Chapter # 07

Chemical Equilibrium

Major Concepts

7.1 Reversible Reactions and Dynamic Equilibrium
7.2 Factors Affecting Equilibrium (Le-Chatelier's Principle)
7.3 Industrial Applications of Le-Chatelier's Principle (Haber's Process)
7.4 Solubility Product and Precipitation Reactions
7.5 Common Ion Effect

Learning Outcomes

The students will be able to:

- Define chemical equilibrium in terms of a reversible reaction. (Remembering)
- Write both forward and reverse reactions and describe the macroscopic characteristics of each.(Understanding)
- State the necessary conditions for equilibrium and the ways that equilibrium can be recognized.(Understanding)
- Describe the microscopic events that occur when a chemical system is in equilibrium.(Understanding)
- Write the equilibrium expression for a given chemical reaction.(Understanding)
- Relate the equilibrium expression in terms of concentration, partial pressure, number of moles and mole fraction.
- Write expression for reaction quotient.
- Determine if the equilibrium constant will increase or decrease when temperature is changed, given the equation for the reaction.(Applying)
- Propose microscopic events that account for observed macroscopic changes that take place during a shift in equilibrium.(Applying)
- Determine if the reactants or products are favored in a chemical reaction, given the equilibrium constant.(Analyzing)
- State Le-Chatelier's Principle and be able to apply it to systems in equilibrium with changes in concentration, pressure, temperature, or the addition of catalyst.(Applying)
- Explain industrial applications of Le-Chatelier's Principle using Haber's Process as an example.(Analyzing)
- Define and explain solubility product.(Understanding)
- Define and explain common ion effect giving suitable examples. (Applying)

Introduction

The digestion of food in our body, the rusting of iron, the spoilage of milk and many other reactions occur in our daily life. A large number of reactions are carried out in different industries which give us a large number of useful products like plastics, fibers, drugs, dyes, soaps and detergents and many other useful products. Some reactions are reversible while others are irreversible.

The reactions which occur only in one direction are called *irreversible reactions*. In these reactions, reactants are completely converted into products and products are not reconverted into reactants. These reactions go to completion. They are shown by putting a single headed arrow ($\longrightarrow$) between the reactants and products. Examples of such reactions are:

i) $2H_2O_{(g)} \xrightarrow{\text{Electric discharge}} 2H_{2(g)} + O_{2(g)}$

ii) $AgNO_{3(aq)} + NaCl_{(aq)} \longrightarrow AgCl_{(s)} + NaNO_{3(aq)}$

iii) Burning of fuel

iv) Digestion of food

A chemical reaction which occurs in forward as well as reverse directions is called reversible reaction. In these reactions, reactants are converted into products and products are reconverted into reactants. These are slow reactions. These reactions never go to completion, hence called incomplete reactions. They are shown by putting the double arrow with double barbs ($\rightleftharpoons$), pointing in opposite directions, between the reactants and products. The double arrows of equal length also show equilibrium. Examples of some reversible reactions are:

i) $H_{2(g)} + I_{2(g)} \underset{\text{Reverse reaction}}{\overset{\text{Forward reaction}}{\rightleftharpoons}} 2HI_{(g)}$

ii) $N_{2(g)} + 3N_{2(g)} \underset{\text{Reverse reaction}}{\overset{\text{Forward reaction}}{\rightleftharpoons}} 2NH_{3(g)}$

iii) $2SO_{2(g)} + O_{2(g)} \underset{\text{Reverse reaction}}{\overset{\text{Forward reaction}}{\rightleftharpoons}} 2SO_{3(g)}$

iv) $H_2O_{(l)} \underset{\text{Reverse reaction}}{\overset{\text{Forward reaction}}{\rightleftharpoons}} H_2O_{(g)}$

All chemical reactions are considered to be reversible and they reach a s of equilibrium under suitable conditions. A reversible chemical reaction is dynamic process. The word equilibrium means "a state in which opposing fo are balanced". It may be static (at rest) or dynamic (in constant motion). A pen finger at rest is the example of static equilibrium and the earth that revolves ar the sun is the example of dynamic equilibrium.

7.1 Reversible Reactions and Dynamic Equilibrium

7.1.1 Concept and Explanation

The state in which the rates of forward and reverse reactions are same and the concentrations of the reactants and products remain unchanged with time is called chemical equilibrium. Chemical equilibrium may be physical or chemical. Equilibrium between two phases of the same substance is called physical equilibrium because the changes that take place are physical processes. The conversion of water into vapours in a closed container at a given temperature is an example of physical equilibrium. The rate of evaporation is higher than rate of condensation at the start when water vaporizes within a closed container at constant temperature, but after some times, the rate of evaporation becomes equal to rate of condensation. At this stage liquid and vapours are in the state of dynamic equilibrium i.e. the number of molecules leaving the liquid surface is equal to the number of molecules returning back to the liquid. At equilibrium the pressure exerted by the water molecules at a given temperature remains constant and is called the equilibrium vapour pressure of water.

$$\text{Liquid (water)} \xrightleftharpoons[\text{Condensation}]{\text{Evaporation}} \text{Vapours (steam)}$$

Chemical equilibrium is a *dynamic* state because reactions continue to occur, but because they occur at the same rate, no net change is observed on the macroscopic level.

The study of physical equilibrium gives useful information such as the equilibrium vapour pressure. However, chemists are particularly interested in chemical equilibrium processes because they are involved in many biological, industrial, and environmental processes. Consider the reversible reaction which involves the decomposition of colourless frozen dinitrogen tetraoxide into dark brown nitrogen dioxide:

$$N_2O_{4(g)} \xrightleftharpoons[\text{Reverse reaction}]{\text{Forward reaction}} 2NO_{2(g)}$$

When some amount of pure N_2O_4 is placed in an evacuated flask at room temperature, some brown colour gas appears which shows the formation of NO_2 molecules. The concentration of NO_2 in the flask increases and the brown colour deepens. However, the reverse reaction can also starts. As the reaction proceeds, the concentration of reactant (N_2O_4) goes on decreasing, so the rate of forward reaction also goes on decreasing. On the other hand, the concentration of product (NO_2) goes on increasing, so the rate of reverse reaction also goes on increasing. When the rate of forward reaction becomes equal to rate of reverse reaction, the reaction reaches state of chemical equilibrium and the concentrations of reactants and products become constant. Now the change in colour is stopped. In fact, you see no net change at this stage, although the forward and reverse reactions are going on. The continuing forward and reverse reactions make the equilibrium a *dynamic* process. All chemical equilibriums are dynamic. Once the state of chemical equilibrium is established, it will last forever if conditions are not changed.

Consider a general reaction, in which A reacts with B to produce C and D.

$$\underset{\text{(Reactants)}}{A + B} \underset{\text{Reverse reaction}}{\overset{\text{Forward reaction}}{\rightleftharpoons}} \underset{\text{(Products)}}{C + D}$$

Let us consider initial concentrations of A and B are equal. The concentration of reactants A and B decreases and that of products C and D increases when reaction proceeds in forward direction. Hence, the rate of forward reaction goes on decreasing while that of reverse reaction goes on increasing and a point is reached at which rate of forward reaction becomes equal to rate of reverse reaction. This is called equilibrium point. At equilibrium, product and reactant lines are parallel to each other. The change in concentration of reactants or products is called rate of reaction.

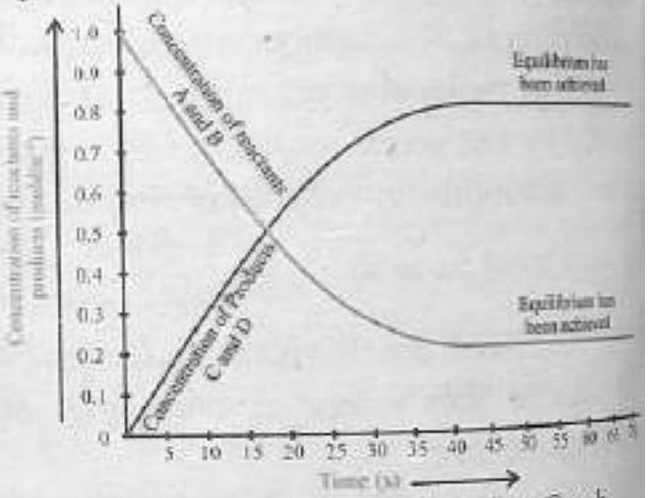

Figure 7.1: Concentration-time Graph

The mixture of reactants and products in the equilibrium state is known as equilibrium mixture and the unvarying amounts of reactants and products are called equilibrium concentrations.

