



Equilibrium

Chemical equilibrium is a state in a chemical reaction where the rates of the forward and reverse reactions are equal so the concentrations of the reactants and products remain constant. At equilibrium, there is no net change in the amounts of reactants and products. The equilibrium position (where the concentrations stabilize) depends on factors like temperature, pressure, and concentration of reactants and products. Changing these factors can shift the equilibrium position.

Law of chemical equilibrium or mass action

- For a general reaction,



- The equilibrium constant in terms of concentrations,

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

where [] denotes the molar concentration

- The equilibrium constant in terms of partial pressure,

$$K_p = \frac{P_C^c \cdot P_D^d}{P_A^a \cdot P_B^b}$$

where p_A, p_B, p_C and p_D denote the partial pressure of chemical species and a, b, c, and d denote the stoichiometric coefficients A, B, C, and D respectively.

- The relationship between K_p and K_c is as under:

$$K_p = K_c (RT)^{\Delta n}$$

where, Δn is the change in moles of the gaseous product and reactant.

Relations between equilibrium constant for a general reaction and its multiples

- $aA + bB \rightleftharpoons cC + dD$ K
- $cC + dD \rightleftharpoons aA + bB$ $K_2 = \frac{1}{K}$
- $naA + nbB \rightleftharpoons ncC + ndD$ $K_2 = K^n$
- $\frac{1}{n}aA + \frac{1}{n}bB \rightleftharpoons \frac{1}{n}cC + \frac{1}{n}dD$ $K_3 = (K)^{1/n}$

Equilibrium

Reaction Quotient and direction of the reaction:

- Unlike K_c which uses concentrations or pressures at equilibrium, Q_c uses the actual concentrations or pressures of reactants and products in the system, whether they are at equilibrium or not.
- For a general reaction:



$$Q_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

- If $Q_c > K_c$ then the reaction will shift in the reverse direction.
- If $Q_c < K_c$ then the reaction will shift in the forward direction.
- If $Q_c = K_c$, the reaction mixture is at equilibrium.

Le-Chatelier's principle: If any factor that determines the equilibrium state of a system (such as concentration, pressure, or temperature) is altered, the system will spontaneously undergo changes to counteract or oppose the imposed change.

a) Effect of concentration –

- The addition of reactant shifts the equilibrium in the forward direction.
- The removal of reactant shifts the equilibrium in the reverse direction.

b) Effect of temperature –

- If the temperature of a system at equilibrium is increased, the reaction will shift in the direction that absorbs or is endothermic with respect to heat.
- When the temperature of a system at equilibrium is lowered, the reaction will shift in the direction that releases or is exothermic with respect to heat.

c) Effect of pressure –

- When the pressure on a system at chemical equilibrium is increased, the equilibrium will shift in the direction that results in a decrease in the total number of moles of gas.
- If the pressure acting on a system at equilibrium is lowered, the reaction will shift in the direction that results in an increase in the total number of moles of gas.

d) Effect of catalyst –

- A catalyst does not affect the equilibrium constant of the reaction.

Acid-Base concept

a) Arrhenius concept of Acids and Bases-

- Acids are substances that donate/release hydrogen ions (H^+) in aqueous solution.
- Bases are substances that donate/release hydroxide ions (OH^-) in aqueous solution.

b) The Brønsted-Lowry Acids and Bases –

- An acid is a proton donor - it is a species that can donate a proton (H^+) to another molecule or ion.

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- A Base is a proton acceptor - it is a species that can accept a proton (H+) donated by an acid.
- If Brønsted acid is a strong acid then its conjugate base is a weak base and vice versa.

c) Lewis Acids and Bases –

- A Lewis acid is an electron pair acceptor. It is a substance capable of accepting an electron pair from another molecule to form a coordinate covalent bond.
- A Lewis base is an electron pair donor. It is a substance capable of donating an electron pair to form a coordinate covalent bond with a Lewis acid.

