 mol^{-1} respectively. The dissociation constant of the acid is approximately.

(A) 2×10^{-3}	(B) 0.02
(C) 4.0×10^{-4}	(D) None of these

8. For which of the following electrolytes, molar conductance will be three times that of equivalence conductance at any dilution?

(A) $Al_2(SO_4)_3$ (B) Na_3PO_4

(C) $MgCl_2$ (D) NaCl

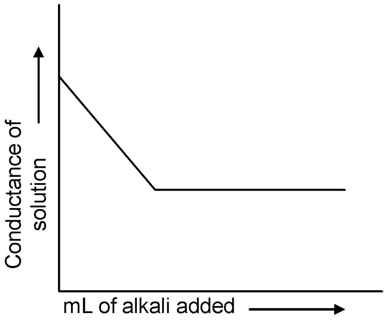
9. The titration curve shown in the parenthesis represents that for the

(A) Titration of HCl is NaOH

(B) Titration of CH_3COOH vs NaOH

(C) Titration of HCOOH vs KOH

(D) Titration of HCl vs NH_4OH



10. The conductance that decreases with dilution is

(A) Equivalence conductance (B) Molar conductance

(C) Specific conductance (D) Ionic conductance

Answers

Subjective

1. 1.82×10^{-5} mol dm^{-3}
2. 1.89×10^{-3}g dm^{-3}
3. 1.9×10^{-14}
4. 1.465×10^{-4} S m^{2} mol^{-1}
5. 4.172%

Objective

1. **B**
2. **B**
3. **C**
4. **B**
5 **B**
6. **A**
7. **C**
8. **B**
9. **D**
10. **C**