

OSWALD'S DILUTION LAW

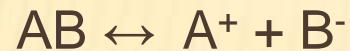
ARRHENIUS THEORY

- According to Arrhenius Theory of dissociation, an electrolyte dissociates into water solutions. These ions are in a state of equilibrium with the undissociated molecules. This is called the **ionic equilibrium**
- **Oswald** noted that the law of mass action can be applied to the ionic equilibrium as in the case of chemical equilibria.

OR

- It also tells us the variation of degree of dissociation of an electrolyte with dilution

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- Consider a binary electrolyte AB which dissociates into A⁺ and B⁻ ions and the equilibrium state is represented by the equation:



Initially t = 0 C 0 0

At equilibrium C(1-α) Cα Cα

- Let **C** moles per litre be the concentration of the electrolyte and **α** (alpha)

its degree of dissociation. The concentration terms at equilibrium may be

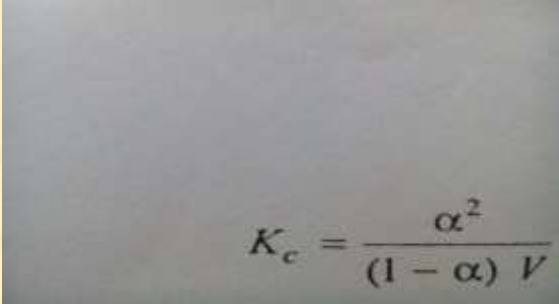
written as

EXPERIMENTAL VERIFICATION OF OSTWALD'S LAW

- The Ostwald's Dilution law can be verified if the values of α (alpha), the degree of dissociation, at different dilution are known.
- The values of α are determined experimentally by using the relation

$$\alpha = \Lambda_v / \Lambda_\infty$$

- where Λ_v and Λ_∞ are the equivalent conductance at dilution V and infinite respectively.
- Their values are found by conductance measurements and Kohlrausch's law.
- The values of α (alpha) at various dilution thus determined are inserted in expression


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

- if the values of **K_c** come out to be constant, the **Ostwald's law** stands verified

LIMITATION OF OSTWALD DILUTION LAW

Limitations of Ostwald's dilution law:

- The law holds good only for weak electrolytes and fails completely in the case of strong electrolytes. The value of ' α ' is determined by conductivity measurements by applying the formula Λ/Λ_{∞} . The value of ' α ' determined at various dilutions of an electrolyte when substituted in gives a constant value of K only in the case of weak electrolytes like CH_3COOH , NH_4OH , etc. "

THE CAUSE OF FAILURE OF OSTWALD'S DILUTION LAW I

- **OSTWALD'S law fails due to following reasons**
- **(i) The law is based on the fact that only a portion of the electrolyte is dissociated into ions at ordinary dilution and completely at infinite dilution. Strong electrolytes are almost completely ionized at all dilutions and Λ/Λ_{∞} does not give accurate value of ' α '.**

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- **(ii) When concentration of the ions is very high, the presence of charges on the ions appreciably effects the equilibrium. Hence, law of mass action its simple form cannot be strictly applied in the case of strong electrolytes.**

Thank you!
Jimmy