Table 7.1: The Explanation of the Characteristics of Equilibrium State

Characteristics of Equilibrium State	Explanation
Most of the reactions are reversible	The reactions can proceed in both forward and reverse directions.
Equilibrium is dynamic	The reaction has not stopped but the oppo rates are equal (both forward and reve reactions are still taking place at the equal
The macroscopic properties of a system are constant at equilibrium.	The reaction has not stopped but the op rates are equal (both forward and re reactions are still taking place at the equal

Characteristics of Equilibrium State	Explanation
The microscopic processes continue	The forward and reverse reactions are going on but nothing appears to be happening because the forward and reverse reactions occur at the same rates.
Equilibrium is achieved in a closed system	A closed system is a system that does not allow the exchange of matter with the surroundings, so the equilibrium is attained where both reactants and products can react and recombine with each other.
The concentrations of products and reactants remain constant at equilibrium	There is no change in the concentrations of reactants or products in a system of dynamic equilibrium. They are being produced and destroyed at an equal rate. Equilibrium does not mean that concentrations of reactants and products are all equal.
Equilibrium can be approached from either side	The same equilibrium mixture will result under the same conditions, regardless of whether the reaction is started with all reactants, all products or a mixture of both. For example, the proportions of $N_{2(g)}$, $H_{2(g)}$ and $NH_{3(g)}$ are the same at equilibrium no matter whether the reaction is started with $N_{2(g)}$, $H_{2(g)}$ or whether the reaction is stated with $NH_{3(g)}$ or mixture of both. $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 3NH_{3(g)}$
Catalysts do not affect equilibrium concentrations	Catalysts speed up the rate of forward and reverse reactions equally. We get the same concentrations of reactants and products at equilibrium, whether the catalyst is present in the reaction mixture or not.

Types of Chemical Equilibriums

There are two types of chemical equilibriums:

Homogeneous Chemical Equilibrium

Chemical equilibrium in which reactants and products are in same physical state is called homogeneous chemical equilibrium. For example,

$$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$$

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

Heterogeneous Chemical Equilibrium

Chemical equilibrium in which reactants and products are in different physical states is called heterogeneous chemical equilibrium. For example:

$$CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$$

$$2Fe_{(s)} + 3H_2O_{(g)} \rightleftharpoons Fe_2O_{3(s)} + 3H_{2(g)}$$

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7.1.2 Law of Mass Action and Expression for Equilibrium Constant

C. M. Guldberg (1836-1902) Peter Waage (1833-1900)

The law of mass action was postulated by professor of applied mathematics and technology Cato Maximilian Guldberg and professor of chemistry Peter Waage in 1864 at the university of Oslo, Norway. This law states that:

"The rate of reaction is directly proportional to the product of active masses of the reactants".

By active masses we mean molar concentrations of the reactants and products for dilute solution. It is expressed in moles dm^{-3}. Consider a general reversible reaction.

$$\underset{\text{(Reactants)}}{A + B} \underset{\text{Reverse}}{\overset{\text{Forward}}{\rightleftharpoons}} \underset{\text{(Products)}}{C + D}$$

According to law of mass action, the rate of forward reaction is directly proportional to the product of molar concentration of reactants A and B.

$$R_f \propto [A][B] \qquad \text{or}$$

$$R_f = K_f[A][B]$$

Where, K_f is the rate constant of forward reaction. Similarly, the rate of reverse reaction is directly proportional to the product of molar concentration of products C and D.

$$R_r \propto [C][D] \qquad \text{or}$$

$$R_r = K_r[C][D]$$

Where, K_r is the rate constant of reverse reaction. At equilibrium state, rate of forward reaction is exactly equal to the rate of reverse reaction.

Rate of forward reaction = Rate of reverse reaction

$$R_f = R_r$$

or $$K_f[A][B] = K_r[C][D]$$

or $$\frac{K_f}{K_r} = \frac{[C][D]}{[A][B]}$$

$$\boxed{\frac{K_f}{K_r} = K_c}$$

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

or $$K_c = \frac{\text{Product of molar concentrations of products}}{\text{Product of molar concentrations of reactants}}$$

K_c is called equilibrium constant of the reaction. It is defined as: The ratio of concentrations of products to the concentrations of reactants at equilibrium is called equilibrium constant. It has concentration of products in the numerator and concentration of reactants in the denominator. In gaseous equilibriums, concentrations of gases are shown by partial pressure and K_p is used instead of K_c. Consider the more general reversible reaction:

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

Where a, b, c and d are the coefficients of balanced chemical equation. At equilibrium state,

Concentration of products

$$\underset{\underset{\text{Equilibrium constant}}{\uparrow}}{K_c} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Concentration of reactants

$$K_c = \frac{\text{Product of concentrations of products (raised to power equal to coeffcients)}}{\text{Product of concentrations of reactants (raised to power equal to coeffcients)}}$$

The coefficients appear as exponents (powers) of concentrations in the equation of K_c.

Characteristics of Equilibrium Constant

) Equilibrium constant is independent of initial concentrations of reactants and roducts at a given temperature.

i) It does not depend upon the direction of reaction. The same equilibrium onstant value is obtained whether the reaction is started from the reactants side or om the products side.

) Its value changes with temperature and is constant at constant temperature.

) Its value depends upon the coefficients of reactants and products in a balanced emical equation.

The higher value of equilibrium constant is the indication of higher value of oducts as compared to the reactants at equilibrium and vice versa.

) The molar concentrations of pure solids, pure liquids (in heterogeneous equilibria), and solvents (in homogeneous equilibria) do not appear in equilibrium constant expressions.

Units of Equilibrium Constant

When the number of moles of reactants and products in balanced chemi equations are equal, then K_c has no unit. For example:

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$

$$K_c = \frac{[CO_2][H_2]}{[CO][H_2O]} = \frac{(\text{mol dm}^{-3})(\text{moles dm}^{-3})}{(\text{mol dm}^{-3})(\text{mol dm}^{-3})} = \text{No unit}$$

When the number of moles of reactants and products are unequal, then the K has units. For example:

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

$$\begin{aligned} K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} &= \frac{(\text{mol dm}^{-3})^2}{(\text{mol dm}^{-3})(\text{mol dm}^{-3})^3} \\ &= \frac{(\text{mol}^2\text{dm}^{-6})}{(\text{mol dm}^{-3})(\text{mol}^3\text{dm}^{-9})} \\ &= \frac{\text{mol}^2\text{dm}^{-6}}{\text{mol}^4\text{dm}^{-12}} \\ &= \text{mol}^{2-4}\,\text{dm}^{-6+12} \\ &= \text{mol}^{-2}\,\text{dm}^{+6} \end{aligned}$$

But in usual practice, the units of K_c and K_p are not written.

7.1.3 Relationship Between K_c, K_p, K_x and K_n

Relationship Between K_c and K_p

When concentration of reactants and products are taken in moles dm^{-3} t equilibrium constant is expressed by K_c. Consider the general reversible reactio

$$A + B \rightleftharpoons C + D$$

Hence,

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b} \quad \text{or} \quad K_c = \frac{C_C^c \cdot C_D^d}{C_A^a \cdot C_B^b}$$

Square brackets or "C" show molar concentration in moles dm^{-3}.

When all the reactants and products are in gaseous state, then concentration of each gas is taken in terms of partial pressure, and the equilibrium constant is expressed by K_p.

$$K_p = \frac{P_C^c \cdot P_D^d}{P_A^a \cdot P_B^b} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (i)$$

Where P_A is the partial pressure of gas A and P_B is the partial pressure of gas B.

