STUDY MATERIAL AND NUMERICAL PROBLEMS: ION CONDUCTANCE

INTRODUCTION TO ION CONDUCTANCE

Ion conductance is a fundamental concept in electrochemistry, describing the ability of ions in a solution to carry electric current. The movement of charged ions under the influence of an electric field constitutes an electric current. The magnitude of this current depends on the concentration of ions, their charge, and their mobility.

CONDUCTANCE AND ITS MEASUREMENT

Conductance (G) is the reciprocal of electrical resistance (R). It measures how easily electric current flows through a conductor.

Formula: $G = 1/R$

The unit of conductance is Siemens (S), formerly mho.

Electrical resistance is measured using a Wheatstone bridge, and conductance can be calculated from the measured resistance.

Cell Constant (K)

The **cell constant** is a geometric factor characteristic of the conductivity cell used. It is defined as the ratio of the distance (l) between the two electrodes to the area (A) of each electrode:

Formula: $K = l/A$

The unit of cell constant is typically cm^{-1} or m^{-1}.

Specific Conductance (Conductivity, κ)

Specific conductance (or conductivity, κ) is the conductance of a solution that is contained in a cell with electrodes of 1 cm^2 area and 1 cm distance between them (i.e., a 1 cm^3 volume). It is the conductance of a unit cube of the electrolyte solution.

Formula: $\kappa = G \times (l/A) = G \times K$

The unit of specific conductance is Siemens per centimeter ($S\ cm^{-1}$) or Siemens per meter ($S\ m^{-1}$).

Molar Conductance (Λ_m)

Molar conductance is the conductance of a solution containing one mole of electrolyte, such that all the ions produced from the mole of electrolyte are contained in volume V between the electrodes. It is defined as the specific conductance divided by the molar concentration (C) of the electrolyte.

Formula: $\Lambda_m = \kappa / C$

The unit of molar conductance is Siemens centimeter squared per mole ($S\ cm^2\ mol^{-1}$) or Siemens meter squared per mole ($S\ m^2\ mol^{-1}$).

Note: Sometimes, Equivalent Conductance (Λ_{eq}) is used, defined as specific conductance divided by the equivalent concentration. $\Lambda_{eq} = \kappa / N$, where N is the normality.

VARIATION OF SPECIFIC AND MOLAR CONDUCTANCE WITH DILUTION

As the dilution of an electrolyte solution increases (i.e., volume of solvent per mole of electrolyte increases, or concentration decreases), the conductance properties change:

Strong Electrolytes

Specific Conductance (κ): Decreases with dilution because the total number of ions per unit volume decreases, even though the mobility of individual ions might increase slightly.

Molar Conductance (Λ_m): Increases with dilution. This is because as the volume increases, ions are further apart, leading to reduced interionic attraction and increased mobility of ions, which more than compensates for the decrease in concentration.

Weak Electrolytes

Specific Conductance (κ): Decreases significantly with dilution, similar to strong electrolytes, due to the reduced number of ions per unit volume.

Molar Conductance (Λ_m): Increases sharply with dilution. This is primarily due to the significant increase in the degree of dissociation (α) with dilution, leading to a larger number of ions available for conduction.

KOHLRAUSCH'S LAW OF INDEPENDENT MIGRATION OF IONS

Kohlrausch's law states that the molar conductance of an electrolyte at infinite dilution (Λ_m^∞) is equal to the sum of the molar conductances of its cation and anion at infinite dilution, each multiplied by their respective stoichiometric coefficients. At infinite dilution, the ions migrate independently of each other, and interionic interactions are negligible.

For an electrolyte like $M_{n+}X_{m-}$*:*

$\Lambda_m^\infty(M_{n+}X_{m-}) = n * \lambda_+^\infty + m * \lambda_-^\infty$

where λ_+^∞ and λ_-^∞ are the molar conductances of the cation and anion at infinite dilution, respectively.

EQUIVALENT AND MOLAR CONDUCTANCE AT INFINITE DILUTION

Molar conductance at infinite dilution (Λ_m^∞) is the molar conductance when the electrolyte is completely dissociated and interionic attractions are zero. It represents the maximum possible molar conductance for that electrolyte.

Determination for Strong Electrolytes:

For strong electrolytes, Λ_m can be extrapolated to zero concentration from plots of Λ_m vs. $\sqrt{C}$. The relationship is approximately linear at low concentrations:

$\Lambda_m = \Lambda_m^\infty - A\sqrt{C}$

where A is a constant that depends on the solvent, temperature, and the charge of the ions.

