7

CHEMICAL EQUILIBRIUM

This is a 8 days unit

After completing this lesson, you will be able to:

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

Reading

INTRODUCTION

When we presented stoichiometery in Chapter – 1, we described that reactions proceed virtually to completion when the limiting reactant is completely consumed. This is true for reactions that virtually go to completion i.e., reactants are completely consumed and converted into the products. Such reactions are called irreversible reactions. Such reactions stop when the limiting reactant is consumed. However in many reactions the net formation of products comes to an end before all the limiting reactant has been consumed. Such reactions actually proceed in both the directions i.e. forward and backward and are called reversible reactions. These reactions reach at a stage called chemical equilibrium. At this stage the concentration of reactants and products become constant. But the reaction continues to proceed in both the directions without any change in concentration of reactants and products under existing conditions. Such reactions never go to completion and are called reversible reactions.

In this chapter we will discuss how and why a chemical reaction comes to equilibrium. We will discuss the principles and applications of chemical equilibrium.

7.1 REVERSIBLE REACTIONS AND DYNAMIC EQUILIBRIUM

A reversible reaction is one in which the products once formed can react to form reactants. Such reactions do not go to completion even if stoichiometric amounts of the reactants are taken. These reactions take place both in the forward and backward directions under the existing conditions. Some examples of reversible reactions are given below: which reaction is forward reaction?

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

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

$$2NO_{(g)} + Cl_{2(g)} \rightleftharpoons 2NOCl_{(g)}$$

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

The double arrow $\rightleftharpoons$ tells that the reaction is reversible.

Consider the reaction between steam and carbon monoxide under appropriate conditions. On mixing macroscopic changes are observed (e.g, changes in concentration).

Suppose that the reaction is started with same number of moles of both the reactants. When steam and carbon monoxide are mixed, a maximum number of collisions per second between them will occur. Therefore the forward reaction has its maximum speed at the beginning. This leads to a decrease in the concentration of the reactants.

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

As H_2O and CO are gradually used up, the forward reaction gradually slows down. As the molecules of H_2 and CO_2 accumulate reverse reaction also starts. With the increase in concentration of H_2 and CO_2 more and more collisions per second between these molecules occur. Therefore reverse reaction proceeds with increasing speed. This means that forward reaction starts with maximum speed and gradually slows down, whereas the reverse reaction starts at zero speed and gradually increases its speed.

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

Eventually a time comes when both reactions proceed at the same speed. The reaction at this stage is said to be in chemical equilibrium. The concentration of reactants and products become constant.

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

Unless the system is somehow disturbed no further changes in concentration will occur. "The state of a reversible reaction at which composition of the reaction mixture does not change is called the state of chemical equilibrium. The

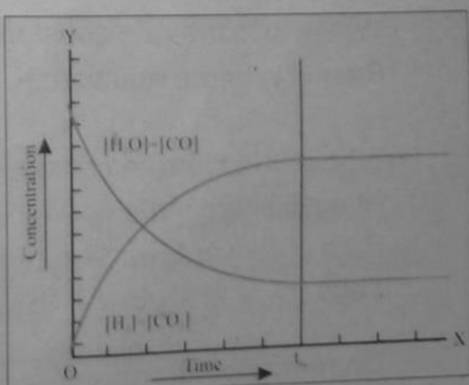

Figure.7.1: The plots of concentration of reactants and products versus time

The student should be guided to identity forward and reverse reactions and explain state of equilibrium.

plots of the concentrations of reactants and products versus time are shown in Fig.7.1 what these plots show? Why have they become parallel?

Since the concentration of reactants and products become constant it may appear that the reaction has stopped. But this is not true. On the microscopic level there is excited activity. Individual molecules of reactants continue to combine. Individual molecules of products also continue to combine. But the rate of one process is exactly balanced by the rate of the other. Therefore this is a dynamic equilibrium. The system is dynamic because individual molecules react continuously, but the rate of the forward and reverse reactions are equal. It is at equilibrium because no net change occurs.

7.1.1 The Equilibrium Constant

Two chemists C.M Guldberg and P. Wage in 1864 proposed the law of mass action as a general description of the equilibrium state. This Law you have learnt in a grade IX-X.

It states that **"the rate at which a substance reacts is proportional to its active mass and the rate of a chemical reaction is proportional to the product of the active masses of the reacting substances"**. It can also be defined as "the rate of chemical reaction is proportional to the product of molar concentration of each reacting substance raised to a power equal to its stoichiometric coefficient in the balanced chemical equation. The term active mass means, the concentration of the reactants and products in moles dm^{-3} for a dilute solution.

Consider the following general reversible reaction.

$$aA_{(g)} + bB_{(g)} \rightleftharpoons cC_{(g)} + dD_{(g)}$$

Where A, B C and D represent chemical species and a, b, c and d are their coefficients in the balanced equation.

According to the law of mass action.

Rate of forward reaction, $R_f \ \alpha\ [A]^a\,[B]^b$

$$= k_f\,[A]^a\,[B]^b$$

Where k_f is the rate constant for the forward reaction. .... (1)

Rate of reverse reaction, $R_r \ \alpha\ [C]^c\,[D]^d$

$$= k_r\,C]^c\,[D]^d$$

Where k_r is the rate constant for the reverse reaction. .... (2)

At equilibrium state

Rate of forward reaction = Rate of reverse reaction

Thus

$$k_f\,[A]^a\,[B]^b = k_r\,C]^c\,[D]^d$$

On rearranging

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

$$K_c = \frac{C]^c\,[D]^d}{[A]^a\,[B]^b} \qquad .... (3)$$

Where $K_c = \frac{k_f}{k_r}$ and is known as equilibrium constant, and the equation (3) is known as equilibrium constant expression. The square brackets indicate the concentration of the chemical species at equilibrium. Concentration of which species are taken in the numerator in K_c expersion?

Thus the equilibrium constant expression for any reaction can be written from its balanced equation. Concentration of products are taken in the numerator and concentration of reactants in the denominator.

Conditions for Equilibrium

Important features of equilibrium constant expression are as follows:

- K_c applies only at equilibrium. The subscript c indicates the concentration of reactants and products in moles per dm^3 at equilibrium state.
- K_c is independent of initial concentration of reactants and products but depends upon temperature. At a given temperature, it has only one value. Whether we start reaction with pure reactants or pure products or any composition in between, the value of K_c remains unchanged.
- K_c is related to the coefficients of the balance chemical equation. The concentration of the products are placed in the numerator and those of reactants in the denominator. Each concentration is raised to a power equal to its coefficient in the balance chemical chemical equation.
- The magnitude of K_c indicates the position of equilibrium. When K_c is less then 1, the denominator is greater in magnitude than the numerator. This means the concentration of the reactants are greater than those of products when the equilibrium is established. Whereas, when K_c is greater than 1, the numerator is greater in magnitude than the denominator. This means the concentration of the products are greater than those of the reactants at equilibrium.

It is important to recognize the difference between the equilibrium constant expression and rate law of a reaction. You will learn about rate law expression in chapter on chemical kinetics. In both these expressions, concentration terms are raised to powers. The rate law describes how the rate of a reaction changes with concentration. It cannot be written from the balanced chemical equation. Whereas the equilibrium expression describes the concentration of reactants and products when the net rate of reaction is zero. It can be written from a balance chemical equation.

7.1.2 Examples of Equilibrium Constant Expression

Problem solving strategy

1. Write products in the numerator and reactants in the denominator in square brackets.

2. Raise each concentration to the power that correspond to the co-efficient of each species in the balanced chemical equation.