The value of K_c is generally different from K_p because the partial pressures of reactants and products are not equal to their concentrations expressed in moles per decimeter cube. If we know the value of one, then we can calculate the value of the other by using the general gas equation.

According to combined gas law:

$$PV = nRT \quad \text{or}$$

$$P = \frac{n}{V}(RT)$$

The conventional unit for **n/V** is mol/dm^3 that is equal to Molarity.

Hence, for gaseous reactants A, B and gaseous products C, D the above equation can be written as:

$$P_A = \frac{n_A}{V}(RT) \quad \text{or} \quad P_A = [A](RT)$$

$$P_B = \frac{n_B}{V}(RT) \quad \text{or} \quad P_B = [B](RT)$$

$$P_C = \frac{n_C}{V}(RT) \quad \text{or} \quad P_C = [C](RT)$$

$$P_D = \frac{n_D}{V}(RT) \quad \text{or} \quad P_D = [D](RT)$$

By putting the value of P_A, P_B, P_C, and P_D in equation (i), we get:

$$K_p = \frac{[C]^c (RT)^c \cdot [D]^d (RT)^d}{[A]^a (RT)^a \cdot [B]^b (RT)^b} \quad \text{or}$$

$$K_p = \frac{[C]^c [D]^d (RT)^{c+d}}{[A]^a [B]^b (RT)^{a+b}} \quad \text{or}$$

$$K_p = \frac{[C]^c [D]^d}{[A]^a [B]^b} (RT)^{(c+d)-(a+b)}$$

As, $\frac{[C]^c [D]^d}{[A]^a [B]^b} = K_c$, hence, the above equation can be written as,

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

Where, R is general gas constant, T is absolute temperature and Δn is in the number of moles between products and reactants of gases. So,

$\Delta n = (c+d)-(a+b)$

Δn = (Sum of moles of gaseous products) – (Sum of moles of gaseous

When number of moles of reactants and products are equal, then Δn is to zero, and $K_p = K_c$.

Example 7.1

Write the equilibrium constant expressions (K_c & K_p) for the two reactions below:

(a) $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$

(b) $N_2 + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$

Solution:

(a) $$K_c = \frac{[NO_2]^2}{[N_2O_4]}$$

As we know,

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

Hence,

$$K_p = \frac{[NO_2]^2}{[N_2O_4]}(RT)$$ Where, $\Delta n = 1$

(b) $$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

As we know,

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

Hence,

$$K_p = \frac{[NH_3]^2}{[N_2][H_2]^3}(RT)^{-2}$$ Where, $\Delta n = 2-4=-2$

Practice Exercise 1:

Write the equilibrium constant expressions (K_c & K_p) for the reaction below:

$$2SO_{3(g)} \rightleftharpoons 2SO_{2(g)} + O_{2(g)}$$

Relationship between K_p and K_x

According to Dalton's Law, the partial pressure of a gas is equal to the product of its mole fraction and total pressure.

$$P_i = X_i \cdot P_T$$

Where, P_i is the partial pressure of a gas, X_i is the mole fraction of a gas and P_T is the total pressure of the gases. The values of partial pressures of gases A, B, C, and D are:

$$P_A = X_A \cdot P_T$$

$$P_B = X_B \cdot P_T$$

$$P_C = X_C \cdot P_T$$

$$P_D = X_D \cdot P_T$$

By putting the value of P_A, P_B, P_C and P_D in equation (i), we get

$$K_p = \frac{(X_C P_T)^c (X_D P_T)^d}{(X_A P_T)^a (X_B P_T)^b} \qquad \text{or}$$

$$K_p = \frac{(X_C^c)(X_D^d)(P_T)^{c+d}}{(X_A^a)(X_B^b)(P_T)^{a+b}} \qquad \text{or}$$

$$K_p = \frac{(X_C^c)(X_D^d)}{(X_A^a)(X_B^b)} (P_T)^{(c+d)-(a+b)}$$

$$\frac{(X_C^c)(X_D^d)}{(X_A^a)(X_B^b)} = K_x$$

Therefore,

$$K_p = K_x(P_T)^{(c+d)-(a+b)} \qquad \text{or} \qquad K_p = K_x(P_T)^{\Delta n}$$

For one mole of a gas:

$$P_T = \frac{RT}{V}$$

Therefore:

$$K_p = K_x\left(\frac{RT}{V}\right)^{\Delta n} \qquad \text{................. (iii)}$$

When number of moles of reactants and products are equal, then Δn is equal to zero, and $K_x = K_p$.

Relationship between K_p and K_n

When concentrations of reactants and products are taken in terms of number of moles, then equilibrium constant is expressed by K_n. According to Dalton's Law, the mole fraction of a gas is equal to number of moles of a particular gas divided by total number of moles of all gases present in the mixture.

$$X_i = \frac{n_i}{n_T}$$

Where, X_i is the mole fraction of a gas, n_i is the number of moles of a gas, and n_T is the total number of moles of gases. We know that,

$$P_i = X_i \, . \, P_T$$

Hence, by putting the value of X_i in this equation, we obtain

$$P_i = \frac{n_i}{n_T} \, . \, P_T$$

For the reactant gases (A and B) and product gases (C and D), the equation will be:

$$P_A = \frac{n_A}{n_T} \, . \, P_T$$

$$P_B = \frac{n_B}{n_T} \, . \, P_T$$

$$P_C = \frac{n_C}{n_T} \, . \, P_T$$

$$P_D = \frac{n_D}{n_T} \, . \, P_T$$

By putting the value of P_A, P_B, P_C, and P_D in equation (i), we get

$$K_p = \frac{(\frac{n_C}{n_T} \, . \, P_T)^c \, (\frac{n_D}{n_T} \, . P_T)^d}{(\frac{n_A}{n_T} \, . \, P_T)^a \, (\frac{n_B}{n_T} \, . P_T)^b} \qquad \text{or}$$

$$K_p = \frac{(\frac{n_C}{n_T})(\frac{n_D}{n_T})(P_T)^{c+d}}{(\frac{n_A}{n_T})(\frac{n_B}{n_T})(P_T)^{a+b}}$$

As, $$\frac{(\frac{n_C}{n_T})(\frac{n_D}{n_T})}{(\frac{n_A}{n_T})(\frac{n_B}{n_T})} = K_n$$

Therefore,

$$K_p = K_n(P_T)^{(c+d)-(a+b)} \quad \text{or} \quad K_p = K_n(P_T)^{\Delta n}$$

For one mole of a gas,

$$P_T = \frac{RT}{V}$$

Therefore,

$$K_p = K_n\left(\frac{RT}{V}\right)^{\Delta n} \quad \text{..................} \quad \text{(iv)}$$

When number of moles of reactants and products are equal, then Δn is equal zero, and all the equilibrium constants have the same values, hence

$$K_c = K_p = K_x = K_n$$

7.4 Calculation of Equilibrium Constant

Equilibrium constant of chemical reaction is calculated from the values of concentration or partial pressures at equilibrium. In cases where the equilibrium constant is known, the concentration or partial pressure values at equilibrium may determined.

Example 7.2

The ammonia, used in the manufacture of fertilizer, is prepared by the reaction of nitrogen and hydrogen gases. At equilibrium, the concentrations of nitrogen, hydrogen, and ammonia are 0.030M, 0.037M and 0.016M respectively. Calculate the value of K_c at 500°C for the reaction given below:

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

Concentration of nitrogen $= [N_2] = 0.030M$

Concentration of hydrogen $= [H_2] = 0.037M$

Concentration of ammonia $= [NH_3] = 0.016M$

Value of K_c for reaction $= ?$

$$\begin{array}{lccccc} & N_{2(g)} & + & 3H_{2(g)} & \rightleftharpoons & 2NH_{3(g)} \\ \text{Equilibrium concentration (M)} = & 0.030 & & 0.037 & & 0.016 \end{array}$$

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} \quad \text{or}$$

$$K_c = \frac{[0.016]^2}{[0.030][0.037]^3} = 168.46 \quad \text{or} \quad 1.68 \times 10^2$$

Practice Exercise 2:

Phosgene gas (carbonyl chloride, $COCl_2$) is a highly poisonous gas that was used in the First World War as a chemical weapon. This gas is prepared by the reaction of CO and Cl_2 gases. At equilibrium, the concentrations of CO, Cl_2 and $COCl_2$ are 0.011 M, 0.045M and 0.012M respectively. What is the value of K_c at 100°C for the reaction given below?

$$CO_{(g)} + Cl_{2(g)} \rightleftharpoons COCl_{2(g)}$$

Example 7.3

Calculate the concentration of SO_3 gas, used in the manufacture of H_2SO_4, with the help of the reaction give below:

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$

The concentration of SO_2 gas is 0.59M and that of O_2 gas is 0.45M. The K_c value of this reaction is 4.32.

