

Chemical Equilibrium

After studying this unit, 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. (Applying)
- Write expression for reaction quotient. (Understanding)
- Determine if the equilibrium constant will increase or decrease when temperature is changed in given 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 favoured in a chemical reaction from the given equilibrium constant. (Analysing)
- 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)

Teaching

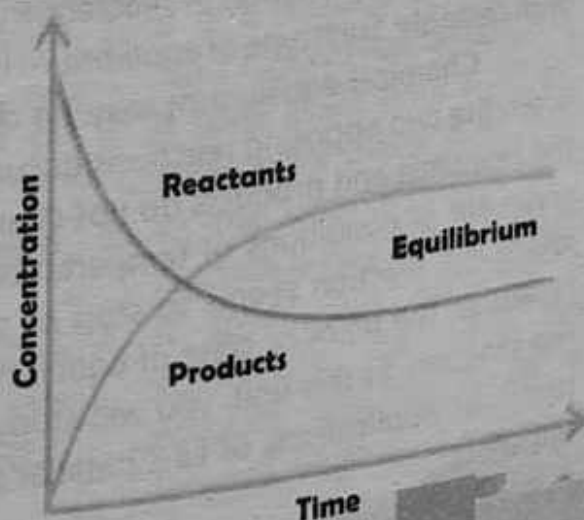
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Assessment

01

Weightage %

07



- Explain industrial application of Le-Chatelier's Principle using Haber's process as example. (Analysing)
- Define and explain solubility product. (Understanding)
- Define and explain common ion effect giving suitable examples. (Applying)

Introduction

It is a well-established fact that many reactions do not go to completion even if favourable conditions are maintained. Such reactions proceed to certain extent and then apparently stop. This is because the products react themselves to give back the original reactants and a time reaches when there is no further change in composition of the reaction mixture occurs. The reaction when reaches the stage where no more products are formed is said to be at equilibrium state. Such reactions are called reversible reactions.

At the start of a reversible reaction, the reaction proceeds towards the formation of products. As soon as some product molecules are formed, the reverse process begins to take place and reactant molecules are formed from the product molecules. At the beginning rate of forward reaction is fast since the reactant concentration is high and rate of reverse reaction is low since the concentration of product is low. With the passage of time, rate of forward reaction gradually becomes slow and rate of reverse reaction becomes fast. Ultimately, a stage reaches where both the rates become equal; this stage is called the equilibrium state.

At equilibrium state:

- Rate of forward reaction is equal to rate of reverse reaction.
- The concentrations of reactants and products become constant (not necessarily equal) and can be recognised by chemical and physical methods.

Although at molecular level formation of product molecules from reactant molecules and formation of reactant molecules from product molecules continue undetectably. Such type of equilibrium is called dynamic equilibrium.

Chemical equilibrium may be defined as the state of a reversible reaction when the two opposing reactions occur at the same rate and the concentrations of the reactants and products do not change with time. It is observed that under a given set of conditions of temperature, pressure, and concentration the point at which the reaction seems to stop or equilibrium is attained, is always the same. However, the point or state of equilibrium changes by changing the conditions of the reaction. In this unit, you will study about dynamic equilibrium, Le-Chatelier's principle, applications of Le-Chatelier's principle, solubility product and common ion effect.

7.1 Reversible Reactions and Dynamic Equilibrium

7.1.1 Concept and Explanation

The reactions that do not go to completion and the products formed react to re-form the reactants are called reversible reactions.

A reversible reaction can be represented by two arrows ($\rightleftharpoons$) between the reactants and products. Let us consider a general reaction taking place in a closed vessel.



Let the initial concentration of A and B be the same. As the forward reaction proceeds, the concentrations of the reactants (A, B) decrease and those of the products (C, D) increase continuously. Therefore, the rate of forward reaction goes on decreasing while that of backward reaction keeps on increasing. Ultimately, a stage reaches when the rate of forward reaction becomes equal to the rate of backward reaction. At this stage the concentrations of the reactants and products become constant. This is called the state of chemical equilibrium.

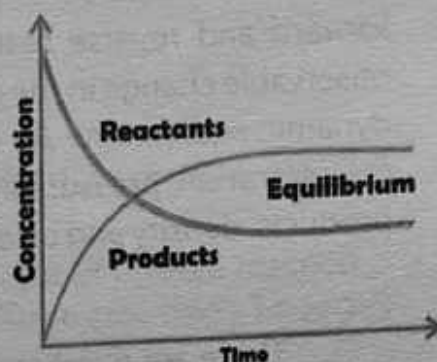


Fig: 7.1 Reversible Reaction and Equilibrium state

Some examples of reversible reactions in a closed vessel are given below.



Table 7.1. Macroscopic Characteristics of Forward and Reverse Reactions

Forward Reaction	Reverse Reaction
a. It is a reaction in which reactants react to form products.	1. It is a reaction in which products react to form reactants.
b. It takes place from left to right as given in chemical equation.	2. It takes place from right to left as given in the chemical equation.
c. At initial stage the rate of forward reaction is fast.	3. At the beginning rate of reverse reaction is very slow.
d. The rate of reaction slows down gradually and at equilibrium its rate becomes constant and equals to that of reverse reaction.	4. It speeds up gradually and at equilibrium its rate becomes constant and equals to that of forward reaction.

The necessary conditions of equilibrium are as follows:

- 1) The equilibrium state can only be reached if the reaction is taking place in closed vessel wherein substances can neither leave nor enter.
- 2) Catalyst helps to attain equilibrium earlier but it does not change the position of equilibrium.
- 3) The state of equilibrium is maintained only as long as the reaction conditions such as temperature and pressure etc. do not change.

Once the equilibrium composition has been attained no further change in the quantities of the components will occur as long as the system remains undisturbed, although microscopically, (at molecular level) reactants are converted to products and product molecules are reacting to give the reactants back; both the forward and reverse reactions taking place at the same rate. Thus, there is no observable change in the concentration of both reactants and products, this is called dynamic equilibrium. An equilibrium state can be recognized by the constancy of concentration, pressure in the case of gaseous reactants or products, density and colour, etc. of the reaction mixture.