Example 7.1

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

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

Example 7.2

$$CO_{(g)} + \frac{1}{2}O_{2(g)} \rightleftharpoons CO_{2(g)}$$

$$K_c = \frac{[CO_2]}{[CO][O_2]^{\frac{1}{2}}}$$

Self Check Exercise 7.1

The following equations represent various industrial reactions at equilibrium. Write K_c

1. Expression for each of these reactions. Do not forget to balance the equations:
   (i) $SO_{3\,(g)} + O_{2(g)} \rightleftharpoons SO_{3(g)}$
   (ii) $NH_{3(g)} + O_{2(g)} \rightleftharpoons NO_{(g)} + H_2O_{(g)}$
   (iii) $CH_{4(g)} + H_2O_{(g)} \rightleftharpoons CO_{(g)} + H_{2(g)}$
2. Give the balanced equations that correspond to following equilibrium expressions.

$$K_c = \frac{[CH_3OH]}{[CO][H_2]^2}$$

$$K_c = \frac{[N_2][H_2O]^2}{[NO]^2[H_2]^2}$$

7.1.3 Units of Equilibrium Constant

Problem solving strategy

1. Write equilibrium constant expression.
2. Write mol dm^{-3} as units of concentration of each species within square brackets.
3. Simplify the expression.

Equilibrium constant may or may not have units. Equilibrium constant has no units if the number of moles of the reactants are equal to the number of moles of the products. For instance Kc for the following reaction has no units.

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

$$K_c = \frac{[H_2[CO_2]}{[H_2O[CO]}$$

$$K_c = \frac{(mol\,dm^{-3})(mole\,dm^{-3})}{(mole\,dm^{-3})(mole\,dm^{-3})} = \text{No units}$$

On the other hand if the number of moles of products and reactants are not equal, K_c has units. For example

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

$$k_c = \frac{[NO_2]^2}{[N_2O_4]}$$

$$k_c = \text{mole dm}^{-3}$$

In this way we can determine the units for k_c. However units of equilibrium constant is not usually written.

Self Check Exercise 7.2

Determine the units for Kc for the following reactions:

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

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

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

The value of K_C at a given temperature can be calculated if we know the equilibrium concentration of the reaction components.

Example 7.3

The following equilibrium concentrations were observed for the reaction at 500°C.

$$A_{(g)} + 3B_{(g)} \rightleftharpoons 2AB_{(g)}$$

[A] = 0.399M, [B] = 1.197M, [AB] = 0.203M

Calculate K_C

Solution

$$K_c = \frac{[AB]^2}{[A][B]^3}$$

$$K_c = \frac{(0.203 \text{ mol dm}^{-3})^2}{(0.399\text{mole dm}^{-3})(1.19 \text{ mol dm}^{-3})^3}$$

$$= 6 \times 10^{-2} \text{ dm}^6 \text{ mole}^{-2}$$

7.1.4 Equilibrium Expressions Involving Partial Pressure, Number of Moles and Mole Fraction.

Consider the general gaseous reversible reaction.

$$aA_{(g)} + bB_{(g)} \rightleftharpoons cC_{(g)} + dD_{(g)}$$

The student should be guided to use information to solve different data.

For gases the expression is often expressed in terms of partial pressure of each gas. According to Henry's law "At constant temperature, the partial pressure of a gas is directly proportional to its molar concentration.

Equilibrium constant K_p in term of partial pressures is given by:

$$K_P = \frac{P_C^c \times P_D^d}{P_A^a \times P_B^b}$$

Where P_A, P_B, P_C and P_D are partial pressures of gas A, B, C and D respectively K_p is related with K_c by the following equation.

$$K_P = K_c(RT)^{\Delta n}$$ $\Delta n = n_P - n_R$

Where Δn is the difference between the total number of moles of the products and the reactants.

When equilibrium concentrations of reactants and products are expressed in terms of their moles, the equilibrium constant is represented by K_n and is given by the following equation.

$$K_n = \frac{n_C^c \times n_D^d}{n_A^a \times n_B^b}$$

Where n_A. n_B, n_C and n_D are the moles of A, B, C and D respectively at the equilibrium state. K_P is also related with K_n.

$$K_P = K_n\left(\frac{P}{N}\right)^{\Delta n}$$

Where P is the pressure of reaction mixture at equilibrium and N is the total number of moles of reactants and products as shown by the balanced equation.

When the equilibrium concentration of the reactants and products are expressed by their mole fractions, the equilibrium constant is represented by K_x and is given by the following equations.

$$K_x = \frac{x_C^c \times x_D^d}{x_A^a \times x_B^b}$$ $x_c = \frac{n_c}{n_t}$

Where X_A, X_B, X_C and X_D are mole fractions of A, B, C and D respectively. K_P is related with K_x by the following expression.

$$K_P = K_x(P)^{\Delta n}$$

Where P is the pressure of the equilibrium mixture.

Example 7.4

Following reaction was studied at 25°C. Calculate its K_P and K_C.

$$2NO_{(g)} + Cl_{2(g)} \rightleftharpoons 2NOCl_{(g)}$$

The partial pressures at equilibrium were found to be

$P_{NOCl} = 1.2$ atm

$P_{NO} = 5.0 \times 10^{-2}$ atm

$P_{Cl_2} = 3.0 \times 10^{-1}$ atm

Problem Solving Strategy

1. Write K_P expression
2. Substitute the partial pressures of each species.
3. Simplify to get K_P
4. Calculate Δn
5. Write expression relating K_P and K_C
6. Substitute known values in it and find K_C

$$K_P \frac{(P_{NOCl})^2}{(P_{NO})^2 (P_{Cl_2})}$$

$$K_P = \frac{(1.2)^2}{(5.0\times10^{-2})^2 (3.0\times10^{-1})}$$

$$K_P = 1.9\times10^3$$

Now

$$K_P = K_C (RT)^{\Delta n}$$

$\Delta n = 2 - (2 + 1) = -1$

$R = 0.0821 dm^3\ atm K^{-1}\ mole^{-1}$

$T = 25^oC + 273 = 298K$

$K_P = K_C (RT)^{\Delta n}$

$1.9\times10^3 = K_C(0.0821\times298)^{-1}$

$1.9\times10^3 = \times \dfrac{K_C}{(0.0821\times298)}$

$K_C = 1.9\times10^3 \times 0.0821\times298$

$K_C = 4.65\times10^4$

Self Check Exercise 7.3

The contact process prepares purest sulphuric acid commercially. Following reaction takes place in the contact chamber in the presence of V_2O_5.

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

Calculate K_P if the following concentrations are found at equilibrium.

$[SO_2] = 0.59M$, $[O_2] = 0.05M$ & $[SO_3] = 0.259M$ **(Ans:** 0.1576)

7.1.5 Types of Equilibrium

With respect to the physical states of reactants and products, there are two types of Chemical Equilibrium.

i. **Homogeneous Equilibria**

An equilibrium system in which all of the reactants and products are in the same phase. For example

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

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

$$2NO_{(g)} + Cl_{2(g)} \rightleftharpoons 2NOCl_{(g)}$$

$$CH_3COOH(\ell) + C_2H_5OH_{(\ell)} \rightleftharpoons CH_3COOC_2H_5(\ell) + H_2O(\ell)$$

ii. Heterogeneous Equilibria

Equilibria which involve more than one phases are called Heterogeneous equilibria. For example

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

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

$$3Fe_{(s)} + 4H_2O_{(g)} \rightleftharpoons Fe_3O_{4(s)} 4H_{2(g)}$$

If pure solids or pure liquids are involved in an equilibrium system, their concentrations are not included in the equilibrium constant expression. This is because the change in concentration of any pure solid or liquid has no effect on the equilibrium system.

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

$$K_C = [H_2]^2[O_2]$$

and $K_P = P_{H_2}^2 \times P_{O_2}$

ii) $3Fe_{(s)} + 4H_2O_{(g)} \rightleftharpoons Fe_3O_{4(s)} + 4H_{2(g)}$

$$K_C = \frac{[H_2]^4}{[H_2O]^4}$$

and $K_P = \dfrac{P^4_{H_2}}{P^4_{H_2O}}$

Self Check Exercise 7.4

Write K_C and K_P expressions for each of the following reactions.