Solution:

Concentration of SO_3 = $[SO_3]$ = ?

Concentration of SO_2 = $[SO_2]$ = 0.59M

Concentration of O_2 = $[O_2]$ = 0.45M

Value of K_c = 4.32

At equilibrium,

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$

$$K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]} \quad \text{or}$$

$$[SO_3]^2 = K_c\,[SO_2]^2[O_2]$$

By putting the values we get,

$$[SO_3]^2 = (4.32)(0.59)^2(0.045)$$

$$[SO_3]^2 = 0.0677$$

By taking under root on both sides we have,

$$[SO_3] = \sqrt{0.0677}$$

$$[So_3] = 0.26M$$

Practice Exercise 3:

Consider the reaction:

$$2\,NO_{(g)} \rightleftharpoons N_{2(g)} + O_{2(g)}$$

Suppose NO gas is allowed to reach to equilibrium at 900°C. The measured equilibrium concentrations are 0.021M for N_2, 0.021M for O_2. The value of K_c for the equilibrium system is 76.56. Calculate the concentration of NO.

7.1.5 Importance of Equilibrium Constant

The equilibrium constants of reactions can be used to determine:

i) the direction of reaction.

ii) the extent of reaction.

Determination of Direction of Reaction and the Reaction Quotient

The ratio of concentrations of products to the concentrations of reactants when the reaction is at equilibrium is called equilibrium constant (K_c) whereas, the ratio of concentrations of products to the concentrations of reactants when the reaction is not at equilibrium is called reaction quotient (Q_c).

The ratio $[C]^c[D]^d / [A]^a[B]^b$ at equilibrium is equal to K_c.

The ratio $[C]^c[D]^d / [A]^a[B]^b$ that is not at equilibrium is equal to Q_c.

We say that, the reaction quotient is an expression which has the same form as the equilibrium constant except that the concentrations in reaction quotient are not necessarily those at equilibrium.

The equilibrium quotient is also used to determine whether the reaction is at equilibrium or is not at equilibrium. The reaction is at equilibrium when Q_c is equal to $K_c (Q_c = K_c)$ and the reaction is not at equilibrium when Q_c is not equal to $K_c (Q_c \neq K_c)$.

The reaction quotient is helpful to determine the direction of reaction. We can determine the direction of chemical reaction by comparing the values of Q_c and K_c. There are three possibilities:

The Q_c may be less than K_c, greater than K_c or equal to K_c.

i) If Q_c is less than K_c ($Q_c < K_c$), then reaction will proceed in forward direction (from left to right) to attain the equilibrium.

$$aA + bB \longrightarrow cC + dD$$

ii) If Q_c is greater than K_c ($Q_c > K_c$), the reaction will proceed in a reverse direction (from right to left) to attain the equilibrium.

$$aA + bB \longleftarrow cC + dD$$

iii) If Q_c is equal to K_c ($Q_c = K_c$), then the reaction is at equilibrium. It wil not move in any direction.

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

Determination of Extent of Reaction

Extent of chemical reaction means that how much reactant is converted into produc at equilibrium. There are three possibilities:

i) **If K_c is very large:** It means that if K_c value is greater than 10^3 ($K_c > 10^3$), the forward reaction takes place to greater extent and reverse reaction take place to smaller extent. The forward reaction is almost near to completion. Fo example:

$$2O_3 \rightleftharpoons 3O_2$$

$$K_c = \frac{[O_2]^3}{[O_3]^2} = 10^{55} \quad \text{at } 25^\circ C$$

The equilibrium constant value for this reaction is very large which show that the concentration of product is very large as compared to the concentration of reactant at equilibrium. The large value of K_c at equilibrium tells us that the maj amount of reactant is changed into product.

ii) **If K_c is very small:** It means that if K_c value is less than 10^{-3} ($K_c < 10^{-3}$), the reverse reaction takes place to greater extent and forward reaction takes place smaller extent. For example:

$$2HF \rightleftharpoons H_2 + F_2$$

$$K_c = \frac{[H_2][F_2]}{[HF]^2} = 10^{-13} \quad \text{at } 2000^\circ C$$

The equilibrium constant value for this reaction is very small which sho that the concentration of product is very small as compared to the concentratio reactant at equilibrium. The small value of K_c at equilibrium tells us that the mi quantity of reactant is changed into products.

iii) **If K_c is neither very large nor very small:** It means that if K_c value is in range of 10^{-3} to 10^3, then both the forward and reverse reactions take place almo an equal extent. For example:

(a) $N_2O_4 \rightleftharpoons 2NO_2$

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} = 0.36 \text{ at } 25^\circ C$$

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

$$K_c = \frac{[NO]^2}{[N_2][O_2]} = 0.1 \text{ at } 2000^\circ C$$

At equilibrium, the molar concentration of products and reactants are almost equal.

7.2 Factors Affecting Equilibrium

The ratio of products to reactants in the equilibrium mixture is known as the position of chemical equilibrium or equilibrium position. The ratio of the reactants and products can be changed by changing the conditions of a reaction at equilibrium. Many useful chemical reactions are reversible in which the reactants are not completely converted into products and the amount of products decreases. The chemists are interested to increase the amount of products by shifting the equilibrium in forward direction. The factors that affect the equilibrium state of a chemical reaction are concentration, pressure and temperature. The effect of such changes on equilibrium state can be best explained with the help of Le Chatelier's Principle.

LeChatelier's Principle

imp

Henri Louis Le
Chatelier
(1850-1936)

Henri Louis Le Chatelier was a French chemist specialized n mining engineering and interested in glass and ceramic. He studied the effect of concentration, pressure and emperature on a number of reactions in equilibrium state in 984. This principle states that, if a system in equilibrium is isturbed by some change, the system will shift so as to ounteract the effect of the change.

This principle can be applied to all types of dynamic quilibrium i.e. for physical and chemical systems.

pplications of Le-Chatelier's Principle

et us explain some of the most common applications of this principle in the llowing changes.

7.2.1 The Effect of Concentration Change

Consider a system is in equilibrium:

$$\underset{\text{(Reactants)}}{A + B} \rightleftharpoons \underset{\text{(Products)}}{C + D}$$

i) If we increase the concentration of anyone reactant A or B or both of them, then the reaction moves from left to right in forward direction. The equilibrium is reestablished with a higher concentration of product.

ii) If we increase the concentration of anyone product C or D or both of them, then the reaction moves from right to left in the reverse direction to increase the amount of reactant at time of equilibrium.

iii) If we decrease the concentration of reactant A or B or both of them, then the reaction moves from right to left in reverse direction. This effect is reduced by the decomposition of products to produce reactants.

iv) If we decrease the concentration of product C or D or both of them, then the reaction moves from left to right in forward direction forming more product when equilibrium is reestablished.

In all of the above cases the equilibrium position changes due to change in the concentration of reactants and product. But the equilibrium constant (K_c) value does not change when we change the concentration of reactants and products.

Consider the example of the reaction of equilibrium mixture of N_2, H_2 and NH_3

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

If the concentrations of N_2 or H_2 or both of them are increased, the equilibrium will shift in the forward direction and greater amount of NH_3 is produced when the equilibrium is reestablished. If we remove some amount of N_2, H_2 or both of them from the equilibrium mixture, then the equilibrium will shift in the reverse direction and NH_3 is decomposed to produce N_2 and H_2. Hence, the increase in the concentration of reactants favours the forward reaction whereas the decrease in the concentration of reactants favours the reverse reaction.