Determination for Weak Electrolytes:

Direct extrapolation is not possible for weak electrolytes due to their low degree of dissociation. Instead, Kohlrausch's law is used, often in conjunction with conductance data for related strong electrolytes. For example, to find $\Lambda_m^\infty(CH_3COOH)$:

$$\Lambda_m^\infty(CH_3COOH) = \Lambda_m^\infty(CH_3COONa) + \Lambda_m^\infty(HCl) - \Lambda_m^\infty(NaCl)$$

DEBYE–HÜCKEL THEORY OF ION ATMOSPHERE (QUALITATIVE)

The Debye-Hückel theory explains the behavior of ions in electrolyte solutions, particularly why molar conductance increases with dilution. It introduces the concept of an 'ion atmosphere'.

Ion Atmosphere

Each ion in solution is surrounded by a cluster of oppositely charged ions, forming a dynamic 'ionic atmosphere'. This atmosphere neutralizes the charge of the central ion, reducing its effective charge and influencing its movement.

Asymmetric Effect, Relaxation Effect, and Electrophoretic Effect

Asymmetric Effect (or Relaxation Effect): When an ion moves under an applied electric field, it tends to drag its surrounding ion atmosphere with it. However, the ion atmosphere cannot respond instantaneously to the movement of the central ion. This asymmetry means that the ion atmosphere exerts a retarding force on the central ion, opposing its motion and thus reducing its mobility. This effect is more pronounced at higher concentrations.

Electrophoretic Effect: The ions in the ion atmosphere are also in motion within the solvent. As the central ion moves, it encounters the solvent molecules that are being dragged by the counter-ions in the atmosphere. This movement of solvent due to the motion of counter-ions creates a backflow that opposes the motion of the central ion, further reducing its mobility.

Both these effects lead to a decrease in the effective mobility of ions as concentration increases, explaining why molar conductance decreases with increasing concentration.

DEBYE–HÜCKEL LIMITING LAW

The Debye-Hückel limiting law mathematically describes the activity coefficients of ions in dilute solutions. It predicts that the activity coefficient (γ) of an ion decreases as the square root of the ionic strength (I) increases:

Formula (for a single ion): $\log(\gamma_{\pm}) = -A|z_{+}z_{-}|\sqrt{I}$

where:

$\gamma_{\pm}$ is the mean activity coefficient

A is a constant dependent on temperature and solvent properties

z_{+} and z_{-} are the charges of the cation and anion, respectively

I is the ionic strength of the solution ($I = \frac{1}{2} \Sigma c_i z_i^2$)

The law is 'limiting' because it is valid only for very dilute solutions where ion-ion interactions are minimal and the ions can be treated as point charges.

Estimation of Activity Coefficient

The law allows for the estimation of activity coefficients, which are crucial for accurate thermodynamic calculations in electrolyte solutions. A more general form used is:

$\log(\gamma_i) = -(z_i^2 A \sqrt{I}) / (1 + B a_0 \sqrt{I})$

where 'a_0' is the effective size of the ion and 'B' is another constant. For dilute solutions (where $B a_0 \sqrt{I} << 1$), this simplifies to the limiting law.

OSTWALD'S DILUTION LAW

Ostwald's dilution law relates the molar conductance of a weak electrolyte at a given concentration to its molar conductance at infinite dilution. It is based on the concept of degree of dissociation (α) and assumes that only the undissociated molecules are in equilibrium with the ions. For a weak electrolyte $A_{\nu+}B_{\nu-} \rightleftharpoons \nu_{+}A^{+} + \nu_{-}B^{-}$:

Degree of dissociation: $\alpha = \Lambda_m / \Lambda_m^{\infty}$

Dissociation constant (K_a): $K_a = (C \alpha^2) / (1 - \alpha)$

Substituting α:

$K_a = (C (\Lambda_m / \Lambda_m{}^{\infty})^2) / (1 - \Lambda_m / \Lambda_m{}^{\infty})$

$K_a = (C (\Lambda_m)^2 / (\Lambda_m{}^{\infty})^2) / ((\Lambda_m{}^{\infty} - \Lambda_m) / \Lambda_m{}^{\infty})$

Simplified form: $K_a = C (\Lambda_m)^2 / (\Lambda_m{}^{\infty} (\Lambda_m{}^{\infty} - \Lambda_m))$

This law holds well for weak electrolytes at low concentrations.

IONIC MOBILITY (U)

Ionic mobility is defined as the velocity of an ion under a unit electric field (field strength of 1 V/cm). It is a measure of how fast an ion can move through a solution.