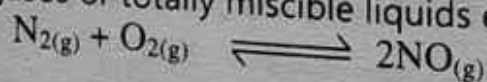
Reading Check

Define chemical equilibrium.

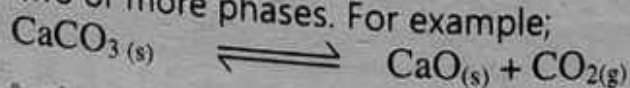
Types of chemical equilibrium

There are two types of chemical equilibrium:

- Homogeneous Equilibrium:** In homogeneous equilibrium all the components of reaction occur only in one phase. For example, a system containing only gases or totally miscible liquids e.g.



- Heterogeneous Equilibrium:** In heterogeneous equilibrium the reaction components occur in two or more phases. For example;



7.1.2. The law of Mass Action and expression for Equilibrium Constant

This law was first enunciated by C.M. Guldberg and P. Waage in 1864 that helps us to find the relations between the concentrations of reactants and products at equilibrium in a chemical reaction. It states that "The rate at which a substance reacts is proportional to its active mass and the rate of chemical reaction is proportional to the product of the active masses of the reacting substances". By the term active mass (or activity) we mean the molar concentration, or number of moles dm^{-3} in a dilute solution. Consider a general reaction;



Where A and B are the reactants while C and D are the products. The equilibrium concentrations in mol dm^{-3} of A, B, C and D are represented in square brackets like [A], [B], [C], and [D], respectively. According to the law of mass action the rate of forward reaction is proportional to the product of molar concentrations of A and B.

$$\text{Rate of forward reaction} \propto [A] [B]$$

$$\text{Rate of forward reaction} = k_f [A] [B]$$

k_f is the proportionality constant known as rate constant for the forward reaction. Since C and D are the reactants for the backward reaction so the rate of reverse reaction is given by

$$\text{Rate of reverse reaction} \propto [C] [D]$$

$$\text{Rate of reverse reaction} = k_r [C] [D]$$

Where, k_r is the rate constant for the backward (or reverse) reaction.

At equilibrium,

$$\text{The rate of forward reaction} = \text{The rate of reverse reaction}$$

Therefore,

$$k_f [A] [B] = k_r [C] [D]$$

On rearranging the above relation we get,

$$\frac{[C][D]}{[A][B]} = \frac{k_f}{k_r} = K_c \quad (7.1)$$

Where, K_c is the ratio of the rate constants (k_f/k_r). It is known as equilibrium constant of the reaction. K_c of the form as given in Eq.7.1 is defined as *the ratio of the product of the molar concentration of the products to that of the reactants*.

For a more general reaction of the following type



Where a, b, c, and d represents the number of moles of the species taking part in the chemical reaction. They are called the coefficient of the species (reactants or products) present in the balanced chemical equation. According to the law of mass action, the equilibrium constant expression is;

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad (7.2)$$

Eq. (7.2) is a general form of the mathematical representation of the equilibrium constant which can more appropriately be defined as *the ratio of the*

product of the molar concentrations of the products to that of the reactants each raised to the power equal to the coefficients of the respective species that occur in the balanced chemical equation. Thus, in the light of the above discussion the law of mass action can more appropriately be defined as *the rate of any chemical reaction is proportional to product of the active masses (or activity) of the reactants, with each reactant raised to a power equal to the coefficients of the reactants that occurs in the (balanced) chemical equation at a given temperature*. The value of K_c is independent of the initial concentrations of the reactants and products but changes only with change in temperature. Remember that the concentrations of reactants and the products appearing in equilibrium constant expression (Eq.7.2) are the equilibrium concentrations.

For a gaseous equilibrium, it is some times more convenient to express the concentration of gases in terms of their partial pressures at any given temperature. Let P_A , P_B , P_C , and P_D are the partial pressures of the gaseous species then the equilibrium constant K_p may be expressed as;

$$K_p = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b} \quad (7.3)$$

If the concentrations are expressed in terms of mole fractions, then the equilibrium constant K_x can be represented as;

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

Similarly, in terms of number of moles, the equilibrium constant K_n is written as

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

Here it should be mentioned that how to recognize that equilibrium has been reached. For this purpose the concentration of any of the reactant or product species is monitored, at different time intervals, by analysing them using any suitable physical or chemical method of analysis. When the concentration of the chosen species becomes constant, after the elapsed interval, it is an indication of the fact that the equilibrium state has been reached.

Self-Assessment

- Define forward and backward reactions with examples.
- Explain law of mass action with an example.
- Differentiate between homogeneous and heterogeneous equilibrium.

Example 7.1

An equilibrium mixture is found to contain 7g of N_2 , 0.3g of H_2 and 1.53g of NH_3 per dm^3 at $300^\circ C$. Find K_c for the reaction.



Solution

$$[N_2] = \text{mol } dm^{-3} \text{ of } N_2 = \frac{7g}{28g \text{ mol}^{-1}} = 0.25 \text{ mol}$$

$$[H_2] = 0.15 \text{ mol} = \frac{0.3g}{2g \text{ mol}^{-1}} = 0.15 \text{ mol}$$

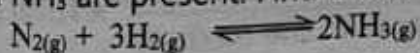
$$[NH_3] = \frac{1.53g}{17g \text{ mol}^{-1}} = 0.09 \text{ mol}$$

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

$$K_c = \frac{[0.09]^2}{[0.25][0.15]^3} = \frac{9.6 \text{ (dm}^3)^2}{\text{mol}^2} \text{ or } 9.6 M^{-2}$$

Practice Problem 7.1

Nitrogen and hydrogen are placed in an empty 5.00 dm^3 container at $500^\circ C$. When equilibrium is established, 3.01 mol of N_2 , 2.10 mol of H_2 , and 0.565 mol of NH_3 are present. Find the K_c for the following reaction at $500^\circ C$.

**7.1.3. Relationship between Equilibrium Constants (K_c , K_p , K_x , K_n)****i) Relation between K_p and K_c**

Consider a general reaction



For an ideal gaseous system, the equilibrium constant expression is written as,

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

Where P represents the partial pressure of the individual gas components present in the equilibrium state.