Consider another familiar example of equilibrium mixture of N_2, O_2 and N

$$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$$

If we increase the concentration of NO by adding some amount of it to equilibrium mixture, then the system will shift in the reverse direction. This eff reduced by the decomposition of NO to produce N_2 and O_2. If we decreas concentration of NO by removing some amount of it from the equilibrium mi then the system will shift in the forward direction to produce more nitric (NO). Hence, the increase in the concentration of products favours the rev reaction whereas the decrease in the concentration of products favours the forward reaction.

Table 7.2: The Effect of Concentration Change on Equilibrium Position and K_c

Change to System	Change in Direction	Effect on Equilibrium Position	Effect on K_c
Increase in the concentration of reactants	Equilibrium shifts to the product side	Changes	No effect
Decrease in the concentration of reactants	Equilibrium shifts to the reactant side	Changes	No effect
Increase in the concentration of products	Equilibrium shifts to the reactant side	Changes	No effect
Decrease in the concentration of products	Equilibrium shifts to the product side	Changes	No effect

7.2.2 Effect of Pressure or Volume Change

According to Le Chatelier's principle, if the pressure of an equilibrium mixture of gases is increased by decreasing the volume, at constant temperature, the reaction shifts in the direction of fewer moles of gas molecules. If the pressure of an equilibrium mixture of gases is decreased by increasing the volume, at constant temperature, the reaction shifts in the direction of more moles of gas molecules.

Pressure or volume change produces sharp effect in gaseous equilibriums where the total number of moles of reactants on the left side of equation is not equal to the total number of moles of products on the right side of equation. Examples are:

Formation of Ammonia

Consider the reaction,

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

When pressure is increased or volume is decreased at equilibrium, the reaction moves from left to right in the forward direction to increase the amount of product (NH_3). In this case, the equilibrium position shifts to the right (product side) but K_c value remains constant.

Dissociation of PCl_5

Consider the reaction,

$$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$$

When pressure is increased at equilibrium; the reaction moves from right to left in the direction of decreased volume to increase the amount of reactant (PCl_5).

In this case, the equilibrium position shifts to the left (reactant side) but K_c remains constant.

The effect of pressure or volume change is not applicable:

(a) When the system involves solids and liquids. They are not affected by the changes in pressure because they are almost incompressible. Consider the example the water gas (mixture of CO gas and H_2 gas) is produced when steam is passed through red hot coke (carbon).

$$H_2O_{(g)} + C_{(s)} \rightleftharpoons CO_{(g)} + H_{2(g)}$$

When pressure is increased by decreasing volume, the equilibrium will shift from right to left in the direction of fewer moles of gas molecules. In this reaction we ignore the volume or concentration of carbon because it is present in solid state.

(b) When the total number of moles of reactants is equal to the total number of moles of products in gaseous phase homogeneous equilibriums.

Consider the following reaction,

$$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$$

When pressure is increased at equilibrium, the rate of both the forward and reverse reactions will increase to the same extent and the equilibrium will not shift in any direction because the total number of moles of reactants is equal to the total number of moles of products in this reaction. In this case, both the equilibrium position and K_c are not changed.

(c) When an inert gas is added to the equilibrium mixture. When a non-reactive gas (inert gas) such as neon which is not part of the equilibrium system(reactants and products) is added, the total pressure of the gases increases in a rigid container but it has no effect on the partial pressures or concentrations of the reactants or products. Thus it cannot affect the equilibrium position (i.e. the relative amounts of reactants and products) of the system. Nitrogen and noble gases are frequently used as inert gases.

Table 7.3: The Effect of Pressure Change on Equilibrium Position and K_c

Change to System	**Change in Direction**	**Effect on Equilibrium Position**	**Effect on K**
Increase in pressure or decrease in volume	Equilibrium shifts to the side that has fewer moles of gas molecules	Changes	No effect
Decrease in pressure or increase in volume	Equilibrium shifts to the side that has greater moles of gas molecules	Changes	No effect

7.2.3 Effect of Temperature Change

Changes in concentration, pressure, or volume alter the equilibrium position without altering the value of the equilibrium constant. The value of equilibrium constant can be altered only when the temperature of the system is changed.

According to Le-Chatelier's Principle, exothermic reactions are favoured by decrease in temperature and endothermic reactions are favoured by increase in temperature. A reaction in which heat is evolved is said to be exothermic whereas a reaction in which heat is absorbed is said to be endothermic. For exothermic reactions heat is regarded as one of the products and for endothermic reactions heat is regarded as one of the reactants.

(a) **Consider the example of the formation of nitric oxide:**

$$N_{2(g)} + O_{2(g)} \underset{\text{Exothermic}}{\overset{\text{Endothermic}}{\rightleftharpoons}} 2NO_{(g)} \qquad \Delta H = +90.25\ \text{Kjmol}^{-1}$$

Here, the forward reaction is endothermic and the reverse reaction is exothermic. In this case the forward reaction is favoured by rise in temperature and the reverse reaction is favoured by fall in temperature. Actually a temperature above 3000°C is used to increase the concentration of product.

(b) **Consider the example of the formation of ammonia:**

$$N_{2(g)} + 3H_{2(g)} \underset{\text{Endothermic}}{\overset{\text{Exothermic}}{\rightleftharpoons}} 2NH_{3(g)} \qquad \Delta H = -46.11\ \text{KJmol}^{-1}$$

Here, the forward reaction is exothermic and the reverse reaction is endothermic. In this case, the formation of ammonia is favoured by decrease in temperature. The increase in temperature shifts the equilibrium to the left direction and the ammonia will decompose to produce nitrogen and hydrogen gases. Thus the ammonia should be synthesized at low temperature. But at low temperature, the forward reaction is very slow and takes a long time to reach the equilibrium state. Therefore, a moderate temperature of 450-500°C is used to decrease time of equilibrium and a pressure of 200-300atm is used to prevent the decomposition of ammonia and get the sufficient amount of product (ammonia).

Keep in mind

A reaction which is exothermic in the forward direction will be endothermic in the reverse direction.

The effect of temperature on equilibrium mixture is summarized as, for an endothermic reaction, an increase in temperature shift the equilibrium to the right and increases the amount of product. As a result of this, the value of K_c increases. For an exothermic reaction, an increase in temperature shift the equilibrium to the left and increases the amount of reactant as a result of this the value of K_c decreases.

Table 7.4: The Effect of Temperature Change on Equilibrium Position and K_c

Change to System	Direction of Change	Effect on Equilibrium Position	Effec on K_c
Increase in temperature for an endothermic reaction	Equilibrium shifts to the product side	Changes	Increases
Decrease in temperature for an endothermic reaction	Equilibrium shifts to the reactant side	Changes	Decreases
Increase in temperature for an exothermic reaction	Equilibrium shifts to the reactant side	Changes	Decreases
Decrease in temperature for an exothermic reaction	Equilibrium shifts to the product side	Changes	Increases

7.3 Industrial Application of Le-Chatelier's Principle (Synthesi of Ammonia by Haber's Process)

Ammonia is unusually valuable compound and is used in the manufacture fertilizer such as urea, $(NH_2)_2CO$ and diammonium hydrogen phosph $(NH_4)_2HPO_4$. It is also used in the manufacture of explosives such as TN (trinitrotoluene), as a refrigerant and as a cleaning agent. It can also be used in t manufacture of polymers such as nylon and rayon. Chemists earlier discovered th the ammonia is produced by passing electric spark through a mixture of hydro and nitrogen gases.

$$N_{2(g)} + 3H_{2(g)} \xrightleftharpoons{\text{Electric spark}} 2NH_{3(g)}$$

But unluckily they failed to produce the maximum amount of ammo because the reaction is reversible and its rate of forward reaction is very slow room temperature. This problem was solved in 1912 by a German chemist Fritz Haber (1868-1934) who developed the process for the synthesis of ammonia. The Haber discovered that the adequate yield of ammonia is obtained by the reaction of hydrogen and nitrogen at about 450-500°C at a pressure of about 200-300 atmospheres in the presence of an iron catalyst. This method is known as Haber's process.