(i) $FeO_{(s)} + CO_{(g)} \rightleftharpoons Fe_{(s)} + CO_{2(g)}$

(ii) $P_{4(s)} + 5O_{2(g)} \rightleftharpoons P_4O_{10(s)}$

(iii) $CH_{4(g)} + 4Cl_{2(g)} \rightleftharpoons CCl_{4(l)} + 4HCl_{(g)}$

7.1.6 Ways to Recognize Equilibrium and Determination of Equilibrium Constant

Equilibrium constant expression can be determined by physical as well as chemical methods.

a) Physical Method (spectrometric method)

This method is based on the measurement of a physical property of the reaction mixture. This physical property is measured during the course of reaction without removing the sample

The student should be guided to operate the following information in practical uses.

from the reaction mixture. We will discuss spectrometric method. This method is applicable if a reactant or product absorbs ultraviolet, visible or infrared radiation. The concentration can be determined by measuring the amount of radiation absorbed. Equilibrium constant for $N_2O_4 - NO_2$ system can be determined by the spectrophotometer.

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

N_2O_4 is a colourless gas whereas NO_2 is reddish brown gas. The progress of the reaction can be studied by measuring the absorbance at regular Intervals. Absorbance is proportional to the concentration of NO_2. At equilibrium spectrometer will show constant value of absorbance. Suppose reaction is started with "a" moles of N_2O_4 at 100°C. and x moles of it, is converted to NO_2. By applying stoichiometery, the amount of NO_2 present in equilibrium will be 2x, which is measured by the spectrophotometer. Suppose the volume of the reaction mixture is V dm^{-3}, then we can write.

	$N_2O_{4(g)} \rightleftharpoons$	$2NO_{2(g)}$
Initial Conc. (in moles)	a	zero
Eq. Conc. (in moles)	$a - x$	$2x$
Eq. Conc. (moles/dm^3)	$\frac{a-x}{V}$	$\frac{2x}{V}$

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

$$K_c = \frac{\left(\frac{2x}{V}\right)^2}{\left(\frac{(a-x)}{V}\right)}$$

$$K_c = \frac{4X^2}{(a-x)V}$$

Example 7.5

At 100°C, 0.1mole of N_2O_4 is heated in a one dm³ flask. At equilibrium concentration of NO_2 was found to be 0.12 moles. Calculate K_c for the reaction.

Problem Solving Strategy

1. Write equilibrium reaction.
2. Write initial conc. of each species below equilibrium reaction.
3. Workout equilibrium conc. of each species.
4. Use equilibrium conc. of each species in K_c expression and find K_c

Solution

$[NO_2] = 0.12$ mole

Since one mole of N_2O_4 gives 2 moles of NO_2

$2X = 0.12$

$X = \frac{0.12}{2}$

$X = 0.06$

$[N_2O_4] = 0.1 - 0.06$

$= 0.04$ mole

	$N_2O_{4(g)} \rightleftharpoons$	$2NO_{2(g)}$
Initial Conc. (in moles)	0.1	zero
Eq. Conc. (in moles)	$0.1 - 2x$	0.12
Eq. Conc. (mole/dm^3)	$\frac{0.04}{1}$	$\frac{0.12}{1}$
	0.04	0.12

$K_C = \frac{[NO_2]^2}{[N_2O_4]}$

$K_C = \frac{(0.12)^2}{(0.04)}$

$K_C = 0.36$

Example7.6

Consider the following reaction

$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$ $K_C = 0.1$ at 2000°C

If original concentrations of N_2 and O_2 were 0.1M each. Calculate the concentrations of NO at equilibrium.

Solution

	$N_{2(g)}$ +	$O_{2(g)} \rightleftharpoons$	$2NO_{(g)}$
Initial Conc.	0.1M	0.1M	0
Eq. Conc. (mole/dm^3)	(0.1 - X)	(0.1 – X)	2X

$K_c = \frac{[NO]^2}{[N_2][O_2]}$

$0.1 = \frac{(2X)^2}{(0.1-X)(0.1-X)}$

Taking square root of both the sides

$0.32 = \frac{2X}{0.1-X}$

$X = 0.014M$

$[N_2] = [O_2] = 0.1 - X$

$= 0.1 - 0.014$

$= 0.086M$ each

$[NO] = 2X$

$= 2 \times 0.014$

$= 0.028$ M

Self Check Exercise 7.5

For the reaction

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

$K_c = 0.60$ at $500^\circ C$. If a mixture of 0.30M of each H_2 and CO_2 is heated at 500°C, calculate the concentration of CO at equilibrium.

b) Chemical Method

In this method, the amount of a reactant or product is determined by a suitable chemical reaction. Consider the reaction between acetic acid and ethanol to form ethyl acetate and water. It is an example of reversible reaction in the solution state.

$$CH_3COOH(\ell) + C_2H_5OH(\ell) \rightleftharpoons CH_3COOC_2H_5(\ell) + H_2O(\ell)$$

Suppose this reaction is started by taking 'a' moles of acetic acid and 'b' moles of ethanol in a stoppered flask at room temperature. A small amount of mineral acid is added in the mixture to catalyse the reaction.

The progress of the reaction can be studied by determining the concentration of acetic acid after regular intervals. For this purpose small portion of mixture is withdrawn. The concentration of acetic acid is determined by titrating it against a standard solution of NaOH using phenolphthalein as indicator. Concentration of acetic acid will decrease until equilibrium is attained. Suppose x moles of acetic acid has reacted with ethanol. Since one mole of acetic acid reacts with one mole of ethanol, the amount of ethanol reacted with acetic acid will also be x moles. As one mole of each of the product is formed. At equilibrium x moles of ethyl acetate and x moles of water are produced. This data is shown in table 7.1

Table 7.1. Data for the equilibrium reaction between acetic acid and ethyl alcohol.

Reaction	$CH_3COOH(\ell)$ +	$C_2H_5OH(\ell) \rightleftharpoons$	$CH_3COOC_2H_5(\ell)$ +	$H_2O(\ell)$
Initial Conc (in moles)	a	b	Zero	Zero
Eq. Conc (in moles)	a - x	b - x	x	x

$$K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$$

$$K_c = \frac{(x)\,(x)}{(a-x)(b-x)}$$

$$K_c = \frac{x^2}{(a-x)(b-x)}$$

Example7.7

When 60g of acetic acid and 46g of ethyl alcohol are heate to give and equilibrium mixture 12g water and 58.7g of ethyl acetate are formed. Find K_c for the reaction.

Initial moles of $CH_3COOH = \frac{60g}{60g/mole} = 1$ mole

Initial moles of $C_2H_5OH = \frac{46g}{46g/mole} = 1$mole

At equilibrium

Moles of $CH_3COOC_2H_5 = \frac{58.7g}{88g/mole} = 0.666$mole.

Moles of $H_2O = \frac{12g}{18g/mole} = 0.666$mole

	$CH_3COOH(\ell)$ +	$C_2H_5OH(\ell) \rightleftharpoons$	$CH_3COOC_2H5(\ell)$ +	$H_2O(\ell)$
Init. conc (in moles)	1	1	0	0
Eq.conc. (moles)	1- 0.666 0.333	1 – 0.666 0.333	0.666	0.666

$$K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$$

$$K_c = \frac{(0.666)(0.666)}{(0.333)(0.333)}$$

$$K_c = 4$$

Self Check Exercise 7.6

1. When dissolved in water, glucose and fructose exists in equilibrium as follows:

$$\text{Fructose} \rightleftharpoons \text{Glucose}$$

An analyst prepared a 0.25M fructose solution at room temperature. At equilibrium he found that its concentration decreased by 0.038M. Calculate K_c for the reaction. (Ans: 0.179)

3. When 3.88 moles of NO and 0.88 moles of CO_2 were heated in a flask at a certain temperature. At equilibrium 0.11 moles of each of the product were present. Calculate K_c for the reaction.

$$CO_{2(g)} + NO_{(g)} \rightleftharpoons CO_{(g)} + NO_{2(g)}$$

(**Ans:** 0.0042)

7.1.7 Applications of the Equilibrium Constant

Equilibrium constant for a reaction can be used to predict many important features of the reactions. For instance, it can be used to predict (1) Direction of the chemical reaction (2) Extent of the chemical reaction (3) Effect of changes in condition of the chemical reaction on the equilibrium position and equilibrium constant.

