8 CHEMICAL EQUILIBRIUM

Student Learning Outcomes [C-11-A-135 to C-11-A-148]

After studying this chapter, students will be able to:

- Describe the microscopic events that occur when a chemical system is in equilibrium. Define with examples. **(Understanding)**
- Differentiate between microscopic and macroscopic events in a chemical reaction. **(Understanding)**
- Propose microscopic that account for observed macroscopic changes that take place during a shift in equilibrium. **(Understanding)**
- Describe what is meant by a reversible reaction and dynamic equilibrium in terms of the rate of forward and reverse reactions being equal and the concentration of reactants and products remaining constant. **(Understanding)**
- Define dynamic equilibrium between two physical states. **(Knowledge)**
- Deduce the equilibrium constant expression [K_c] from an equation for homogeneous reaction. **(Understanding)**
- Determine the relationship between different equilibrium constants (K_c) for the same reaction at the same temperature. **(Understanding)**
- Write the equilibrium expression for a given chemical reaction in terms of concentration, K_c, partial pressure K_p, number of moles K_n and mole fraction K_x. **(Application)**
- State the necessary conditions for equilibrium and the ways that equilibrium can be recognized. **(Knowledge)**
- 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. **(Knowledge)**
- Determine if Kc will increase or decrease when temperature is changed, given the equation for the reaction. **(Understanding)**
- Explain industrial applications of Le Chatelier's Principle using Haber's process and the contact process as an example. **(Understanding)**
- Discuss the industrial applications of chemical equilibria and how it can be used to optimize chemical reactions to maximize yields and minimize waste products. **(Understanding)**
- Use of concept of hydrolysis to explain why aqueous solutions of some salts are acidic or basic. **(Application)**

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The reactions in which the reactants are completely consumed and converted into products are called **irreversible reactions**. Such reactions stop when the limiting reactant is used up. However, some reactions continue in both directions, i.e., forward and reverse, without changing the concentration of reactants and products under the existing conditions. Such reactions never stop and are called **reversible reactions**. When a reversible chemical reaction takes place in a container which prevents the entry or escape of any of the substances involved in the reaction, the quantities of these components change as some are consumed and others are formed. These reactions eventually reach a stage called **chemical equilibrium**. At this point, the concentrations of reactants and products become constant and the rates of the forward and reverse reactions become equal.

This chapter will deal with the equilibria of reversible processes, both physical and chemical changes. Examples of some reversible reactions are given below :

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

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

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

The double arrow tells that the reaction is reversible.

8.1 MACROSCOPIC EVENTS AND MICROSCOPIC EVENTS

8.1.1 Macroscopic Events

Macroscopic events refer to the phenomena that can be observed with the naked eye without considering the individual particles or molecules involved in the process. Change in colour, the evolution or absorption of heat, the formation of precipitate, evolution of a gas, change in volume or pressure and change in the composition of a substance in a chemical reaction are examples of macroscopic properties.

8.1.2 Microscopic Events

Microscopic events refer to the phenomena that cannot be observed with the naked eye. The collisions between molecules, breaking and forming bonds, rearrangement of atoms in molecules and loss or gain of electrons are examples of microscopic events.

8.2 REVERSIBLE REACTIONS, MICROSCOPIC EVENTS AND DYNAMIC EQUILIBRIUM

When a reversible reaction is at equilibrium, it would apparently seem to be static. However, at microscopic level, the reaction never stops and molecules are continuously under change. The reactant molecules convert into products, while at the same time, the reverse process happens. To study at micro scale that affect the macroscopic properties of the system.

Consider the reaction between steam and carbon monoxide under appropriate conditions. On mixing these gases, macroscopic changes are observed (e.g., changes in concentration). Suppose that the reaction is started with same number of moles of both reactants. When

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steam and carbon monoxide are mixed, a maximum number of collisions per second between them will occur as microscopic events. Bonds in CO and H_2O are broken and new bonds are formed to produce H_2 and CO_2. Therefore, the forward reaction has its maximum rate at the beginning. This leads to a decrease in the concentration of the reactants. As H_2O and CO are gradually used up, the forward reaction slows down.