Fritz Haber (1868-19

The experimental conditions must be adjusted to get the maximum yield of ammonia in a suitable time and at a reasonable price.

(i) Reactions occur more rapidly when the reactant concentrations are high. According to Le Chatelier's principle, at equilibrium, an increase in the concentration of any one reactant (N_2 or H_2) shifts the equilibrium to the right and increases the amount of product (NH_3).

(ii) According to Le Chatelier's principle, the high temperature increases the rate of reaction, but for exothermic reactions, it shifts equilibrium to the left and equilibrium constant value decreases.

(iii) The total number of moles of reactants is greater than the total number of moles of products; hence, according to Le Chatelier's principle, the greater amount of product is obtained at higher pressures. The pressure is, therefore, increased on the equilibrium mixture to shift the equilibrium to the right.

(iv) The high temperature does not favour the forward reaction; therefore, the increase in the reaction rate is achieved by the use of catalyst. The use of catalyst enhances the speed of reaction. Hence the synthesis of ammonia is carried out at a moderate temperature of about 450-500°C in the presence of an effective catalyst such as Fe_3O_4 mixed with KOH, SiO_2 and Al_2O_3. The catalyst is not effective below 400°C.

(v) The equilibrium mixture has nearly 35% ammonia by volume. The equilibrium mixture is cooled by refrigeration coils below 0°C (B.P. -33°C) until ammonia liquefies. The liquefied ammonia is then removed from the reaction vessel, which reduces the concentration of the product. The continual removal of ammonia shifts the equilibrium to the product side and increase the yield of ammonia. It also prevents the decomposition of ammonia into reactants.

Haber was awarded a Nobel Prize in chemistry in 1918 for the synthesis of ammonia. After nearly five years Carl Bosch (1874-1940), the engineer, solved the engineering problems and developed the industrial process on a large scale. The Haber process is, therefore, sometimes also called the Haber-Bosch process. The Bosch was awarded the Nobel Prize in 1931 for his work on high pressure reactions. All of the ammonia that is produced worldwide is synthesized by Haber-Bosch process. Industrial plants are usually situated near the reservoirs of natural gas. The natural gas is used to get hydrogen gas which is used in the production of ammonia.

$$CH_{4(g)} + H_2O_{(g)} \longrightarrow CO_{(g)} + 3H_{2(g)}$$

The nitrogen gas is obtained from air which is an endless source of nitrogen.

7.4 Solubility Product and Precipitation Reactions

The process of solubility is very important. For example, we flavour foods because of the solubility of table salt and sugar in water. X-rays technicians give patients the suspension of barium sulphate to drink before taking X-ray of the large gastrointestinal tract (intestine and stomach). Barium sulphate is a sparingly soluble salt. It is a good absorber of X-rays and is used to improve the clarity of X-rays. The Ba^{2+} ions present in the $BaSO_4$ are toxic. Since it is very slightly soluble, hence it is taken orally without threat. The concept of solubility and solubility product helps doctors to reduce the prevalence of painful kidney stones, and tooth decay. It enables the doctors to make the ingestion of compounds safe. The concept of these reactions helps engineers prevent the formation of deposits in water processing and distribution systems.

Keep in mind

If the solubility of substance is greater than gram per 100 gram of wa it is said to be soluble. It the solubility of a substance less than 0.1 gram, then the substance is said to insoluble. If the solubili ranges between these tw limits, the substance is sai to be sparingly soluble. Th insoluble substances ar actually very slightl soluble in water.

Some ionic compounds are soluble (NaCl, $NaNO_3$ etc.) and the others a slightly soluble or insoluble in water.

For very slightly soluble salts (AgCl, $PbCl_2$, PbI_2, $BaSO_4$), the dissociation very small and concentration of salt may be considered as constant. For examp when $BaSO_4$, a slightly soluble salt, is placed in water, it dissolves until a satura solution is obtained, and then equilibrium is established between the ions and so $BaSO_4$ in the solution.

$$BaSO_{4(s)} \rightleftharpoons Ba^{2+}_{(aq)} + SO^{2-}_{4(aq)}$$

According to law of mass action,

$$K_c = \frac{[Ba^{2+}][SO_4^{2-}]}{[BaSO_4]}$$

Where,

K_c is equilibrium constant and $[Ba^{2+}]$, $[SO_4^{2-}]$, $[BaSO_4]$ are concentrations Ba^{2+}, SO_4^{2-} and $BaSO_4$ in the solution.

As the salt is slightly soluble, the concentration of undissolved salt, [BaS remains same.

Therefore, $[BaSO_4] = K$

Thus,

$$K_c = \frac{[Ba^{2+}][SO_4^{2-}]}{K}$$

or

$$K_c . K = [Ba^{2+}][SO_4^{2-}]$$

or

$$K_{sp} = [Ba^{2+}][SO_4^{2-}]$$

K_{sp} is the product of two constants K_c and K and is known as solubility product. The product of molar concentrations of positive and negative ions in equilibrium state with solid salt at a given temperature is called solubility product. It is represented by K_{sp}. The value of K_{sp} shows how much salt is soluble in water.

Solubility product is temperature dependent and increases by increase in temperature.

Applications of Solubility Product

Prediction of Precipitation

Many environmental and biological processes involve the precipitation of slightly soluble ionic compounds. The calcium oxalate, a slightly soluble salt, precipitates out in the kidney and forms a kidney stone. A common problem for chemists is to determine the direction in which a reaction proceeds to reach equilibrium. For example, will the precipitation reaction of $BaSO_4$ proceeds in the forward direction or in the reverse direction or the reaction is at equilibrium when we mix the aqueous solutions of $BaCl_2$ and Na_2SO_4? To answer this question we need to calculate ionic product and then compare it with K_{sp}. There are three possible relationships between ionic product and K_{sp} that are as follows:

Keep in mind

Reaction that occurs when cations and anions of two different aqueous solutions combine to form an insoluble solid (precipitate) is called precipitation reaction.

) If $K_{sp} >$ ionic product, solution is unsaturated and precipitation does not occur. n this case more solid dissolves and increasing the ionic concentration until ionic product $= K_{sp}$.

i) If $K_{sp} <$ ionic product, the solution is supersaturated and precipitation occurs, educing ionic concentrations until ionic product $= K_{sp}$.

iii) If K_{sp} = ionic product, solution is saturated and precipitation does not occ because the reaction is at equilibrium.

The solubility and Solubility Product

The solubility and the solubility product of a slightly soluble salt are not the same. Solubility is expressed in g/dm^3. It can also be expressed in mol/dm^3. The solubility product is unit less.

The solubility is temperature dependent. It can be increased for most of the ionic compounds, by increasing temperature. The solubility of ionic compounds is determined by experiments, and by the use of solubility data, the value of solubility product is calculated. The values of solubility can also be calculated from solubility product values. Solutes with very low solubility have very small solubility product values.

Table 7.5: Solubility product constant values for some ionic compounds at 25°C

Name	Formula	K_{sp}
Aluminum hydroxide	$Al(OH)_3$	2.0×10^{-32}
Barium sulphate	$BaSO_4$	1.5×10^{-9}
Cadmium sulphide	CdS	8.0×10^{-27}
Calcium carbonate	$CaCO_3$	8.7×10^{-9}
Calcium fluoride	CaF_2	4.0×10^{-11}
Calcium hydroxide	$Ca(OH)_2$	1.3×10^{-6}
Calcium phosphate	$Ca_3(PO_4)_2$	1.3×10^{-32}
Calcium sulphate	$CaSO_4$	6.1×10^{-5}
Iron (II) sulphide	FeS	6.0×10^{-18}
Lead (II) chromate	$PbCrO_4$	2.0×10^{-16}
Silver bromide	$AgBr$	5.0×10^{-13}
Silver chloride	$AgCl$	1.6×10^{-10}
Zinc sulphide	ZnS	3.0×10^{-23}

Example 7.4

The solubility product constant value (K_{sp}) for ZnS is 3.0×10^{-23}. Calculate its solubility at 25°C.

