

Equilibrium

Equilibrium in physical processes:

- Solid-liquid equilibrium

For any pure substance at atmospheric pressure, the temperature at which the solid and liquid phases are at equilibrium is called the normal melting point or normal freezing point of the substance.

- Liquid-vapour equilibrium
- Solid-vapour equilibrium

Equilibrium in chemical processes-Dynamic equilibrium:

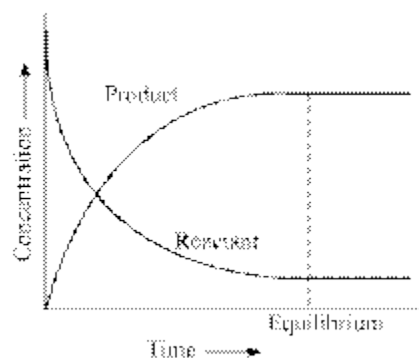
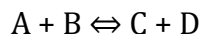


Fig: Attainment of chemical equilibrium

Law of chemical equilibrium and equilibrium constant:

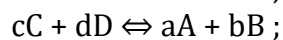
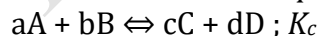


Equilibrium equation:

$$K_c = \frac{[C][D]}{[A][B]}$$

Where, K_c = Equilibrium constant

- Relations between equilibrium constants for a general reaction and its multiples:



$$K'_c = (1/K_c)$$

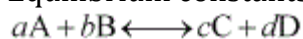


$$K_c^{\circ} = (K_c^{\circ})$$

Homogeneous equilibria:

All the reactants and products are in the same phase.

- Equilibrium constants in gaseous systems:

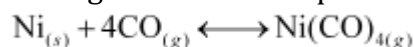


$$K_p = \frac{(p_C^c)(p_D^d)}{(p_A^a)(p_B^b)}$$

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

Heterogeneous equilibria:

Having more than one phase:



$$K_c = \frac{[\text{Ni}(\text{CO})_{4(g)}]}{[\text{CO}_{(g)}]^4} \quad \left(\text{Because } [\text{Ni}_{(s)}] = \text{Constant} \right)$$

[As the molar concentration of a pure solid or liquid is constant, therefore, $[\text{Ni}_{(s)}]$ is constant]

Applications of equilibrium constants:

- Predicting the extent of a reaction
 - If $K_c > 10^3$, then products predominate over reactants.
 - If $K_c < 10^{-3}$, then reactants predominate over products.
 - If K_c is in the range of 10^{-3} to 10^3 , then appreciable concentrations of both reactants and products are present at equilibrium.
- Predicting the direction of the reaction,

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

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

Reaction quotient,

(The concentrations in Q_c are not necessarily equilibrium values)

- If $Q_c > K_c$, then the reaction will proceed in the reverse direction.

2. If $Q_c < K_c$, then the reaction will proceed in the forward direction.
3. If $Q_c = K_c$, then the reaction mixture is already at equilibrium.

Relation between K, Q, and G (Gibbs energy):

$$\Delta G = \Delta G^\ominus + RT \ln Q$$

At equilibrium, $\Delta G = 0$, and $Q = K$

Therefore, $\Delta G^\ominus = -RT \ln K$

Or, $\ln K = -\Delta G^\ominus / RT$

Or, $K = e^{-\Delta G^\ominus / RT}$

- If $\Delta G^\ominus < 0$, then $-\Delta G^\ominus / RT$ is positive and $e^{-\Delta G^\ominus / RT} > 1$, therefore, $K > 1$. That is a spontaneous reaction.
- If $\Delta G^\ominus > 0$, then $-\Delta G^\ominus / RT$ is negative and $e^{-\Delta G^\ominus / RT} < 1$, therefore, $K < 1$. That is a non-spontaneous reaction.

Le Chatelier's principle 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.

Concentration change

- When a reactant/product is added, the net reaction proceeds in the direction in which the added substance is consumed.
- When a reactant/product is removed, the net reaction proceeds in the direction in which the removed substance is replenished.

Pressure change

When pressure is increased, the equilibrium shifts in the direction in which the number of moles of gas or pressure decreases.

Addition of inert gas

At constant volume, addition of inert gas does not affect the equilibrium of a reaction.

Temperature change

- The equilibrium constant for an exothermic reaction decreases with increase in temperature.
- The equilibrium constant for an endothermic reaction increases with increase in temperature.

Effect of catalyst

Catalyst does not affect the equilibrium of a reaction.

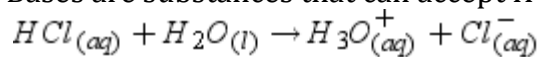
Acids, Bases, and Salts

- Arrhenius concept of acids and bases:

1. Acids are substances which dissociate in water to give H^+ ions.
2. Bases are substances which dissociate in water to give OH^- ions.