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

As the molecules of H_2 and CO_2 accumulate, the reverse reaction also starts. With the increase in the concentration of H_2 and CO_2, more and more collisions per second between these molecules will occur as microscopic events. As bonds in H_2 and CO_2 are broken, the bonds in CO and H_2O are formed.

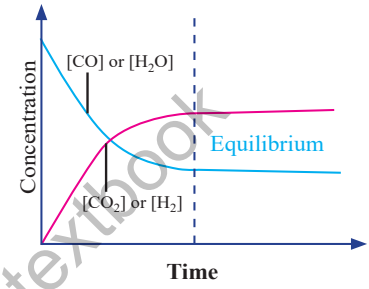

Figure 8.1 Plot of concentration vs time

This means that forward reaction starts with maximum rate and gradually slows down, whereas at the start, the rate of the reverse reaction is low, gradually increases, and finally becomes constant.

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

Eventually, a time comes when both reactions proceed at the same rate. The reaction at this stage is said to be in chemical equilibrium and 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 the concentrations will occur. The state of a reversible reaction at which composition of the reaction mixture does not change and forward and reverse rates are equal is called the **state of chemical equilibrium**. The plots of the concentrations of reactants and products versus time for a general reaction are shown in **Figure 8.1**.

Suppose the reactant A is converted into the product B in a chemical reaction. The graphs in the figure show different possibilities after the equilibrium is established. At the equilibrium position, the concentrations of the reactant and the product may be equal as shown in **Figure 8.2 (a)**, or the amount of reactant may be lower or greater than that of the product as shown in **Figure 8.2 (b and c)**. However, for all of these graphs, it is clear that after the equilibrium is established, the concentrations become constant.

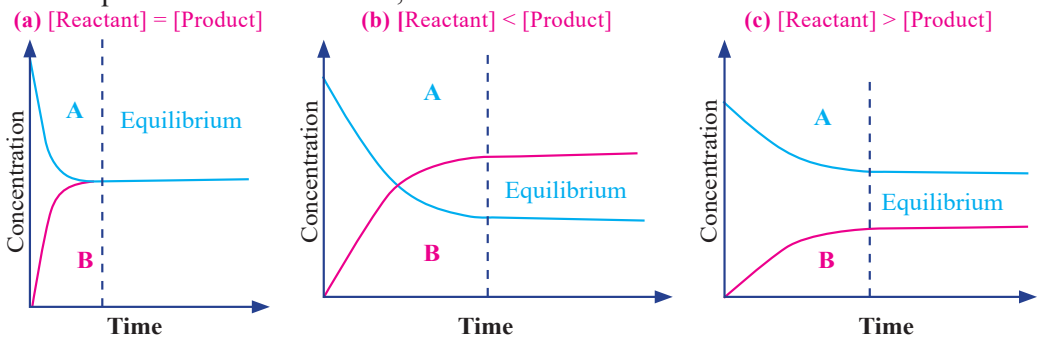

Figure 8.2 Plots of concentration vs time

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When the concentrations of reactants and products become constant, the reaction may apparently seem to have stopped. But it is not true. At the microscopic level, there is intense activity. The individual molecules of the reactants continue to react. Individual product molecules also react to combine to go back to the reactants. The rate of forward process, is exactly equal to the rate of the reverse process. Therefore, it is a **dynamic equilibrium**. The system is dynamic because the individual molecules are constantly reacting, but the rates of forward and reverse reactions are the same.

8.3 RELATION BETWEEN MACROSCOPIC AND MICROSCOPIC EVENTS

Macroscopic events are the result of multiple simultaneous microscopic events. Understanding the microscopic events helps us to explain and predict the observed macroscopic changes in the equilibrium system.

When a change in equilibrium occurs in a chemical reaction, the microscopic events that explain the observed changes in equilibrium are the collisions and formation of new bonds between particles or molecules. These collisions change the rates of forward and reverse reactions, which are affected by activation energy and external factors. These microscopic events collectively appear as macroscopic changes which are observable by naked eye.