For 'n' number of moles the ideal gas equation is given as;

$$PV = nRT$$

$$P = (n/V)RT$$

Where P is the partial pressure of the gas and the volume ' V ' is constant. Since, $n/V = C$, the molar concentration

$$\text{Hence, } P = CRT$$

Substituting the values of partial pressures in Eq.7.3, we get

$$K_p = \frac{(C_c RT)^c}{(C_a RT)^a} \times \frac{(C_d RT)^d}{(C_b RT)^b}$$

$$K_p = \frac{[C_c]^c [C_d]^d}{[C_a]^a [C_b]^b} \times \frac{(RT)^{c+d}}{(RT)^{a+b}}$$

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

$$K_p = K_c (RT)^{\Delta n} \quad (7.4)$$

Where $\Delta n = (c+d) - (a+b)$ is the difference in co-efficients of the products and reactants in balanced chemical equation. Furthermore, Δn may be positive, negative or zero. When $\Delta n = 0$, the number of moles of the reactants are equal to the number of moles of the products and Eq. (7.4) becomes $K_p = K_c$.

ii) Relation between K_p and K_x

According to the Raoult's law of partial pressure, P_A , of any gas component for example, is given by

Partial pressure of gas,

$$P_A = \frac{\text{No. of moles of gas A}}{\text{Total number of moles of gases in the mixture}} \times \text{Total pressure}$$

$$\text{Or } P_A = \text{Mole fraction of gas A} \times \text{total pressure i.e. } P_A = X_A P$$

Where X_A is the mole fraction of the gas component A, and P is the total pressure of the system. Eq. (7.3) becomes;

$$K_p = \frac{X_c^c P^c}{X_a^a P^a} \times \frac{X_d^d P^d}{X_b^b P^b}$$

$$K_p = \frac{X_c^c X_d^d}{X_a^a X_b^b} \times \frac{P^{c+d}}{P^{a+b}}$$

$$K_p = \frac{X_c^c X_d^d}{X_a^a X_b^b} \times P^{(c+d)-(a+b)}$$

$$K_p = \frac{X_c^c X_d^d}{X_a^a X_b^b} \times P^{\Delta n}$$

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

$$K_p = K_x P^{\Delta n}$$

Since $P = \frac{RT}{V}$ for one mole of an ideal gas

$$K_p = K_x \left(\frac{RT}{V} \right)^{\Delta n} \dots\dots\dots (7.5)$$

(ii) Relation between K_p and K_n

K_p can be expressed in terms of K_n when the concentrations are expressed in terms of moles of the gases in the system. Dalton's law of partial pressure can be written as;

$$P_A = X_A P \left(\frac{n_A}{N} \right) = P \left(n_A \cdot \frac{P}{N} \right)$$

Where n_A is the number of moles of the component gas A and N is the total number of moles of all the gases in the system. Substituting the values of partial pressures of the gases into Eq.(7.3), we get;

$$K_p = \frac{n_C^c \left(\frac{P}{N} \right)^c \times n_D^d \left(\frac{P}{N} \right)^d}{n_A^a \left(\frac{P}{N} \right)^a \times n_B^b \left(\frac{P}{N} \right)^b}$$

$$K_p = \frac{n_C^c \times n_D^d}{n_A^a \times n_B^b} \times \left(\frac{P}{N} \right)^{(c+d)-(a+b)}$$

$$K_p = \frac{n_C^c \times n_D^d}{n_A^a \times n_B^b} \times \left(\frac{P}{N} \right)^{\Delta n}$$

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

$$K_p = K_n \left(\frac{P}{N} \right)^{\Delta n} \dots\dots\dots (7.6)$$

Thus, Eqs. (7.4), (7.5) and (7.6) show the relationship between K_p , K_c , K_x and K_n . These are related to each other as follows;

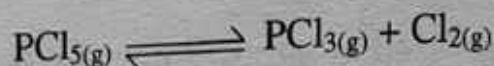
$$K_p = K_c (RT)^{\Delta n} = K_x \left(\frac{RT}{V} \right)^{\Delta n} = K_n \left(\frac{P}{N} \right)^{\Delta n}$$

If the number of moles of the reactants is equal to the number of moles of the products, then $\Delta n=0$ and $(RT)^\circ = 1$, $\frac{P}{P^\circ} = 1$ and $(P/N)^\circ = 1$, for such reaction;

$$K_p = K_c = K_x = K_n$$

Example 7.2

Equilibrium constant, K_p at 523 K is 0.82. Find K_c at the same temperature for the following reaction.



Solution:

$$T = 523\text{K}$$

$$R = 0.082\text{dm}^3 \text{ atmK}^{-1} \text{ mol}^{-1}$$

$$K_p = 0.82$$

$$\Delta n = (1+1) - 1 = 1 \text{ mol}$$

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

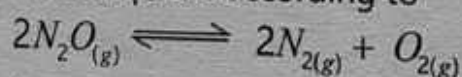
$$0.82 = K_c (0.082 \times 523)^1$$

$$K_c = 0.82 / 0.082 \times 523$$

$$= 1.91 \times 10^{-2} \text{ mol.dm}^{-3}$$

Practice Problem 7.2

We put 10.0 moles of N_2O into a 2.00 dm^3 container at some temperature where it decomposes according to



At equilibrium, 2.20 moles of N_2O remain. Calculate the value of K_c for the reaction.

7.1.4 Importance of K_c and Reaction Quotient

The equilibrium constant can be used to predict the following:

1. The direction in which a chemical system would proceed to acquire an equilibrium state.
2. The extent to which a reaction will proceed before equilibrium is reached.
3. To calculate equilibrium concentrations of reactants and products if the initial concentrations are known.
4. The effect of change in conditions upon a chemical system in a state of equilibrium.

