

Equilibrium

The concept of equilibrium is applicable for both physical and chemical processes. At equilibrium, the chemical reaction does not stop but instead both the forward as well as the backward reactions takes place at the same time.

1. Law of Chemical Equilibrium and Equilibrium Constant

Consider a homogeneous reversible reaction,

$$aA + bB \rightleftharpoons cC + dD$$

At equilibrium,

rate of forward reaction

= rate of backward reaction

i.e. $k_f[A]^a[B]^b = k_b[C]^c[D]^d$

$$\therefore \frac{k_f}{k_b} = \frac{[C]^c[D]^d}{[A]^a[B]^b} \text{ or } K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Equilibrium constant in gaseous systems

$$K_p = \frac{p_C^c \cdot p_D^d}{p_A^a \cdot p_B^b}$$

Relation between K_p and K_c

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

If $\Delta n_g = 0$ then $K_p = K_c$.

If $\Delta n_g = +ve$ then $K_p > K_c$.

If $\Delta n_g = -ve$ then $K_p < K_c$.

Characteristics of Equilibrium Constant

- Equilibrium constant of a reaction is constant at constant temperature and does not depend upon the concentrations of reactants.
- If reaction is reversed, equilibrium constant is inversed. e.g. If it is K for $A + B \rightleftharpoons C + D$, then for $C + D \rightleftharpoons A + B$, it is $1/K$.
- If equation with equilibrium constant K is divided by 2 then new equilibrium constant is \sqrt{K} .
- If equation with equilibrium constant K is multiplied by 2, then equilibrium constant for the new equation will be K^2 .

(v) If equation with equilibrium constant K takes place in two steps having equilibrium constants K_1 and K_2 and if the equation is added, then $K = K_1 \times K_2$ and if the equation is subtracted then $K = K_1/K_2$.

2. Le-Chatelier's Principle It states that "a change in any of the factors that determine the equilibrium conditions of a system will cause the system to change in such a manner so as to reduce or to counteract the effect of the change".

3. Factors Affecting Equilibrium Following are the various factors that affect the state of equilibrium:

(i) Effect of change in concentration

If concentration of the reactants are increased or products is removed, the equilibrium will shift in the forward direction.

(ii) **Effect of change in pressure** If pressure is increased, the equilibrium will shift in a direction where decrease in number of moles takes place.

(iii) Effect of change in temperature

(a) An increase in temperature for exothermic reactions decreases the concentration of products at equilibrium and *vice-versa*.

(b) An increase in temperature for endothermic reactions increases the concentration of products at equilibrium and *vice-versa*.

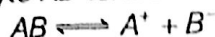
(iv) **Effect of catalyst** Catalyst increases (or decreases) both forward and backward reactions equally, therefore, equilibrium will be attained in less or more time.

Catalyst does not affect equilibrium constant.

(v) **Effect of the addition of inert gas** Addition of inert gas to an equilibrium (if $\Delta n \neq 0$) has no effect, if addition is made at constant volume. But addition at constant pressure, it will favour the direction of reaction where total number of moles at equilibrium shows an increase.

4. **Ionic Equilibrium** In the solutions of weak electrolytes, an equilibrium is established between the ions and unionised electrolytes. Such equilibrium is called ionic equilibrium.

e.g. An electrolyte AB ionises as,



The fraction of total number of molecules that undergo ionisation or dissociation is called the **degree of ionisation or dissociation** (α).