The molar ionic conductivity at infinite dilution ($\lambda_{\pm}{}^{\infty}$) is related to ionic mobility ($u_{\pm}$) by:

$\lambda_{\pm}{}^{\infty} = F u_{\pm}$

where F is the Faraday constant.

APPLICATIONS OF CONDUCTANCE MEASUREMENT

Determination of Solubility Product (K_{sp})

The solubility of sparingly soluble salts can be determined using conductivity measurements. For a salt M_xY_y, its solubility S (in mol/L) can be related to its molar conductance at infinite dilution ($\Lambda_m{}^{\infty}$) and the specific conductance of its saturated solution ($\kappa_{solution}$) when the conductivity of the solvent (κ_{water}) is known:

$\Lambda_m{}^{\infty}(M_xY_y) = (\kappa_{solution} - \kappa_{water}) / S$

From $\Lambda_m{}^{\infty}$ and S, the K_{sp} can be calculated, as $K_{sp} = [M^+]^x[Y^-]^y = (xS)^x(yS)^y$.

Determination of Ionic Product of Water (K_w)

The ionic product of water (K_w) can be determined by measuring the specific conductance of pure water at a given temperature, which is primarily due to H^+ and OH^- ions.

$K_w = [H^+][OH^-] = (\Lambda_m^\infty(H_2O) \times \kappa_{water}) / (1000)$

Where κ_{water} is the specific conductance of pure water, and $\Lambda_m^\infty(H_2O)$ is the molar conductivity of water (which is very small but can be determined from data of H^+ and OH^- ions).

Conductometric Titrations

Conductometric titration is a method of determining the equivalence point of a titration by monitoring the change in the conductance of the solution as a titrant is added. It is useful for titrations where other indicators fail, such as the titration of a weak acid with a strong base or vice versa, or the titration of salts that do not have sharp color changes.

Example: Titration of HCl (strong acid) with NaOH (strong base):

Initially, conductance is high due to H^+ ions. As NaOH is added, H^+ ions are replaced by less mobile Na^+ ions, causing conductance to decrease. At the equivalence point, conductance is minimum. Beyond the equivalence point, excess NaOH (containing highly mobile OH^- ions) increases conductance rapidly.

TRANSPORT NUMBER

Transport number (t_+ or t_-) represents the fraction of total charge carried by a specific ion (cation or anion) during electrolysis. It is the ratio of the mobility of a cation to the sum of the mobilities of both cation and anion, weighted by their concentrations.

For a 1:1 electrolyte:

$t_+ = U_+ / (U_+ + U_-)$

$t_- = U_- / (U_+ + U_-)$

$t_+ + t_- = 1$

The transport number is also related to molar conductances at infinite dilution:

$t_+ = \lambda_+^\infty / (\lambda_+^\infty + \lambda_-^\infty) = \lambda_+^\infty / \Lambda_m^\infty$

$t_- = \lambda_-^\infty / (\lambda_+^\infty + \lambda_-^\infty) = \lambda_-^\infty / \Lambda_m^\infty$

Principles of Hittorf’s Method

Hittorf's method determines transport numbers by measuring the change in concentration of ions in the electrolyte solution near the electrodes during electrolysis. The method accounts for the ions that migrate towards the electrodes and the ions that are discharged at the electrodes. By carefully measuring the amount of metal deposited at the cathode and the change in electrolyte concentration in the anode and cathode compartments, transport numbers can be calculated.

Principles of Moving-boundary Method

The moving-boundary method directly measures the speed of ions relative to the solvent. It involves electrolysis of a solution containing a specific ion (e.g., K^+ in KCl) moving between a leading electrolyte (e.g., LiCl) and a trailing electrolyte (e.g., $CdCl_2$). The boundary between these ions is sharp. When an electric field is applied, the ions move at different speeds. The transport number is calculated from the ratio of the speed of the ion of interest to the speed of the boundary.

NUMERICAL PROBLEMS

PROBLEM 1: SPECIFIC AND MOLAR CONDUCTANCE

A conductivity cell has a cell constant of 0.5 cm^{-1}. If the resistance of a 0.01 M KCl solution measured in this cell is 400 Ω, calculate the specific conductance and molar conductance of the solution.