7.1.4.1 Prediction of Direction of Reactions and Reaction Quotient

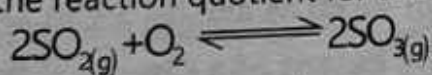
According to law of mass action, equilibrium constant for any reaction is given by the relationship,

$$K_c = \frac{[\text{Products}]}{[\text{Reactants}]}$$

Where [Reactants] and [Products] are the equilibrium concentrations of the reactants and products, respectively. Hence, we come to know that at equilibrium only certain concentrations of the reactants and products are possible for a given reaction. The direction of a reaction at any time during the reaction can be predicted by means of the above relationship, before the reaction attains equilibrium. Initially, we can bring together the reactants or products in just about any concentrations (or partial pressures). An expression is built up which has the same form as K_c .

$$Q_c = \frac{[\text{Products}]_0}{[\text{Reactants}]_0}$$

Such an expression is called expression for the reaction quotient, Q_c . The reaction quotient is not constant for the given reaction but it is quite useful in predicting the direction in which a net reaction must proceed to establish equilibrium. For example, the reaction quotient for the synthesis of $\text{SO}_{3(g)}$ is



$$Q_c = \frac{[\text{SO}_3]_0^2}{[\text{SO}_2]_0^2 [\text{O}_2]_0}$$

Q_c has the same algebraic form of the concentration terms as does the K_c . We call them initial concentrations, represented as $[\]_0$ and they are not necessarily the equilibrium concentrations. A certain value of Q_c is obtained when a set of initial concentrations are substituted into the equation of reaction quotient. In order to predict whether the system is at equilibrium or not, the magnitude of Q_c must be compared with that of K_c . Therefore, when

- i. $Q_c = K_c$, the reaction is at equilibrium.
- ii. $Q_c > K_c$, the system is not at equilibrium and the net reaction will occur in the reverse direction until equilibrium is reached.
- iii. $Q_c < K_c$, the system is not at equilibrium and the net reaction will occur in the forward direction until equilibrium is established.

Example 7.3

For the dissociation of HI



K_c at 520°C is 1.6×10^{-2} . Predict the direction in which the system will move to attain the equilibrium if the initial concentration of HI is 1.02M and that of H_2 and I_2 are 0.01M each.

Solution:

$$Q_c = \frac{[\text{H}_2]_o [\text{I}_2]_o}{[\text{HI}]_o^2} = \frac{[0.01]_o [0.01]_o}{[1.02]_o^2} = 9.61 \times 10^{-5} \text{ M}$$

Since the initial concentration ratio, 9.61×10^{-5} , is less than the given value of K_c , 1.6×10^{-2} , hence, the reaction will proceed in the forward direction and HI will dissociate further.

Practice Problem

At a very high temperature, $K_c = 65.0$ for the following reaction.



The following concentrations were detected in a mixture. Is the system at equilibrium? If not, in which direction must the reaction proceed for equilibrium to be established?

$[\text{HI}] = 0.500 \text{ M}$, $[\text{H}_2] = 2.80 \text{ M}$, and $[\text{I}_2] = 3.40 \text{ M}$

7.1.4.2 Prediction of the Extent of a Chemical Reaction

The extent of the reaction can be found from the value of the equilibrium constant.

- If the equilibrium constant, K_c , is very large, then this indicates that the reaction is almost complete. The concentration of products is much greater than those of reactant at equilibrium.
- If the value of K_c is very small, then the reaction proceeds a little in the forward direction, and a small amount of product is formed at equilibrium.
- If the value of K_c is neither very small nor very large, this shows that both the reactants and products are in appreciable quantities at equilibrium.

Example 7.4

Predict the extent of the given reaction for which the equilibrium constant is 1×10^{-30} at 25°C .

Solution:



Since the value of $K_c = 1 \times 10^{-30}$, which is very small for this system, an equilibrium mixture of the three gases at 25°C will contain very little NO as

compared to N_2 and O_2 .

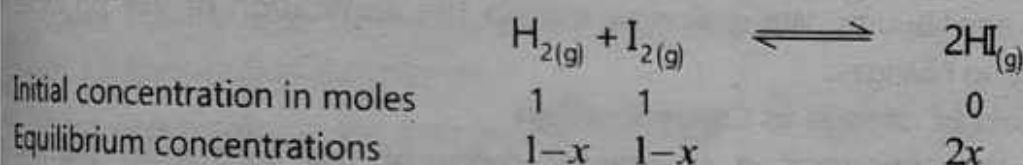
7.1.4.3. Calculation of the Equilibrium Concentrations

If the value of equilibrium constant and the initial concentrations of the reactants are known for a particular reaction, we can calculate the concentrations in the equilibrium mixture. This will be illustrated by following example.

Example 7.5

1.0 mole of hydrogen and 1.0 mole of iodine come to equilibrium at 457.7°C in a one dm^3 flask. What will be the concentration of each substance at equilibrium? Where $K_c = 48.9$

Solution:



$$K_c = 48.9 = \frac{[HI]^2}{[H_2][I_2]} = \frac{(2x)^2}{(1-x)(1-x)} = \frac{(2x)^2}{(1-x)^2}$$

$$\frac{2x}{(1-x)} = \sqrt{48.9}$$

$$x = \frac{6.99}{8.99} = 0.778$$

Hence,

$$[H_2] = 1.0 - 0.778 = 0.222 \text{ M}$$

$$[I_2] = 1.0 - 0.778 = 0.222 \text{ M}$$

$$[HI] = 2 \times 0.778 = 1.556 \text{ M}$$

Practice Problem 7.4

The equation for the following reaction and the value of K_c at a given temperature are given. An equilibrium mixture in a 1.00 liter container contains 0.25 mol of PCl_5 and 0.16 mol of PCl_3 . What equilibrium concentration of Cl_2 must be present? $K_c = 1.9$



7.2 Factors Affecting Equilibrium

Once a system has attained equilibrium, it is possible to change its position by changing the external conditions i.e., concentration, pressure, temperature etc. Chemists are interested in finding the best conditions to obtain maximum yield of the products in reversible reactions by favorably shifting the position of equilibrium of a reaction. For this purpose Le-Chatelier's principle is used.

