Kohlrausch's law.

(1) Kohlrausch law states that, "At time infinite dilution, the molar conductivity of an electrolyte can be expressed as the sum of the contributions from its individual ions" i.e., $\boxed{\Lambda_m^\infty = \nu_+ \lambda_+^\infty + \nu_- \lambda_-^\infty}$, where, ν_+ and ν_- are the number of cations and anions per formula unit of electrolyte respectively and, λ_+^∞ and λ_-^∞ are the molar conductivities of the cation and anion at infinite dilution respectively. The use of above equation in expressing the molar conductivity of an electrolyte is illustrated below,

(i) **Molar conductivity of HCl**: The molar conductivity of HCl at infinite dilution can be expressed as,

$\Lambda_{HCl}^\infty = \nu_{H^+} \lambda_{H^+}^\infty + \nu_{Cl^-} \lambda_{Cl^-}^\infty$; For HCl, $\nu_{H^+} = 1$ and $\nu_{Cl^-} = 1$. So,

$\Lambda_{HCl}^\infty = (1 \times \lambda_{H^+}^\infty) + (1 \times \lambda_{Cl^-}^\infty)$; Hence, $\Lambda_{HCl}^\infty = \lambda_{H^+}^\infty + \lambda_{Cl^-}^\infty$

(ii) **Molar conductivity of $MgCl_2$** : For $MgCl_2$, the molar conductivity at infinite dilution can be expressed as,

$\Lambda_{MgCl_2}^\infty = \nu_{Mg^{2+}} \lambda_{Mg^{2+}}^\infty + \nu_{Cl^-} \lambda_{Cl^-}^\infty$; For $MgCl_2$, $\nu_{Mg^{2+}} = 1$ and $\nu_{Cl^-} = 2$

So, $\Lambda_{MgCl_2}^\infty = 1 \times \lambda_{Mg^{2+}}^\infty + 2 \times \lambda_{Cl^-}^\infty$; Hence, $\Lambda_{MgCl_2}^\infty = \lambda_{Mg^{2+}}^\infty + 2\lambda_{Cl^-}^\infty$

(iii) **Molar conductivity of CH_3COOH** : CH_3COOH in solution ionizes as,

$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$; So, the molar conductivity of CH_3COOH (acetic acid) at infinite dilution can be expressed as, $\Lambda_{CH_3COOH}^\infty = \nu_{H^+} \lambda_{H^+}^\infty + \nu_{CH_3COO^-} \lambda_{CH_3COO^-}^\infty$; For, CH_3COOH, $\nu_{H^+} = 1$ and $\nu_{CH_3COO^-} = 1$

So, $\Lambda_{CH_3COOH}^\infty = 1 \times \lambda_{H^+}^\infty + 1 \times \lambda_{CH_3COO^-}^\infty$ or $\Lambda_{CH_3COOH}^\infty = \lambda_{H^+}^\infty + \lambda_{CH_3COO^-}^\infty$

The molar conductivities of some ions at infinite dilution and 298 K

Cation	$\lambda_+^\infty S\ cm^2 mol^{-1}$	Cation	$\lambda_+^\infty S\ cm^2 mol^{-1}$	Anion	$\lambda_-^\infty S\ cm^2 mol^{-1}$	Anion	$\lambda_-^\infty S\ cm^2 mol^{-1}$
H^+	349.8	Ba^{2+}	127.2	OH^-	198.0	ClO_4^-	68.0
Tl^+	74.7	Ca^{2+}	119.0	Br^-	78.4	SO_4^{2-}	159.2
$K^=$	73.5	Sr^{2+}	119.0	I^-	76.8	CH_3COO^-	40.9
Na^+	50.1	Mg^{2+}	106.2	Cl^-	76.3		

Li^+	38.7			NO_3^-	71.4		

(2) **Applications of Kohlrausch's law:** Some typical applications of the Kohlrausch's law are described below,

(i) **Determination of Λ_m^∞ for weak electrolytes**: The molar conductivity of a weak electrolyte at infinite dilution (Λ_m^∞) cannot be determined by extrapolation method. However, Λ_m^∞ values for weak electrolytes can be determined by using the Kohlrausch's equation. For acetic acid this is illustrated below. According to the Kohlrausch's law, the molar conductivity of acetic acid (CH_3COOH) is given by,

$\Lambda_{CH_3COOH}^\infty = \nu_{H^+}\lambda_{H^+}^\infty + \nu_{CH_3COO^-}\lambda_{CH_3COO^-}^\infty = 1\times\lambda_{H^+}^\infty + 1\times\lambda_{CH_3COO^-}^\infty$; Taking the values of $\lambda_{H^+}^\infty$ and $\lambda_{CH_3COO^-}^\infty$ (from table), we can write, $\lambda_{CH_3COOH}^\infty = (349.8+40.9)\,S\,cm^2mol^{-1} = 390.7\,S\,cm^2mol^{-1}$.

Sometimes, the molar conductivity values for the ions may not be available. In such cases, the following procedure may be followed,

(a) Select a series of strong electrolytes, so that their sum or difference gives the weak electrolyte. Generally, three strong electrolytes are selected.

(b) Measure Λ_m values of these salts at various concentrations (C_m) and plot Λ_m against $\sqrt{C_m}$ for each salt separately. Determine Λ_m^∞ for each salt (Strong electrolyte) by extrapolation method.

