Chemistry Study Materials for Class 12
(NCERT Based Notes of Chapter -03)
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Electrochemistry

Molar conductivity (λm)

It is the conductivity of 1 mole of an electrolytic solution kept between two electrodes with unit area of cross section and at a distance of unit length. It is related to conductivity of the solution by the equation,

$\lambda m = \kappa/C$ (where C is the concentration of the solution)

Or, $\lambda m = 1000\ \kappa/M$ (where M is the molarity)

The unit of molar conductivity is $\Omega^{-1}cm^{2}\ mol^{-1}$ or $S\ cm^{2}\ mol^{-1}$.

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Variation of conductivity and Molar conductivity with concentration (dilution)

Both conductivity and molar conductivity change with the concentration of the electrolyte. We know that when a solution is diluted, its concentration decreases. *For both strong and weak electrolytes, conductivity always decreases with dilution*. This is because conductivity is the conductance of unit volume of electrolytic solution. *As dilution increases, the number of ions per unit volume decreases and hence the conductivity decreases*.

For both strong and weak electrolytes, the molar conductivity increase with dilution (or decrease with increase in concentration), but due to different reasons.

For strong electrolytes, as dilution increases, the force of attraction between the ions decreases and hence the ionic mobility increases. So, molar conductivity increases. When dilution reaches maximum or concentration approaches zero, the molar conductivity becomes maximum and it is called the limiting molar conductivity ($\lambda^{0}m$).

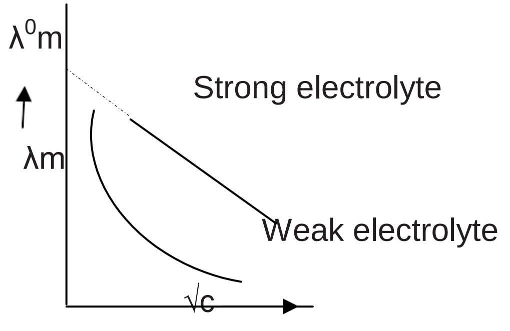
For strong electrolytes, the relation between λm and concentration can be given as:

$\lambda m = \lambda^{0}m - A\sqrt{c}$

Where 'c' is the concentration and A is a constant depends on temperature, the nature of the electrolyte and the nature of the solvent. All electrolytes of a particular type have the same value for 'A'.

For weak electrolytes, as dilution increases, the degree of dissociation increases. So the number of ions and hence the molar conductivity increases.

The variation of λm for strong and weak electrolytes is shown in the following graphs:



For strong electrolytes, the value of $\lambda^{0}m$ can be determined by the extrapolation of the graph. But for weak electrolytes, it is not possible since the graph is not a straight line. So their $\lambda^{0}m$ values are calculated by applying Kohlrausch's law of independent migration of ions.

Kohlrausch's law of independent migration of ions

The law states that the limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and the cation of the electrolyte.

Thus if an electrolyte on dissociation gives $n_{(+)}$ cations and $n_{(-)}$ anions, its limiting molar conductivity is given as: $\lambda^0 m = n_{(+)}\lambda^0_{(+)} + n_{(-)}\lambda^0_{(-)}$

For NaCl, $\lambda^0 m_{\ (NaCl)} = \lambda^0_{(Na+)} + \lambda^0_{(Cl-)}$

For $CaCl_2$, $\lambda^0 m_{\ (CaCl2)} = \lambda^{(0a2+)} + 2 \times \lambda^0_{(Cl-)}$

Applications of Kohlrausch's law

1) ***Determination of $\lambda^0 m$ of weak electrolytes***

By knowing the $\lambda^0 m$ values of strong electrolytes, we can calculate $\lambda^0 m$ of weak electrolytes. For e.g. we can determine the $\lambda^0 m$ of acetic acid (CH_3COOH) by knowing the $\lambda^0 m$ of CH_3COONa, NaCl and HCl as follows:

$\lambda^0 m\ (CH_3COONa) = \lambda^0 CH_3COO^- + \lambda^0 Na^+$ .... (1)

$\lambda^0 m\ (HCl) = \lambda^0 H+ + \lambda^0 Cl$............... (2)

$\lambda^0 m\ (NaCl) = \lambda^0 Na+ + \lambda^0 Cl$............. (3)

(1) + (2) - (3) gives:

$$\lambda^0 m\ (CH_3COONa) + \lambda^0 m\ (HCl) - \lambda^0 m\ (NaCl) = \lambda^0 CH_3COO^- + \lambda^0 Na^+ + \lambda^0 H^+ + \lambda^0 Cl^- - \lambda^0 Na^+ - \lambda^0 Cl^-$$

$$= \lambda^0 CH_3COOH$$

2) ***Determination of degree of dissociation of weak electrolytes***

By knowing the molar conductivity at a particular concentration ($\lambda^c m$) and limiting molar conductivity ($\lambda^0 m$), we can calculate the degree of dissociation (α) as,

$$\boxed{\alpha = \frac{\lambda^c m}{\lambda^0 m}}$$

By using α, we can calculate the dissociation constant of acid as:

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

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