The Direction of a Reaction

i. The direction of reaction when reactants and products of a given chemical reaction are mixed, it is important to know whether the mixture is at equilibrium and if not, in which direction it will move to achieve equilibrium state. For this purpose we use the reaction quotient (Q). **The ratio of concentration of products to reactant at any particular time is called reaction quotient**. It is obtained by applying the law of mass action, using initial concentration or concentration at any particular time instead of equilibrium concentration.

$$Q = \frac{[Products]}{[Reactants]}$$

he value Q leads to one of the following possibilities.

$< K_c$ $\quad R \longrightarrow P$

is indicates that more product is needed to acquire equilibrium.
refore system must shift to the right until equilibrium is attained.

K_c $\quad R \longleftarrow P$

This indicates that less product or more reactant is needed to acquire equilibrium. Therefore system must shift to the left until equilibrium in reached.

(c) **$Q = K_c$** $\quad R \rightleftharpoons P$

This shows that reaction is at equilibrium. No shift will occur.

Example7.8

For the synthesis of ammonia at 500°C, $K_c = 6.0 \times 10^{-1}$

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

Predict the direction in which the system will shift to attain equilibrium when the concentration of species were found to be

$[H_2] = 1.0 \times 10^{-2}$ M

$[N_2] = 1.0 \times 10^{-3}$ M

$[NH_3] = 1.0 \times 10^{-3}$ M

Problem Solving Strategy

1. Write the reaction quotient expression for the reaction
2. Substitute the given values of conc. of each species in the expression and find Q
3. Compere Q. with K_c. If Q is > K_c, the system will shift to the left to achieve equilibrium.

Solution

$$Q = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

$$Q = \frac{(1.0\times10^{-3})^2}{(1.0\times10^{-3})(1.0\times10^{-2})^3}$$

$Q = 1.0 \times 10^3$

But

$K_c = 6.0 \times 10^{-2}$

Therefore $Q > K_c$. The system will shift to the left to achieve equilibrium.

Self Check Exercise 7.7

Phosgene is potent chemical warfare agent and has been used in World War II. It decomposes by the following reaction.

$COCl_{2(g)} \rightleftharpoons CO_{(g)} + Cl_{2(g)}$ $K_c = 8.3 \times 10^{-4}$ at 350°C

Predict the direction in which system will shift to attain equilibrium, when the concentrations of species were found to be

$[COCl_2] = 0.5M$

$[CO] = 2.5 \times 10^{-2}M$

$[Cl_2] = 2.5 \times 10^{-2}M$

(**Ans:** Towards left)

ii. The Extent of Chemical Reaction

The extent of a chemical reaction can be predicated by considering the magnitude of equilibrium constant. Again three are three possibilities.

a. K_c is very large

Many reactions have very large equilibrium constant, for example

$$H_{2(g)} + Br_{2(g)} \rightleftharpoons 2HBr_{(g)} \qquad K_c = 5.4 \times 10^{18} \text{ at } 25°C$$

If concentration of each of the reactant at equilibrium is 1 mole then concentration of HBr would be

$$\frac{[HBr]^2}{1 \times 1} = 5.4 \times 10^{18}$$

$K_c = \frac{[P]}{[R]}$

$$[HBr] = \sqrt{5.4 \times 10^{18}}$$

$$= 2.32 \times 10^9 M$$

It mean that the concentration of HBr is very large as compared to that of reactants. At equilibrium the mixture will have mainly products. Thus large value of Kc indicates that the reaction goes virtually to completion.

b. K_c is very small

Reactions having very small Kc do not proceed appreciably in the forward direction. For example.

$$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)} \qquad K_c = 1.0 \times 10^{-30} \text{ at } 25°C$$

$$K_c = \frac{[NO]^2}{[N_2][O_2]} = 1.0 \times 10^{-30}$$

If one mole of each of the reactant is present at equilibrium, then the concentration of NO would be

$$\frac{[NO]^2}{1 \times 1} = 1 \times 10^{-30}$$

$$[NO] = \sqrt{1 \times 10^{-30}}$$

$[NO] = 1 \times 10^{-15}$ moles

Thus concentration of NO will be very small. Equilibrium mixture will have mainly reactants. Therefore, small value of K_c indicates that the reaction has very little tendency to move in the forward direction.

c. **K_c is neither very small nor very large**

When K_c in neither very small nor very large, the equilibrium mixture contains appreciable amounts of both products and reactants. For example:

$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)} \qquad K_c = 0.36 \text{ at } 25°C$$

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} = 0.36$$

If 1 mole of N_2O_4 is present at equilibrium, 0.6 mole of NO_2 will be present in the equilibrium mixture. Hence the equilibrium mixture will contain appreciable amount of reactants and products. In such cases neither forward nor the reverse reaction go to completion.

Self Check Exercise 7.8

White phosphorus P_4 is produced by the reaction of phosphorite rock, $Ca_3(PO_4)_2$ with coke. When exposed to air it bursts into smoke and fumes and releases a large amount of heat. Predict whether K_c for this reaction is large or small.

$$P_{4(g)} + 5O_{2(g)} \rightleftharpoons P_4O_{10(s)}$$

7.2 FACTORS AFFECTING EQUILIBRIUM

It is necessary to understand the factors that control the position of a chemical equilibrium. A knowledge of such factors help industrial chemists to choose conditions which favour desired product as much as possible. We can predict the effect of various factors such as concentration, pressure and temperature on a system at equilibrium by using Le Chatelier's principle. **"It states that if a change is imposed on a system at equilibrium, the position of the equilibrium will shift in a direction which tends to reduce that change".**

7.2.1 The Effect of a Change in Concentration

When the concentration of one or more of the reactants or products present in equilibrium mixture is disturbed, the system will not remain at equilibrium state. According to Le Chatelier's principle, the equilibrium shifts to accommodate the substance added or removed and restore equilibrium again.

Consider the following gas phase equilibrium:

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

The student should be guided to demonstrate this knowledge in various ways.

When CO_2 is added to this equilibrium system, it is no longer in equilibrium. Higher concentration of CO_2 increases the rate of forward reaction relative to the reverse reaction. Thus more CO_2 and H_2 combine and more CO and H_2 form. As time passes the concentrations of CO_2 and H_2 decrease, lowering the rate of forward reaction. At the same time increased concentration of the products accelerate the reverse reaction ultimately the two rates become equal again and equilibrium is re-established. At the new equilibrium concentration of CO and H_2O are higher than were present before the CO_2 was added. Thus equilibrium is said to have shifted to the products side.

In all chemical systems, an increase in concentration of any reactant shifts the equilibrium towards the formation of the products. If concentration of a product is increased, the equilibrium shifts towards the reactants. A shift towards the reactant lowers the concentration of the added product.

The opposite happens when we decrease the concentration of a reactant or product. If the reactant concentration is decreased, the equilibrium system shifts towards the reactants. Removal of product shifts equilibrium towards the products. Let us understand the microscopic events that take place in an equilibrium system. The rate of chemical reaction depends on the numbers of effective collisions between the reacting molecules. At equilibrium the number of effective collisions for the forward and reverse reactions are equal. Increase in concentration of reactant increases such collisions for the forward reaction. Thus equilibrium shifts towards right with the formation of more molecules of products. Number of effective collisions for the reverse process also increase. As time passes the effective collisions of reactant molecules decrease, lowering the rate of forward reaction. Ultimately the number of effective collisions for both the processes again become equal and equilibrium is re-established.

