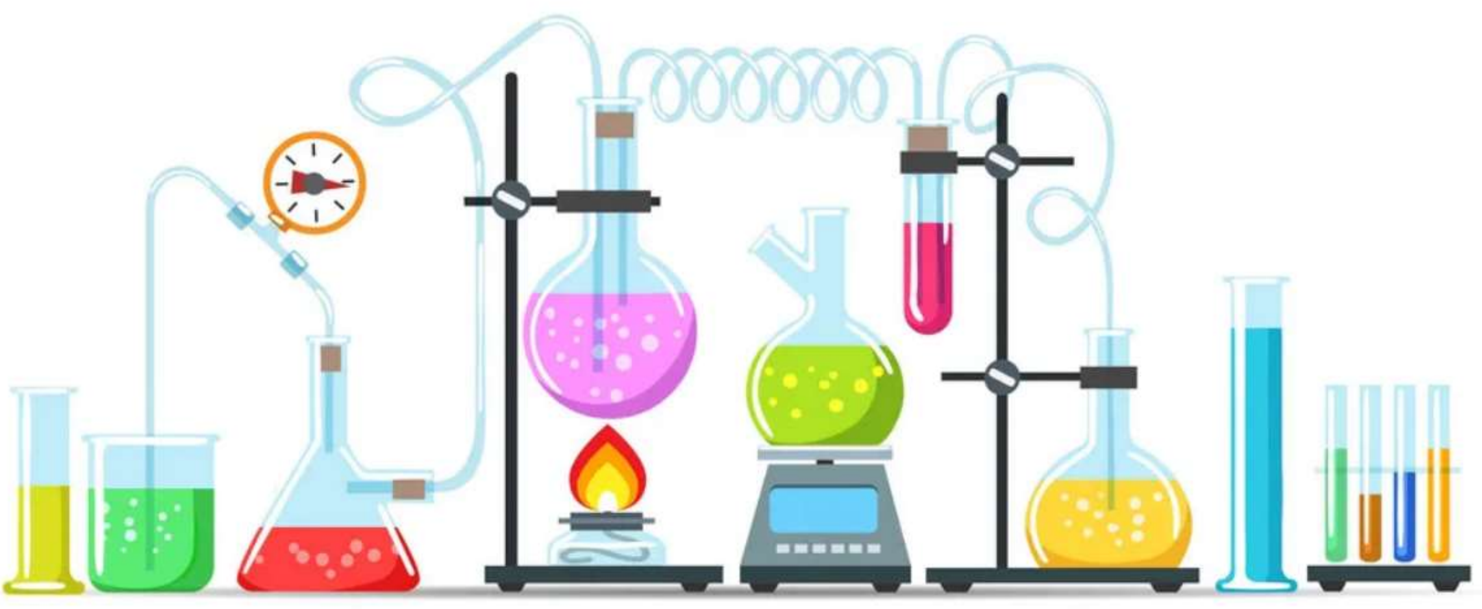
CHEMISTRY



EQUILIBRIUM

Introduction

Equilibrium is the most important characteristic property of reversible reactions. These reactions for which the forward reaction occurs to a much greater extent are considered to be unidirectional in nature and whenever the rate of forward reaction is equal to rate of backward reaction, equilibrium is attained, not to forget that equilibrium exists only in closed system.

It is the state of system at which temperature, pressure, volume and composition have fixed value and does not vary with time. Chemical Reactions can be divided into two categories:

Irreversible Reactions: The reactions which proceed to completion and the products fail to recombine to give back reactants. For example:

$$AgNO_3 + NaCl \rightarrow AgCl + NaNO_3$$

Reversible Reactions: The reactions which never go to completion and products recombine to give back reactants. For example:

$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

Physical Equilibrium

We know that solid, liquid and gas are the three states of substance. Therefore, three types of physical equilibrium are possible. These are

Solid(s) $\rightleftharpoons$ liquid (l)

Liquid(l) $\rightleftharpoons$ gas(g)

Solid(s) $\rightleftharpoons$ gas(g)

Here the sign double half arrows ($\rightleftharpoons$) pointing in the opposite directions is both for the reversible change as well as for the equilibrium state.

1. **Solid(s) – liquid(l) equilibrium:** At equilibrium two processes takes place at the same rate i.e.,

   Ice(s) $\rightleftharpoons$ water(l)

   $H_2O(s) \rightleftharpoons H_2O(l)$

At equilibrium,

Rate of melting of ice = Rate of freezing of water

The temperature at which the solid and liquid states of a pure substance are in equilibrium at the atmospheric.

pressure is called the normal freezing point or melting point of that substance.

2. Liquid(l) – gas(g) equilibrium:

   $H_2O(l) \rightleftharpoons H_2O(g)$

   In such type of equilibrium,

   Rate of vaporisation of water = Rate of condensation of water vapour

3. **Solid(s) – gas(g) equilibrium:** Such type of equilibrium is attained in case of volatile solids.

   Example: If solid iodine is placed in a closed vessel, violet vapours starts appearing in the vessel.

   The intensity of violet vapour increases with time and ultimately it becomes constant.

