Kohlrausch law

EFFECT OF DILUTION ON CONDUCTANCE

(i) When we increase the dilution of electrolyte, magnitude of specific conductance decreases, because number of ions in 1 cm^3 volume of electrolyte decreases.

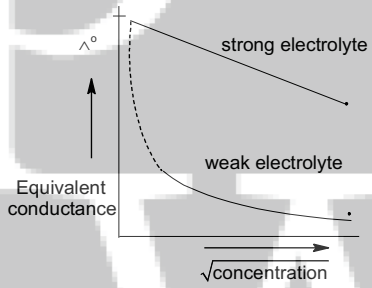
(ii) When dilution of electrolyte increases, magnitude of molar conductance and equivalent conductance increases, because number of ions increases after dilution.

(iii) The molar conductivity of strong electrolytes is found to vary with concentration according to the equation.

$$\wedge_m^c = \wedge_m^o - b\sqrt{c}$$

where $\wedge^c$ = equivalent conductivity at fixed concentration

$\wedge^o$ = equivalent conductivity of infinite dilution



(iv) Degree of dissociation $(\alpha) = \frac{\wedge_m^c}{\wedge_m^o}$

The maximum (limiting) value of equivalent conductivity (value obtained at infinite dilution or zero concentration) for a strong electrolyte can be obtained by extrapolating the equivalent conductance graph to zero concentration.

However, in weak electrolytes the value of equivalent conductance at infinite dilution (λ_∞) or at zero concentration (λ_0) cannot be obtained by extrapolating the concerned graphs. The value of λ_∞ for weak electrolytes is actually obtained by an indirect method based on Kohlrausch's law.

According to this law "the equivalent conductance of an electrolytes at inifinite dilution is the sum of two values , one depending upon the cation and the other upon the anion"

Mathematically, $\lambda_\infty = \lambda_c + \lambda_a$ where λ_c and λ_a are the equivalent conductivities (ionic conductances) of the cation and anion respectively.Based on Kohlrausch's law, it is possible to calculate the molar conductivity of a weak electrolyte at infinite dilution by simply adding and subtracting Λ_∞ values of appropriate electrolytes. Taking, for example, acetic acid, we have

$$\Lambda^\infty(HAc) = \Lambda^\infty(NaAc) + \Lambda^\infty(HCl) - \Lambda^\infty(NaCl)$$

$$= \lambda^\infty(Na^+) + \lambda^\infty(Ac^-) + \lambda^\infty(H^+) + \lambda^\infty(Cl^-) - \lambda^\infty(Na^+) - \lambda^\infty(Cl^-)$$

$$= \lambda^\infty(H^+) + \lambda^\infty(Ac^-) = \Lambda^\infty(HAc)$$

Example

Calculate molar conductivities at infinite dilution and 25°C for potash alum

$K_2SO_4Al_2(SO_4)_3 \cdot 24\ H_2O$ Given

$$\lambda^\infty(K^+) = 73.52\ Scm^2mol^{-1}$$

$$\lambda^\infty\ (Al^{3+}) = 189\ Scm^2mol^{-1}$$

$$\Lambda^\infty(SO_4^{2-}) = 160\ Scm^2mol^{-1}$$

Solution: $\Lambda_m^\infty = 2\lambda^\infty(K^+) + 2\lambda^\infty\ (Al^{3+}) + 4\Lambda^\infty(SO_4^{2-})$

$= 2 \times 73.52 + 2 \times 189 + 4 \times 160 = 1165.04\ S\ cm^2\ mol^{-1}$

Application of Kohlrausch's Law

(i) **Determination of Λ_m^0 of a weak electrolyte:**

In order to calculate Λ_m^0 of a weak electrolyte say CH_3COOH, we determine experimentally Λ_m^0 values of the following three strong electrolytes:

(a) A strong electrolyte containing same cation as in the test 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.

Λ_m^0 of CH_3COOH is then given as:

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

Proof:

$$\Lambda_m^0 (HCl) = \lambda_{H}^0 + \lambda_{Cl^-} \quad \ldots I$$

$$\Lambda_m^0 (CH_3COONa) = \lambda^0_{CH_3COO^-} + \lambda_{Na^+} \quad \ldots II$$

$$\Lambda_m^0 (NaCl) = \lambda^0_{Na^+} + \lambda^0_{Cl^-} \quad \ldots III$$

Adding equation (I) and equation (II) and subtracting (III) from them:

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

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

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

(iv) **Determination of ionic product of water:**

From Kohlrausch's law, we determine Λ_m^0 of H_2O where Λ_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.

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

Again using the following equation,

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

$\Rightarrow \wedge_m = \frac{\kappa}{C}$, where C = concentration in mol m^{-3}

Assuming that $\wedge_m$ differs very little from $\wedge_m^0$

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

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

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

K_w is then calculated as:

$K_w = C^2$