Ionic Equilibria I

Paper-III, Bsc II, General Chemistry

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In this section, we will learn about the ionic equilibrium in ionic solutions. Substances in Ionic Equilibrium can be classified into two categories on the basis of their ability to conduct electricity given as under,

Non-Electrolytes

These are substances that consist of molecules that bear no electric charge, do not dissociate into their constituent ions and thus do not conduct electricity in their aqueous solution or molten state. For example sugar solution.

Electrolytes

These are substances that dissociate into their constituent ions in their aqueous solution and thus conduct electricity in their aqueous solutions or molten state. Example, salt solution, acid solution, base solution etc.

Electrolytes in ionic equilibrium can be further classified into strong and weak electrolytes.

Strong electrolytes are substances that upon dissociation in their ionic solution ionize completely while in the case of **weak electrolytes**, the dissociation is partial in nature.

For example, NaCl undergoes complete ionization in its aqueous solution to render sodium ions (Na⁺) and chloride (Cl⁻) ions, whereas, acetic acid undergoes partial ionization to render some amount of acetate ions(CH₃COO⁻) and hydrogen(H⁺) ions.

- In case of a strong electrolyte, the dissociation reaction is said to be complete, thus moving in the forward direction only, whereas, in case of a weak electrolyte, the reaction is said to be reversible in nature.
- In the case of the weak electrolyte, the equilibrium is established between the ions and the unionized molecules, which can be termed as ionic equilibrium. The same can be understood with the following example.

 $CH_3COOH \implies CH_3COO^- + H^+$

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Oswald Dilution Law

Degree of ionisation of any weak electrolyte is inversely proportional to the square root of concentration.

Degree of dissociation or ionisation,
$$\alpha = \frac{\text{number of molecules ionized}}{\text{total number of molecules}}$$
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If we consider the reaction 1 and initial concentration of the acid is C moles/litre. Then concentration of the dissociated species would be α C and undissociated acid as (1- α)C.

The dissociation constant can be expressed as

$$K = \frac{[CH_3 CO O^-][H^+]}{[CH_3 CO OH]} = \frac{\alpha^2 C}{(1-\alpha)}$$
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For weak electrolyte $\alpha \ll 1$, so $(1-\alpha) \sim 1$, So $K = \alpha^2 C$ or $\alpha = \sqrt{\frac{K}{C}}$

Ionisation or dissociation Constant of Weak Acid

Consider the Acid HA which dissociation can be written as the following equation

$$HA \rightleftharpoons H^+ + A^- 5$$

Considering equation 3 expression of ionisation constant of the acid, $K_{a} \mbox{ would be }$

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

Ionisation or dissociation Constant of Weak Base

Consider the base BOH which dissociation can be written as the following equation

BOH
$$\rightleftharpoons$$
 B⁺ + OH⁻ 5

Considering equation 3expression of ionisation constant of the base, K_b would be

$$K_{\rm b} = \frac{[{\rm B}^+][{\rm OH}^-]}{[{\rm BOH}]}$$
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Ionic Product of water

Ionisation of water can be expressed as $H_2O \implies H^+ + OH^-$ and dissociation constant, K can be expressed as

$$K = \frac{[H^+][OH^-]}{[H_2O]} \text{ or } K[H_2O] = [H^+][OH^-] \text{ or } K_w = [H^+][OH^-]$$
and K_w is called ionic product of water.

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