   $I_2(s) \rightleftharpoons I_2(g)$

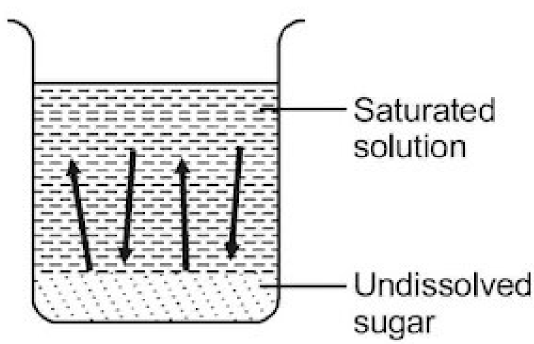
   In this equilibrium,

   Rate of sublimation = Rate of condensation

4. **Solids in liquids:** Suppose sugar is added continuously into a fixed volume of water at room temperature and stirred thoroughly with a glass rod. First the sugar will keep on dissolving but then a stage will come when no more sugar dissolves. Instead it settles down at the bottom. The solution is now said to be saturated and in a state of equilibrium. In this state

   Rate of dissolution = Rate of precipitation

   Sugar(s) $\rightleftharpoons$ Sugar (in solution)



The amount of the solid in grams that dissolves in 100 g of the solvent to form a saturated solution at a particular temperature is called the solubility of that solid in the given solvent at that temperature.

Gases in liquids

Such type of equilibrium is present in soda water bottle in which CO_2 gas is dissolved in water under high pressure. There is a state of dynamic equilibrium between the CO_2 present in the solution and the vapours of the gas above the liquid surface at a given temperature.

$CO_2(g) \rightleftharpoons CO_2(aq)$

Henry's law

Periodic table may be defined as the tabular arrangement of elements in such a way that the elements having same properties are kept together.

$m \propto p$

$m = kp$

where k is Henry's constant and its value depends upon the nature of the gas, nature of liquid and temperature.

General Characteristics of Physical Equilibrium:

1. Equilibrium is possible only in a closed system at a given temperature.
2. Both the opposing processes occur at the same rate and there is a dynamic but stable condition.
3. All measurable properties of the system remain constant.
4. When equilibrium is attained for a physical process, it is characterised by constant value of one of its parameters at a given temperature.
5. The magnitude of such quantities at any stage indicates the extent to which the physical process has proceeded before reaching equilibrium.

Chemical Equilibrium

Every reversible reaction consists of one pair of reaction, one is forward and other is backward reaction. At one stage during reversible reactions, forward and backward reaction proceed at the same time with the same rate, the reaction is then said to be in equilibrium. If the opposing processes involve chemical reactions, the equilibrium is called Chemical equilibrium.

1. **Law of Chemical Equilibrium:** This law states that the rate of an elementary reaction is proportional to the product of the concentration of the reactants. At a constant temperature, the rate of a chemical reaction is directly proportional to the product of the molar concentrations of the reactants each raised to a power equal to the

corresponding stoichiometric coefficients as represented by the balanced chemical equation. Let us consider the reaction,

$A + B \rightleftharpoons C + D$

$r_f = K_f[A][B]$

$r_b = K_b[C][D]$

At equilibrium $r_f = r_b$.

$K_f[A][B] = K_b[C][D]$

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

Kc is called the equilibrium constant, [ ] ⟶ denotes active masses.

For a general reversible reaction,

$aA + bB \rightleftharpoons cC + dD$

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

2. **Equilibrium constant of reverse reaction:** Equilibrium constant for the reverse reaction is the inverse of the equilibrium constant for the reaction in the forward direction.

$$K'^c = \frac{1}{K_c}$$

Relation between K_p and K_c

For a general reversible reaction

$aA + bB \rightleftharpoons cC + dD$

$$K_c = \frac{[C_C]^C[C_D]^d}{[C_A]^a[C_B]^b} \ldots (1)$$

$$K_p = \frac{[P_C]^C[P_D]^d}{[P_A]^a[P_B]^b}$$

$$K_p = \frac{[C_C]^C \times [RT]^C . [C_D]^d \times [RT]^d}{[C_A]^a \times [RT]^a . [C_B]^b \times [RT]^b}$$

$$K_p = \frac{[C_C]^C[C_D]^d(RT)^{c+b}}{[C_A]^a[C_B]^b(RT)^{a+b}}$$

From Eq. (1),

$$K_p = K_C(RT)^{(c+d)-(a+b)}$$

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

Where, Δn = difference of stoichiometric coefficients of gaseous products and reactants.

3. Characteristics of Equilibrium

i. At the state of equilibrium, certain available properties like pressure, concentration and density becomes constant.

ii. Chemical equilibrium can be established from either side.

iii. A catalyst can cause the state of equilibrium to be reached faster, but does not alter the state of equilibrium.

iv. Chemical equilibrium is dynamic in nature.

v. Any change in external stress (Pressure, temperature or concentration) causes disturbance in equilibrium state. The state of equilibrium being stable, is again reached by some adjustment.

vi. If temperature is changed, a new equilibrium is achieved with a new value for relative concentration of products and reactants.

vii. If temperature is kept constant, pressure and concentration of reactants / products is altered, system shifts in forward or backward direction in order to nullify the alteration (stress).

Factors Affecting Equilibria

i. **Change in Concentration:** When the concentration of any of the reactants or products in an equilibrium reaction is altered, the equilibrium mixture's composition changes in order to minimize the effect of the concentration change.

ii. **Change in Temperature:** According to Le-Chatelier's principle if the temperature of an equilibrium system is increased, the equilibrium will move in the direction of the added heat.

iii. **Change in Pressure:** The pressure has no effect on the equilibrium if the number of moles of gaseous reactants and products does not change. The change in pressure in both liquids and solids can be neglected in heterogeneous chemical equilibrium.

iv. **Change in Volume:** When the volume of a gaseous mixture at equilibrium is increased, the equilibrium moves in the direction of a larger number of gaseous molecules.

v. **Effect of a Catalyst:** The equilibrium is unaffected by the catalyst. This is due to the fact that the catalyst favours both forward and backward reactions equally.

Homogeneous Equilibria

When in an equilibrium reaction, all the reactants and the products are present in the same phase (i.e., gaseous or liquid) it is called a homogeneous equilibrium. For example,

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

Heterogeneous Equilibria

When in an equilibrium reaction, the reactants and the products are present in two or more than two phases, it is called a heterogeneous equilibrium.