Thus,

$$\alpha = \frac{\text{Number of molecules of electrolyte ionised as ions}}{\text{Total number of molecules of electrolyte dissolved}}$$

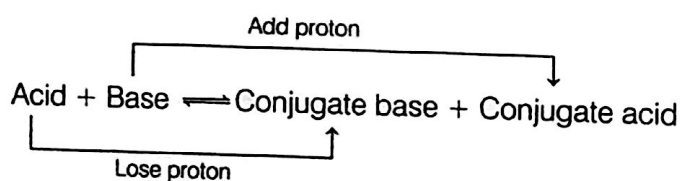
$$\text{or } \alpha = \frac{\text{Amount of electrolyte ionised}}{\text{Initial amount}}$$

5. Arrhenius Concept of Acids and Bases

According to this concept, all substances that give hydrogen ions, $H^+(aq)$ in their aqueous solutions are called acids, while that, which furnish hydroxyl ions, $OH^-(aq)$ in water are called bases.

6. Bronsted-Lowry Concept of Acids and Bases

According to this concept, an acid is a substance (molecule or ion) which can donate H^+ to some other substance and a base is a substance which can accept a proton from an acid.



7. **Lewis Concept of Acids and Bases** According to this concept, a base is a substance that have a tendency to donate an electron pair to form a coordinate bond and an acid is a substance that accepts the electron pair donated by the Lewis base.

8. The Ionisation Constant of Water and Its Ionic Product

$$K_w = [H_3O^+] [OH^-]$$

$$\text{or } K_w = [H^+] [OH^-]$$

[∵ $[H_3O^+]$ and $[H^+]$ are same]

K_w is called the **ionic product of water**. From the experiments, it is found that at 298 K,

$$[H^+] = [H_3O^+] = 1.0 \times 10^{-7} \text{ M}$$

Since, water produces $[H_3O^+]$ and $[OH^-]$ in equal numbers, so

$$[H_3O^+] = [OH^-] = 1.0 \times 10^{-7} \text{ M}$$

On substituting the values, we get

$$K_w = (1 \times 10^{-7})^2 = 1 \times 10^{-14} \text{ M (at 298 K)}$$

9. Ionisation Constants (K_a and K_b)

Ionisation constants are of two types:

(i) **Ionisation constant of acid** (K_a)

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

where, α = degree of ionisation,
 C = concentration

If α is very smaller than 1, i.e. $\alpha \ll 1$

$$\text{So, } K_a = \alpha^2 C$$

$$\Rightarrow \alpha = \sqrt{\frac{K_a}{C}} = \sqrt{K_a V}$$

(ii) **Ionisation constant of base** (K_b)

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

If α is smaller than 1, then, $K_b = \alpha^2 C$

$$\alpha = \sqrt{K_b / C} = \sqrt{K_b V}$$

where, V = volume of solution containing 1 mole.

10. **pK Value** p stands for negative logarithm. Thus, pK is the negative logarithm of dissociation constant.

$$\therefore pK_a = -\log K_a$$

$$\text{and } pK_b = -\log K_b$$

$$\text{or } pK_a + pK_b = 14 \quad (\text{at } 298 \text{ K})$$

11. **The pH Scale** "The negative logarithm to base 10 of the activity of hydrogen ion (a_{H^+}).

If the solution is very dilute (i.e. $< 0.01\text{M}$), the activity of hydrogen ion becomes equal to its molarity,

$$\text{i.e. } a_{H^+} = [H^+] \quad (a_{H^+} \text{ is a dimensionless quantity})$$

From the definition of pH,

$$pH = -\log (a_{H^+})$$

$$\text{or } pH = -\log [H^+] = \log \frac{1}{[H^+]}$$

12. **pOH Value** Just as pH indicates H^+ ion concentration, pOH represents the OH^- ion concentration.

$$\text{i.e. } pOH = -\log [OH^-]$$

13. Relation between pH and pOH

We know that at 298 K in aqueous solution,

$$[H^+] [OH^-] = K_w = 1 \times 10^{-14}$$

$$\therefore pH + pOH = 14$$

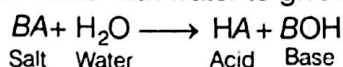
(i) In case of pure water as $[H^+] = [OH^-] = 1 \times 10^{-7}$, thus $pH = pOH = 7$ represents neutrality.