Le-Chatelier's Principle

A French chemist Henry Le-Chatelier (1884) studied the effect of concentration, temperature, and pressure on a large number of systems in equilibrium. He summed up his conclusions in the form of a generalization known as Le-Chatelier's Principle. The principle states that "if a system at equilibrium is subjected to a stress by a change in temperature, pressure or concentration, the system tends to adjust itself so as to minimize the effect of that change".

This principle is a general one and is applicable to all physical and chemical equilibria. We shall now explain the application of this principle to the following changes.

7.2.1 Effect of change in Concentration

If the concentration of one or more of the substances present in equilibrium is changed, the system is no longer in a state of equilibrium. According to Le-Chatelier's Principle the system will undergo changes in the concentration of various components so as to restore the equilibrium in the system. Consider for example the formation of NO.



$$K_c = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]}$$

- Adding N_2 or O_2 disturbs the position of equilibrium and as a result the reaction moves in the forward direction so a greater yield of NO is obtained till equilibrium is re-established.
- Removing nitric oxide (NO) causes the forward reaction to occur so that part of the NO removed from the system is reproduced.

7.2.2 Effect of change in Pressure or Volume

Liquids are relatively incompressible, changing the pressure above a liquid solution has negligible effect on the concentration of dissolved substance. Consequently, changes in external pressure have very little effect on equilibrium systems that contain only solids (incompressible) or liquids. In contrast, because gases are highly compressible, their concentrations vary considerably with pressure. From the ideal gas law, $PV = nRT$, the concentration (C) of a gas is related to its pressure as follows:

$$C = \frac{n}{V} = \frac{P}{RT}$$

Hence, the concentration in any gaseous reactant or product is directly

proportional to the applied pressure and inversely proportional to the total volume (V). Consequently, the equilibrium compositions of system that contain gaseous substances are quite sensitive to changes in pressure, volume and temperature.

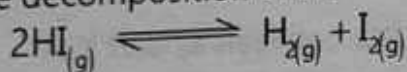
Consider the following examples:

(a) Effect of pressure on the formation of NO_2



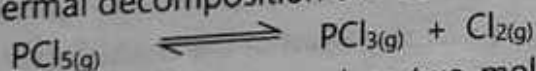
From the stoichiometry of the reaction, the ratio of N_2O_4 to 2NO_2 is 1 to 2. Hence, by Avogadro's law this can be expressed as 1 to 2 volume ratio (1:2). By increasing pressure, a state of lower volume is favoured. Hence, the equilibrium moves towards the lower volume side i.e. reactant side and more will be produced (i.e. reverse reaction is favoured) and vice versa.

(b) Effect of pressure on the decomposition of HI.



The reaction shows that there is no change in volume during the decomposition of HI. Hence, there will be no effect of change in pressure on the equilibrium concentrations of reactants and products.

(c) Effect of pressure on thermal decomposition of PCl_5



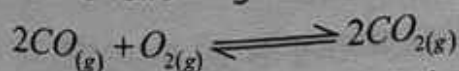
In this reaction, one mole of reactant gives two moles of product after decomposition, all in gaseous state. The effect of pressure on this system will result in decrease in volume which results when reaction goes from right to left in the reactant side. Thus this reaction is favourable under low pressure.

7.2.3 Effect of change in Temperature

If the temperature of a system at equilibrium is changed, the value of the equilibrium constant also changes. According to the Le-Chatelier's principle, *if the temperature of a reaction increases, the equilibrium shifts in the endothermic direction i.e. the direction in which heat is absorbed in an attempt to lower the temperature.*

Consider the following reactions,

$$\Delta H = -41.84 \text{ kJ mol}^{-1}$$



Since the reaction is exothermic in the forward direction and its reverse direction is endothermic so an increase in temperature would shift the equilibrium in the backward direction.

$$\Delta H = 180.5 \text{ kJ mol}^{-1}$$



The formation of NO_2 is an endothermic reaction. Thus according to Le-Chatelier Principle, a high temperature will favour the formation of NO_2 . Practically, the temperature used for its formation is about 3000°C .

7.2.4 Effect of Catalyst on Equilibrium

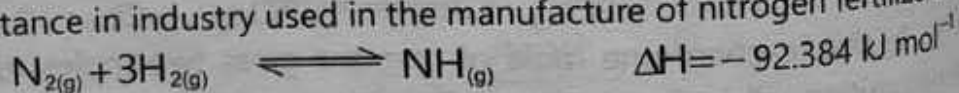
The presence of a catalyst does not affect the equilibrium constant value of a reaction. A catalyst only increases the rate of a reaction by lowering the activation energy of the reaction and thus equilibrium state is reached earlier. Since the increase in rate constant applies to both forward and reverse reactions so the net effect is that there is no change in the value of the equilibrium constant or the position of equilibrium.

Self-Assessment

1. What are the effects of change in concentration and pressure on equilibrium.
2. Explain the relationship between K_p and K_x .
3. What are the uses of equilibrium constant.
4. Define Le-Chatelier's Principle.

7.3 Industrial Applications of Le-Chatelier's Principle

Haber's Process: Let us consider the synthesis of ammonia which is of great importance in industry used in the manufacture of nitrogen fertilizers.



$$K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$$

i. Effect of Concentration

If nitrogen or hydrogen is added to the equilibrium mixture then more amount of ammonia will be formed according to Le-Chatelier's principle. This is due to the fact that an increase in the concentration of N_2 or H_2 will result in shifting the equilibrium towards right. If ammonia is removed from reaction chamber, the forward reaction must be favoured. Hence, efficient removal of ammonia results in a greater yield of ammonia.

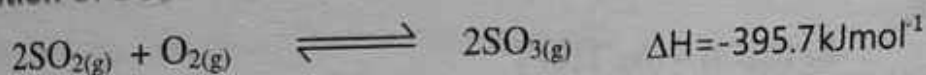
ii. Effect of Pressure

According to the Le-Chatelier's principle, an increase in pressure on this system in equilibrium state, will change the system in a direction in which the volume is decreased. Since one volume of nitrogen and three volumes of hydrogen react to form two volumes of ammonia or a decrease in volume takes place in the forward direction, hence, the formation of ammonia will be favoured by high pressure.