The equilibrium between water vapour and liquid water in a closed container is an example of heterogeneous equilibrium.

$H_2O(l) \rightleftharpoons H_2O(g)$

Le Chatelier's Principle

It states that if a stress is applied to a system in equilibrium, the equilibrium for the time being gets disturbed. As a result system moves in a direction which tends to relieve the external stress and finally a new equilibrium is attained.

Ionic Equilibrium

Electrolyte: Electrolytes are the substances which conduct electricity in molten state or in solution. Example HCl, NaCl, KCl, CH_3COOH etc.

Arrhenius theory of Electrolytic dissociation: When an electrolyte is dissolved in a solvent it spontaneously dissociates into oppositely charged particles called ions, to a considerable extent. Electrolytic ionization or dissociation gives ions and unionized molecules in solution. For neutrality, the total charge on cations is equal to the total charge on the anions.

Degree of Dissociation (α): It is the fraction of one mole of the electrolyte that has dissociated under the given conditions. The value of α depends on temperature, dilution of electrolyte, nature of electrolyte and solvent.

α = No. of ionized moles/ Total mo. Moles

Ostwald's Law of Dilution:

According to this law, "The degree of ionization (or dissociation) of any weak electrolyte is inversely proportional to the square root of concentration."

$$\alpha = \sqrt{\frac{K}{C}}$$

Where, K = proportionality constant

Concepts of Acids and Bases

1. **Arrhenius Concept:**
   - **Acid:** Any substance when dissolved in water, increases the concentration of H+. e.g., HCl, H_2SO_4, HNO_3 etc.
   - **Base:** Any substance when dissolved in water, increases the concentration of OH-. e.g., NaOH, KOH etc.

2. **Bronsted - Lowry Concept:**
   - **Acid:** Species (Molecule or ion) that donates a proton to another species.
   - **Base:** Species (Molecule or ion) that accepts a proton from another species.
   HCl(Acid) + NH_3(Base) $\longrightarrow$ NH^+_4 + Cl^-

3. **Lewis acids and bases:**

   According to Lewis concept of acids and bases, a Lewis acid is an electron pair acceptor and a Lewis base is an electron pair donor.

   Lewis acids: H^+, Ag^+, Fe^{2+}, $AlCl^3$, BF^3, BCl^3, $BeCl^2$ etc.

   Lewis Bases: Cl^-, CN^-, OH^-, X^-, NH^{-2}, SH^- etc.

   An acid base reaction is the sharing of an electron pair with an acid by a base. This process is simply defined as coordination or neutralisation.

   a. A strong acid is an acid that ionizes completely in water.

      $HCl(aq) + H_2O\ (l) \longrightarrow H_3O^+\ (aq) + Cl^-(aq)$

   b. A weak acid is an acid that is only partially ionized in water

      $CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_2COO^-(aq) + H_3O^+(aq)$

   c. A strong base is a base that ionizes completely in water.

      $KOH(aq) \longrightarrow K^+(aq) + OH^-(aq)$

   d. A weak base is a base which is partially ionized in water

      $NH_3(aq) + H_2O(l) \rightleftharpoons$ NH+4(aq) + $OH^-(aq)$

The pH Scale

pH of solution may be defined as negative logarithm of hydronium ion concentration.

$$pH = -\log [H_3O^+]$$

$$pH = \log \frac{1}{[H_3O^+]}$$

The pH range at 25°C is taken as 0 to 14.
pH = 7 Neutral
pH > 7 Basic
pH < 7 Acidic

Common Ion Effect

The suppression in the dissociation of a weak electrolyte by the addition of a strong electrolyte having a common ion is called common ion effect.

For example: Ionisation of acetic acid (CH_3COOH) and effect of addition of a small amount of acetate ion.

$CH_3COOH(aq) \longrightarrow CH_3COO$-(aq) + H+(aq)

$CH_3COONa(aq) \longrightarrow CH_3COO$-(aq) + Na+(aq)

Buffer Solution

A buffer solution is that solution which resists any change in its pH value on addition of small amount of acid or base. Although the pH of buffer changes on doing so, but the change in pH value will be less than the expected change. There are three types of buffer solution.

Acidic Buffer: This consists of solution of a weak acid and its salt with strong base. Example; CH_3COOH and CH_3COONa.

Basic Buffer: This consists of solution of weak base and its salt with strong acid. e.g., NH_4OH and NH_4Cl

Salt Buffer: It is a solution of salt which itself can act as a buffer. Such a salt is the salt of weak acid and weak base. For example,

$CH_3COONH_4 \rightleftharpoons NH_4^+ + CH_3COO^-$

When an acid is added, it reacts with CH_3COO^- to produce CH_3COOH and when a base is added, it react with NH^{4+} to produce NH_4OH.

Buffer Capacity

It is the number of moles of acid or base required by one litre of a buffer solution for changing its pH by one unit.

Buffer Capacity = No. of moles of acid or base adder per litre / Change in pH

Solubility and Solubility Product

The number of moles of solute in one litre of a saturated solution (mole / L) is defined as solubility. Let us calculate solubility of salt AgCl.

$AgCl \rightleftharpoons Ag^+ + Cl^-$

$Ksp = [Ag^+][Cl^-]$

Ksp is called solubility product.

In pure water,

$Ksp = [Ag^+][Cl^-]$

$Ksp = S_2 \quad \{\because S = [Ag^+] = [Cl^-]\}$

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

Summary

1. **Equilibrium:** It represents the state of a process in which the properties like temperature, pressure, concentration of the system do not show any change with the passage of time.