(ii) In case of acidic solution, $[H^+] > [OH^-]$, thus $pH < 7$ and $pOH > 7$.

(iii) Also, in case of alkaline solution, $[H^+] < [OH^-]$, thus, $pH > 7$ and $pOH < 7$.

14. Common Ion Effect The degree of dissociation of an electrolyte of weak acid or weak base is suppressed by the addition of another electrolyte containing a common ion. This phenomenon is termed as common ion effect.

15. Hydrolysis of Salts Salt hydrolysis is a process in which salt reacts with water to give acid and base.



Hydrolysis process is the reverse of neutralisation process.

Summary of Salt Hydrolysis

Salt	Nature	Degree of hydrolysis	pH
NaCl (strong acid + strong base)	Neutral	No hydrolysis	—
CH ₃ COONa (weak acid + strong base)	Basic	$h = \sqrt{\frac{K_w}{CK_a}}$	$\frac{1}{2} [pK_w + pK_a + \log C]$
NH ₄ Cl (strong acid + weak base)	Acidic	$h = \sqrt{\frac{K_w}{CK_b}}$	$\frac{1}{2} [pK_w - pK_b - \log C]$
CH ₃ COONH ₄ (weak acid + weak base)	*	$h = \sqrt{\frac{K_w}{K_a \times K_b}}$	$\frac{1}{2} [pK_w + pK_a - pK_b]$

16. Buffer Solutions The solutions that resist change in their pH on dilution or on addition of small amounts of acids or alkalies are called buffer solutions and the ability of a buffer solution is to resist changes in pH on adding acid or base is called the buffer action of the buffer solution.

17. Types of Buffer Solutions Buffer solutions are generally of three types:

(i) **Natural buffer** It is a salt of weak acid and weak base, e.g. CH₃COONH₄.

(ii) **Acidic buffer** It is a mixture of a weak acid and its conjugate base (or salt with strong base).

e.g. CH₃COOH + CH₃COONa

pH of an acidic buffer is given by **Henderson-Hasselbalch equation** or **Henderson equation** which is represented as

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

$$pH = pK_a + \log \frac{[\text{Conjugate base}]}{[\text{Acid}]}$$

where, K_a is dissociation constant of the acid.

(iii) **Basic buffer** It is a mixture of weak base and its conjugate acid (or its salt with strong acid).

e.g. NH₄OH + NH₄Cl

$$pOH = pK_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$$

$$\text{or } pOH = pK_b + \log \frac{[\text{Conjugate acid}]}{[\text{Base}]}$$

where, K_b is dissociation constant of the base.

18. Buffer Capacity (ϕ)

Number of moles of acid or base added to 1 L of buffer

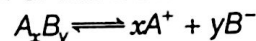
$$= \frac{\text{Change in pH}}{\text{Change in pH}}$$

19. Solubility It is defined as the concentration of the solute in its saturated solution at a given temperature.

Solubility of solution (in moles/litre)

$$= \frac{\text{Solubility of solute (in gL}^{-1}\text{)}}{\text{Molecular weight of solution}}$$

20. Solubility Product It is defined as the product of molar concentration of its ions in a concentrated solution, each concentration term raised to the power equal to the number of ions produced on dissociation of one molecule of electrolyte.



$$\therefore K_{sp} = [A^+]^x [B^-]^y$$

Relation between solubility and solubility product

• For salts of AB type (NaCl, BaSO₄, AgCl etc.),

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

• For salts of AB₂ type (BaCl₂, CaF₂, PbI₂ etc.)

$$s = \sqrt[3]{\frac{K_{sp}}{4}}$$

• For salts of AB₃ type (AlCl₃ etc), $s = \sqrt[4]{\frac{K_{sp}}{27}}$

21. Effect of pH on Solubility The solubility of salts of weak acids such as phosphates, increases with decrease in pH as at lower pH, the anion gets protonated and hence, its concentration decreases.