Solution:

The equation for the dissociation of ZnS is:

$$ZnS_{(s)} \rightleftharpoons Zn^{2+}_{(aq)} + S^{2-}_{(aq)}$$

Initial concentrations (M): 0 0

Equilibrium concentrations (M): s s

The expression for the solubility product constant is:

$$K_{sp} = [Zn^{2+}][S^{2-}]$$
$$3.0\times10^{-23} = (s)(s)$$
$$3.0\times10^{-23} = s^2$$

By taking under root on both sides,

$$s = \sqrt{3.0\times10^{-23}}$$
$$s = 5.48\times10^{-12}M$$

Practice Exercise 4:

Calculate the solubility of $CaCO_3$ at room temperature. The solubility product value of $CaCO_3$ is 8.7×10^{-9}.

Example 7.5

Calculate the solubility product constant, K_{sp} value for $BaSO_4$. The solubility of $BaSO_4$ at room temperature is $1.03\times10^{-5}M$.

Solution:

Value of K_{sp} for $BaSO_4$ = ?

Solubility of $BaSO_4$ = $1.03\times10^{-5}M$

The solubility equation for $BaSO_4$ is:

$$BaSO_{4(s)} \rightleftarrows Ba^{2+}_{(aq)} + SO^{2-}_{4(aq)}$$

Initial concentrations (M): 0 0

Equilibrium concentrations (M): 1.03×10^{-5} 1.03×10^{-5}

The solubility product expression for solubility product constant is:

$$K_{sp} = \left[Ba^{2+}\right]\left[SO_4^{2-}\right]$$
$$K_{sp} = (1.03\times10^{-5})(1.03\times10^{-5})$$
$$K_{sp} = 1.06\times10^{-10}$$

Practice Exercise 5:

The solubility of PbF_2 is $2.25\times10^{-3}mol/dm^{-3}$ at room temperature. What is the value of solubility product constant for PbF_2?

7.5 Common Ion Effect

The process in which the degree of ionization of a weak electrolyte is decreased by the addition of a strong electrolyte having a common ion is called common ion effect.

This process is used to decrease the solubility of slightly soluble electrolyte (salt) by the addition of strong electrolyte (more soluble electrolyte) having a common ion. For example:

Consider the ionization of less soluble salt:

$$CaCO_{3(s)} \rightleftharpoons Ca^{2+}_{(aq)} + CO^{2-}_{3\,(aq)}$$

According to law of mass action,

$$K_c = \frac{[Ca^{2+}][CO_3^{2-}]}{[CaCO_3]}$$

Keep in mind

Electrolyte is a compound that conducts electricity either in molten state or in an aqueous solution. Those compounds such as NaCl, KOH, which ionize almost completely in the solution are called strong electrolytes while those compounds such as $CaCO_3$, CH_3COOH, which are ionized partially in the dilute solutions are called weak electrolytes.

When $CaCl_2$, a more soluble salt, is added to the solution of $CaCO_3$, Then it will increase the concentration of Ca^{2+} ion (common ion) and it will shift the equilibrium from right to left, hence $CaCO_3$ precipitates out from the solution.

$$CaCl_{2(s)} \rightleftharpoons Ca^{2+}_{(aq)} + 2Cl^-_{(aq)}$$

$$CaCO_{3(s)} \longleftarrow Ca^{2+}_{(aq)} + CO^{2-}_{3(aq)}$$

This is according to Le-Chatelier's Principle.

Consider the ionization of moderately soluble $KClO_4$ in water,

$$KClO_{4(s)} \rightleftharpoons K^+_{(aq)} + ClO^-_{4(aq)}$$

According to law of mass action,

$$K_c = \frac{[K^+][ClO_4^-]}{[KClO_4]}$$

When more soluble salt of KCl is added to the saturated solution of less soluble $KClO_4$, then as a result of this the concentration of K^+ ion (common ion) increases, it will shift equilibrium from right to left, hence $KClO_4$ precipitates out from the solution.

$$KCl_{(s)} \rightleftharpoons K^+_{(aq)} + Cl^-_{(aq)}$$

$$KClO_{4(s)} \longleftarrow K^+_{(aq)} + ClO^-_{4(aq)}$$

This is according to Le-Chatelier's Principle and is known as common ion effect.

Summary of Facts and Concepts

- Dynamic chemical equilibrium occurs when the rates of forward and reverse reactions are equal and the reactants and products concentrations do not change with time.
- Chemical equilibrium in which all the reactants and products are in the same phase is called homogeneous chemical equilibrium whereas the chemical equilibrium in which all the reactants and products are not in the same phase is called heterogeneous chemical equilibrium.
- According to Law of Mass Action, the rate of forward reaction is directly proportional to the product of active masses of the reactants.
- The ratio of the molar concentrations of the products divided by the molar concentrations of reactants, each raised to powers equal to their coefficients is called equilibrium constant. The equilibrium constants are shown as K_c, K_p, K_n, and K_x. The equilibrium constants of reactions are used to determine the direction and extent of the chemical reaction.
- The reaction quotient, Q_c is defined in the same way as equilibrium constant except that the concentrations in the reaction quotient expression are not necessarily equilibrium concentrations.
- If $Q_c < K_c$, then reaction will proceed in forward direction to attain the equilibrium. If $Q_c > K_c$, then reaction will proceed in reverse direction to attain the equilibrium. If $Q_c = K_c$, then the system is at equilibrium.
- If K_c is very large ($K_c > 10^3$), the equilibrium mixture is mostly products and if K_c is very small ($K_c < 10^{-3}$), the equilibrium mixture is mostly reactants. If K_c is in the range of 10^{-3} to 10^{-3}, then both the forward and reverse reactions take place almost to an equal extent.
- According to Le Chatelier's principle, when a change in concentration, pressure, and temperature is applied to a system at equilibrium, the equilibrium is shifted in the direction that counteracts (minimizes) the effect of the change.
- The value of K_c is temperature dependent. Its value increases for an endothermic reaction and decreases for an exothermic reaction when the temperature increases.
- A catalyst does not affect the equilibrium constant or the equilibrium concentrations. However it increases the rate of chemical reaction by decreasing activation energy at which chemical equilibrium is reached.

- The product of molar concentrations of positive and negative ions equilibrium state with solid salt at a given temperature is called solubi product constant. It reflects the solubility of a compound. The greater th solubility products value of a compound, the greater the solubility of compound.
- The process of common ion effect is used for the purification of so compounds like NaCl, in the preparation of buffers and in qualitative analy

Questions and Problems

Q.1. Four answers are given for each question. Select the correct one:

i) The reactions that occur only in one direction are known as:

(a) Reversible reaction (b) irreversible reaction

(c) spontaneous reaction (d) non-spontaneous reaction

ii) The reaction will proceed in the reverse direction when

(a) $Q_c < K_c$ (b) $Q_c > K_c$

(c) $Q_c = K_c$ (d) $Q_c = (K_c)^3$

iii) Which of the following change will favour the formation o adequate amount of ammonia at equilibrium in the reaction gi below:

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

(a) By decreasing pressure (b) by increasing pressure

(c) by adding ammonia (d) by removing nitrogen

iv) A dynamic equilibrium is disturbed by

(a) Concentration change (b) pressure change

(c) temperature change (d) all of these

v) What is the unit of K_c for the reaction:

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$

(a) $mol\,dm^{-3}$ (b) $mol^{-1}dm^{-3}$

(c) $mol^{-1}dm^{+3}$ (d) $mol^{2}dm^{-6}$

vi) When the total number of moles of reactants and products are e then the equilibrium state is **NOT** disturbed by:

(a) Concentration change (b) pressure change

(c) temperature change (d) catalyst

vii) Exothermic reactions are favoured in the forward direction by

(a) Decrease in temperature (b) increase in temperature
(c) adding a catalyst (d) removal of reactant

viii) When HCl is added to the aqueous solution of NaCl, the ionization of NaCl:

(a) Increases (b) decreases
(c) remains same (d) first decreases and then increases

ix) Precipitation occurs when

(a) $K_{sp} <$ ionic product (b) $K_{sp} >$ ionic product
(c) $K_{sp} =$ ionic product (d) $\sqrt{K_{sp}} <$ ionic product

x) The forward reaction almost near completion if the value of K_c is:

(a) Very small (b) very large
(c) unity (d) zero

Q.2. Fill in the blanks with suitable words given in the brackets:

i) The reactions in which products are reconverted into reactants are called ________. (reversible/irreversible)

ii) All chemical equilibria are ________. (static/dynamic)

iii) Law of mass action was given by ________ in 1864. (Bosch / Guldberg)

iv) For the reaction, $CH_{4(g)} + H_2O_{(g)} \rightleftharpoons CO_{(g)} + 3H_{2(g)}$, the increase in pressure favours the ________ of products. (decomposition / formation)

v) If K_{sp} is ________ to / than ionic product, the solution is saturated. (greater / equal)

vi) The removal of the amount of any one reactant from the container at equilibrium will shift the system ________. (to the left/to the right)

vii) Solutes with very high solubility have very ________ solubility product values. (small/high)

viii) For endothermic reactions, the equilibrium constant value ________ by increase in temperature. (increases/decreases)

ix) Catalyst ________ the activation energy of chemical reaction. (decreases/increases)

x) Haber was awarded a Nobel Prize in chemistry in ________. (1931/1918)

Q.3. Label the following statement as True or False:

i) The concentrations of products and reactants remain constant equilibrium.

ii) The same equilibrium constant value is obtained whether reaction is started from the reactants side or from the products side.

iii) The concentrations of reactants are equal to the concentrations products at equilibrium.

iv) The reaction is at equilibrium when Q_c is equal to K_c ($Q_c = K_c$).

v) When the number of moles of reactants and products are equal in balanced chemical equation, then $K_c = K_p = K_x = K_n$.

vi) A catalyst does not change the equilibrium constant but it changes the equilibrium position of the reaction.

vii) The NaCl can be purified by passing HCl gas through its saturat solution by common ion effect.

viii) Molar solubility is the number of moles of solute dissolved in one liter of solvent.

ix) As the reaction proceeds in the forward direction, the concentratio of product goes on decreasing and that of reactant goes increasing.

x) Haber solved the engineering problems for the synthesis of ammon

Q.4: Write the equilibrium constant expressions for K_c for each of following processes:

i) $CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2(g)} + H_{2(g)}$

ii) $2\,CO_{(g)} + O_{2(g)} \rightleftharpoons 2\,CO_{2(g)}$

iii) $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$

iv) $2O_{3(g)} \rightleftharpoons 3O_{2(g)}$

v) $CH_3COOH_{(aq)} \rightleftharpoons CH_3COO^-_{(aq)} + H^+_{(aq)}$

Q.5: What is the value of K_p at 1050°C if K_c value is 2.30×10^{22} for following reaction?

$2\,CO_{(g)} + O_{2(g)} \rightleftharpoons 2\,CO_{2(g)}$

Q.6: Write the balanced chemical equation corresponding to the equilib constant expressions given below:

a) $K_c = \dfrac{[N_2O_5][O_2]}{[N_2O_4][O_3]}$

b) $K_c = \dfrac{[NH_4Cl]}{[NH_3][HCl]}$

c) $K_c = \dfrac{[CH_4]^2[Cl_2]^3}{[CHCl_3]^2[H_2]^3}$

Q.7: How will you predict the direction and extent of a chemical reaction with the help of a chemical equilibrium expression?

Q.8: Define reaction quotient. What is the difference between equilibrium constant and reaction quotient?

Q.9: What does it mean when (a) $Q_c > K_c$ (b) $Q_c < K_c$ (c) $Q_c = K_c$?

Q.10: What is dynamic chemical equilibrium? Explain why the concentrations of reactants and products are not necessarily the same at equilibrium?

Q.11: What are homogeneous and heterogeneous equilibria? Give two examples for each.

Q.12: Explain, what is the law of mass action? Derive the equilibrium constant expression for a general reversible reaction.

Q.13: What is the characteristics of equilibrium constant?

Q.14: How will you relate the equilibrium expression in terms of concentration, partial pressure, number of moles and mole fraction?

Q.15: Explain Le Chatelier's principle. How this principle help chemists to maximize the yield of products. Explain industrial applications of Le-Chatelier's Principle using Haber's Process as an example.

Q.16: Lime, $CaO_{(s)}$ is prepared by heating lime stone, $CaCO_{3(s)}$ to decompose it.

a) Write the balanced chemical equation for the reaction.

b) Predict the sign of enthalpy change for the reaction.

c) Is the reaction favoured by increase in temperature or decrease in temperature.

Q.17: What is the effect of the following changes on the value of equilibrium constant for the exothermic gas phase reaction (a) removal of product (b) addition of product (c) increase in the pressure (d) increase in the volume (e) decrease in the temperature (f) addition of a catalyst?

Q.18: What is the effect of the following changes at equilibrium if we:

a) increase the concentration of reactants in a reaction mixture

b) increase the concentration of products in a reaction mixture

c) decrease the pressure of a reaction mixture if the product side has greater number of moles of gases than reactant side

(d) increase the temperature of an endothermic reaction mixture?

Q.19: What is the effect of catalyst on:

(a) the rate of chemical reaction
(b) the position of equilibrium in a chemical reaction
(c) the value of equilibrium constant?

Q.20: What is the significance of catalyst in chemistry?

Q.21: Describe the effect of increasing pressure on each of the following reactio systems at equilibrium.

i) $2O_{3(g)} \rightleftharpoons 3O_{2(g)}$

ii) $H_{2(g)} + Cl_{2(g)} \rightleftharpoons 2\,HCl_{(g)}$

iii) $PCl_{3(g)} + Cl_{2(g)} \rightleftharpoons PCl_{5(g)}$

Q.22: Define and explain common ion effect giving suitable examples.

Q.23: What is a solubility product constant? Determine the solubility produ expression for slightly soluble AgBr, $Ca(OH)_2$ and $PbCrO_4$.

Q.24: Answer the following questions:

a) There is only one value of the equilibrium constant for a particu system at a particular temperature, how?

b) Why the value of equilibrium constant does not depend on the init concentrations of reactants and products mixed together?

c) Why the equilibrium vapour pressure of a liquid increases w increasing temperature?

d) Can the equilibrium constant value ever be zero or negativ Explain.

e) How are rates of forward and reverse reactions related in a system chemical equilibrium?

f) The solubility of $KClO_4$ is decreased by adding KCl to its saturat solution, how?

Q.25: The equilibrium concentrations of hydrogen, iodine, and hydrogen iod are 0.530M, 0.033M, and 0.934M respectively at 450°C. What is the v of K_c for the following reaction?

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

Q.26: Calculate the concentration of PCl_5 at 250°C. The equili concentration for both PCl_3 and Cl_2 gases are 0.005M. The value of K the reaction is 1.2×10^{-2}.

$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$

Q.27: $Ca(OH)_2$ is a slightly soluble base and has a K_{sp} value equal to 1.3×10^{-6}. Calculate its solubility at room temperature.

Q.28: AgCl is a sparingly soluble salt and has a K_{sp} value equal to 1.7×10^{-10}. Calculate its solubility at 25°C.

Q.29: The solubility of PbI_2 at 25°C is 0.55 g/dm^3. What is the solubility product constant value at this temperature?

Q.30: The solubility of CaF_2 at 25°C is 8.60 g/100g of water. What is the solubility product constant value at this temperature?

Q.31: Consider the reaction

$$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)} \qquad \Delta H = +92.5 kJ/mol$$

What is the effect on the concentrations of reactants and products if we:

a) Increase the pressure
b) increase the temperature
c) add a catalyst
d) add a neon gas.

32: Consider the gas phase reaction:

$$2CO_{(g)} + O_{2(g)} \rightleftharpoons 2CO_{2(g)} \qquad \Delta H = -283.0 kJ/mol$$

i) What is the effect of the pressure change on this reaction?
ii) What is the effect of the temperature change on this reaction?
iii) What is the effect of the concentration change on this reaction?