Example7.9

K_c for, the following reaction is 1.0×10^{-3} at 230°C

$$2\,ICl_{(g)} \rightleftharpoons Cl_{2(g)} + I_{2(g)}$$

1.6 moles of ICl, 0.05 mole of I_2 and 0.05 mole of Cl_2 is present in the equilibrium mixture in 2dm^3 container at 230°C. Determine the equilibrium concentrations of I_2, Cl_2 and ICl when the equilibrium is restored after the addition of another mole of ICl.

Solution

On adding one mole of ICl into the equilibrium mixture will shift equilibrium in the forward direction. Thus the concentration of ICl will decrease and concentration of I_2 and Cl_2 will increase by x whereas concentration of ICl will decrease by 2x.

	$2ICl_{(g)}$ $\rightleftharpoons$	$Cl_{2(g)}$ +	$I_{2(g)}$
Initial Conc. (in moles)	1.6 + 1 = 2.6	0.05	0.05
Conc. at new Equilibrium (in moles)	2.6 – 2x	0.05 + x	0.05 + x

Eq.Conc in moles dm^{-3} $\frac{2.6-2x}{2}$ $\frac{0.05+x}{2}$ $\frac{0.5+x}{2}$

$$K_c = \frac{[Cl_2][I_2]}{[ICl]^2}$$

$$1.0\times10^{-3} = \frac{\left(\frac{0.05+x}{2}\right)\left(\frac{0.05+x}{2}\right)}{\left(\frac{2.6-2x}{2}\right)}$$

Taking square root of both the sides

$$\sqrt{1.0\times10^{-3}} = \frac{\left(\frac{0.05+x}{2}\right)}{\frac{2.6-2x}{2}}$$

$$3.1\times10^{-2} = \frac{0.05-x}{2.6-2x}$$

$x = 0.029$ moles dm^{-3}

$[ICl] = 2.6 - 2x$

$= 2.6 - 2\times 0.029$

$= 2.571$ moles dm^{-3}

$[I_2] = [Cl_2] = 0.05 + x$

$= 0.05 + 0.029$

$= 0.079$ moles dm^{-3}

Self Check Exercise 7.9

K_c for, the following reaction is 1.0×10^{-3} at 230°C

$$2ICl_{(g)} \rightleftharpoons Cl_{2(g)} + I_{2(g)}$$

1.6 moles of ICl, 0.05 mole of I_2 and 0.05 mole of Cl_2 is present in the equilibrium mixture in 2dm^3 container at 230°C. Determine the equilibrium concentrations of I_2, Cl_2 and ICl when the equilibrium is restored after the removal of one mole of ICl. (**Ans:** 0.0208M, 0.0208M, 0.658M

Do you know?

Cigarette smoke is a major source of CO. Smokers inhale it directly through burning cigarette, even non- smoker also inhale CO when they are exposed to cigarette smoke of others. CO combines with hemoglobin to form carboxy-hemoglobin. Because carboxy-hemoglobin is unable to transport oxygen, the heart must pump more blood to get the needed oxygen. Also heavy smokers do not give their hemoglobin much opportunity to recover. Thus chronic exposure to CO from smoking is believed to cause heart disease and heart attacks. Other substances in cigarette smoke can cause lung cancer and respiratory problems. Infact, smoking is a habit with many higher risks.

7.2.2 The Effect of Pressure Change

Equilibria that contain gases are influenced by pressure changes. When pressure on a gaseous system at equilibrium is increased, the system tends to reduce the volume to undo or minimize the effect of increased pressure. This is done by decreasing the total number of gaseous molecules in the system. This is because at constant temperature and pressure, the volume of a gas is directly proportional to the total number of molecules of the gas present.

Consider the following equilibrium system. Which side contains smaller numbers of molecules?

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

If we suddenly increase pressure on the system. What will happen to the equilibrium position? The reaction system will reduce its volume by reducing the number of molecules present. This means that the reaction will shift to the right, because in this direction three molecules (two of SO_2 and one of O_2) react to produce two molecules (of SO_3), thus reducing the total number of gaseous molecules present. This means the equilibrium position will shift towards the side involving the smaller number of gaseous molecules in the balance chemical equation.

When the pressure is reduced the system will shift so as to increase its volume.

There are certain equilibrium in which the total number of molecules are same on either side. For example

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

Whenever the pressure is changed on such a system, neither forward nor the reverse reaction is favoured because the number of molecules is the same on each side. Such equilibria are not affected by pressure or volume changes.

Self Check Exercise 7.10

The formation of methanol is an important industrial reaction in the processing of new fuels

$$CO_{(g)} + 2H_{2(g)} \rightleftharpoons CH_3OH_{(g)}$$

A student decreases pressure over the system in an attempt to increase the yield of methanol. Is this approach reasonable? Explain.

7.2.3 The Effect of Change in Temperature

You have already learnt in grade IX-X that chemical reactions are always associated with energy changes. Chemical reactions that liberate heat are called exothermic and those that absorb heat are called endothermic. This has also been discussed in section 11.1.4. Heat is placed on the right side of the equation in case of exothermic reactions. In endothermic reactions, it is placed on the left side of the equation. We can use Le Chatelier's Principle to predict the direction of change. Treat energy as a reactant in the endothermic process. Predict the direction of shift in the same way as an actual reactant or product is added or removed. Therefore an increase in temperature adding heat favours the endothermic reaction and decrease in temperature (removing heat) favours the exothermic reaction. Consider the following reaction. Which reaction is endothermic, forward or reverse rection.

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)} \quad \Delta H^{\circ} = -198kJ$$

A+heat ⇌ B (Endothermic)

Because the reaction is exothermic, we can write

(Favourable condition) high heat is

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

Heat can be treated as if it were a substance involved in the reaction. According to the Le Chatelier's Principle an increase in temperature will shift reaction from right to left in order to absorb the added heat and to counteract the temperature increase. As a result of this change concentration of SO_3 will decrease and concentrations of SO_2 and O_2 will increase. As a result, the value of equilibrium constant will decrease.

$$K_c = \frac{[SO_3]^2 \longleftarrow \text{increases}}{[SO_2]^2[O_2] \longleftarrow \text{decreases}}$$

A ⇌ B+heat (Exothermic)
(low heat is favourable)

That is why $K_c = 2.8 \times 10^2$ at 1000K whereas at 298K the value of $K_c = 1 \times 10^{26}$. The equilibrium production of SO_3 is favoured at lower temperature. This is because K_c is much larger at 298K than at 1000K.

Now consider the following reaction

$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)} \quad \Delta H^{\circ} = +57.2kJ$$

Because the reaction is endothermic, we can write

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

As the temperature is increased, heat enters the system and the reaction will shift from left to right. As a result of this change, concentration of NO_2 will increase and that of N_2O_4 will decrease. This will increase the value of K_c.

$$K_c = \frac{[NO_2]^2 \longleftarrow \text{increases}}{[N_2O_4] \longleftarrow \text{decreases}}$$

That is why K_c for this reaction is 7.7×10^{-5} at 0°C and 0.4 at 100°C.

Self Check Exercise 7.11

Consider the following equilibrium

$$2I_{(g)} \rightleftharpoons I_{2(g)}$$

What would be the effect on the position of equilibrium when temperature is decreased?

Predict the effect of increasing the temperature on the amount of product in the following reaction.

$$CO_{(g)} + 2H_{2(g)} \rightleftharpoons CH_3OH_{(\ell)} \qquad \text{(exothermic)}$$

Encourage sutdents to demonstrate effects of change in concentration, pressure and temperature with some other examples.

7.2.4 The Effect of Addition of Catalyst

A catalyst added to a reaction mixture speeds up both the forward and the reverse reaction to the same degree. Thus catalyst has no effect on the equilibrium concentrations of reaction mixture. However, the catalyst is important in enhancing the rate at which equilibrium is established.

7.3 INDUSTRIAL APPLICATION OF LECHATELIER'S PRINCIPLE (SYNTHESIS OF AMMONIA BY HABER'S PROCESS)

For industrial processes it is important to maximise the concentration of the desired product and minimise the leftover reactants. Le chatellier's principles and reaction kinetics can both be used to design best conditions to give the highest possible yield of the product in an economic way.