- Bronsted-Lowry acids and bases:

1. Acids are substances that can donate H^+ ions.
2. Bases are substances that can accept H^+ ions.



Acid Base Conjugate Conjugate
acid base

3. The conjugate base of a strong acid is a weak base and vice-versa.

- Lewis acids and bases:

1. Acids are species that accept electron pair.
2. Bases are species that donate electron pair.

- Arrhenius concept of acids and bases
- Strong acids and bases completely dissociate in aqueous solutions producing H_3O^+ and OH^- ions, respectively
- Bronsted-Lowry concept of acids and bases
- Based on conjugate pairs of acids and bases
- Strong acid or base has weak conjugate base or acid
- Strong and weak electrolytes
- Strong electrolytes ionise in water completely
- Weak electrolytes undergo partial ionisation in water
- Degree of dissociation
- Extent to which an electrolyte dissociates in a solvent
- Depends on the following factors:
- Nature of solvent and electrolyte

- Dilution
- Temperature
- The pH scale
- $\text{pH} = -\log [\text{H}^+]$
- $\text{p}K_w = \text{pH} + \text{pOH} = 14$
- For acidic solution, $\text{pH} < 7$
- For basic solution, $\text{pH} > 7$
- For neutral solution, $\text{pH} = 7$

- Ionization constant and ionic product of water:

$$K = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]}$$

Ionization constant of water,

Ionic product of water, $K_w = [\text{H}^+][\text{OH}^-]$

At 298K, $K_w = 1 \times 10^{-14} \text{ M}^2$

For acidic solution, $[\text{H}_3\text{O}^+] > [\text{OH}^-]$

For neutral solution, $[\text{H}_3\text{O}^+] = [\text{OH}^-]$

For basic solution, $[\text{H}_3\text{O}^+] < [\text{OH}^-]$

- The pH scale
 $\text{pH} = -\log [\text{H}^+]$
 $\text{p}K_w = \text{pH} + \text{pOH} = 14$
 For acidic solution, $\text{pH} < 7$
 For basic solution, $\text{pH} > 7$
 For neutral solution, $\text{pH} = 7$

- $\text{pH} = -\log a_{\text{H}^+}$
 $= -\log \{[\text{H}^+] / \text{mol L}^{-1}\}$ ($a_{\text{H}^+} = [\text{H}^+] / \text{mol L}^{-1} = \text{activity of H}^+ \text{ ion}$)
- For pure water:
 $\text{pH} = -\log (10^{-7})$
 $= 7$
- For acidic solution – $\text{pH} < 7$
- For basic solution – $\text{pH} > 7$
- For neutral solution – $\text{pH} = 7$

- $K_w = [\text{H}_3\text{O}^+] [\text{OH}^-] = 10^{-14}$
 $\Rightarrow \text{p}K_w = \text{pH} + \text{pOH} = 14$

- Determination of pH: Using pH paper



- Can be accurately determined by a pH meter.

- Ionization constant for weak acids:

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

$$\text{p}K_a = -\log(K_a)$$

- Ionization constants for weak bases:

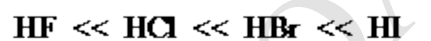
$$K_b = \frac{c \alpha^2}{1-\alpha}$$

- Relation between K_a and K_b

$$K_a \times K_b$$

$$\text{p}K_a \times \text{p}K_b = \text{p}K_w = 14$$

- Factors affecting acid strength (the strength of H-A bonds is an important factor in determining the strength of acids):



Size of A increases

Acid strength increases



Electronegativity of A increases

Acid strength increases

- Hydrolysis:

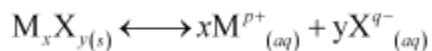
Interaction of the anion or the cation (or both) of a salt with water to produce an acidic or a basic solution.

- Salts of strong acids and strong bases are neutral ($\text{pH} = 7$).
- Salts of strong acids and strong bases are acidic ($\text{pH} < 7$).
- Salts of weak acids and strong bases are basic ($\text{pH} > 7$).

- **Buffer solutions:**

Buffer solutions are the solutions in which pH does not change on dilution or with the addition of small amounts of acid or alkali.

- General formula:



Where, $xp^+ = yq^-$

Solubility product:

$$K_{\text{sp}} = [\text{M}^{p+}][\text{X}^{q-}]$$

$$\Rightarrow K_{\text{sp}} = (xS)^x (yS)^y$$

$$\Rightarrow S^{x+y} = \frac{K_{\text{sp}}}{x^x y^y}$$

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