Science, Technology and Society

For industrial processes, it is important to maximize the concentration of the desired products and minimize the 'leftover' reactants. Le-Chatelier's Principle and the principles of reaction kinetics can both be used to design the best reaction conditions to give the highest possible yield of product in an economic way.

Formation of SO_3 for the Manufacture of H_2SO_4



Applying law of mass action

$$K_c = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2 [\text{O}_2]}$$

According to Le-Chatelier's principle, the addition of SO_2 or O_2 at equilibrium results in a greater yield of SO_3 . The process is accompanied by a decrease in volume so it is favoured by slightly higher pressure (1.5 — 1.7 atm.). Since the forward reaction is exothermic, the equilibrium will be shifted towards the product side by lowering the temperature. The optimum temperature for this reaction is 400—500°C.

iii. Effect of Temperature

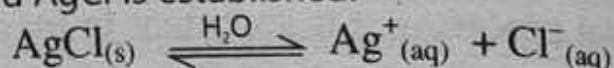
The formation of ammonia from its elements is an exothermic reaction, and its reverse reaction is endothermic. Thus, the increase of temperature results in the increased dissociation of ammonia and decrease in temperature results in the increased production of ammonia. In practice, at lower temperature the reaction proceeds rather slowly and equilibrium is attained in a longer time.

Thus, a suitable temperature at which reaction occurs at reasonable rate and results in a reasonable production of products is selected, which is called optimum temperature. Hence, the synthesis of ammonia is carried out at 400 to 450°C (optimum temperature) in the presence of finely divided iron which acts as a catalyst and a high pressure of 200—500 atm.

7.4 Solubility Product and Precipitation Reactions

When a sparingly soluble salt such as AgCl is shaken with water it dissolves until a saturated solution is formed. The solution contains Ag^+ , Cl^- ions and un-dissolved AgCl . It means that equilibrium between dissolved Ag^+ and Cl^-

ions, and un-dissolved AgCl is established.



Applying law of mass action, the equilibrium constant is

$$K_c = \frac{[\text{Ag}^+][\text{Cl}^-]}{[\text{AgCl}]}$$

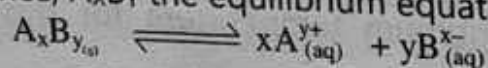
Since the concentration of a pure solid [AgCl] is constant, therefore can write,

$$K_c [\text{AgCl}] = [\text{Ag}^+][\text{Cl}^-]$$

If $K_c [\text{AgCl}] = K_{sp}$

then $K_{sp} = [\text{Ag}^+][\text{Cl}^-]$

K_{sp} is called the solubility product. In general, *the solubility product of a substance is the product of molar concentrations of its ions in the saturated solution each raised to an exponent equal to the coefficient of each ion in the balanced equation*. K_{sp} is usually very small quantity at room temperature. The value of K_{sp} is temperature dependent. In general, for a sparingly soluble substance, A_xB_y the equilibrium equation is



$$K_{sp} = [A^{y+}]^x [B^{x-}]^y$$

Example 7.6

Calculate the concentration of Pb^{+2} ions when solid PbSO_4 is added to water. The solubility product of PbSO_4 is 1.6×10^{-8} .



$$K_{sp} = [\text{Pb}^{+2}][\text{SO}_4^{-2}] = 1.6 \times 10^{-8}$$

From the above chemical equation $[\text{Pb}^{+2}] = [\text{SO}_4^{-2}]$

Let $[\text{Pb}^{+2}] = x \text{ mol dm}^{-3}$

Then $[\text{SO}_4^{-2}] = x \text{ mol dm}^{-3}$

$$K_{sp} = [x][x] = 1.6 \times 10^{-8}$$

$$[\text{Pb}^{+2}] = [x]^2 = 1.6 \times 10^{-8}$$

$$[\text{Pb}^{+2}] = x^2 = \sqrt{1.6 \times 10^{-8}}$$

$$[\text{Pb}^{+2}] = 1.265 \times 10^{-4} \text{ M}$$

Applications

The solubility product principle can be used to predict whether precipitation will occur or not under given concentrations and conditions. Solubility product constant is the product of concentration of ions of electrolyte in a saturated solution each raised to the power of their coefficients in the balanced chemical equation. It is valid only for saturated solution and is constant for a solution at a given temperature. On the other hand, ionic product is the product of concentrations of ions of electrolyte at any concentration of solution each raised to the power of their coefficients in the balanced chemical equation.

The values of ionic product (IP) and solubility product constant (K_{sp}) of a solution help to know whether the solution is saturated, unsaturated or supersaturated. These three situations are discussed below.

(1) $IP = K_{sp}$

When actual amount of ions in solution is maximum, the resulting solution will be saturated but there is no precipitation.

(2) $IP < K_{sp}$

When actual amount of ions is less than equilibrium concentration, the solution will be unsaturated and there is no precipitation.

(3) $IP > K_{sp}$

When actual amount of ions is more than equilibrium concentration, the solution will be supersaturated and is accommodating more ions than it can keep in solution.

A supersaturated solution does not stay supersaturated and it has to precipitate out the excess ions that it cannot handle or hold in solution. The resultant outcome will be saturated solution and precipitate.

Practice Problem 7.5

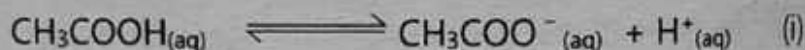
Calculate the solubility of silver acetate, CH_3COOAg , in mol/dm^3 , given the K_{sp} value for silver acetate, CH_3COOAg is $K_{sp} = 1.9 \times 10^{-3}$.

7.5 Common Ion effect

It is a phenomenon in which the extent of dissociation (or solubility) of any weak electrolyte is suppressed by the presence of small amount of a strong electrolyte having a common ion with the weak electrolyte. In other words, the shift of equilibrium towards left side, caused by the addition of an electrolyte having an ion in common with the dissolved electrolyte is called common ion effect. Consider the following examples for explanation of common ion effect.

