

NEET Revision Notes

Chemistry

Equilibrium

Introduction to Equilibrium

Equilibrium is the state during a reaction in which there is no change in the temperature, pressure, or concentration of reactants and products with time.

An equilibrium is represented by a **double arrow**, \rightleftharpoons , in a chemical reaction.

When equilibrium is attained, the forward reaction rate becomes equal to the reverse reaction rate.

There are two types of equilibria:

1. Physical equilibrium and
2. Chemical equilibrium.

Physical equilibrium: This equilibrium exists between the two different physical states of the substance. There is no change in the chemical composition of the substances. Example:

- Solid-Liquid equilibrium: $\text{H}_2\text{O(s)} \rightleftharpoons \text{H}_2\text{O(l)}$
- Liquid-Gas equilibrium: $\text{H}_2\text{O(l)} \rightleftharpoons \text{H}_2\text{O(g)}$
- Solid-Gas equilibrium: $\text{I}_2\text{(s)} \rightleftharpoons \text{I}_2\text{(g)}$
- Solid- Solution equilibrium: $\text{NaCl (s)} \rightleftharpoons \text{NaCl (aq)}$

Chemical equilibrium: In this type of equilibrium, the reactants and products are different but their concentration is not changing with time. This is due to the fact that the rate of formation of products (forward reaction) is equal to the rate of formation of reactants (Reverse reaction).

Example: Decomposition of calcium carbonate



In this reaction, the rate of decomposition of CaCO_3 is equal to the rate of combination of CaO and CO_2 .

Type of chemical equilibria:

- Homogeneous equilibrium: In such reactions, both reactants and products are in the same physical phase. Example: $\text{N}_2\text{(g)} + 3\text{H}_2\text{(g)} \rightleftharpoons 2\text{NH}_3\text{(g)}$
- Heterogeneous equilibrium: In such reactions, reactants and products are in different physical phases. Example: $\text{MgO (s)} + \text{CO}_2\text{(g)} \rightleftharpoons \text{MgCO}_3\text{(s)}$

Dynamic nature of equilibrium:

Dynamic equilibrium means that the rate of forward reaction has become equal to the rate of the reverse reaction. Although there is no change is observed in the concentration of reactants and products at equilibrium, it does not mean that the reaction has stopped. The rate at which products are forming has become equal to the rate by which reactants are again changing in the products.

Dynamic equilibrium

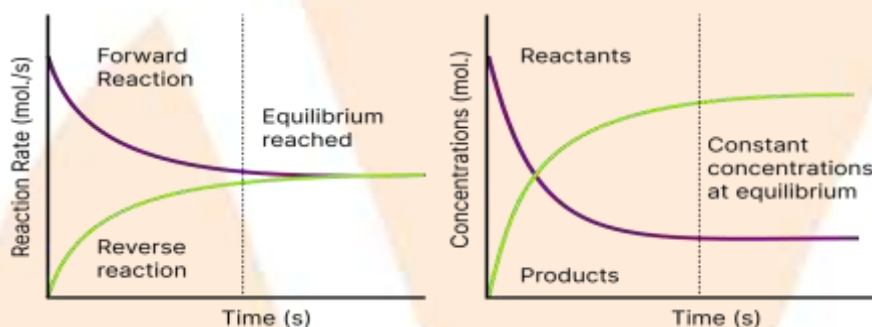


Image: Dynamic equilibrium

Law of chemical equilibrium:

According to this law, the ratio of the concentration of the products to the concentration of the reactants, each term raised to the power of their stoichiometric coefficients, is a constant and this constant is called the equilibrium constant.

For a general reaction: $aA + bB \rightleftharpoons cC + dD$

Equilibrium constant is expressed as: $K_c = \frac{[C]^c \cdot [D]^d}{[A]^a \cdot [B]^b}$

Equilibrium constant:

- The equilibrium constant shows the relationship between the concentration of reactants and products at equilibrium.

It is derived as:

For the reaction: $aA + bB \rightleftharpoons cC + dD$

Rate of the forward reaction, $R_f = K_f [A]^a [B]^b$

Rate of the reverse reaction, $R_b = K_b [C]^c [D]^d$

At equilibrium, rate of forward reaction = rate of reverse reaction.

Therefore,

$$K_f[A]^a[B]^b = K_b[C]^c[D]^d$$

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

- For the reverse reaction, the value of K_c is the inverse of the equilibrium constant for the forward reaction.

$$K_f = \frac{1}{K_b}$$

- When the equation is multiplied by any factor (say n), then the equilibrium constant for the new equation is: $K'_c = K_c \cdot n$

Reaction quotient (Q):

At any point other than equilibrium during a reaction, the ratio of the concentration of products to the concentration of reactants, each term raised to the power of their stoichiometric coefficients, is known as reaction quotient.

- When $Q = K_c$, then the reaction is at equilibrium.
- When $K_c > Q$, then the reaction proceeds in the forward direction. More products are formed.
- When $K_c < Q$, then the reaction proceeds in the reverse direction. More reactants are formed.

Le-Chatelier's Principle:

According to Le-Chatelier's principle, if any change is made to equilibrium then the position of equilibrium shifts in order to counteract that change to re-establish the equilibrium.

- **Effect of change in temperature:**

For exothermic reactions, when the temperature of the system is increased, more heat is added to the reaction system, thus to counteract this rise in heat, the equilibrium will go in the reverse direction to absorb this extra heat and vice-versa.