2. **Physical equilibrium:** It is a state of equilibrium in which the two opposing processes involve changes in physical state only.

3. **Chemical equilibrium:** It is a state of equilibrium in which the two opposing processes involve change of chemical species.

4. **Reversible reaction:** A reversible reaction is one which proceeds in both the forward and backward directions.

5. **Law of mass action:** This law states that at constant temperature, the rate of chemical reaction is directly proportional to the product of molar concentrations of the reacting substances.

6. **Equilibrium constant (K):** It is the ratio of the product of the molar concentrations of the substances formed to that of the reacting substances raised to the powers equal to their stoichiometric coefficients in the chemical equation at a particular temperature.

7. **Henry's law:** The mass of a gas dissolved in a given mass of a solvent at any temperature is directly proportional to the pressure of the gas above the solvent.

8. **Le Chatelier's Principle:** When a system in dynamic equilibrium is subjected to a stress such as a change in concentration, pressure or temperature, the equilibrium shifts in a direction that opposes or reduces the stress.

9. **Strong electrolytes:** Electrolytes which are ionized almost completely in aqueous solution under similar conditions of concentration and temperature are called strong electrolytes.

10. **Weak electrolytes:** Electrolytes which are poorly ionized in aqueous solution under similar conditions of concentration and temperature are called weak electrolytes.

11. **Solubility product:** It is the product of concentration of ions in a saturated solution of a sparingly soluble salt at a given temperature.

12. **Arrhenius acid-base concept:** According to Arrhenious, an acid is a substance which gives hydrogen ions and base is a substance which gives hydroxyl ions in aqueous solutions.

13. **Bronsted-Lowry acid-base concept:** According to this concept, an acid is a proton donor and base is a proton acceptor.

14. **Lewis acid-bases concept:** According to this concept, an acid is an electron pair acceptor and base is an electron pair donor.

15. **pH value:** pH value of a solution is the negative logarithm of the hydrogen ion concentration (in moles per litre) present in it. Thus $pH = -\log[H^+]$

16. **Irreversible reaction:** If a reaction cannot take place in the reverse direction i.e., the products formed do not react to give back the reactants under the same conditions is called an irreversible reaction.

17. **Homogeneous equilibria:** When in an equilibrium reaction, all the reactants and the products are present in the same phase (i.e., gaseous or liquid), it is called a homogeneous equilibrium.

18. **Heterogeneous equilibrium:** When in an equilibrium reaction, the reactants and the products are present in two or more than two phases, it is called a heterogeneous equilibrium.

19. **Buffer solution:** It is defined as a solution which resists in its pH value even when small amounts of the acid or the base are added to it.

20. **Conjugate base:** A base formed by the loss of proton by an acid is called conjugate base of the acid.

MIND MAP : LEARNING MADE SIMPLE CHAPTER - 7

Equilibrium

Factors Affecting Equilibra

- **Le Chatelier's principle:** 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 counteract the effect of the change.
- **Effect of Concentration Change:** If concentration of reactants is increased, equilibrium will shift in forward direction and vice-versa.
- **Effect of Pressure Change:** No effect if moles of reactants and products are same. If there is change in number of moles , equilibrium will shift in the direction having smaller number of moles when the pressure is increased and vice-versa.
- **Effect of Inert Gas Addition:** If volume is constant, ie addition does not change partial pressure or molar concentrations, equilibrium is not affected.
- **Effect of Temperature change:** For exothermic, low temperature favours formation of reactants; for endothermic, high temperature favours formation of products.

Acids and Bases

Acids turn blue litmus into red and liberate dihydrogen on reacting with some metals.
Bases turn red litmus into blue, taste bitter and feel soapy. Salts are formed when acids and bases are mixed in right proportion. Lewis Acid accepts an electron pair. Lewis Base donates an electron pair.
Acidic: $[H_3O^+] > [OH^-]$
Neutral $[H_3O^+] = [OH^-]$
Basic $[H_3O^+] < [OH^-]$

Predicting the Extent of a Reaction

- $K_c < 10^{-3}$ reaction proceeds rarely.
- $K_c > 10^3$ reaction proceeds nearly to completion
- $K_c \rightarrow 10^{-3}$ to 10^3, reaction is at equilibrium

Predicting the Direction of a Reaction

- If $Q_c < K_c$, net reaction goes from left to right.
- If $Q_c > K_c$, net reaction goes from right to left.
- If $Q_c = K_c$, no net reaction occurs

Calculating Equilibrium Concentrations

Step 1: Write the balanced equation for the reaction.
Step 2: Make a table that lists for each substance involved in reaction; Initial concentration, change in concentration, equilibrium concentration.
Step 3: Substitute the equilibrium concentrations into the equilibrium equation for the reaction and solve.
Step 4: Calculate equilibrium concentrations from the calculated value of concentration of substances.
Step 5: Check results by substituting them into the equilibrium equation.
Buffer Solutions are the solutions which reside change in pH on dilution or addition of acid or alkali.
Solubility Product (ksp):
For a sparingly soluble salt, it is the product of molar concentration of ions raised to power equal to numbers of times each ion.

Relationship Between Equilibrium Constant K, Reaction Quotient Q And Gibbs Energy G

G is negative, reaction is spontaneous and proceeds in forward reaction.
G is positive, reaction is non-spontaneous and proceeds in reserve reaction.
G is 0, reaction has achieved equilibrium.
$K = e^{-\Delta G^\circ/RT}$
Arrhenius Concept of Acids and Bases: Arrhenius theory states that acids are substances that dissociates in water give hydrogen ions and bases are substances that produce hydroxyl ions.
Bronsted Lowry Theory states that acid is a substance that is capable of donating hydrogen ion and bases are substances capable of accepting a hydrogen ion.
•Weak acids have very strong conjugate bases.

