(3) Lewis conc

DISSOCIATION / IONISATION OF ACIDS AND BASES

Arrhenius concept of acids and bases is most useful as most of the ionisations in chemical and biological systems occur in aqueous medium. Acids and bases dissociate in water , to give H^+ and OH^- ions respectively. Acids as well as bases are of two types. **Strong acids** such as HCl, HNO_3, H_2SO_4 and $HClO_4$ are almost completely dissociated in water and produce large number of H^+ ions. Acids like HF, HCOOH, CH_3COOH, H_3PO_4 etc dissociate only to a small extent and produce small number of H^+ ions in solution. These are called **weak acids**. Bases like LiOH, NaOH, $Ba(OH)_2$ etc are almost completely dissociated in water and produce large number of OH^- ions, and are called **strong bases.** Bases like NH_4OH, $Al(OH)_3$ etc dissociate to a small extent producing small number of OH^- ions in aqueous solution and are called **weak bases.** According to Bronsted–Lowry concept, strong acids are good proton donor and strong bases are good proton acceptor. Let us consider the dissociation of an acid HA in aqueous solution.

$$\underset{\text{acid}}{HA\,(aq)} + \underset{\text{base}}{H_2O} \rightleftharpoons \underset{\text{conjugate acid}}{H_3O^+(aq)} + \underset{\text{conjugate base}}{A^-(aq)}$$

The above equilibrium is dynamic and involves the transfer of one proton in forward as well as reverse direction. If HA is a strong acid, equilibrium lies in forward direction. Strong acid HA produces a weak conjugate base A^- which will have little tendency to accept proton and shift the equilibrium in backward direction.

$$HB(aq) + H_2O(aq) \rightleftharpoons H_3O^+\,(aq) + B^-\,(aq)$$

If HB is a weak acid, equilibrium lies in backward direction. Weak acid HB will produce a strong base B^- having strong tendency to accept a proton and shift the equilibrium in backward direction.

Ionisation Constants of Weak Acids and Weak Bases

Strong acids and strong bases are almost completely dissociated in water. But weak acids and weak bases dissociate to a small extent in aqueous solution. Let us consider the dissociation of a weak acid (HA).

$$HA\,(aq) + H_2O \rightleftharpoons A^-\,(aq) + H_3O^+\,(aq)$$

Applying law of chemical equilibrium

$$K = \frac{[A^-][H_3O^+]}{[HA][H_2O]}$$

As H_2O is solvent and its concentration remains almost constant (55.5 mol/L), let $K\,[H_2O] = K_a$

$$K_a = \frac{[A^-][H_3O^+]}{[HA]}$$

K_a is called ionisation constant or dissociation constant of weak acid. The chemical equation for the dissociation of weak acid and Ka may also be represented as :

$$HA + aq \rightleftharpoons A^-(aq) + H^+(aq)$$

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

Similarly, dissociation of a weak base in water may be represented as :

$$BOH + aq \rightleftharpoons B^+(aq) + OH^-(aq)$$

Applying law of chemical equilibrium ,

$$K_b = \frac{[B^+][OH^-]}{[BOH]}$$

K_b is called dissociation constant or ionisation constant of the weak base.

Calculation of degree of dissociation (α) for the weak acid and weak base

Let the concentration of weak acid (HA) be C mol/lit and degree of dissociation at this concentration and constant temperature is α. Moles of acid dissociated will be Cα. Moles of acid left at equilibrium will be (C – Cα).

	$HA(aq)$ $\rightleftharpoons$	$H^+(aq)$ +	$A^-(aq)$
Initial molar conc.	C	0	0
Molar conc. at equilibrium	$C - C\alpha$	$C\alpha$	$C\alpha$

$$K_a = \frac{[H^+][A^-]}{[HA]} \quad \text{or} \quad K_a = \frac{C\alpha \times C\alpha}{C - C\alpha} \quad \text{or} \quad \boxed{K_a = \frac{C\alpha^2}{1-\alpha}}$$

As degree of dissociation (α) is very small, (1 – α) may be taken equal to one.

$$\therefore \quad \boxed{K_a = C\alpha^2, \quad \alpha = \sqrt{\frac{K_a}{C}} \quad \text{and } [H^+] = C\alpha \quad \text{or} \quad [H^+] = \sqrt{K_a \times C}}$$

K_a is constant at a given temperature. K_a is a dimensionless quantity with the understanding that the standard state concentration is 1 M.

Let us calculate the degree of dissociation (α) of a weak base (BOH).

	$BOH(aq)$ $\rightleftharpoons$	$B^+(aq)$ +	$OH^-(aq)$
Initial molar conc.	C	0	0
Molar conc. at equilibrium	$C - C\alpha$	$C\alpha$	$C\alpha$

$$\boxed{K_b = \frac{[B^+][OH^-]}{[BOH]} \quad \text{or} \quad K_b = \frac{C\alpha \times C\alpha}{C - C\alpha} \quad \text{or} \quad K_b = \frac{C\alpha^2}{1-\alpha}}$$