(c) Add or subtract the equations to get the Λ_m^∞ of the weak electrolyte.

Suppose we have to determine the molar conductivity of a weak electrolyte MA at infinite dilution. For this purpose, we take three salts, viz., MCl, NaA and NaCl, and determine their Λ_m^∞ values by extrapolation method. Then, according to the Kohlrausch's law, $\Lambda_{MCl}^\infty = \lambda_{M^+}^\infty + \lambda_{Cl^-}^\infty$; $\Lambda_{NaA}^\infty = \lambda_{Na^+}^\infty + \lambda_{A^-}^\infty$; $\Lambda_{NaCl}^\infty = \lambda_{Na^+}^\infty + \lambda_{Cl^-}^\infty$

From these equations, we can write,

$$\Lambda_{MCl}^\infty + \Lambda_{NaA}^\infty - \Lambda_{NaCl}^\infty = (\lambda_{M^+}^\infty + \lambda_{Cl^-}^\infty) + (\lambda_{Na^+}^\infty + \lambda_{A^-}^\infty) - (\lambda_{Na^+}^\infty + \lambda_{Cl^-}^\infty) = \lambda_{M^+}^\infty + \lambda_{A^-}^\infty = \Lambda_{MA}^\infty$$

So, $\Lambda_{MA}^\infty = \Lambda_{MCl}^\infty + \Lambda_{NaA}^\infty - \Lambda_{NaCl}^\infty$

Thus, we can obtain the molar conductivity of a weak electrolyte at infinite dilution from the Λ_m^∞ values of three suitable strong electrolytes.

(ii) **Determination of the degree of ionization of a weak electrolyte**: The Kohlrausch's law can be used for determining the degree of ionization of a weak electrolyte at any concentration. If λ_m^c is the molar conductivity of a weak electrolyte at any concentration C and, λ_m^∞ is the molar conductivity of an electrolyte at infinite dilution. Then, the degree of ionization is given by,

$$\boxed{\alpha_c = \frac{\Lambda_m^c}{\Lambda_m^\infty} = \frac{\Lambda_m^c}{(\nu_+\lambda_+^\infty + \nu_-\lambda_-^\infty)}}$$

Thus, knowing the value of Λ_m^c, and Λ_m^∞ (From the Kohlrausch's equation), the degree of ionization at any concentration (α_c) can be determined.

(iii) **Determination of the ionization constant of a weak electrolyte:** Weak electrolytes in aqueous solutions ionize to a very small extent. The extent of ionization is described in terms of the degree of ionization (α). in solution, the ions are in dynamic equilibrium with the unionized molecules. Such an equilibrium can be described by a constant called **ionization constant**. For example, for a weak electrolyte AB, the ionization equilibrium is, $AB \rightleftharpoons A^+ + B^-$; If C is the initial concentration of the electrolyte AB in solution, then the equilibrium concentrations of various species in the solution are, $[AB] = C(1-\alpha), [A^+] = C\alpha$ and $[B^-] = C\alpha$

Then, the ionization constant of AB is given by, $K = \frac{[A^+][B]}{[AB]} = \frac{C\alpha.C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)}$

We know, that at any concentration C, the degree of ionization (α) is given by, $\alpha = \Lambda_m^c / \Lambda_m^\infty$

Then, $K = \frac{C(\Lambda_m^c/\Lambda_m^\infty)^2}{[1-(\Lambda_m^c/\Lambda_m^\infty)]} = \frac{C(\Lambda_m^c)^2}{\Lambda_m^\infty(\Lambda_m^\infty - \Lambda_m^c)}$; Thus, knowing Λ_m^∞ and Λ_m^c at any concentration, the ionization constant (K) of the electrolyte can be determined.

(iv) **Determination of the solubility of a sparingly soluble salt**: The solubility of a sparingly soluble salt in a solvent is quite low. Even a saturated solution of such a salt is so dilute that it can be assumed to be at infinite dilution. Then, the molar conductivity of a sparingly soluble salt at infinite dilution (Λ_m^∞) can be obtained from the relationship, $\Lambda_m^\infty = \nu_+\lambda_+^\infty + \nu_-\lambda_-^\infty$ ....(i)

The conductivity of the saturated solution of the sparingly soluble salt is measured. Form this, the conductivity of the salt (κ_{salt}) can be obtained by using the relationship, $\boxed{\kappa_{\text{salt}} = \kappa_{\text{sol}} - \kappa_{\text{water}}}$, where, κ_{water} is the conductivity of the water used in the preparation of the saturated solution of the salt.

$$\Lambda_{\text{salt}}^\infty = \frac{1000\,\kappa_{\text{salt}}}{C_m} \qquad \text{........(ii)}$$

From equation (i) and (ii);

$$\boxed{C_m = \frac{1000\ \kappa_{\text{salt}}}{(\nu_+ \lambda_+^{\infty} + \nu_- \lambda_-^{\infty})}},$$

C_m is the molar concentration of the sparingly soluble salt in its saturated solution. Thus, C_m is equal to the solubility of the sparingly soluble salt in the mole per liter units. The solubility of the salt in gram per liter units can be obtained by multiplying C_m with the molar mass of the salt.