Types

Homogeneous Equilibria

Reactants and products are in same phase.

Hetrogeneous Equilibria

Reactants and products are present in two or more phases.

Physical

Equilibrium set up in physical processes like evaporation of water, etc.
- Solid $\rightleftharpoons$ Liquid
- Liquid $\rightleftharpoons$ Gas
- Solid $\rightleftharpoons$ Gas

Characteristics:
- Possible only in a closed system at a given temperature.
- Both the reactions occur at same rate.
- All measurable property remains constant.
- When equilibrium is attained one of its parameter remains constant at given temperature.
- Magnitude of such quantities at any stage indicates the extent to which process has proceeded before reaching equilibrium.

Chemical

Speed of forward reaction equals that of backward reaction.
Characteristics:
- Can be achieved from either side.
- Dynamic in nature.
- There is no change in concentration of various species.
- Observable physical properties become constant.
- Equilibrium is attained rapidly by the presence of catalyst.

pH of a solution is negative logarithm to base 10 of the activity of hydrogen ion

Size increases
HR<<HCl<<HB<<HI
Size increases
Acidic strength increases

Under given set of conditions

if a chemical reaction is carried out in a closed container, a constancy in some observable properties like colour, pressure is observed. Such a state is referred as equilibrium state.

Equilibrium In Chemical Processes

Dynamic Equilibrium: Chemical reactions reach a state of dynamic equilibrium in which the rate of forward and reverse reactions are equal and there is no net change in composition.

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 concentration of the reactions raised to their individual stoichiometric coefficients has a constant value: $aA + bB \rightleftharpoons cC + dD$

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

Equilibrium Constant

for the reverse reaction is the inverse of the equilibrium constant for reaction in the forward direction.
Applications of Equilibrium Constants:
- Applicable only when concentrations of the reactants and products have attained constant value at equilibrium state.
- Value of K_c is independent of initial concentrations of the reactants and products.
- Equilibrium constant is temperature dependent.
  K_c reverse $= \frac{1}{K_c}$
- Equilibrium constant for a reacting is related to equilibrium constant of corresponding reaction.

Important Questions

Multiple Choice questions-

Question 1. Which of the following fluoro-compounds is most likely to behave as a Lewis base?

(a) BF_3

(b) PF_3

(c) CF_4

(d) SiF_4

Question 2. Calculate the pOH of a solution at 25°C that contains 1×10^{-10} M of hydronium ions, i.e. H_3O^+.

(a) 4.000

(b) 9.000

(c) 1.000

(d) 7.000

Question 3. When two reactants, A and B are mixed to give products C and D, the reaction quotient, Q, at the initial stages of the reaction

(a) is zero

(b) Decreases With Time

(c) Is Independent of Time

(d) Increases With Time

Question 4. 1 M NaCl and 1 M HCl are present in an aqueous solution. The solution is

(a) Not a buffer solution with pH < 7

(b) Not a buffer solution with pH > 7

(c) A buffer solution with pH < 7

(d) A buffer solution with pH > 7

Question 5. If, in the reaction N_2O_4 $2NO_2$, x is that part of N_2O_4 which dissociates, then the number of molecules at equilibrium will be

(a) 1

(b) 3

(c) (1 + x)

(d) $(1 + xy)^2$

Question 6. The solubility product of a salt having general formula MX_2. In water is: 4×10^{-12}. The concentration of M^{2+}ions in the aqueous solution of the salt is

(a) 4.0×10^{-10} M

(b) 1.6×10^{-4} M

(c) 1.0×10^{-4} M

(d) 2.0×10^{-6} M

Question 7. Equimolar solutions of the following were prepared in water separately. Which one of the solutions will record the highest pH?

(a) $CaCl_2$

(b) $SrCl_2$

(c) $BaCl_2$

(d) $MgCl_2$

Question 8. Oxidation number of Iodine varies from

(a) -1 to +1

(b) -1 to +7

(c) +3 to +5

(d) -1 to +5

Question 9. Which of the following molecular species has unpaired electrons?

(a) N_2

(b) F_2

(c) O^-_2

(d) O_2^{-2}

Question 10. A certain buffer solution contains equal concentration of X– and HX. The ka for HX is 10-8. The pH of the buffer is

(a) 3

(b) 8

(c) 11

(d) 14

Question 11. Among the following the weakest Bronsted base is

(a) F–

(b) Cl–

(c) Br–

(d) I–

Question 12. Which of the following statements is correct about the equilibrium constant?

(a) Its value increases by increase in temperature

(b) Its value decreases by decrease in temperature

(c) Its value may increase or decrease with increase in temperature

(d) Its value is constant at all temperatures

Question 13. pH value of which one of the following is NOT equal to one.

(a) 0.1 M CH_3COOH

(b) 0.1 M HNO_3

(c) 0.05 M H_2SO_4

(d) $50cm^3$ 0.4 M HCl + $50cm^3$ 0.2 M NaOH

Question 14. [OH–] in a solution is 1 mol L–. The pH the solution is

(a) 1

(b) 0

(c) 14

(d) 10^{-14}

Question 15. What is the pH of a 0.10 M solution of barium hydroxide, $Ba(OH)_2$?

(a) 11.31

(b) 11.7

(c) 13.30

(d) None of these

Very Short:

1. Write the expression for the equilibrium constant K_p for the reaction $3Fe (s) + 4H_2O (g) \rightleftharpoons Fe_3O_4 (s) + 4H_2 (g)$

2. How are Kc and Kp related to each other in the reaction

$N_2 (g) + O_2 (g) \rightleftharpoons 2NO (g)$

3. What is the equilibrium constant expression for the reaction

$Al (s) + 3H^+ (aq) \rightleftharpoons Al^3+ (aq) + \frac{3}{2}H_2 (g)$

4. What happens to the equilibrium

PCl_5 (g) $\rightleftharpoons$ PCl_3 (g) + Cl_2 (g) if nitrogen is added to it

(i) at constant volume

(ii) at constant pressure?