The manufacture of ammonia by Haber's process is represented by the following equation.

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \qquad \Delta H^\circ = -92.46kJ$$

This equation provides the following information.

i) The reaction is exothermic.

ii) The reaction proceeds with a decrease in number of molecules or moles.

Le Chatelier's principle suggests three ways to get maximum yield of ammonia.

i. **Low Temperature**

The forward reaction is exothermic therefore, low temperature will favour the formation of ammonia. The suitable temperature is 400°C.

ii. **High Pressure**

Since four molecules (one of N_2 and three of H_2) react to produce two molecules of NH_3. Thus high pressure will shift the equilibrium to the right side i.e. formation of NH_3. The most suitable pressure is 200 – 300 atm.

Thus optimum condition for equilibrium production of ammonia is low temperature and high pressure. Although at low temperature yield of ammonia is high, but the rate of its formation is so slow that the process becomes uneconomical. Therefore, a catalyst is used to increase the rate of reaction. Usually a piece of iron with other metal oxides is used as catalyst. The equilibrium mixture contains 35% NH_3 by volume.

iii. **Continual removal of ammonia**

A final factor which greatly increases the production of ammonia is the continuous removal of ammonia as it is formed. This is done by liquefying ammonia. The equilibrium mixture is cooled by refrigeration coils until ammonia condenses at -33.4°C and is removed. N_2 and H_2 which do not liquefy at this temperature are recycled into the reaction chamber. The stress caused by the continual removal of ammonia shifts the equilibrium toward the

The student should be guided to interpret information and appraise the importance of Le chatellier's principle.

production of more ammonia. In fact the mixture need not to be allowed to come to equilibrium at all. In this way practically 100% conversion of N_2 and H_2 to NH_3 is possible.

7.4 SOLUBILITY PRODUCT AND PRECIPITATION REACTIONS

Now we will discuss some of the important equilibria which have some analytical importance.

7.4.1 Solubility Product

When an excess of slightly soluble ionic compound is mixed with water. Some of it dissolves and remaining compound settle at the bottom. Dynamic equilibrium is established between undissolved solid compound and its ions in the saturated solution. For example when CaF_2 is mixed with water. Following equilibrium is established.

$$CaF_{2(s)} \rightleftharpoons Ca^{2+}_{(aq)} + 2F^{-}_{(aq)}$$

K_c for this equilibrium can be written as

$$K_c = \frac{[Ca^{+2}][F^{-}]^2}{[CaF_2]}$$

Do You Know

. Precipitates are insoluble ionic solid product of a reaction in which certain cations and anions combine in an aqueous solution.

Since CaF_2 is slightly soluble salt its concentration almost remains constant.

Therefore,

$$K_c[CaF_2] = [Ca^{+2}][F^{-}]^2$$

$$K_{SP} = [Ca^{+2}][F^{-}]^2$$

Where K_{SP} is a constant known as the solubility product constant. **It is defined as the product of the equilibrium concentrations of ions, each raised to a power which is the coefficient of the ion in the balance chemical equation.**

In general, K_{SP} expression of any slightly soluble ionic compound A_mB_n can be written as

$$A_mB_{n(s)} \rightleftharpoons mA^{+n}_{(aq)} + nB^{-m}_{(aq)}$$

$$K_{SP} = [A^{+n}]^m[B^{-m}]^n$$

This means that the solubility product constant is equal to the product of the equilibrium concentration of ions each raised to a power equal to the number of such ions in the formula unit of the compound.

7.4.2 Precipitation Reactions

In the previous section, we have considered solids dissolving in solutions. Now we will consider the reverse process i.e the formation of a solid from solution. **An aqueous reaction that takes place when two or more solution are mixed together, yielding a solid insoluble substance is called precipitation reaction**. In this section we will show how to predict whether a precipitate will form when two solutions are mixed. We will use the term ion product (Q'). It is obtained by substituting initial concentrations instead of equilibrium concentrations in the expression for K_{SP}. For example, ion product expression for solid CaF_2 is given by

$$Q' = [\text{Initial conc. of } Ca^{+2}][\text{Initial conc. of } F^{-}]^2$$

If we add a solution containing Ca^{+2} ions to a solution containing F^- ions, precipitate may or may not form. To predict whether a precipitation will occur, we compare Q' and K_{SP}. There are two possibilities.

a) If $Q' > K_{SP}$, precipitation occurs and will continue until the concentration satisfy K_{SP}.

b) If $Q' < K_{SP}$, precipitation does not occur.

Example 7.10

$50cm^3$ of 0.001M NaOH is mixed with $150cm^3$ of 0.01M $MgCl_2$. Will Mg $(OH)_2$ precipitate?

K_{SP} for Mg $(OH)_2$ = 2×10^{-11}

Problem Solving Strategy

1. Write ion product expression for solid $Mg(OH)_2$
2. Find total volume of solution in dm^3
3. Find the molar concentration of OH^- ions of given NaOH Solution in the total volume of solution.
4. Find the molar concentration of Mg^{+2} ions of given $MgCl_2$ solution in the total volume of solution.
5. Find Q' and compare it with K_{SP} value. If $Q' > K_{SP}$ precipitation will occur. If $Q' < K_{SP}$ Precipitation will not occur.

Solution

First we will determine the concentration of the ions present after mixing

Total volume of solution

$= 50cm^3 + 150cm^3$

$= 200\ cm^3$

$= 0.2dm^3$

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

0.001M   0.001M   0.001M

$50cm^3$ NaOH solution = $0.05dm^3$

$$[OH^-] = \frac{\text{Given volume}}{\text{Required volume}} \times \text{Conc.}$$

$$[OH^-] = \frac{0.05dm^3 \times 0.001M}{0.2dm^3}$$

$= 2.5 \times 10^{-4}M$

$$MgCl_2 \rightleftharpoons Mg^{+2}_{(aq)} + 2Cl^-_{(aq)}$$

0.01M   0.01M $2 \times 0.01M$

$150cm^3$ $MgCl_2$ solution = $0.15dm^3$

$$[Mg^{+2}] = \frac{0.01M \times 0.15dm^3}{0.2dm^3}$$

$= 7.5 \times 10^{-3}$ M

The student should be guided to choose useful information to solve various problems.

Now

$Q' = [Mg^{+2}][OH]^2$

$= (7.5 \times 10^{-3})(2.5 \times 10^{-4})^2$

$= 47 \times 10^{-11}$

As $Q' > K_{SP}$, therefore precipitation will occur.

Example7.11

The solubility of Ag Br is 7.1×10^{-7} M at 25°C. Calculate its K_{SP}.

Solution

7.1×10^{-7} M of dissolved Ag Br produces equal moles of Ag^+ and Br^- ions.

$$AgBr_{(s)} \rightleftharpoons Ag^+_{(aq)} + Br^-_{(aq)}$$

$$7.1 \times 10^{-7}M \quad 7.1 \times 10^{-7}M \quad 7.1 \times 10^{-7}M$$

$K_{SP} = [Ag^+][Br^-]$

$K_{SP} = (7.1 \times 10^{-7})(7.1 \times 10^{-7})$

$K_{SP} = 5.041 \times 10^{-13}$

Self Check Exercise 7.12

i. Write K_{SP} expressions for

Iron(II)Hydroxide

Calcium Sulphate

ii. Lead (II) Sulphate is used as white pigment. What is the solubility of $PbSO_4$?

$K_{SP} = 1.96 \times 10^{-8}$ at 25°C (**Ans:** 1.4×10^{-4} M)

iii. Phosphate in natural water often precipitates as insoluble $Ca_3((PO_4)_2$. In Indus river concentration of Ca^{+2} and PO_4^{-3} ions is 1.0×10^{-9}M each. Will calcium phosphate precipitate?

