

**Subject: Chemistry**

**Class: XI**

**Chapter: Equilibrium**

**Top concepts**

1. When the reactants in a closed vessel at a particular temperature react to give products, the concentrations of the reactants keep on decreasing, while those of products keep on increasing for some time after which there is no change in the concentrations of either of the reactants or products. This stage of the system is the dynamic equilibrium. At equilibrium rates of the forward and reverse reactions become equal.
2. General characteristics of equilibrium involving physical processes
  - Measurable properties of system becomes constant at equilibrium
  - Equilibrium can be established only in case of closed system
  - Equilibrium is always dynamic in nature i.e. the process does not stop but changes take place in forward and reverse direction with same rate
  - When equilibrium is attained for a physical process, it is characterised by constant value of one of its parameters at a given temperature. For example for equilibrium  $\text{H}_2\text{O(l)} \rightleftharpoons \text{H}_2\text{O(g)}$ , the pressure becomes constant
  - The magnitude of the constant value of the concentration related expression gives an indication of the extent to which the reaction proceeds before acquiring equilibrium.
3. During a chemical reaction when the rates of the forward and reverse reactions become equal, the concentrations of the reactants and the products remain constant. This is the stage of chemical equilibrium. Chemical equilibrium is dynamic in nature.
4. General characteristics of equilibrium involving chemical processes
  - Chemical equilibrium is dynamic in nature
  - Properties of system becomes constant at equilibrium and remains unchanged thereafter
  - Equilibrium can be established only in case of closed system
  - Equilibrium can be approached from either direction
  - A catalyst does not alter the equilibrium point

5. Law of mass action: Rate of a chemical reaction is directly proportional to the product of molar concentration of the reactants at a constant temperature at any given time.
6. Equilibrium Law or Law of Chemical Equilibrium: At a given temperature, the product of concentrations of the reaction products raised to the respective stoichiometric coefficient in the balanced chemical equation divided by the product of concentrations of the reactants raised to their individual stoichiometric coefficients has a constant value
7. Equilibrium reactions in which all reactants and products are in same phase are called homogeneous equilibrium reactions.
8. Equilibrium reactions in which all reactants and products are in different phases are called heterogeneous equilibrium reactions
9. For a general reaction of the type:  
 $aA + bB \rightleftharpoons cC + dD$

The equilibrium constant may be represented as

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

A and B are reactants

C and D are products

Exponents a, b, c and d have same values as in balanced chemical equation

If the concentration expressed is in molar concentrations then  $K = K_c$

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

10. For a gaseous reaction of the type:  
 $aA + bB \rightleftharpoons cC + dD$

The equilibrium constant may be represented as

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

$p_A, p_B, p_C, p_D$  are the partial pressures of A, B, C and D respectively  
Exponents a, b, c and d have same values as in balanced chemical equation

## 11. Relation between $K_p$ and $K_c$

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

$\Delta n = (\text{number of moles of gaseous products}) - (\text{number of moles of gaseous reactants})$   
in the balanced chemical equation.

## 12. In heterogeneous equilibrium pure solids or liquids are present but their concentrations or partial pressures do not appear in the expression of the equilibrium constant.

## 13. Characteristic of equilibrium constant

- Equilibrium constants is applicable only when the concentration of reactants and products have attained their equilibrium state
- The value of equilibrium constant is independent of initial concentrations of the reactants and products
- Equilibrium constant has a definite value for every reaction at a particular temperature
- Equilibrium constant for the reverse reaction is the inverse of the equilibrium constant for the reaction in the forward direction
- The value of equilibrium constant tells the extent to which a reaction proceeds in forward or reverse reaction
- Equilibrium constant is independent of presence of catalyst

## 14. Applications of equilibrium constant

### 1) Predicting the Extent of a Reaction

- If  $K_c > 10^3$ , products predominate over reactants, i.e., if  $K_c$  is very large, the reaction proceeds nearly to completion
- If  $K_c < 10^{-3}$ , reactants predominate over products, i.e., if  $K_c$  is very small, the reaction proceeds rarely
- If  $K_c$  is in the range of  $10^{-3}$  to  $10^3$ , considerable concentrations of both reactants and products are present

## 2) Predicting the Direction of the Reaction.

Reaction quotient (Q) is the ratio of product of concentration (or partial pressure) of products to that of reactants at any stage of the reaction

- If  $Q_c > K_c$ , the reaction will proceed in the direction of reactants (reverse reaction).
- If  $Q_c < K_c$ , the reaction will proceed in the direction of the products (forward reaction)
- If  $Q_c = K_c$ , the reaction mixture is already at equilibrium.