For endothermic reactions, when the temperature of the system is increased, the forward reaction is favored and vice-versa.

- **Effect of change in pressure:**

If the pressure of the system is increased, the equilibrium will go in the direction which decreases the pressure to counteract this increase. Thus, the reaction will go towards lesser gaseous molecules and vice-versa.

- **Effect of change in concentration:**

When the concentration of reactants increases, the reaction favors the forward reaction. And when the concentration of the products increases, the reaction favors the reverse reaction.

- **Effect of addition of inert gas:**

At constant volume, there is no effect on the Equilibrium. At constant pressure, equilibrium shifts towards the greater number of gaseous molecules. There is no effect of the addition of a catalyst on the equilibrium.

Thermodynamics of Chemical equilibrium:

The equation that relates G (Gibbs free energy change) and the K_{eq} (equilibrium constant) of a reaction is:

$$\Delta G = \Delta G^\circ + RT \ln K_{eq}$$

Where

G° is the standard Gibbs free energy change

R : Universal gas constant

T : Temperature

When the reaction is at equilibrium, the value of G becomes zero.

Thus,

$$\Delta G = 0 = \Delta G^\circ + RT \ln K_{eq}$$

$$\therefore \Delta G^\circ = -RT \ln K_{eq} = -2.303RT \log K_{eq}$$

Relation between K_{eq} (equilibrium constant) and ΔH° (Standard enthalpy change) and ΔS° (Standard entropy change)-

$$\log K_{eq} = \frac{-\Delta H^\circ}{2.303RT} + \frac{\Delta S^\circ}{2.303RT}$$

Ionic equilibrium

An ionic equilibrium is established between an ionic compound and its dissociated ions in the solution.

Example: $X_a Y_b \rightleftharpoons aX^+ + bY^-$

The substances that dissociate into their constituent ions when dissolved in solution and also conduct electricity are referred as electrolytes. They include acids, bases and salts.

Electrolytes can be divided into two categories:

1. Strong electrolytes and

2. Weak electrolytes.

Strong electrolytes:

They completely ionize in their solution. Strong acids (HCl, HBr, HI, HNO₃, H₂SO₄), strong bases, and water-soluble salts like NaCl are strong electrolytes.

Weak electrolytes:

They ionize partially when dissolved. Weak acids, weak bases and insoluble salts like AgCl.

Ostwald dilution law:

According to this law, the degree of dissection (α) of any weak electrolyte and equilibrium constant are related as-

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

For weak electrolytes, since $\alpha \ll 1$, thus $(1-\alpha) = 1$

$$\therefore K = C\alpha^2 \text{ or } \alpha = \sqrt{K/C}$$

Next, the dissociation constant of an acid is represented by K_a and the dissociation constant of a base is represented by K_b . The relationship between K_a and K_b is:

$$K_a \times K_b = K_w = 1.0 \times 10^{-14}$$

Where K_w is the ion-product constant of liquid water.

The acid strength is defined by its pH.

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

For a weak dibasic acid: $\text{pH} = \frac{(\text{p}K_{a_1} + \text{p}K_{a_2})}{2}$ where K_{a_1} is the first dissociation constant of the acid and K_{a_2} is the second dissociation constant of the acid.

The strength of a base is defined by its pOH.

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

The relation between pH and pOH is: $\text{pH} + \text{pOH} = 14$

Common ion effect: When equilibrium is established between an ionic compound and its ions, then adding a common ion will shift the direction of the equilibrium in order to consume that ion as per the Le-Chatelier's principle.

Salts: Salts are produced when an acid reacts with a base.

Ionization of Salts: When salts ionize in a solution, their ions further react with water forming either an acidic, a basic, or a neutral solution.

Salt formed from	Salt solution
Strong acid + Strong base	Neutral
Weak acid + Strong base	Basic
Strong acid + Weak base	Acidic

Buffer Solution

Buffer solutions are those that resist the change in their pH on small addition of acid or base. They are formed by mixing a weak acid and its strong conjugate base or a weak base and its strong conjugate acid.

Henderson-Hasselbalch equation: The pH of the buffer solution is to be determined using the Henderson-Hasselbalch equation which is expressed as:

$$\text{pH} = \text{pK}_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

Where,

$[\text{A}^-]$ is the concentration of the conjugate base

$[\text{HA}]$ is the concentration of the acid.

When a basic buffer (Weak base + conjugate acid) is given, pOH is calculated using Henderson-Hasselbalch equation as-

$$\text{pOH} = \text{pK}_b + \log \frac{[\text{BH}]}{[\text{B}^-]}$$

Where,

$[\text{B}^-]$ is the concentration of the base

$[\text{BH}]$ is the concentration of the conjugate acid.

Solubility and Solubility product

The solubility of a substance is defined as the maximum amount that can be dissolved in a solvent at a specific temperature.

For an ionic compound XY which dissociates in water as: $\text{XY} \rightleftharpoons \text{X}^+ + \text{Y}^-$

The solubility product (K_{sp}) is written as: $K_{sp} = [\text{X}^+][\text{Y}^-]$

Ionic product (I.P.): The product of the concentration of ions present in the solution.

- When $\text{I.P.} < K_{sp}$, it means the solution is unsaturated.

- When $I.P. > K_{sp}$, it means the solution is supersaturated and precipitate will form.
- When $I.P. = K_{sp}$, it means the solution is saturated and no precipitate formation will occur.

