B.Sc. (Honours) Part-I

Paper-IA

Topic: **Dissociation constant of acids and bases**

UG

Subject-Chemistry

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Dissociation Constants of Weak Acids and Bases

Strong acids (hydrochloric acid, sulfuric acid, etc.) and bases (sodium hydroxide, potassium hydroxide, etc.) are those that are completely ionized in dilute aqueous solutions.

In biological systems one generally encounters only weak acids and bases. Weak acids and bases do not completely dissociate in solution. They exist instead as an equilibrium mixture of undissociated and dissociated species. For example, in aqueous solution, acetic acid is an equilibrium mixture of acetate ion, hydrogen ion, and undissociated acetic acid. The equilibrium between these species can be expressed as:

$$CH_3COOH \underset{k_2}{\overset{k_1}{\rightleftarrows}} H^+ + CH_3COO^-$$

where k_1 represents the rate constant of dissociation of acetic acid to acetate and hydrogen ions, and k_2 represents the rate constant for the association of acetate and hydrogen ions to form acetic acid. The rate of dissociation of acetic acid,

$-d[CH_3COOH]/dt$, is dependent on the rate constant of dissociation (k_1) and the concentration of acetic acid $[CH_3COOH]$ and can be expressed as:

$$\frac{d\,[CH_3COOH]}{dt} = k_1\,[CH_3COOH]$$

Similarly, the rate of association to form acetic acid, d[HAc]/dt, is dependent on the rate constant of association (k_2) and the concentration of acetate and hydrogen ions and can be expressed as:

$$\frac{d\,[CH_3COOH]}{dt} = k_2\,[H^+]\,[CH_3COO^-]$$

Since the rates of dissociation and reassociation are equal under equilibrium conditions:

$$k_1\,[CH_3COOH] = k_2\,[H^+]\,[CH_3COO^-]$$

or

$$\frac{k_1}{k_2} = \frac{[H^+]\,[CH_3COO^-]}{[CH_3COOH]}$$

$$K_a = \frac{[H^+]\,[CH_3COO^-]}{[CH_3COOH]}$$

where

$$\frac{k_1}{k_2} = K_a \textbf{ (Equilibrium constant)}$$

This equilibrium expression can now be rearranged to

$$[H^+] = K_a \frac{[CH_3COOH]}{[CH_3COO^-]}$$

where the hydrogen ion concentration is expressed in terms of the equilibrium constant and the concentrations of undissociated acetic acid and acetate ion. The equilibrium constant for ionization reactions is called the ionization constant or dissociation constant.

Using Ka and pKa To Predict Equilibrium and Strength of Acids

K_a may be used to measure the position of equilibrium:

- If K_a is large, the formation of the products of the dissociation is favored.
- If K_a is small, the undissolved acid is favored.

K_a may be used to predict the strength of an acid:

- If K_a is large (pK_a is small) this means the acid is mostly dissociated, so the acid is strong. Acids with a pK_a less than around -2 are strong acids.
- If K_a is small (pK_a is large), little dissociation has occurred, so the acid is weak. Acids with a pK_a in the range of -2 to 12 in water are weak acids.

- K_a is a better measure of the strength of an acid <u>than pH</u> because adding water to an acid solution doesn't change its acid equilibrium constant, but does alter the H^+ ion concentration and pH.