Example 7.7 Dissociation of Weak Acid

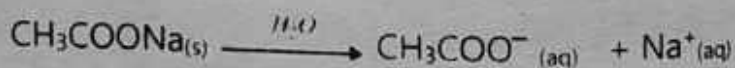
Ionization of weak electrolyte, acetic acid (CH_3COOH), is suppressed by adding strong electrolyte such as sodium acetate (CH_3COONa), containing common ion that is acetate ion (CH_3COO^-). Acetic acid in water dissociates and an equilibrium exists as follows.



The acid dissociation constant, K_a , for this dissociation is written as;

$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]}$$

When a small amount of strong electrolyte, like sodium acetate (CH_3COONa), is added to the aqueous solution of CH_3COOH , it gets dissociated as follows.



Here acetate ions (CH_3COO^-) are common in CH_3COOH and CH_3COONa . According to Le-Chatelier's principle equilibrium, (i), shifts towards left to keep the value of K_a constant, thus the concentration of CH_3COOH molecules is increased. In this way ionization of CH_3COOH is suppressed by adding CH_3COONa .

Example 7.8 Dissociation of Weak Base

Ionization of weak electrolyte such as ammonium hydroxide (NH_4OH), is suppressed by adding strong electrolyte, i.e. ammonium chloride (NH_4Cl) containing common ammonium ions (NH_4^+). NH_4OH dissociates in water as follows,



The equilibrium constant i.e. base dissociation constant, K_b , is written as

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]}$$

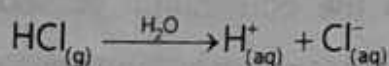
If a small amount of strong electrolyte like ammonium chloride (NH_4Cl) is added to the aqueous solution of NH_4OH , it gets dissociated as follows



Here ammonium ions are common in NH_4OH and NH_4Cl and addition of NH_4Cl increases the concentration of NH_4^+ ions. Thus according to Le-Chatelier's principle, equilibrium of NH_4OH shifts towards left to keep the value of K_b constant, the concentration of NH_4OH molecules is increased. In this way ionization of NH_4OH is suppressed by adding NH_4Cl .

Example 7.9

Purification of NaCl is carried out by passing HCl gas through a saturated solution of NaCl .



Cl^- is a common ion due to which equilibrium shifts to the backward direction whereby NaCl precipitates.

Reading Check

- Define common ion effect.
- Explain the solubility product of a substance with an example.

KEY POINTS

- In a chemical reaction when the rate of forward reaction becomes equal to the rate of backward reaction, the reaction is in the state of dynamic equilibrium.
- According to the Law of Mass Action, the rate at which a substance reacts, is directly proportional to its active mass and the rate of reaction is directly proportional to the product of active masses of the reacting substances.
- Equilibrium constant of the reaction, K_c , is defined as the ratio of the product of the molar concentrations of the products to that of the reactants.
- A large value of equilibrium constant, K_c , indicates that the reaction is almost complete. If the value of K_c is very small, then the reaction proceeds a little in the forward direction rather the reverse reaction is favoured.
- Le-Chatelier's Principle states that "if a stress is applied to a system at equilibrium, the equilibrium will shift in the forward or backward direction to reduce the effect of stress".
- The catalyst has no effect on the equilibrium composition of a reaction. However, it increases the rate of the reaction by lowering its energy of activation.
- If a soluble salt (say A^+C^-) is added to another less soluble salt (A^+B^-) containing a common ion A^+ , the dissociation of A^+B^- is suppressed. It is called common ion effect.

EXERCISE

Choose the correct answer.

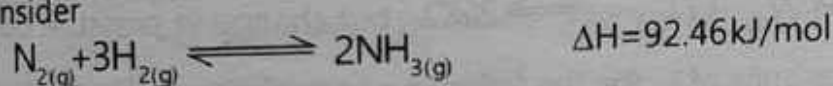
1. In which of the following values of K_c , the reaction goes to completion in the forward direction:

a) 10^2 b) 10^{30} c) 10^{-30} d) 1

2. An appreciable amount of the product and reactants is present in a reaction if its equilibrium constant value is:

a) Negative and large b) Negative and small
c) Zero d) Neither large nor small.

3. Consider



The optimum temperature for the production of ammonia is:

a) 5000°C b) 450°C c) 0°C d) Constant temperature

4. In the production of SO_3 from SO_2 and oxygen. The yield of SO_3 is increased by

a) increasing temperature b) adding a catalyst
c) adding more SO_2 d) removing O_2

5. Le-Chatelier's principle applies to

a) mechanical system b) physical system
c) chemical system d) both b and c

6. The unit of K_c for the system $\text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{Cl}_2$ is

a) mol^2/dm^6 b) dm^3/mol
c) mol/dm^6 d) mol/dm^3

7. Forward reaction goes virtually to completion when K_c is

a) positive and small b) positive and large
c) negative and large d) unity

8. Endothermic reactions are favoured in the forward direction by

a) cooling b) freezing
c) heating d) adding a catalyst

9. Molecules of chlorine decompose to a very small extent into atomic chlorine i.e. $\text{Cl}_2 \rightleftharpoons 2\text{Cl}$; this is because K_c of this reaction is

a) very large b) very small c) zero d) 1

10. How much reaction is complete when $K_c = 1$ for the system



- a) 10% b) 25% c) 50% d) 100%

11. HCl when added to H_2S solution

- a) suppresses the ionization of H_2S b) enhances the ionization
c) solution becomes coloured d) does not affect

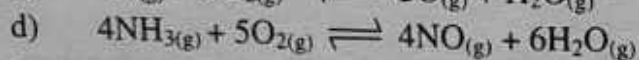
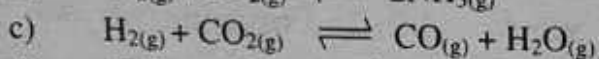
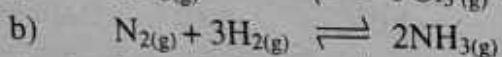
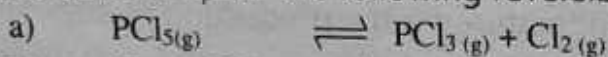
12. The value of K_p is greater than K_c when the difference of the moles of the products and reactants is

- a) zero b) positive c) negative d) one

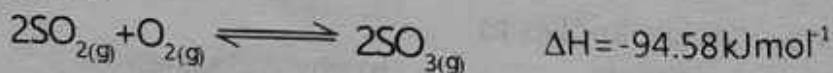
Write answers for the given short questions.