Solution

Given:

Cell constant (K) = 0.5 cm^{-1}

Resistance (R) = 400 Ω

Concentration (C) = 0.01 M = 0.01 mol/L = 0.01 mol/1000 cm^3

1. Calculate Specific Conductance (κ):

$\kappa = G \times K$

First, calculate Conductance (G): $G = 1/R = 1/400\ \Omega = 0.0025\ \text{S}$

Now, calculate κ:

$\kappa = 0.0025\ \text{S} \times 0.5\ \text{cm}^{-1} = 0.00125\ \text{S cm}^{-1}$

2. Calculate Molar Conductance (Λ_m):

Convert concentration to mol/cm^3: $C = 0.01\ \text{mol/L} = 0.01\ \text{mol} / 1000\ \text{cm}^3 = 1 \times 10^{-5}\ \text{mol/cm}^3$

$\Lambda_m = \kappa / C$

$\Lambda_m = (0.00125\ \text{S cm}^{-1}) / (1 \times 10^{-5}\ \text{mol/cm}^3)$

$\Lambda_m = 125\ \text{S cm}^3\ \text{mol}^{-1} = 125\ \text{S cm}^2/\text{mol}$

PROBLEM 2: KOHLRAUSCH'S LAW

The molar conductances at infinite dilution for NaCl, HCl, and NaAc (Sodium Acetate) are 126.4, 426.1, and 91.0 S cm^2/mol, respectively. Calculate the molar conductance at infinite dilution for acetic acid (HAc).

Solution

Using Kohlrausch's Law: $\Lambda_m^\infty(\text{HAc}) = \Lambda_m^\infty(\text{H}^+) + \Lambda_m^\infty(\text{Ac}^-)$

We can express the given values as:

$\Lambda_m^\infty(\text{NaCl}) = \Lambda_m^\infty(\text{Na}^+) + \Lambda_m^\infty(\text{Cl}^-) = 126.4\ \text{S cm}^2/\text{mol}$

$\Lambda_m^\infty(\text{HCl}) = \Lambda_m^\infty(\text{H}^+) + \Lambda_m^\infty(\text{Cl}^-) = 426.1\ \text{S cm}^2/\text{mol}$

$\Lambda_m^\infty(\text{NaAc}) = \Lambda_m^\infty(\text{Na}^+) + \Lambda_m^\infty(\text{Ac}^-) = 91.0\ \text{S cm}^2/\text{mol}$

We want to find $\Lambda_m^\infty(\text{HAc}) = \Lambda_m^\infty(\text{H}^+) + \Lambda_m^\infty(\text{Ac}^-)$.

We can combine the given equations:

$\Lambda_m^\infty(\text{HAc}) = \Lambda_m^\infty(\text{HCl}) + \Lambda_m^\infty(\text{NaAc}) - \Lambda_m^\infty(\text{NaCl})$

Λ_m^{∞}(HAc) = 426.1 + 91.0 - 126.4 S cm²/mol

Λ_m^{∞}(HAc) = 517.1 - 126.4 S cm²/mol

Λ_m^{∞}(HAc) = 390.7 S cm²/mol

PROBLEM 3: OSTWALD'S DILUTION LAW

The molar conductance of a 0.01 M acetic acid solution at 25°C is 150 S cm²/mol. The molar conductance of acetic acid at infinite dilution is 390 S cm²/mol. Calculate the dissociation constant (K_a) for acetic acid at this concentration.

Solution

Given:

Concentration (C) = 0.01 M

Molar conductance (Λ_m) = 150 S cm²/mol

Molar conductance at infinite dilution (Λ_m^{∞}) = 390 S cm²/mol

1. Calculate the degree of dissociation (α):

$\alpha = \Lambda_m / \Lambda_m^{\infty}$

$\alpha = 150 \text{ S cm}^2\text{/mol} / 390 \text{ S cm}^2\text{/mol} \approx 0.3846$

2. Calculate the dissociation constant (K_a) using Ostwald's dilution law formula:

$K_a = C \alpha^2 / (1 - \alpha)$

$K_a = (0.01 \text{ M}) \times (0.3846)^2 / (1 - 0.3846)$

$K_a = (0.01) \times (0.1480) / (0.6154)$

$K_a = 0.001480 / 0.6154$

$K_a \approx 0.002405 \text{ M}$

Alternatively, using the simplified form:

$K_a = C (\Lambda_m)^2 / (\Lambda_m^{\infty} (\Lambda_m^{\infty} - \Lambda_m))$

$K_a = (0.01 \text{ M}) \times (150 \text{ S cm}^2\text{/mol})^2 / (390 \text{ S cm}^2\text{/mol} \times (390 - 150) \text{ S cm}^2\text{/mol})$

K_a = (0.01) × (22500) / (390 × 240)

K_a = 225 / 93600

K_a ≈ 0.002403 M

The dissociation constant for acetic acid at this concentration and temperature is approximately 0.0024 M.