$K_{SP} = 1.2 \times 10^{-29}$ at 25°C (**Ans**: No)

7.5 COMMON ION EFFECT

An interesting situation arises when a weak electrolyte and a salt containing a common ion are present simultaneously in an aqueous solution. For example in a solution of weak acid, hydrofluoric acid $K_a = 7.2 \times 10^{-4}$, its salt sodium fluoride produces the common ion.

$$HF_{(aq)} \underset{}{\overset{H_2O}{\rightleftharpoons}} H^+_{(aq)} + F^-_{(aq)}$$

$$NaF_{(s)} \xrightarrow{H_2O} Na^+ + F^-_{(aq)}$$

Since HF is a weak electrolyte, it slightly dissociates. NaF being strong electrolyte breaks up completely into its ions. The common ion F^- is produced by NaF will upset its equilibrium. This will increase concentration of F^- ions. According, to the Le Chatelier's principle, the equilibrium will shift to the left to use some of F^- ions. This will decrease the dissociation of HF. Thus dissociation of HF will decrease in the presence of dissolved NaF. This means as a result of equilibrium shift, the concentration of HF will increase. See section 7.2.1 to understand the effect of change in concentration on equilibrium.

Do You Know

Separation and identification of cations into analytical groups is based on solubility product principle and common ion effect. In general any procedure that involves precipitation follows these principles

Similarly when a highly soluble salt is added to the saturated solution of less soluble salt containing a common ion. The degree of dissociation of less soluble salt decreases. Therefore it causes to decrease its solubility.

The term common ion effect is used to describe the behaviour of a solution in which same ion is produced by two different compounds. **"The phenomenon in which the degree of ionization or solubility of an electrolyte is suppressed by the addition of highly soluble electrolyte containing a common ion is called common ion effect".**

Examples 7.12

i. Potassium per chlorate $KClO_4$ is moderately soluble in water. When highly soluble KCl is added to the saturated solution of $KClO_4$. It causes to increase the concentration of K^+ ion.

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

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

According to the Le Chatelier's principle K^+ ions will react with ClO_4^- ions to form $KClO_{4(s)}$. This will suppress, the ionization of $KClO_4$. Thus it will precipitate out.

ii. When HCl gas is passed through the saturated solution of NaCl (Brine), it causes to increases the concentration of Cl^{-1} ion.

$$NaCl_{(s)} \rightleftharpoons Na^+_{(aq)} + Cl^-_{(aq)}$$

$$HCl_{(aq)} \rightleftharpoons H^+_{(aq)}(aq) + Cl^{-1}_{(aq)}$$

According to Le Chatelier's principle Cl^- ions will combine with Na^+ ions to form precipitate of pure NaCl.

Self Check Exercise 7.12

i. Ammonium Chloride, NH_4Cl is a water soluble salt. What will happen if this salt is added to a solution containing ammonium hydroxide.

$NH_4OH_{(aq)} \rightleftharpoons NH^+_{4(aq)} + OH^-_{(aq)}$ $NH_4Cl \rightleftharpoons NH_4^+ + Cl^-$

ii. Carbonic acid is a weak acid. It ionizes in water as follows

$H_2CO_{3(aq)} \rightleftharpoons 2H^+_{(aq)} + CO^{-2}_{3(aq)}$ $Na_2CO_3 \rightleftharpoons 2Na^+ + CO_3^{-2}$

What will happen if a strong electrolyte such as Na_2CO_3 is added to a solution containing carbonic acid.

Key Points

- Chemical Equilibrium is a dynamic state in which the reaction proceeds with equal rates in both the directions.
- At equilibrium state reactants are converted continuously into products and vice versa, as molecules collide with each other.
- The law of mass action is a general description of the equilibrium condition. It states that for the reaction of type

$$aA_{(g)} + bB_{(g)} \rightleftharpoons cC_{(g)} + dD_{(g)}$$

The equilibrium equation is given by

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

where K_c is equilibrium constant

- The equilibrium can be expressed in terms of the equilibrium partial pressure of gases as K_P.
- The reaction quotient Q has the same form as the equilibrium constant expression, but it applies to the reaction that may not be at equilibrium. If $Q > K_c$, the reaction will proceed from right to left to achieve equilibrium. If $Q < K_c$, the reaction will proceed from left to right to achieve equilibrium. If $Q = K_c$, the reaction is at equilibrium.
- There is only value of K_c for each reaction at a given temperature. However, there are infinite numbers of equilibrium positions. An equilibrium position is defined as a particular set of equilibrium concentration that satisfies the equilibrium expressions.
- The concentration of pure solids, pure liquids and solvents are constant and do not appear in equilibrium constant expression of a reaction.
- Le Chatelier's Principle allows us to predict the effect of changes in concentration, pressure and temperature on a system at equilibrium. It states that when a change is imposed on a system equilibrium, the equilibrium position will shift in a direction that tends to undo the effect of imposed change.
- Only a change in temperature changes the value of K_c for a particular reaction.
- The addition of catalyst has no effect on the equilibrium concentration of reactants and products. However, it decreases time to achieve equilibrium state.
- The principle of equilibrium can also be applied when an excess of solid is added to form a saturated solution.

References for Further Information

- Advanced Chemistry, Philip Matthews
- Fundamental's of Chemistry, David E.Guldberg
- Raymond Chang, Essential Chemistry

Exercise

1. CHOOSE THE CORRECT ANSWER

(i) K_c is independent of

(a) Temperature (b) Pressure

(c) Both temperature and pressure (d) K_P

(ii) For which of the following reactions, Kc has units of concentration.

(a) $2A_{(g)} \rightleftharpoons B_{(g)}$ (b) $A_{(g)} \rightleftharpoons B_{(g)}$

(c) $A_{(g)} \rightleftharpoons 2B_{(g)}$ (d) $3_{(g)} \rightleftharpoons 2C_{(g)}$

(iii) For the following reaction

$2A_{(g)} + B_{(g)} \rightleftharpoons 3C_{(g)}$

We can write

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

(c) $K_P - K_c = 0$ (d) $K_P - K_c = -1$

(iv) When a catalyst is added to an equilibrium mixture, it decreases

(a) Reverse reaction (b) Forward reaction

(c) Concentrations of reaction mixture

(d) Enthalpy of reaction (e) It has not effect

$M_3X_2 \rightleftharpoons 3M^{+2} + 2X^{-3}$

(v) If $K_{sP} = [M^{+2}]^3[X^{-3}]^2$, the chemical formula of compound is

(a) MX_2 (b) M_2X_3 (c) M_3X_2 (d) M_2X_2 (e) None of these

(vi) NaCl can be purified by passing HCl gas through the ________ solution of NaCl.

(a) Dilute (b) Concentrated (c) Hot (d) Cold

(vii) $K_c = K_P$ when Δn is equal to

(a) Zero (b) +1 (c) -1 (d) -2

(viii) Consider the following reaction:

$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)} \quad \Delta H^\circ = -198kJ$

Yield of sulphur trixoxide can be increased by

a) increasing pressure
b) increasing temperature
c) adding catalyst
d) increasing concentration of oxygen

1. a, b
2. a, b, c
3. a, b, c, d
4. a, d

2. Define chemical equilibrium

2. State the necessary conditions for equilibrium and the ways that equilibrium can be recognized.
3. Describe the microscopic events that occur when a chemical system is in equilibrium
4. Define and explain the following terms
   (i) Reaction quotient
   (ii) Solubility product
   (iii) Common ion effect
   (iv) Heterogenous equilibria
   (v) Ion product
6. Explain industrial application of Le Chatelier's principle using Haber's process as an example.
7. Propose microscopic events that account for observed macroscopic changes that take place during a shift in equilibrium.
8. 50 cm^3 of acetic acid (d = 1.049 g cm^{-3}) is mixed with 50 cm^3 of ethanol (d=0.789 g cm^{-3}) what is the equilibrium composition of the mixture at 25°C ($K_c = 4$).