Quick Check 8.1

a) Differentiate between macroscopic and microscopic events

b) The equilibrium is dynamic in nature, explain in terms of microscopic events.

c) In the reaction $H_2O_{(g)} + CO_{(g)} \rightleftharpoons H_{2(g)} + CO_{2(g)}$, the concentration of the products is higher at the equilibrium stage.

i. Plot a graph between concentrations of reactants and products vs time.

ii. Plot a graph between rate of the reaction with respect to time.

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8.4 DYNAMIC EQUILIBRIUM BETWEEN TWO PHYSICAL STATES

Dynamic equilibrium is a state in a reversible process where the rate of change in one direction is equal to the rate of change in the opposite direction. In other words, although there are continuous changes taking place, no net change in the system as a whole is observed. When a reversible phase change takes place for a substance, there is also a dynamic equilibrium between the two physical states. For example, at 0 °C, ice and water coexist in equilibrium. Water changes into ice whereas ice converts back into water at the same rate.

Relationship between dynamic equilibrium and vapor pressure

Studying the behaviour of liquids and their vapour pressures is a significant concept in chemistry. When a liquid is placed in a closed container, some of the liquid molecules near

the surface have enough energy to escape into the gaseous phase. This process is called **evaporation**. As more molecules escape into the gaseous phase, the pressure exerted by the gas molecules on the walls of the vessel increases. At the same time, molecules in vapour phase can also collide with the liquid surface and be captured again by the liquid, a process known as **condensation**.

$$\textbf{Liquid} \underset{\text{Condensation}}{\overset{\text{Evaporation}}{\rightleftharpoons}} \textbf{Gas}$$

As evaporation and condensation continue, the rate of these processes will eventually become equal, and a state of dynamic equilibrium is achieved. In this state, the number of liquid molecules transforming into the gas phase equals the number of gas molecules returning to the liquid phase. At dynamic equilibrium, the vapor pressure remains constant at a given temperature, as long as the system is undisturbed.

As the temperature increases, the average kinetic energy of the liquid molecules also increases. This leads to a higher rate of evaporation, which in turn increases the vapor pressure. Also, the rate of condensation increases at the higher temperature. Finally, the system will reach a new state of dynamic equilibrium, with a higher equilibrium vapor pressure. In short, dynamic equilibrium in terms of the vapor pressure of a liquid describes the state at which the rates of evaporation and condensation are equal.

Quick Check 8.2

a) The dynamic equilibrium exists between water and its vapour at 100°C. Justify the statement.

b) Do you think that dynamic equilibrium exists between ice and water at 0°C? If yes, explain.

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8.5 CONDITIONS FOR EQUILIBRIUM

The equilibrium should be studied when the following conditions are fulfilled:

1. The state of equilibrium only applies to reversible reactions.
2. The equilibrium can be established only if the reaction vessel is closed. No part of the reactants and products is allowed to escape out.

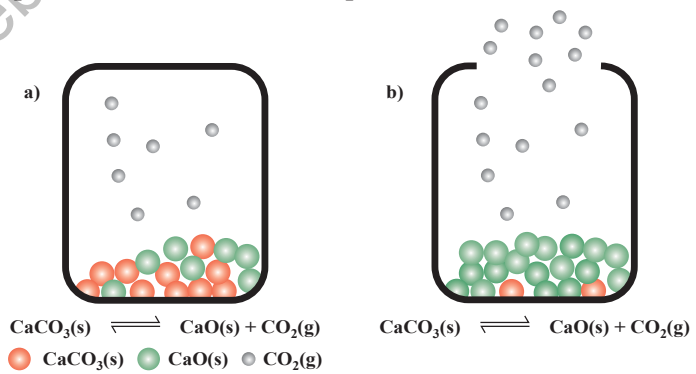

Figure 8.3 (a) Equilibrium is established when the system is closed
(b) Equilibrium can not be established in the open system.

8.6 CHARACTERISTICS OF CHEMICAL EQUILIBRIUM

Important features of equilibrium are as follows:

1. At the stage of chemical equilibrium, the concentrations of reactants and products remain constant.
2. The state of equilibrium in a reversible reaction can be approached from either side whether we start with reactants or products.
3. A catalyst does not change the equilibrium position and the equilibrium constant of the reaction. It helps to attain the equilibrium earlier.
4. The value of equilibrium constant does not depend upon the initial concentrations of reactants, rather it is constant and depends on temperature only.