Ionic product of water:

$$K_w = [H_3O^+][OH^-] \\ = 1.00 \times 10^{-14} \text{ at } 298 \text{ K}$$

- In an acidic solution, the concentration of $[H_3O^+] > [OH^-]$ and $pH < 7$
- In a basic solution, the concentration of $[H_3O^+] < [OH^-]$ and $pH > 7$
- In a neutral solution, the concentration of $[H_3O^+] = [OH^-]$ and $pH = 7$
- $pH + pOH = pK_w = 14$

Ionization constant of weak acid

- For the ionization of weak acid



$$K_a = \frac{c\alpha^2}{(1-\alpha)}$$

where K_a is the ionization constant of the acid HX , α is the degree of dissociation, and c is the initial concentration of the acid HX .

$$\alpha = \sqrt{\frac{K_a}{c}} \quad (\text{When } \alpha \ll 1)$$

$$[H_3O^+] = \sqrt{K_a \cdot c}$$

Ionization constant of a weak base

- For the ionization of weak base



$$K_b = \frac{c\alpha^2}{(1-\alpha)}$$

where K_b is the ionization constant of the base $MOH(aq)$, α is the degree of dissociation, and c is the initial concentration of the base $MOH(aq)$.

$$[OH^-] = \sqrt{K_b \cdot c} \quad (\text{When } \alpha \ll 1)$$

- The larger the value of pK_a weaker the acid.
- The larger the value of pK_b weaker the base.

Equilibrium

Hydrolysis of Salts and pH of their solutions

a) For the salt of a weak acid and strong base

$$K_h = \frac{K_w}{K_a}$$

- where K_h is the hydrolysis constant, K_a is the ionization constant of the acid and K_w is the ionic product of water.

$$h = \sqrt{\frac{K_w}{K_a \cdot c}}$$

- where h is the degree of hydrolysis, c is the initial concentration of salt.

$$pH = \frac{1}{2} pK_w + \frac{1}{2} pK_a + \frac{1}{2} \log c$$

- The hydrolysis of salt of a weak acid and a strong base is basic. For eg. – CH_3COONa , K_2CO_3 etc.
- For the salt of a strong acid and a weak base

$$K_h = \frac{K_w}{K_b}$$

- where K_h is the hydrolysis constant, K_w is the ionization constant of water and K_b is the ionization constant of the base.

$$h = \sqrt{\frac{K_w}{K_b \cdot c}}$$

- where h is the hydrolysis constant of the base and c is the initial concentration of the base.

$$pH = \frac{1}{2} pK_w - \frac{1}{2} pK_b - \frac{1}{2} \log c$$

- The salt of a strong acid and a weak base is acidic in nature. For eg.- NH_4Cl , AlCl_3 , etc.

b) For the salt of a weak acid and a weak base

$$K_h = \frac{K_w}{K_a \cdot K_b}$$

$$h = \sqrt{\frac{K_w}{K_a \cdot K_b}}$$

$$\begin{aligned} pH &= \frac{1}{2} pK_w + \frac{1}{2} (pK_a - pK_b) \\ &= 7 + \frac{1}{2} (pK_a - pK_b) \end{aligned}$$

- The salt of a weak acid and weak base may be neutral, basic, or acidic depending upon acidic or basic strength. For eg.- $\text{CH}_3\text{COONH}_4$, $(\text{NH}_4)_2\text{CO}_3$ etc.
- Salts of a strong acid and a strong base do not undergo hydrolysis.

Equilibrium

Buffer solutions and Henderson Hasselbalch equation

- Buffer solutions are solutions that help resist changes in pH when small amounts of acid or base are added to them. They help maintain pH stability.
- For acidic buffer

$$pH = pK_a + \log \frac{[Salt]}{[Acid]}$$

where [Salt] and [Acid] is the molar concentration of Salt and Acid respectively.

- For Basic buffer

$$pH = 14 - pK_b - \log \frac{[Salt]}{[Base]}$$

- where [Salt] and [Base] is the concentration of Salt and Base respectively.

Solubility equilibria of sparingly soluble salt

- Sparingly soluble salts are salts with a solubility of less than 0.01 M.
For a solid salt with a general reaction



- The solubility product constant is given by

$$\begin{aligned} K_{sp} &= [M^{p+}]^x [X^{q-}]^y \\ &= (xS)^x (yS)^y \end{aligned}$$

- where S is the molar solubility.

$$S = \left(\frac{K_{sp}}{x^x \cdot y^y} \right)^{\frac{1}{(x+y)}}$$

- If the ionic product is greater than K_{sp} precipitation will occur as the solution becomes supersaturated.
- If the ionic product is less than K_{sp} there is no precipitation as the solution is undersaturated.

Solubility from K_{sp}

- a) For the salt of the type AgCl -

$$s = \sqrt{K_{sp}}$$

- b) For the salt of the type Mg(OH)₂ -

$$s = \left(\frac{K_{sp}}{4} \right)^{\frac{1}{3}}$$

- c) For the salt of the type Ca₃(PO₄)₂ -

$$s = \left(\frac{K_{sp}}{108} \right)^{\frac{1}{5}}$$