   (Ans: $CH_3COOH = 17.80g$, $C_2H_5OH = 12.88g$, $CH_3COOC_2H_5 = 50.812$ g, $H_2O = 10g$)
9. Write Kc and Kp expressions for the following reactions
   (i) $SO_{2(g)} + \frac{1}{2}O_{2(g)} \rightleftharpoons SO_{3(g)}$
   (ii) $H_2O_{(g)} + Cl_2O_{(g)} \rightleftharpoons 2HOCl_{(g)}$
   (iii) $O_{3(g)} \rightleftharpoons O_{2(g)} + O_{(g)}$
   (iv) $O_{3(g)} \rightleftharpoons \frac{3}{2}O_2$
   (v) $Fe_3O_{4(s)} + H_{2(g)} \rightleftharpoons 3FeO_{(s)} + H_2O_{(g)}$
   (vi) $2NO_{(g)} + Cl_{2(g)} \rightleftharpoons 2NOCl_{(g)}$
   (vii) $CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$
   (viii) $C_{(s)} + H_2O_{(g)} \rightleftharpoons CO_{(g)} + H_{2(g)}$
10. At a particular temperature Kp = 0.133 atm. Which of the following conditions corresponds to equilibrium position for the reaction.

   $A_{(g)} \rightleftharpoons 2B_{(g)}$
   (a) $P_B = 0.175$ atm, $P_A = 0.102$ atm
   (b) $P_B = 0.064$ atm, $P_A = 0.0308$ atm
   (c) $P_B = 0.144$ atm, $P_A = 0.156$ atm

   (Ans: b and c)
11. Write the expression for K_c and K_P for the following processes.
   (a) Blue vitriol is deep blue solid copper (11) sulphate pentahydrate is heated to drive off water vapours to form white solid copper (11) sulphate.
   (b) The decomposition of solid phosphorus pentachloride to gaseous phosphorus trichloride and chlorine gas

12. Predict the shift in equilibrium position that will occur for each of the following processes when the volume is reduced. (increase in pressure)
(i) $PCl_{3(g)} + 2NH_{3(g)} \rightleftharpoons P(NH_2)_{3(g)} + 3HCl_{(g)}$ (Backward)
(ii) $2NO_{(g)} + O_{2(g)} \rightleftharpoons 2NO_{2(g)}$ (forward)
(iii) $4NH_{3(g)} + 5O_{2(g)} \rightleftharpoons 4NO_{(g)} + 6H_2O_{(g)}$ (Backward)

13. For each of the following reactions, predict how the value of K_c changes as the temperature is increased.
(a) $N_{2(g)} + O_{2(g)} \rightleftharpoons 2N_{(g)}$ $\Delta H^\circ = -180kJ$ (Decrease)
(b) $2SO_{3(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$ $\Delta H^\circ = -198kJ$ (Decrease)
(c) $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$ $\Delta H^\circ = 58kJ$ (increase)
(d) $CH_{4(g)} + H_2O_{(g)} \rightleftharpoons CO_{(g)} + 3H_{2(g)}$ $\Delta H^\circ = 256kJ$ (increase)

14. What is the difference between an equilibrium with a K_c value larger than one compared with an equilibrium that has a K_c smaller than one.

15. Describe the behaviour of the following equilibria with the stated changes
(a) Increasing pressure on
$C_3H_{8(g)} + 5O_{2(g)} \rightleftharpoons 3CO_{2(g)} + 4H_2O_{(g)}$ (Backward)
(b) Adding $I_2(g)$ to $2HI(g) \rightleftharpoons I_2(g) + H_2(g)$ (Backward)
(c) Removing heat from
$CO_{2(g)} \rightleftharpoons CO_{(g)} + \frac{1}{2}O_{2(g)}$ $\Delta H^\circ = 284kJ$ (Backward)
(d) Decreasing pressure on $C_2H_{6(g)} \rightleftharpoons C_2H_{4(g)} + H_2$ (forward)

16. A solution is prepared by mixing 50 cm^3 of 5×10^{-3}M NaCl with 50 cm^3 of 2×10^{-2}M $Pb(NO_3)_2$. Will a precipitate of $PbCl_2$ form? K_{SP} for $PbCl_2$ is 1.7×10^{-5}. (Ans: No)

17. When solid $PbCl_2$ is added to pure water at 25°C, the salt dissolves until the concentration of Pb^{+2} reaches 1.6×10^{-2}M. After this concentration is reached, excess solid remains undissolved. What is K_{SP} for this salt. (Ans: 1.6384×10^{-5})

18. The equilibrium constant for the following reaction is 1.6×10^5 at 1000K
$H_{2(g)} + Br_{2(g)} \rightleftharpoons 2HBr_{(g)}$
Find the equilibrium pressures of all the gases if 10.0 atm of HBr is introduced into a sealed container at 1000K.
(Ans: $H_2 = Br_2 = 0.0249$ HBr = 9.95 atm)

19. Consider the following gas phase reaction
$SO_{2(g)} + Cl_{2(g)} \rightleftharpoons SO_2Cl_{2(g)} + \text{Heat}$
Describe four changes that would derive the equilibrium to left.

20. How would you change the volume of the following reactions to increase the yield of products.
(i) $Cl_{2(g)} + I_{2(g)} \rightleftharpoons 2ICl_{(g)}$ (ii) $2NO_{2(g)} \rightleftharpoons N_2O_{4(g)}$

Think-Tank

22. A figurine device used to predict weather condition is blue on dry, sunny days and pink on damp, rainy days. These figurines are coated with substances containing chemical species that undergo following equilibrium.

$$[Co(H_2O)_6]^{+2} + 4Cl^- \rightleftharpoons [CoCl_4]^{-2} + 6\cancel{4}H_2O$$

(a) Identify the blue substance $[CoCl_4]^{-2}$
(b) Identify the pink substance $[Co(H_2O)_6]^{+2}$
(c) How is Le Chatelier's Principle applied here.

23. The combination of oxygen with hemoglobin (Hb) molecule, which carries oxygen through the blood, is a complex reaction. For our purpose it can be represented by the simplified equation. $Hb_{(aq)} + O_{2(aq)} \rightleftharpoons HbO_{2(aq)}$

where HbO_2 is oxyhaemoglobin that actually transport oxygen to tissues. The equilibrium constant expression is $K_c = \dfrac{[HbO_2]}{[Hb][O_2]}$

Scaling a 3km mountain can cause headache, nausea, extreme fatigue and other discomforts. Give possible explanation for it.

24. Baking Soda undergoes thermal decomposition as follows

$$2NaHCO_{2(s)} \rightleftharpoons Na_2CO_{3(s)} + CO_{2(g)} + H_2O_{(g)}$$

Would we obtain more CO_2 by adding extra baking soda to the reaction mixture in (a) a closed vessel (b) an open vessel.

25. Potassium dichromate solution has beautiful clear orange colour. This is due to the colour of dichromate ion, $Cr_2O_7^{-2}$. When a salt is dissolved in water, the following equilibrium is setup, on heating solution.

$$\underset{\text{(orange)}}{Cr_2O_{7(aq)}^{-2}} + H_2O_{(l)} \rightleftharpoons \underset{\text{(yellow)}}{2CrO_{4(aq)}^{-2}} + 2H^+_{(aq)}$$

$NaOH \rightleftharpoons Na^+ + OH^-$

What will happen if:
i) dilute Sodium hydroxide is added to this solution. forward (Removal of Product)
ii) this is followed by dilute hydrochloric acid addition. backward (common ion effect)

26. If 0.350 moles of SO_3 is placed in a 1.00 dm^3 flask and allowed to come to equilibrium at a high temperature, 0.207 mole of SO_3 remains. Calculate K_c for the reaction. (Ans: 0.034)

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

27. For the reaction between hydrogen and Iodine to form hydrogen Iodide, the value of K_c is 794 at 298K but 54 at 700K what can you deduce from this information?

$H_2 + I_2 \rightleftharpoons 2HI + Heat$ (exothermic)