Keep in Mind!

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 constant.

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8.7 TYPES OF EQUILIBRIUM

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

8.7.1 Homogeneous Equilibrium

An equilibrium system in which all of the reactants and products are in the same phase. The following are examples of homogeneous equilibria:

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

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

$$CH_3COOH_{(\ell)} + C_2H_5OH_{(\ell)} \rightleftharpoons CH_3COOC_2H_{5(\ell)} + H_2O_{(\ell)}$$

8.7.2 Heterogeneous Equilibrium

An equilibrium in which the reactants and products are in more than one phases is called heterogeneous equilibrium. The following are examples of heterogeneous equilibrium:

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

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

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

Quick Check 8.3

a) Differentiate between homogeneous and heterogeneous equilibria.

b) Why do the rates of forward reactions slow down when a reversible reaction approaches the equilibrium stage?

c) In capped soda water bottles, gaseous CO_2 is in equilibrium with the aqueous CO_2 (HCO_3^- and H^+).

$$CO_{2(g)} + H_2O_{(\ell)} \rightleftharpoons HCO^{3-}{}_{(aq)} + H^+{}_{(aq)}$$

i. To which direction will the equilibrium shift if the bottle is opened?

ii. Condition for this equilibrium requires the closed cap of the bottle. Why?

iii. When the cap of the bottle is removed, to which direction the equilibrium shifts?

8.8 EQUILIBRIUM CONSTANT AND POSITION OF EQUILIBRIUM

The position of equilibrium refers to the relative amounts of products and reactants present in an equilibrium mixture.

In 1864, the Norwegian chemists C. Guldberg (1836–1902) and P. Waage (1833–1900) carefully measured the compositions of many reaction systems at equilibrium. They discovered that for any reversible reaction, the ratio of the product of the equilibrium concentrations of the products (raised to their coefficients in the balanced chemical equation) to the product of the equilibrium concentrations of the reactants (raised to their coefficients in the balanced chemical equation) is always a constant under a given set of conditions.

Consider the general reaction:

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

where A and B are reactants, C and D are products, and a, b, c, and d are the stoichiometric coefficients in the balanced chemical equation.

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

The rate of the chemical reaction is directly proportional to the active masses of the reactants, raised to the coefficients present in the balanced equation. By the term active mass, we mean the molar concentration. It is expressed in moles dm^{-3}. This concentration is expressed by square brackets [ ].

Let us consider a general reaction

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

According to the Law of mass action,

Rate of forward reaction α [A][B]

$= k_f$ [A][B]

'k_f' is the proportionality constant, and is known as forward rate constant.

Rate of reverse reaction α [C][D]

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$$= k_r [C][D]$$

'k_r' is the proportionality constant and is known as reverse rate constant.

At the equilibrium stage, the forward and the reverse rates are equal. Hence,

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

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

The left side of this equation is the ratio of two rate constants, so it gives another constant called the equilibrium constant (K_c).

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

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

This expression is known as **equilibrium constant expression**.

Consider the following reversible reaction,

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

where a, b, c and d are the coefficients of balanced equation.

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

8.8.1 Equilibrium Constant Expressions of Some Important Reactions

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

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

(ii) $2N_2O_{5\,(g)} \rightleftharpoons 4NO_{2\,(g)} + O_{2\,(g)}$

$$K_c = \frac{[NO_2]^4\,[O_2]}{[N_2O_5]^2}$$

Sample Problem 8.1

Ethanol reacts with ethanoic acid to form ethyl ethanoate and water.

$$\underset{\textbf{Ethanoic acid}}{CH_3COOH_{(l)}} + \underset{\textbf{Ethanol}}{C_2H_5OH_{(l)}} \rightleftharpoons \underset{\textbf{Ethyl Ethanoate}}{CH_3COOC_2H_{5(l)}} + \underset{\textbf{Water}}{H_2O_{(l)}}$$

500 cm^3 of the reaction mixture at equilibrium contained 0.235 mol of ethanoic acid and 0.0350 mol of ethanol together with 0.182 mol of ethyl ethanoate and 0.182 mol of water. Use this data to calculate a value of K_c for this reaction.