5. What does the equilibrium K < I indicate?

6. For an exothermic reaction, what happens to the equilibrium constant if the temperature is increased?

7. Under what conditions, a reversible process becomes irreversible?

8. What is the effect of increasing pressure on the equilibrium?

N_2 (g) + $3H_2$ (g) $\rightleftharpoons$ $2NH_3$ (g)?

9. For which of the following cases does the reaction go farthest to completion: K = 1, K = 1010, K = 10-10.

10. Under what conditions ice water system is in equilibrium?

(a) at 273 K

(b) below 273 K

(c) above 273 K.

Short Questions:

1. Justify the statement that water behaves like acid as well as a base on the basis of the protonic concept.
2. What is p^{OH}? What is its value for pure water at 298 K?
3. Calculate the p^{H} of a buffer solution containing 0.1 moles of acetic acid and 0.15 mole of sodium acetate. The ionization constant for acetic acid is 1.75×10^{-5}.
4. An aqueous solution of $CuSO_4$ is acidic while that of Na_2SO_4 is neutral. Explain.
5. The dissociation constants of HCN, CH_3COOH, and HF are 7.2×10^{-10}, 1.8×10^{-5}, and 6.7×10^{-4} respectively. Arrange them in increasing order of acid strength.
6. The dissociation of PCl_5 decreases in presence of Cl_2. Why?

Long Questions:

1. Explain chemical equilibrium with th^ help of an example of formation and decomposition of hydrogen iodide.
2. Name and explain the factors which influence the equilibrium state.
3. What is salt hydrolysis? Explain hydrolysis of salts of

   (i) strong acids and strong bases

(ii) strong acids and weak bases

(iii) strong bases and weak acids

(iv) strong acids and weak bases.

4. Calculate the pH of $\frac{N}{1000}$ Sodium hydroxide solution assuming complete ionisation (K_w = 1.0 × 10^{-14}).
5. Calculate the p^H of a 0.01 N solution of acetic acid. K_a for acetic acid is 1.8 × 10^{-5} at 25°C

Assertion Reason Questions:

1. In the following questions, a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the choices given below each question.

   Assertion (A) : Increasing order of acidity of hydrogen halides is HF < HCl < HBr < HI

   Reason (R) : While comparing acids formed by the elements belonging to the same group of periodic table, H–A bond strength is a more important factor in determining acidity of an acid than the polar nature of the bond.

   (i) Both A and R are true and R is the correct explanation of A.

   (ii) Both A and R are true but R is not the correct explanation of A.

   (iii) A is true but R is false.

   (iv) Both A and R are false.

2. In the following questions, a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the choices given below each question.

   Assertion (A) : A solution containing a mixture of acetic acid and sodium

   acetate maintains a constant value of pH on addition of small

   amounts of acid or alkali.

   Reason (R) : A solution containing a mixture of acetic acid and sodium

   acetate acts as a buffer solution around pH 4.75.

   (i) Both A and R are true and R is correct explanation of A.

   (ii) Both A and R are true but R is not the correct explanation of A.

   (iii) A is true but R is false.

   (iv) Both A and R are false.

Case Study Based Question:

1. Le Chatelier's principle is also known as the equilibrium law, used to predict the effect of

change on a system at chemical equilibrium. This principle states that equilibrium adjusts the forward and backward reactions in such a way as to accept the change affecting the equilibrium condition. When factor-like concentration, pressure, temperature, inert gas that affect equilibrium are changed, the equilibrium will shift in that direction where the effects caused by these changes are nullified. This principle is also used to manipulate reversible reactions in order to obtain suitable outcomes.

(1) Which one of the following conditions will favour the maximum formation of the product in the reaction?

$$A_{2(g)} + B_{2(g)} \rightleftharpoons X_{2(g)},\ \Delta_r H = -X\ \text{kJ}\ ?$$

(a) Low temperature and high pressure

(b) Low temperature and low pressure

(c) High temperature and high pressure

(d) High temperature and low pressure

(2) For the reversible reaction,

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} + \text{heat}$$

The equilibrium shifts in forwarding direction

(a) By increasing the concentration of NH3(g)

(b) By decreasing the pressure

(c) By decreasing the concentrations of N2(g) and H2(g)

(d) By increasing pressure and decreasing temperature

(3) Favourable conditions for manufacture of ammonia by the reaction,

$$N_2 + 3H_2 \rightleftharpoons 2NH_3;\ \Delta H = -21.9\ \text{kcal are}$$

(a) Low temperature, low pressure and catalyst

(b) Low temperature, high pressure and catalyst

(c) High temperature, low pressure and catalyst

(d) High temperature, high pressure and catalyst

(4) For the above equilibrium, the reactant concentration is doubled, what would happen then to equilibrium constant?

$$X + Y \rightleftharpoons P + Q$$

(a) Remains constant

(b) Be doubled

(c) Be halved

(d) Cannot be predicted

(5) In which one of the following equilibria will the point of equilibrium shift to left when the pressure of the system is increased?

