



Arrhenius theory and Ostwald dilution law

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▶ **Arrhenius theory of electrolyte dissociation and its limitations:**

- ▶ Arrhenius put forward the theory of electrolyte dissociation in... It is based on the following postulates:
- ▶ When dissolved in water, neutral electrolyte molecules split into charged particles. The positively charged particles are called cations and the negatively charged particles are called anions. The process of formation of ions from the neutral molecules is called ionization.



- ▶ The ions in solution constantly reunite to form neutral molecules and thus there is a state of equilibrium between ions and the dissociated molecules.



Applying the law of mass action;

$$k = \frac{[A^+][B^-]}{[AB]} \quad \text{where } k \text{ is called the dissociation constant}$$

- ▶ Charged ions are free to move through the solution to the oppositely charged electrodes. The movement of these ions constitutes electric current through the solution of electrolyte. This explains the conductivity of electrolytes and the process of electrolysis.
- ▶ Electrical conductivity of an electrolyte solution depends on the number of ions present in solution. i. e. the degree of dissociation determines whether the electrolyte is strong or weak.
- ▶ Degree of dissociation (α) is the fraction of the total number of molecules which undergo dissociation.
- ▶ Degree of dissociation (α) =
$$\frac{\text{Number of molecules dissociated into ions}}{\text{Total number of molecules}}$$

► **Limitations of Arrhenius theory:**

1. Strong electrolytes conduct electricity in fused state also. It is in contradiction with Arrhenius theory, according to which the presence of solvent is essential for ionization.
2. This theory fails to explain the factors affecting the mobility of ions.
3. The Ostwald dilution law which is completely based on the Arrhenius theory is applicable only for weak electrolytes and fails in case of strong electrolytes.

Ostwald dilution law:

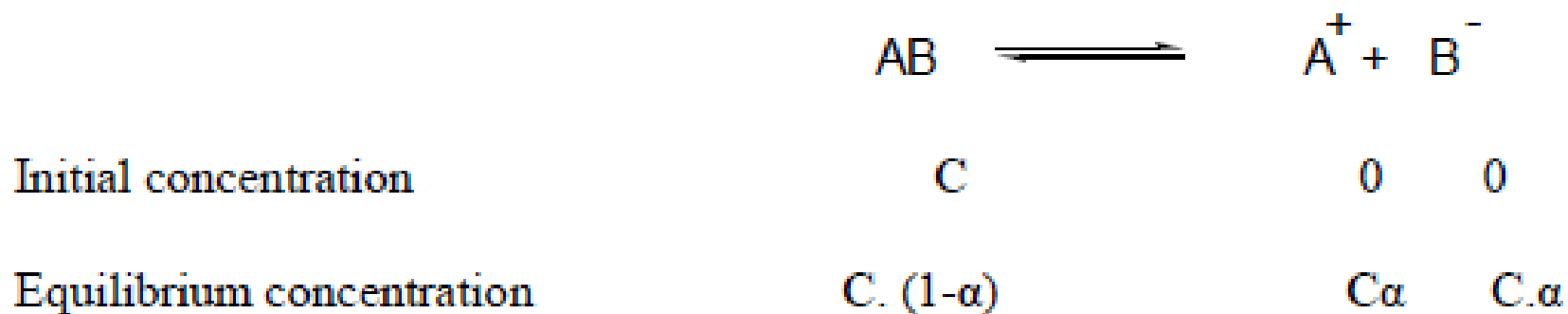
According to Arrhenius theory of electrolyte dissociation, molecules of an electrolyte in aqueous solution undergoes spontaneous dissociation into positive and negatively charged ions and there is a dynamic equilibrium existing between the ions and undissociated molecules.

Consider an electrolyte AB which dissociates into solution as....



Let C moles/ lit be the concentration of electrolyte and

α be the degree of dissociation of the electrolyte.



The equilibrium constant for the reaction is....

$$k = \frac{C\alpha \times C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)}$$

If V is the dilution of solution, ($V = 1/C$)

$$k = \frac{\alpha^2 C}{(1-\alpha)}$$

$$k = \frac{\alpha^2}{(1-\alpha)V}$$

k is the dissociation constant

This expression which represents the variation of degree of dissociation of an electrolyte with dilution is called the Ostwald dilution law.

For weak electrolytes: $\alpha \lll 1$

i.e. $1 - \alpha \approx 1$

Therefore $k = \frac{\alpha^2}{V}$

Or $k = \alpha^2 C$

Or $\alpha = \sqrt{k_c V}$

Or $\alpha = k' \sqrt{V}$

i.e. the degree of dissociation of a weak electrolyte is proportional to square root of dilution.

For strong electrolytes:

α is large and therefore cannot be neglected.

$$k = \frac{\alpha^2}{(1-\alpha)V}$$

Thus $\alpha^2 = kV - \alpha kV$

$$\alpha^2 + \alpha kV - kV = 0$$

From this, the value of α can be calculated.

Limitations of Ostwald dilution law:

1. This law holds good only for weak electrolytes and fails in case of strong electrolytes.
2. The Ostwald dilution law which is completely based upon Arrhenius theory of electrolytic dissociation is not applicable for strong electrolytes. It indicates that Arrhenius theory is applicable only for weak electrolytes.

Degree of dissociation (α) is the fraction of the total number of molecules of an electrolyte dissociated into ions

$$\text{Degree of dissociation } (\alpha) = \frac{\text{Number of molecules dissociated into ions}}{\text{Total number of molecules}}$$

$$\alpha = \sqrt{kV} = \sqrt{\frac{k}{c}}$$

The degree of dissociation can also be defined as the ratio of equivalent conductance at dilution (V) to the equivalent conductance at infinite dilution.