## 3) Calculating Equilibrium Concentrations

### 15. Relation between Equilibrium constant K, Reaction quotient (Q) and Gibbs energy (G)

$$K = e^{-\frac{\Delta G^\theta}{RT}}$$

- If,  $\Delta G^\theta < 0$  then  $-\frac{\Delta G^\theta}{RT}$  is positive, and  $e^{-\frac{\Delta G^\theta}{RT}} > 1$ , making  $K > 1$ . This implies reaction is spontaneous or the reaction proceeds in the forward direction to form products predominantly.
- If,  $\Delta G^\theta > 0$  then  $-\frac{\Delta G^\theta}{RT}$  is negative, and  $e^{-\frac{\Delta G^\theta}{RT}} < 1$ , making  $K < 1$ . This implies reaction is non-spontaneous or the reaction proceeds in the forward direction to such a small degree that only a very minute quantity of product is formed.

### 16. According to Le Chatelier's principle 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

#### 1) Effect of Concentration Change

Increase in concentration of any of the

reactants  $\xrightarrow[\text{equilibrium to}]{\text{Shifts the}}$  Forward direction

Increase in concentration of any of the

products  $\xrightarrow[\text{equilibrium to}]{\text{Shifts the}}$  Backward direction

#### 2) Effect of Pressure Change

Increase in pressure  $\xrightarrow{\text{Shifts the equilibrium in direction of}}$  Lesser number of gaseous moles

Decrease in pressure  $\xrightarrow{\text{Shifts the equilibrium in direction of}}$  Larger number of gaseous moles

3) Effect of Addition of an Inert Gas: Addition of an inert gas at constant volume has no effect on equilibrium

4) Effect of Temperature

Increase in temperature  $\xrightarrow{\text{Shifts the equilibrium in direction of}}$  Endothermic reaction

Decrease in temperature  $\xrightarrow{\text{Shifts the equilibrium in direction of}}$  Exothermic reaction

5) Effect of a Catalyst

Catalyst does not shift the equilibrium in any direction because it favours the forward and backward reaction equally

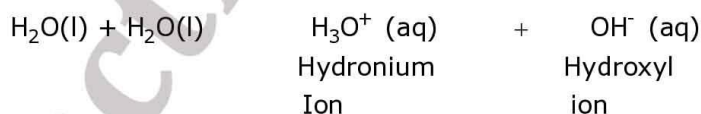
17. Substances that conduct electricity in their molten states or in form of their aqueous solutions are called electrolytes

18. Substances which ionize almost completely into aqueous solutions are called strong electrolytes

19. Ionic Equilibrium: Equilibrium established between unionized molecules and ions in solution of weak electrolytes.



20. Substances which ionize to a small extent in aqueous solution are called weak electrolytes
21. Acids, bases and salts which are electrolytes, conduction of electricity by their aqueous solutions is due to anions and cations produced by the dissociation or ionization of electrolytes in aqueous solution.
22. According to Arrhenius theory, acids are substances that dissociate in water to give hydrogen ions  $\text{H}^+(\text{aq})$  and bases are substances that produce hydroxyl ions  $\text{OH}^-(\text{aq})$ .
23. Limitation of Arrhenius concept of acid and base: The concept is applicable only to aqueous solutions and it does not account for the basicity of substances like, ammonia which do not possess a hydroxyl group.
24. According to Brönsted-Lowry theory, acid is a substance that is capable of donating a hydrogen ion  $\text{H}^+$  and bases are substances capable of accepting a hydrogen ion,  $\text{H}^+$ .
25. The acid-base pair that differs only by one proton is called a conjugate acid-base pair.
26. Conjugate acid has one extra proton and each conjugate base has one less proton.
27. If Brönsted acid is a strong acid then its conjugate base is a weak base and vice versa.
28. According to Lewis concept an acid is a species which accepts electron pair and base which donates an electron pair.
29. Electron deficient species like  $\text{AlCl}_3$ ,  $\text{Co}^{3+}$ ,  $\text{Mg}^{2+}$ , etc. can act as Lewis acids while species like  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{OH}^-$  etc. which can donate a pair of electrons, can act as Lewis bases.
30. Unique ability of water to react with itself to produce a hydronium ion and a hydroxyl ion is called self ionization or autoprotolysis of water.



31. Ionic product of water is the product of concentration of hydronium ions and hydroxyl ions



$$\therefore K = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]^2},$$

K is Equilibrium constant

$$\therefore K[\text{H}_2\text{O}]^2 = [\text{H}_3\text{O}^+][\text{OH}^-]$$

$$\therefore K_w = [\text{H}_3\text{O}^+][\text{OH}^-],$$

$K_w$  is ionic product of water

32. In pure water, the concentration of hydronium ion is always equal to the concentration of hydroxyl ion i.e.  $[\text{H}_3\text{O}^+] = [\text{OH}^-]$

33. The pH of a solution is defined as the negative logarithm to the base 10 of the activity of hydrogen ion i.e.  $\text{pH} = -\log [\text{H}^+]$

