B.Sc. (Honours) Part-II

Paper-IIIA

Topic: Ostwald's dilution law

UG

Subject-Chemistry

Dr. Laxman Singh

Asst. Professor

Department of Chemistry

R.R.S. College (PPU)

(Mokama, Patna)

OSTWALD'S DILUTION LAW

This is an application of the law of mass action for a weak electrolyte dissociation equilibria. Consider ionization of a weak electrolyte say a monoprotic acid, HA

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq) \text{ or}$$

$$HA \rightleftharpoons H^+ + A^-$$

	HA	H^+	A^-
Moles before dissociation	1	0	0
Moles after dissociation	$1-\alpha$	α	a

Where, α is degree of dissociation of a weak acid HA. Let 'c' mol litre^{-1} be the concentration of the acid, HA, then,

$[HA] = c(1-\alpha)$; $[H^+] = c\alpha$; $[A^-] = c\alpha$

According to equilibrium constant expression,

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{(c\alpha.c\alpha)}{c(1-\alpha)}$$

$$K_a = \frac{c\alpha^2}{(1-\alpha)} \quad \text{.... (i)}$$

Where, K_a is the dissociation constant of a weak acid, Since, α is small for weak electrolytes, thus, $1 - a \approx 1$

$$\therefore K_a = c\alpha^2 \text{ or } \alpha = \sqrt{\left(\frac{K_a}{c}\right)} = \sqrt{K_a V} \quad \text{.... (ii)}$$

Where, V is the volume in litre, containing 1 mole of electrolyte. Thus, it may be concluded that the degree of dissociation of a weak electrolyte is inversely proportional to the square root of its concentration.

Similar expression can also be made for a weak base B or BOH as

If $1 - \alpha \approx 1$ and $K_b = c\alpha^2$ .... (iii)

$$\text{or } \alpha = \sqrt{\left(\frac{K_b}{c}\right)} \quad \text{.... (iv)}$$

Where, K_b is the dissociation constant of a weak base.

Eqs. (i) and (iii) also reveals that when $c \rightarrow 0$, $(1 - \alpha) \longrightarrow 0$, i. e. α approaches unity, i. e. at infinite dilution, the whole of the weak electrolyte gets dissociated. This is the Ostwald's dilution law.

Limitations of Ostwald's Dilution Law

The law is applicable 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 $\wedge / \wedge_\infty$

(i) The law is based on the notion 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 dilution and $\wedge / \wedge_\infty$ does not give an accurate value of 'α'

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

Example 1: At 30°C, the degree of dissociation of 0.006 M HA is 0.0145. What would be the degree of dissociation of 0.02 M solution of the acid at the same temperature?

Sol: Solve the problem using Ostwald dilution law. Use the expression relating degree of dissociation and concentration.

Let the ionization constant of the acid be K_a. Degree of dissociation of 0.066 M concentration = 0.0145.

Applying $\alpha = \sqrt{\frac{K_a}{C}}$

$$0.0145 = \sqrt{\frac{K_a}{0.066}} \quad \text{.... (i)}$$

Let the degree of dissociation of the acid at 0.02 M concentration be α.

$$a_1 = \sqrt{\frac{K_a}{0.02}} \quad \text{.... (ii)}$$

$\therefore$

1

$(0.0145)^2 \times 0.066 = \alpha^2 \times 0.02$

$\therefore \alpha_1 = 0.0145 \times$ 9×10^{-16} $\sqrt{\frac{0.066}{0.02}}$

$\alpha_1 = 0.0263$