OSTWALD'S DILUTION LAW

According to Arrhenius theory of electrolyte dissociation, the molecules of an electrolyte in solution are constantly splitting up into ions and the ions are constantly reuniting to form unionized molecules. Therefore, a dynamic equilibrium exists between ions and unionized molecules of the electrolyte in solution. It was pointed out by **Ostwald** that like chemical equilibrium, law of mass action van be applied **to** such systems also.

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

$$AB \leftrightarrow A^+ + B^-$$

Initially t = o   C   0   0

At equilibrium   C(1-α)   Cα   Cα

So, **dissociation constant** may be given as

$$K = [A^+][B^-]/[AB] = (Cα * Cα)/C(1-α)$$

$$= Cα^2/(1-α) \qquad\qquad .... (i)$$

For very weak electrolytes,

$$α <<< 1, \ (1 - α) = 1$$

$$\therefore \qquad\qquad K = Cα^2$$

$$α = \sqrt{K/C} \qquad\qquad .... (ii)$$

Concentration of any ion = Cα = $\sqrt{CK}$.

From equation (ii) it is a clear that degree of ionization increases on dilution.

Thus, **degree of dissociation** of a weak electrolyte is proportional to the square root of dilution.

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 Eq. (i) 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** in the case of strong electrolytes is due to the following factors"

(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'.

(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 string electrolytes.

SOME SOLVED EXAMPLES

Example 1:   A 0.01 M solution of acetic is 5% ionized at 25° C. Calculate its**dissociation constant**.

Solution: According to **Ostwald's dilution law**

$$K_a = \alpha^2/(1-\alpha)V$$

$$\alpha = 0.05, \quad V = 1/0.01 = 100 \text{ litres}$$

 Hence, $K_a = 0.05 * 0.05/(1-0.05)100 = 2.63 * 10^{-5}$

Example 2: Calculate the H+ ion concentration of a 0.02 N weak monobasic acid. The value of **dissociation constant** is 4.0×10^{-10}.

Solution: $HA \leftrightarrow H^+ + A^-$

Applying **Ostwald's dilution law** of a weak acid,

$\alpha = \sqrt{k_a V}$

$Ka = 4.0 \times 10^{-10}$, $V = 1/0.01 = 100$ litres

$\alpha = \sqrt{(4 * 10^{-10} * 10^2)} = 2 * 10^{-4}$

Concentration of hydrogen ions

$a/\sqrt{V} = (2*10^{-4})/100 = 2*10^{-6}$ mol L^{-1}

or Concentration of hydrogen ions

$= \sqrt{(CK)} = \sqrt{(0.01 * 4 *10^{-10})} = 2 * 10^{-6}$ mol L^{-1}