34. Types of solutions based on pH values

Types of solutions	Hydrogen ion concentration i.e. $[\text{H}^+]$ in M	pH
Acidic	$[\text{H}^+] > 1.0 \times 10^{-7}\text{M}$	$\text{pH} < 7.00$
Basic	$[\text{H}^+] < 1.0 \times 10^{-7}\text{M}$	$\text{pH} > 7.00$
Neutral	$[\text{H}^+] = 1.0 \times 10^{-7}\text{M}$	$\text{pH} = 7.00$

35.  $\text{p}K_w = \text{pH} + \text{pOH} = 14$

36. Dissociation constant or ionization constant ( $K_a$ ) of a weak acid (HX) in water is given by equation shown below.

$$K_a = \frac{[\text{H}^+][\text{X}^-]}{[\text{HX}]} = \frac{\alpha^2 c}{(1-\alpha)}$$

At a given temperature T,  $K_a$  is a measure of the strength of the acid HX i.e., larger the value of  $K_a$ , the stronger is the acid.

37. Relation between  $K_a$  and  $\text{p}K_a$ :

$$pK_a = -\log K_a$$

Larger the value of  $pK_a$ , weaker is the acid

38. Dissociation constant or ionization constant ( $K_b$ ) of a weak base (MOH) in water is given by equation shown below.

$$K_b = \frac{[M^+][OH^-]}{[MOH]} = \frac{\alpha^2 c}{(1-\alpha)}$$

At a given temperature  $T$ ,  $K_b$  is a measure of the strength of the base MOH i.e., larger the value of  $K_b$ , the stronger is the base.

39. The degree of ionization  $\alpha$  is defined as the extent of ionization

40. Relation between  $K_b$  and  $pK_b$

$$pK_b = -\log K_b$$

Larger the value of  $pK_b$ , weaker is the base.

41. Relation between  $K_a$  and  $K_b$

$$K_a \times K_b = K_w$$

42.  $pK_a + pK_b = pK_w = 14$  (at 298K)

43. Bronsted acids which can donate more than one protons are called polyprotic acids or polybasic acids.

44. Higher order ionization constants ( $K_{a2}, K_{a3}$ ) are smaller than the lower order ionization constant ( $K_{a1}$ ) of a polyprotic acid. The reason for this is that it is more difficult to remove a positively charged proton from a negative ion due to electrostatic forces.

45. Factors affecting acid strength:

- Extent of dissociation of acid (HA) depends on strength and polarity of H-A bond in acid.
- As strength of H-A bond decreases acid strength increases
- As the electronegativity difference between the atoms H and A increases, charge separation between atoms increases, cleavage of the bond becomes easy. Eventually acid dissociates easily increasing acidity.



46. Common ion Effect: If to an ionic equilibrium, a salt containing a common ion is added, the equilibrium shifts in the backward direction. The shift in equilibrium position caused by the addition or presence of an ion involved in the equilibrium reaction is known as common ion effect

47. Interaction of anion or cation of the salt with water to produce an acidic or basic solution is called hydrolysis of salt.

48. Hydrolysis of Salts and the pH of their Solutions

Type of acid and base used to form salt	Example	Type of solution formed by hydrolysis of salt
Salt of strong acid and weak base	$\text{NH}_4\text{Cl}$	Acidic solutions
Salt of weak acid and strong base	$\text{CH}_3\text{COONa}$	Basic solutions
Salt of weak acid and weak base	$\text{CH}_3\text{COONH}_4$	Neutral solutions
Salt of strong acid and strong base	$\text{NaCl}$	Neutral solutions

49. A buffer solution resists a change in pH caused by dilution or the addition of limited amounts of acid or base.

50. Acidic buffers contain equimolar quantities of a weak acid and one of its salt with a strong base

51. Basic buffers contain equimolar quantities of a weak base and one of its salt with a strong acid

52. Solubility is a measure of amount of solute that can be dissolved in a given amount of solvent at a specific temperature

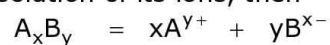
53. In a saturated solution equilibrium exists between the undissolved solute and the solute in the solution.

54. Classification of salts on the basis of solubility

Category I	Soluble	Solubility > 0.1M
Category II	Slightly Soluble	0.01M<Solubility< 0.1M
Category III	Sparingly Soluble	Solubility < 0.01M

55. Solubility product of a salt at a given temperature is equal to product of concentration of the ions in a saturated solution with each concentration term raised to power equal to number of ions produced on dissociation of one mole of substance.

In general if sparingly soluble salt,  $A_xB_y$  is in equilibrium with saturated solution of its ions, then



(solid)

Solubility expression is:  $K_{sp} = [A^{y+}]^x[B^{x-}]^y$

56. Ionic product is defined as the product of the molar concentrations of the constituent ions, each raised to the power of its stoichiometric coefficient in a any solution.

57. Precipitation will occur only when ionic product exceeds the solubility product