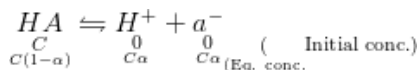


Ostwald's Dilution Law

Ostwald's dilution law is the application of the law of mass action to weak electrolytes in solution. Suppose an acid HA is dissolved in water, it will ionise as under:



Applying law of mass action,

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

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

Where K_a is the dissociation (or ionisation) constant of the acid HA and α is its degree of dissociation.

This equation is known as **Ostwald's dilution law equation**. If $\alpha \ll 1$ then the above equation may be written as:

$$K_a = C\alpha^2 \text{ or } \alpha = \sqrt{\frac{K_a}{C}}$$

$$\text{As } C \propto \frac{1}{V}$$

$$\text{So } K_a = \frac{\alpha^2}{(1-\alpha)V} = \frac{\alpha^2}{V}$$

$$K_a \cdot V = \alpha^2$$

$$\alpha = \sqrt{K_a V}$$

$$\alpha \propto \sqrt{V} \quad \text{At constant temperature}$$

Thus at constant temperature degree of dissociation of weak electrolyte is directly proportional to square root of its dilution. The value of α can be calculated by measuring conductance of the solution as:

$$\alpha = \frac{\lambda_v}{\lambda_{\infty}}$$

Where λ_v is the equivalent conductance at a particular dilution and λ_{∞} is equivalent conductance at infinite dilution.

With the help of this equation; $[H^+]$ or p^H of the acid solution may be calculated.

If we know the value of α and C for any acid then K_a may be calculated. For example, the value of α for 0.05 N acetic acid is 0.03.

Therefore the value of K_a for acetic acid will be,

$$K_a = \frac{0.05 \times 0.03 \times 0.03}{1 - 0.03}$$

$$4.64 \times 10^{-5}$$

Weak electrolytes obey Ostwald's dilution law fairly well, but strong electrolytes do not obey this law; because these electrolytes almost completely ionise at every concentration i. e. , $\alpha = 1$ or $\lambda_v = \lambda_{\infty}$, but in practice it is not so. thus $\alpha = \lambda_v / \lambda_{\infty}$ is not applicable for strong electrolytes. It is observed that $\lambda_v < \lambda_{\infty}$ even though $\alpha = 1$.

This is due to the following two main effects:

1. **The relaxation effect:** According to this effect, each cation is surrounded by a number of anions and vice versa in solution; which is called ionic atmosphere of the oppositely charged ions. On applying e.m.f., the ion moves towards oppositely charged electrode leaving behind the ionic atmosphere. To form a new ionic atmosphere some time is taken which is called **relaxation time** and this effect of the ionic atmosphere is called **relaxation effect**. Due to this effect the value of λ_v , is not limiting.

2. **The electrophoretic effect:** Since solvent molecules attached to the ionic atmosphere moving in the opposite direction produce friction hence reduce the motion of central ion.

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