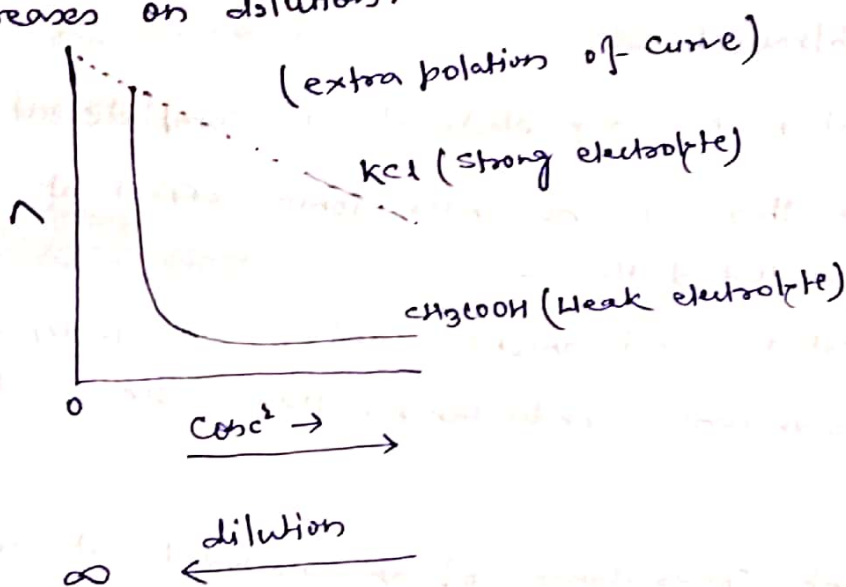


EFFECT of dilution on Conductance :-

When the electrolytic salt is diluted, ionisation increases and the no. of ions increases. So, equivalent conductance and molar conductance increases.

On dilution through no. of ions increases no. of ions per unit volume decreases. So, specific conductance decreases on dilution.



For strong electrolyte Λ_{∞} or Λ_0 can be obtained through extrapolation of curve but this is not possible in case of weak electrolyte.

Degree of Ionisation :-

The fraction of the electrolyte which ionises from one mole of an electrolyte is called degree of ionisation.

It is denoted by α

Where,
$$\alpha = \frac{\Lambda_c}{\Lambda_{\infty}}$$

Where,

$\Lambda_c =$ Equivalent Conductance of 'C' concentration.

$\Lambda_\infty =$ Equivalent Conductance of ∞ dilution.

This is approximately true for weak electrolytes but not in strong electrolytes.

*. Kohlrausch's Law :-

————— x —————

A/c to Kohlrausch —

The dissociation of any electrolyte is complete at ∞ (infinite) dilution and there is no inter-ionic effect at this dilution.

So, he concluded that —

Both cation's and anions contributed independently towards equivalent conductance. Hence, he stated his law as —

Equivalent conductance of an electrolyte at infinite dilution (∞) is composed of two factors — one contributed by cation and the other contributed by an anion. i.e.

$$\Lambda_\infty = v^+ \lambda^+ + v^- \lambda^-$$

Where, λ^+, λ^- are the ionic conductance of cation & anion.
 v^+, v^- are their valencies.

Application of Kohlrausch's law:-

(7)

(1) Determination of molar conductivity of weak electrolyte at infinite dilution. (Λ_{∞}).

It is determined with the help of molar conductivity of strong electrolyte.

for eg -

Gives,

$$\Lambda_{\infty} \text{C}_2\text{H}_5\text{COONa} = 85.1 \text{ ohm}^{-1} \text{cm}^2 \text{eq}^{-1}$$

$$\Lambda_{\infty} \text{HCl} = 426.3 \text{ " " " "}$$

$$\Lambda_{\infty} \text{NaCl} = 126.1 \text{ " " " "}$$

$$\Lambda_{\infty} \text{C}_2\text{H}_5\text{COOH} = ?$$

$$\Lambda_{\infty} \text{C}_2\text{H}_5\text{COONa} = \lambda_{\text{C}_2\text{H}_5\text{COO}^-} + \lambda_{\text{Na}^+} = 85.1 \text{ ohm}^{-1} \text{cm}^2 \text{eq}^{-1} \quad \text{--- (1)}$$

$$\Lambda_{\infty} \text{HCl} = \lambda_{\text{H}^+} + \lambda_{\text{Cl}^-} = 426.3 \text{ " " " "} \quad \text{--- (2)}$$

$$\Lambda_{\infty} \text{NaCl} = \lambda_{\text{Na}^+} + \lambda_{\text{Cl}^-} = 126.1 \text{ " " " "} \quad \text{--- (3)}$$

$$\Lambda_{\infty} \text{C}_2\text{H}_5\text{COOH} = \lambda_{\text{C}_2\text{H}_5\text{COO}^-} + \lambda_{\text{H}^+} = ?$$

on adding eqs - (1) & (2) and then subtracting eqs - (3)

We get -

$$\lambda_{\text{C}_2\text{H}_5\text{COO}^-} + \cancel{\lambda_{\text{Na}^+}} + \lambda_{\text{H}^+} + \cancel{\lambda_{\text{Cl}^-}} - \cancel{\lambda_{\text{Na}^+}} - \cancel{\lambda_{\text{Cl}^-}} = 85.1 + 426.3 - 126.1$$

$$\lambda_{\text{C}_2\text{H}_5\text{COO}^-} + \lambda_{\text{H}^+} = 385.3$$

$$\text{ohm}^{-1} \text{cm}^2 \text{eq}^{-1}$$

$$\therefore \Lambda_{\infty} \text{C}_2\text{H}_5\text{COOH} = 385.3 \text{ ohm}^{-1} \text{cm}^2 \text{eq}^{-1}$$

② Determination of degree of dissociation (α) for weak electrolyte.

It is determined from the formula:-

$$\alpha = \frac{\Lambda_c}{\Lambda_{\infty}}$$

Λ_c = molar conductivity of the electrolyte at any concentration.

Λ_{∞} = molar conductivity of the electrolyte at infinite dilution.

α = degree of dissociation of weak electrolyte.

③ Determination of dissociation constant (K_c) of weak electrolytes -

We know that an equilibrium constant -

$$K_c = \frac{c\alpha^2}{1-\alpha}$$

for weak acid $K_a = \frac{c\alpha^2}{1-\alpha}$

for weak base $K_b = \frac{c\alpha^2}{1-\alpha}$

This formula is not applicable to strong electrolytes such as NaCl, NaOH, AgNO₃, CuSO₄, H₂SO₄ etc because, strong electrolytes are almost 100% dissociated in aq. soln.

Dr. A. P. Gupta
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