(a) $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$

(b) $2NH_{3(g)} \rightleftharpoons N_{2(g)} + 3H_{2(g)}$

(c) $C_{(s)} + O_{2(g)} \rightleftharpoons CO_{2(g)}$

(d) $2H_{2(g)} + O_{2(g)} \rightleftharpoons 2H_2O_{(g)}$

Answer Key:

MCQ

1. (b) PF_3
2. (a) 4000
3. (d) Increases With Time
4. (a) Not a buffer solution with pH < 7
5. (a) 1
6. (c) 1.0×10^{-4} M
7. (c) $BaCl_2$
8. (b) -1 to +7
9. (c) O^{-}_{2}
10. (b) 8
11. (d) I^-
12. (c) Its value may increase or decrease with increase in temperature
13. (a) 0.1 M CH_3COOH

14.(c) 14

15.(c) 13.30

Very Short Answer:

1.

$$K_p = \frac{p^4_{H_2}}{p^4_{H_2O}} = \frac{p_{H_2}}{p_{H_2O}}$$

2. $K_p = K_c$.

3. Kc = $[Al^{3+} (aq)][H2 (g)^{3/2}/[H+ (aq)]^3$.

4. The state of equilibrium remains unaffected.

(ii)Dissociation increases, i.e., the equilibrium shifts forward.

5. The reaction does not proceed much in the forward direction.

6. K = K/K_b.

K_b increases much more than when the temperature is increased in an exothermic reaction. Hence K decreases.

7. If one of the products (gaseous) is allowed to escape out (i.e., in the open vessel).

8. Equilibrium will shift in the forward direction forming more ammonia

9. The reaction having K = 1010 will go farthest to completion because the ratio

(product)/(reactants) is maximum in this case.

10. (a) At 273 K.

Short Answer:

Ans: 1. Water ionizes as $H_2O + H_2O \rightleftharpoons H_3O+ + OH–$

With strong acids, water behaves as a base by accepting a proton from an acid.

$HCl + H_2O \rightleftharpoons H_3O+ (aq) + Cl– (aq)$

While with bases, water behaves as an acid by liberating a proton

$NH_3 + H_2O \rightleftharpoons NH_4+ (aq) + OH (aq)$.

Ans: 2. $p^{OH} = -\log [OH-]$

$pH + p^{OH} = 14$ for pure water at 298 K

$pH = 7$

or

p^{OH} of water at 298 = 7.

Ans: 3.

$$p^{H} = p^{K_a} + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

$$= -\log 1.75 \times 10^{-5} + \log \frac{0.15}{0.10} [p^{K_a} = -\log K_a]$$

$$= -\log 1.75 \times 10^{-5} + \log 1.5 = 4.9.$$

Ans: 4. $CuSO_4 + 2H_2O \rightleftharpoons Cu(OH)_2 + H_2SO_4$ (weak base strong acid)

$CuS0_4$ is the salt of weak base $Cu(OH)_2$ and a strong acid H_2SO_4.

Thus, the solution will have free H^+ ions and will, therefore, be acidic.

Na_2SO_4, being the salt of a strong acid H_2SO_4 and a strong base.

NaOH does not undergo hydrolysis. The solution is, therefore, neutral.

Ans: 5. More the value of Ka, the stronger the acid

Their Ka1S are $6.7 \times 10^{-4} > 1.8 \times 10^{-5} > 7.2 \times 10^{-10}$

$\therefore$ HCN < CH_3COOH < HF.

Ans: 6. For $PCl_5 \rightleftharpoons PCl_3 + Cl_2$.

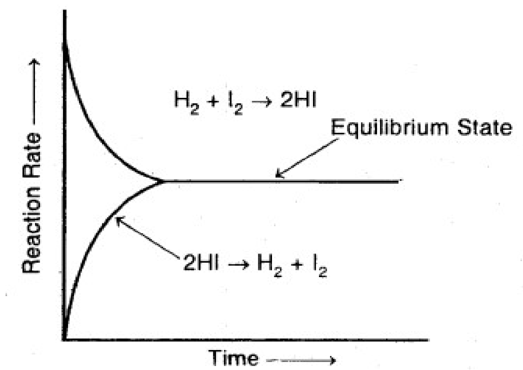
According to Le Chatelier's principle, an increase in the concentration of Cl_2 (one of the products) at equilibrium will favor the backward reaction, and thus the dissociation of PCl_5 into PCl_3 and Cl_2 decreases

Long Answer:

Ans: 1. Consider the reaction between hydrogen and iodide at a constant temperature of 720 K in a closed vessel. The reaction involved is:

$H_2(g) + I_2(g) \rightarrow 2HI(g)$

Accordingly, the effective collision amongst the reactant molecules will result in the production of HI. Since the product molecules are not permitted to leave the vessel (i.e., the reaction is carried out in a closed vessel), they will also collide amongst themselves leading to the formation of reactant molecules. Under these conditions, the reaction takes place in both directions. Hence, it is called a reversible reaction.



Graphical representation of the change of reaction rates with time for the formation and decomposition of hydrogen iodide

Forward reaction: H_2 (g) + I_2 (g) → 2HI (g)

Backward reaction: 2HI (g) → H_2 (g) + I_2 (g)

Reversible reaction: H_2 (g) + I_2 (g) ⇌ 2HI (g).

To begin with, with the concentration of the reactants being higher in comparison to the product molecules, the rate of the forward reaction will be high as compared to the backward reaction. As the reaction proceeds further, the molar concentration of the reactants will gradually decrease while that of the product will gradually increase.

Apparently, the rate of forwarding reaction goes on decreasing while that of the backward reaction. This state is the reversible chemical reaction is called a chemical equilibrium state.

Ans: 2. The various factors which influence the equilibrium state are:

1. Concentration: Concentration change influences the equilibrium state. If the concentration of the reactants is increased, the equilibrium will shift in such a direction in which more to the products are formed and vice-versa.
On the other hand, if the concentration of the products is increased, the equilibrium will

shift in such a direction in which more of the reactants are formed.

