

Class \Rightarrow B.Sc. (Hons.) Part II

Subject \Rightarrow Chemistry

Chapter \Rightarrow Conductance (Group-C)

Topic \Rightarrow Kohlrausch's law and its applications.

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Kohlrausch's Law

The molar conductivity of an electrolyte at infinite dilution is the sum of the ionic conductivities of the cations and the anions each multiplied with the number of ions present in one formula of the electrolyte.

$$\Lambda_m^{\circ} \text{ for } AxBy = x\lambda_A^{\circ} + y\lambda_B^{\circ}$$

\therefore Simply,

$$\Lambda_m^{\circ} = \lambda_+^{\circ} + \lambda_-^{\circ}$$

This is known as Kohlrausch law of independent migration of ions.

Where Λ_m° is the molar conductivity of the electrolyte at infinite dilution.

λ_A° and λ_B° are the molar conductivities of the cation and the anion respectively at infinite dilution.

Thus,

$$\Lambda_m^{\circ} \text{ for NaCl} = \lambda_{Na^+}^{\circ} + \lambda_{Cl^-}^{\circ}$$

$$\Lambda_m^{\circ} \text{ for BaCl}_2 = \lambda_{Ba^{2+}}^{\circ} + 2\lambda_{Cl^-}^{\circ}$$

$$\Lambda_m^{\circ} \text{ for Al}_2(SO_4)_3 = 2\lambda_{Al^{3+}}^{\circ} + 3\lambda_{SO_4^{2-}}^{\circ}$$

In terms of equivalent conductivities, Kohlrausch's law is defined as -

The equivalent conductivity of an electrolyte at infinite dilution is the sum of two values, one depending upon the cation and the other upon the anion.

i.e.

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

where λ_c and λ_a are called the ionic conductivities at infinite dilution of the cation and the anion respectively.

\Rightarrow Molar conductivity Λ_m is related to equivalent conductivity Λ_{eq} according to the equation

$$\Lambda_{eq} = \frac{\Lambda_m}{n_+ z_+} \quad \text{or} \quad \Lambda_{eq} = \frac{\Lambda_m}{n_- z_-}$$

Where n_+ and n_- are the number of cations and anions present per formula unit of the electrolyte and z_+ and z_- are the charges on the cations and the anions respectively.

Applications of Kohlrausch law

(1) calculation of molar conductivity at infinite dilution (Λ°) for weak electrolytes \Rightarrow Molar conductances of strong electrolytes at infinite dilution can be obtained graphically by extrapolation.

However, this can be calculated using Kohlrausch's law.

Consider the example of acetic acid $[CH_3COOH]$ as the weak electrolyte. By Kohlrausch's law,

$$\Lambda^\circ(CH_3COOH) = \lambda_{CH_3COO^-} + \lambda_{H^+}$$

This equation can be arrived at by knowing the molar conductivities at infinite dilution for the strong electrolytes KCl , CH_3COOK and HCl . As per Kohlrausch's law

$$\Lambda^\circ(KCl) = \lambda_{K^+} + \lambda_{Cl^-}$$

$$\Lambda^\circ(CH_3COOK) = \lambda_{CH_3COO^-} + \lambda_{K^+}$$

$$\Lambda^\circ(HCl) = \lambda_{H^+} + \lambda_{Cl^-}$$

Hence we have

$$\lambda_{CH_3COO^-} + \lambda_{H^+} = (\lambda^\circ_{CH_3COO^-} + \lambda^\circ_{K^+}) + (\lambda^\circ_{H^+} + \lambda^\circ_{Cl^-}) - (\lambda^\circ_{K^+} + \lambda^\circ_{Cl^-})$$

$$\text{i.e. } \Lambda^\circ(CH_3COOH) = \Lambda^\circ(CH_3COOK) + \Lambda^\circ(HCl) - \Lambda^\circ(KCl)$$

③

② Calculation of the degree of dissociation \Rightarrow for a weak electrolyte, if Λ_m is the molar conductivity of a solution of any concentration C and Λ_m^{∞} the molar conductivity at infinite dilution (ie zero concentration), then we have

$$\text{Degree of dissociation} (\alpha) = \frac{\Lambda_m}{\Lambda_m^{\infty}}$$

The value of Λ_m^{∞} for the weak electrolytes can be calculated using Kohlrausch's law.

③ Calculation of solubility of a sparingly soluble salt \Rightarrow Salts such as AgCl , BaSO_4 , PbSO_4 etc. which dissolve to a very small extent in water, are called sparingly soluble salts.

Thus by determining the specific conductivity (K) and the molar conductivity (Λ_m) of such a solution, we can obtain solubility as follows -

$$\frac{\Lambda_m}{\text{Molarity}} = K \times 1000 = \frac{K \times 1000}{\text{Solubility}}$$

$$\therefore \text{Solubility} = \frac{K \times 1000}{\Lambda_m}$$

Λ_m^{∞} can be obtained by using Kohlrausch law.

④ Determination of transport number.