1. The change in temperature changes the equilibrium position of the reaction $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$ but change in pressure does not, why?

2. Give the units of K_p for the following reversible reactions.



3. Why does the value of K_c fall with the rise in temperature for the synthesis of SO_3 ?



4. There is a dynamic rather than static equilibrium present between liquid and vapour at constant temperature; explain.

5. The change in concentration of reactants does not change the value of equilibrium constant permanently, elaborate.

6. Discuss the equilibrium of a sparingly soluble salt.

7. Common ion effect operates best in the purification of certain substances; explain.

8. The ionization of calcium oxalate is suppressed by adding $CaCl_2$ to it; why?

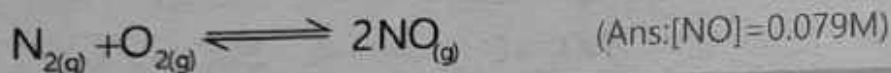
9. The solubility of a sparingly soluble substance is calculated from the solubility product data; explain.

Numerical Questions

1. Calculate K_c for the synthesis of ammonia at 500°C . $K_p = 1.44 \times 10^{-5}$.

(Ans: 5.8×10^{-5})

- The solubility of CaF_2 in water at 25°C is found to be $2.05 \times 10^{-4}\text{M}$. What is the K_{sp} at this temperature? (Ans: 3.446×10^{-11})
- The solubility product of AgCl is 1.8×10^{-10} . Calculate the molar solubility of the salt. (Ans: $1.34 \times 10^{-5}\text{M}$)
- A mixture of 0.5 moles of H_2 and I_2 each was placed in a one litre flask at 400°C . Calculate the concentration of H_2 , I_2 and HI at equilibrium. The K_c for the reaction is 54.3. (Ans: $[\text{H}_2] = [\text{I}_2] = 0.107\text{M}$, $[\text{HI}] = 0.786\text{M}$)
- The equilibrium mixture contains 1 mole of PCl_5 , 0.3 mole of PCl_3 and 0.08 mole of Cl_2 in a 10 L flask. Calculate K_c . (Ans: $K_c = 2.40 \times 10^{-3}$)
- The equilibrium concentration of N_2 and O_2 is 0.25M each while its K_c is 0.1 at 2000°C . Calculate the equilibrium concentration of NO according to the following reaction.

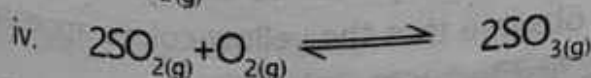
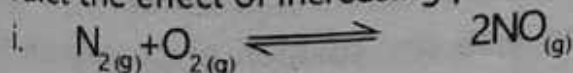


Descriptive Questions

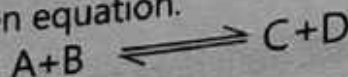
- Write down K_c for the following reversible reactions.



- Predict the effect of increasing pressure on the following gaseous equilibria.



- Derive the relationship between K_p and K_c .
- What is the solubility product? Derive the solubility product expression for slightly soluble AgBr , CaCO_3 , $\text{Al}(\text{OH})_3$ and PbCrO_4 .
- Explain the following.
 - State the Law of Mass Action and derive the equilibrium constant expression for the given equation.



(b) Given the equilibrium concentrations of N_2 , O_2 and NO as $0.05M$, $0.05M$, and $5.5 \times 10^{-4}M$ respectively. Calculate K_c for the decomposition of NO at $1500^\circ C$ for the reaction.

(Ans: 8.26×10^{-3})

- ii. Find the value of equilibrium constant K_c for following reaction.

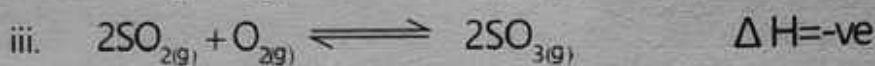
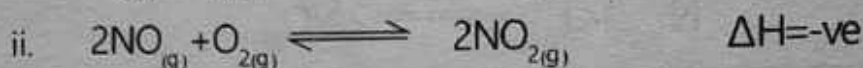
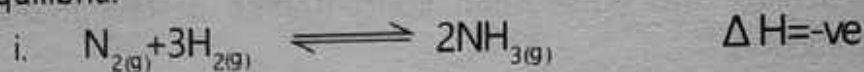


The equilibrium concentrations are $[SO_2] = 0.90M$, $[O_2] = 0.35M$ and $[SO_3] = 1.1M$.

(Ans: 4.3)

- ii. (a) State Le-Chatelier's principle and discuss its application to ammonia system.

(b) What is the effect of raising temperature on each of the following equilibria.



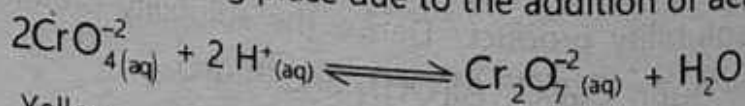
- iv. (a) With the help of chemical equilibrium constant expression, how will you predict the direction and the extent of a chemical reaction?

(b) The equilibrium constant for the reaction, $2O_3 \rightleftharpoons 3O_2$ is 1.0×10^{50} at $25^\circ C$. Predict the extent of the formation of O_2 at room temperature.

Project

Take two test tubes, add about 10 cm^3 solution of potassium chromate (K_2CrO_4) in both of them. Note the colour of the solution. Place one test tube in test tube stand for colour comparison purpose and add dil. HCl solution to the second test tube till the colour changes from yellow to orange. Now add a few cm^3 solution of dil. NaOH. You will observe that the yellow colour appears again. Compare the colour with that of the first test tube solution.

The reaction that is taking place due to the addition of acid is the following:



Questions:

Yellow

Orange

- i. Which principle is governing this reaction to bring it from left to right and back?
- ii. Why the reaction go back from right to left by the addition of base?