2. Temperature: Like concentration, the temperature change also affects the equilibrium state. An increase in temperature of the system will shift the equilibrium in such a direction in which heat is absorbed (i.e. rate of endothermic reaction will increase).

On the other hand, a decrease in temperature of the system will shift the equilibrium in such a direction in which heat is evolved (i.e., rate of exothermic reaction will increase).

3. Pressure: Like concentration and temperature, the pressure also influences the equilibrium state only when the reaction proceeds with a change in volume. An increase in pressure of the system will shift the equilibrium in such a direction in which the volume of the system decreases.

On the other hand, a decrease in pressure of the system will shift the equilibrium in such a direction in which the volume of the system increases.

To explain the effect of temperature, pressure, and concentration on the equilibrium state, consider the combination of N_2 and H_2 to form NH_3

N_2 (g) + $3H_2$ (g) ⇌ $2NH_3$ (g); ΔH = – 93.6 kJ

The reaction is reversible, exothermic, and accompanied by a decrease in volume.

Effect of temperature: According to Le-Chatelier’s principle, an increase in temperature shifts the equilibrium in the direction in which heat is absorbed, and a decrease in temperature shifts the equilibrium in the direction in which heat is evolved. Since the formation of ammonia is accompanied by the evolution of heat, it is favored by a decrease in temperature.

Effect of pressure: According to Le-Chatelier’s principle, an increase of pressure on a system in equilibrium, favors the direction which is accompanied by a decrease in volume and vice-versa. While going from, left to right in the above reaction, there is a decrease in the number of moles or say volume, the formation of ammonia is favored by an increase in pressure.

Effect of concentration: According to Le-Chatelier’s principle, an increase of concentration of any of the substances in the system shifts the equilibrium in the direction in which the concentration of that substance is reduced. Thus, the addition of N_2 or H_2 favors the formation of ammonia.

Ans: 3. Salt hydrolysis: Hydrolysis is a process in which a salt reacts with water to form acid and base.

Salt + Water ⇌ Acid + Base

B A + H_2O ⇌ HA + BOH

That is the interaction of the cations of the salt with OH ions furnished by water and anions of the salt with H+ ions furnished by water to form an acidic or basic solution is called salt hydrolysis.

(i) Salts of strong acids and strong bases like NaCl, KCl, KNO_3 $NaNO_3$, Na_2SO_4, K_2SO_4 do not undergo hydrolysis because the acids and bases furnished by them in aqueous solutions are strong acids and strong bases which are completely dissociated.

$NaCl + H_2O \rightleftharpoons NaOH + HCl$

$NaOH\ (aq) \rightleftharpoons Na^+ + OH^-$

$HCl\ (Aq) \rightleftharpoons H^+ + Cl^-$

Since $[H^+] = [OH^-]$ the resulting solution is neutral and its pH = 7.

(iii) Hydrolysis of salts of strong acids and weak bases:

The salts belonging to this type are NH_4NO_3, NH_4Cl, $(NH_4)_2SO_4$, $CuSO_4$, $AlCl_3$, $Ca(NO_3)_2$, etc.

Let us take the case of NH_4NO_3

$NH_4NO_3 + H_2O \rightleftharpoons NH_4OH + HNO_3$

$NH_4^+ + NO_3^- + H_2O \rightleftharpoons NH_4OH + HNO_3$

or

$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$

The resulting solution after hydrolysis is basic (pH > 7). Since only the anions of the salt have taken place in the hydrolysis, it is called anionic hydrolysis.

(iv) Hydrolysis of salts of weak acids and weak bases:

The salts belonging to this type are:

CH_3COONH_4, $(NH_4)_2CO_3$, $Ca_3(PO_4)_2$ etc.

Let us take the case of hydrolysis of CH_3COONH_4

$CH_3COONH_4 + H_3O \rightleftharpoons CH_3COOH + NH_4OH$

or

$CH_3CO\bar{O} + NH_4 + H_2O \rightleftharpoons CH_3COOH + NH_4OH$

Since both the cations and anions of the salt have participated in the hydrolysis, it is known as cationic as well as anionic hydrolysis. The nature of the solution or pH depends upon the relative strengths of the acid and base that are formed on hydrolysis.

Ans: 4. Since NaOH is completely ionized

$\therefore [NaOH] = [OH^-] = 10^{-3}\ N = 10^{-3}\ M$

Ans: 5. $CH_3COOH \underset{}{\overset{H_2O}{\rightleftharpoons}} CH_3CO\bar{O} + H_3^+O$

Applying the law of chemical equilibrium

Ka = $[CH_3CO\bar{O}][H_3O^+]/[CH_3COOH]$

$\therefore \quad [H_3O^+] = \sqrt{K_a[CH_3COOH]}$

as $\quad [CH_3CO\bar{O}] = [H_3O^+]$

Putting the value of $K_a = 1.8 \times 10^{-5}$ and

$[CH_3COOH] = 0.01\ N = 0.01\ M = 10^{-2}\ M$

$[H_3O^+] = \sqrt{1.8 \times 10^{-5} \times 10^{-2}}$

$= \sqrt{18} \times 10^{-4}$ g ion L^{-1}

$\therefore \quad p^H = -\log[H_3O^+] = -\log(4.242 \times 10^{-4})$

$= -(0.6276 - 4) = 3.37$

Assertion Reason Answer:

1. (i) Both A and R are true and R is the correct explanation of A.
2. (i) Both A and R are true and R is the correct explanation of A.

Case Study Answer:

1. **Answer:**

(1) (a) Low temperature and high pressure

(2) (d) By increasing pressure and decreasing temperature

(3) (b) Low temperature, high pressure and catalyst

(4) (a) Remains constant

(5) (b) $2NH_{3(g)} \rightleftharpoons N_{2(g)} + 3H_{2(g)}$