Electrochemistry ①

Kohlrauch's law of independent migration of ions.

According to this law, at infinite dilution, when the dissociation of an electrolyte is complete, each ion makes a definite contribution towards the molar conductance of the electrolyte, irrespective of the nature of the other ion ~~with~~ with which it is associated. The value of molar conductance at infinite dilution for any electrolyte can be given by the sum of the contribution of cations and anions

$$\Lambda_0 = \nu_c \lambda_c^0 + \nu_a \lambda_a^0$$

Where λ_c^0 and λ_a^0 are the ionic conductances at infinite dilution of cations and anions respectively.

ν_c and ν_a are the number of cations and anions per formula unit of electrolyte

e.g $\nu_c = \nu_a = 1$ for HCl, NaCl etc.

$\nu_c = 1$ & $\nu_a = 2$ for $MgCl_2$

$$\Lambda_m^0 \text{ for } MgCl_2 = \lambda_{Mg^{2+}}^0 + 2\lambda_{Cl^-}$$

In terms of equivalent conductance, Kohlrauch's law may be stated as — The equivalent conductance of an electrolyte at infinite dilution is equal to the sum of the equivalent conductances of the cation and anion.

$$\Lambda_{eq}^0 = \lambda_c^0 + \lambda_a^0$$

Where λ_c^0 and λ_a^0 are the equivalent conduces of cations and anions.

Molar conductance Λ_m is related to the equivalent conductance (Λ_{eq}) according to expression.

$$\Lambda^0_{eq} = \frac{\Lambda^0_m}{\nu_+ Z_+} \quad \text{or} \quad \Lambda^0_{eq} = \frac{\Lambda^0_m}{\nu_- Z_-}$$

Where ν_+ and ν_- are the stoichometric numbers of the cation and anions respectively present in one formula unit of the electrolyte and Z_+ and Z_- are the charges on the cation and anion respectively.

Application of Kohlrauch's law.

I. Calculation of molar conductance at infinite dilution (Λ_0) for weak electrolytes.

The molar conductance of weak electrolytes at infinite dilution cannot be obtained graphically by extrapolation. However, the application of Kohlrauch's law enables indirect evaluation in such cases. For example, molar conductance of acetic acid at infinite dilution can be calculated from the molar conductances at infinite dilution of HCl, CH_3COONa, and NaCl, as illustrated below.

$$\Lambda^0_{CH_3COO^-H} = \Lambda^0_{CH_3COO^-} + \lambda^0_{H^+}$$

$$\Lambda^0_{HCl} = \lambda^0_{H^+} + \lambda^0_{Cl^-}$$

$$\Lambda^0_{CH_3COONa} = \lambda^0_{CH_3COO^-} + \lambda^0_{Na}.$$

$$\Lambda^0_{NaCl} = \lambda^0_{Na^+} + \lambda^0_{Cl^-}$$

$$\Lambda^0_{CH_3COOH} = \Lambda^0_{HCl} + \Lambda^0_{CH_3COONa} - \Lambda^0_{NaCl}.$$

$$= (\lambda^0_{H^+} + \lambda^0_{Cl^-}) + (\lambda^0_{CH_3COO^-} + \lambda^0_{Na^+}) - (\lambda^0_{Na^+} + \lambda^0_{Cl^-})$$

$$= \lambda^0_{CH_3COO^-} + \lambda^0_{H^+}$$

~~Numerical~~

II. Calculation of degree of dissociation of a weak electrolyte.

Calculation of degree of dissociation of a weak electrolyte :- The degree of dissociation of a weak electrolyte at ~~a~~ infinite dilution can be determined by dividing equivalent / molar conductivity of the electrolyte at a given concentration by the equivalent / molar conductivity of the same electrolyte at infinite dilution.

$$\text{Degree of dissociation } (\alpha) = \frac{\Lambda_c}{\lambda^0}$$

Where Λ_c is the conductance at concen^n c,

Numerical problems of Kohlrausch's law.

① Calculate Λ_m^0 for acetic acid from the following data.

