KOHLRAUSCH'S law : Independent migration of ions

A survey of eq. conductances at infinite dilution of a no. of electrolytes having an ion in common will bring to light certain regularities

| Electrolyte | $\Lambda_0$ | Electrolyte | $\Lambda_0$ | Diff |
|---|---|---|---|---|
| $KCl$ | 130 | $NaCl$ | 108.9 | 21.1 |
| $KNO_3$ | 126.3 | $NaNO_3$ | 105.2 | 21.1 |
| $K_2SO_4$ | 133 | $Na_2SO_4$ | 111.9 | 21.1 |

It is seen that the difference between the conductances of $K^+$ and $Na^+$ salts are same and independent on the nature of the anion. Kohlrausch ascribed that every ion makes a definite contribution towards the equivalent conductance of the electrolyte, irrespective of the nature of the other ion. "The equivalent conductance at infinite dilution for any electrolyte is the sum of equivalent conductances for the cation and anion at infinite dilution." This is Kohlrausch's law. The law may be represented as

$$\Lambda_0 = \lambda_+^\circ + \lambda_-^\circ \rightarrow ①$$

where $\lambda_+$ and $\lambda_-$ are known as ion conductances for cation and anion of the electrolyte respectively.

The individual ionic conductances are usually determined from their transport no at infinite dilutions. At infinite dilution, an electrolyte is completely dissociated and there is no interionic attraction. The conductance due to cations depend upon their charge and their speed.

$$\lambda_+^\circ = k_1 n_+ z_+ e u$$

Similarly for anion $\lambda_- = k_1 n_- z_- e v$

$z_+e$ and $z_-e$ are charges of cation and anion. $u$ and $v$ are speeds of cation and anion respectively.

Therefore eq ① will be

$$\Lambda_0 = k_1 n_+ z_+ e u + k_1 n_- z_- e v$$

$$= K(u+v) \text{ where } K = k_1 n_+ z_+ e = k_1 n_- z_- e$$

Then,

$$\frac{\lambda_+^\circ}{\Lambda_0} = \frac{Ku}{K(u+v)} = \frac{u}{u+v} = t_+^\circ$$

and $\frac{\lambda_-^\circ}{\Lambda_0} = t_-^\circ$

$t_+^\circ$ and $t_-^\circ$ are transport no. of cation and anion at infinite dilution.

i.e. $\lambda_+^\circ = t_+^\circ \Lambda_0$ and $\lambda_-^\circ = t_-^\circ \Lambda_0$

In case of weak electrolyte Kohlrausch's law is used to measure $\Lambda_0$.

For example, $\Pi_0$ of $CH_3COOH$ can be calculated from equivalent conductances at infinite dilution of three strong electrolytes HCl, $CH_3COONa$ and NaCl

$$\Pi_{0_{HCl}} = \lambda_{H^+} + \lambda_{Cl^-} \rightarrow ①$$

$$\Pi_{0_{NaAc}} = \lambda^{\circ}_{Na^+} + \lambda^{\circ}_{Ac^-} \rightarrow ②$$

$$\Pi_{0_{NaCl}} = \lambda^{\circ}_{Na^+} + \lambda^{\circ}_{Cl^-} \rightarrow ③$$

Adding eqⁿs ① and ② and substracting eq ③, we have

$$\Pi_{0_{HCl}} + \Pi_{0_{NaAc}} - \Pi_{0_{NaCl}} = \lambda^{\circ}_{H^+} + \lambda^{\circ}_{Cl^-} + \lambda^{\circ}_{Na^+} + \lambda^{\circ}_{Ac^-} - \lambda^{\circ}_{Na^+} - \lambda^{\circ}_{Cl^-}$$

$$= \lambda^{\circ}_{H^+} + \lambda^{\circ}_{Ac^-}$$

$$= \Pi^{\circ}_{0_{CH_3COOH}}$$

$$\therefore \Pi^{\circ}_{0(CH_3COOH)} = \Pi^{\circ}_{0(HCl)} + \Pi^{\circ}_{0(NaAc)} - \Pi^{\circ}_{0(NaCl)}$$

The three values of $\Pi^{\circ}_0$ for HCl, NaAc and NaCl are known by extrapolating the graph $\Pi$ vs $\sqrt{c}$ and $\Pi^{\circ}_{0_{CH_3COOH}}$ can be calculated from the relation.