$\Lambda^0_m(HCl) = 426\ ohm^{-1}\,cm^2\,mol^{-1}$ $\Lambda_m^0(NaCl) = 126\ ohm^{-1}\,cm^2\,mol^{-1}$

and $\Lambda_m^0(CH_3COONa) = 91\ ohm^{-1}\,cm^2\,mol^{-1}$

Sol^n From Kohlrausch's law

$$\Lambda^0_{CH_3COOH} = \Lambda^0_{HCl} + \Lambda^0_{CH_3COONa} - \Lambda^0_{NaCl}.$$

$$= (426 + 91 - 126)\ ohm^{-1}\,cm^2\,mol^{-1}$$

$$= 391\ ohm^{-1}\,cm^2\,mol^{-1}$$

2. The equivalent conductance of acetic acid at 298 K at the concentration of 0.1 N and 0.001 N are 5.20 and 49.2 $ohm^{-1}\,cm^2\,equ^{-1}$, respectively, Calculate the degree of dissociation of acetic acid, at these concentrations. Given that $\lambda^0(H^+)$ and $\lambda^0(CH_3COO^-)$ are 349.8 and 40.9 $ohm^{-1}\,cm^2\,equ^{-1}$ respectively.

Solution

Degree of dissociation is given by $\alpha = \frac{\Lambda_c}{\Lambda^0}$

(1) To calculate $\Lambda^0_{CH_3COOH}$.

$$\Lambda^0_{CH_3COOH} = \lambda^0_{CH_3COO^-} + \lambda^0_{H^+} = 349.8 + 40.9$$
$$= 390 \text{ ohm}^{-1} \text{cm}^2 \text{eq}^{-1}.$$

2. To calculate the degree of dissociation.

At $c = 0.1N$ $\alpha = \frac{\Lambda_c}{\Lambda^0} = \frac{5.20}{390.7} = 0.013$ i.e. $\alpha = 1.3\%$

At $c = 0.001N$ $\alpha = \frac{\Lambda_c}{\Lambda^0} = \frac{49.2}{390.7} = 0.125$ $\alpha = 12.5\%$.

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3. The molar conductivities of $AgNO_3$, KBr and KNO_3 at infinite dilutions were found to be 120.0, 138.0 and 132 mho cm^{2} mol^{-1} respectively. Find the molar conductance of AgBr at infinite dilution. If the specific conductivity of 0.001M solution of AgBr at 25°C is 3×10^{-5} ohm cm^{-1}, what would be the degree of dissociation?

Soln We know that

$$\Lambda^0_{AgBr} = \Lambda^0_{AgNO_3} + \Lambda^0_{KBr} - \Lambda^0_{KNO_3}$$
$$= 120 + 138 - 132 = 126 \text{ mho cm}^2 \text{mol}^{-1};$$

given that the specific conductance of 0.001M AgBr solution is $= 3\times10^{-5}$ mho cm^{-1}.

Hence, the molar conductance of 0.001M solution.

$$= \frac{1000\,\kappa}{M} = \frac{1000 \times 3\times10^{-5}}{0.001}$$
$$= 30 \text{ mho cm}^{-1} \text{mol}^{-1}$$

The degree of dissociation is $\frac{\Lambda_{0.001M}(AgBr)}{\Lambda^0} = \frac{30}{126}$

$$= 0.238 \text{ or } 23.8\%.$$

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The Debye Huchel theory of strong electrolytes. (Debye Huchel Onsagar equation)

A quantitative explanation of the behaviour of dilute solution of strong electrolyte was put forward by Peter Debye and E. Hückel in 1923, and is known as the Debye Hückel theory of strong electrolytes.

☆ In fact the conductance of electrolyte depends upon two factors (i) Number of ions in the solution and (ii) speed or mobility of ions.

In case of weak electrolytes the increase in conductance on dilution is due to the increase in number of ions which is due to the increase in the dissociation of the electrolyte.

Strong electrolytes exist as ions even in solid state and completely ionised in solution at all concentrations.

The electrostatic forces between the ions are inversely proportional to the dielectric constant of the medium. If the solvent has high dielectric constant (e.g water), the interionic attraction will be less, and when the solution is diluted the ions will lie far apart from one another. If the same electrolyte is treated with a solvent of small dielectric constant (e.g alcohol), the electrolyte will completely ionised but not fully dissociated and remain as doublet or ion pair (A^+B^-) ☆

According to the modern theory of strong electrolytes, the degree of ionization of strong electrolytes is unity even at moderate concentrations. Debye and Hückel suggested that the increase in molar conductance of strong electrolytes on dilution is due to the increase in mobility of ions.

The mobility of ions as well as the conductance in case of strong electrolytes decreases due to interionic effect. Thus the interionic effect plays a major role in the molar conductance of a particular electrolyte.

The electrostatic attraction among the oppositely charged ions which effect the speed of the ion in an electric