Step 1 Write out the balanced chemical equation with the concentrations beneath each substance.

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$CH_3COOH_{(\ell)}$	+	$C_2H_5OH_{(\ell)}$	$\rightleftharpoons$	$CH_3COOC_2H_{5(\ell)}$	+	$H_2O_{(\ell)}$
0.235 mol		0.0350 mol		0.182 mol		0.182 mol
0.5 dm^3		0.5 dm^3		0.5 dm^3		0.5 dm^3
0.470 mol dm^{-3}		0.070 mol dm^{-3}		0.364 mol dm^{-3}		0.364 mol dm^{-3}

Step 2 Write the equilibrium constant for this reaction in terms of concentrations.

$$K_c = \frac{[CH_3COOC_2H_5]\,[H_2O]}{[CH_3COOH]\,[C_2H_5OH]} = \frac{(0.364 \text{ mol dm}^{-3})\ (0.364 \text{ mol dm}^{-3})}{(0.470 \text{ mol dm}^{-3})\ (0.070 \text{ mol dm}^{-3})}$$

Step 3 Substitute the equilibrium concentrations into the expression

$$K_c = 4.03 \text{ (to 3 significant figures)}$$

Step 4 Add the correct units by referring back to the equilibrium expression: The units of mol dm^{-3} cancel out, so K_c has no units. Therefore, $K_c = 4.03$.

Sample Problem 8.2

Propanone reacts with hydrogen cyanide as follows:

$$\underset{\textbf{Propanone}}{CH_3COCH_{3\,(\ell)}} + \underset{\textbf{Hydrogen cyanide}}{HCN_{(g)}} \rightleftharpoons \underset{\textbf{Product}}{CH_3C(OH)(CN)CH_{3\,(\ell)}}$$

A mixture of 0.0500 mol dm^{-3} propanone and 0.0500 mol dm^{-3} hydrogen cyanide is left to reach equilibrium at room temperature. At equilibrium the concentration of the product is 0.0233 mol dm^{-3}. Calculate K_c for this reaction.

Solution:

Step 1 Write out the balanced chemical equation with all the data underneath:

	$CH_3COCH_{3\,(l)}$	+	$HCN_{(g)}$	$\rightleftharpoons$	$CH_3C(OH)(CN)CH_{3\,(\ell)}$
Initial conc.	0.0500 mol dm^{-3}		0.0500 mol dm^{-3}		0 mol dm^{-3}
Equil. conc.	?		?		0.0233 mol dm^{-3}

Step 2 Calculate the equilibrium concentrations of the reactants. The chemical equation shows that for every mole of product formed, 1 mole of CH_3COCH_3 and 1 mole of HCN are consumed. So the equilibrium concentrations are as follows:

$$[CH_3COCH_3] = 0.0500 - 0.0233 = 0.0267 \text{ mol dm}^{-3}$$

$$[HCN] = 0.0500 - 0.0233 = 0.0267 \text{ mol dm}^{-3}$$

Step 3 Write the equilibrium constant for this reaction in terms of concentrations:

$$K_c = \frac{[CH_3C(OH)(CN)CH_3]}{[CH_3COH_3]\,[HCN]} = \frac{(0.0233 \text{ mol dm}^{-3})}{(0.0267 \text{ mol dm}^{-3})\ (0.0267 \text{ mol dm}^{-3})} = \frac{0.0233}{0.000712}$$

Step 4 Substitute the equilibrium concentrations into the expression

$$K_c = 32.7 \text{ dm}^3 \text{ mol}^{-1}$$

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Quick Check 8.4

a) Write K_c for the following reactions:

i. $Sn^{2+}_{(aq)} + 2Fe^{3+}_{(aq)} \rightleftharpoons Sn^{4+}_{(aq)} + 2Fe^{2+}_{(aq)}$

ii. $4NH_{3(g)} + 5O_{2(g)} \rightleftharpoons 4NO_{(g)} + 6H_2O_{(g)}$

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

b) Calculate the value of K_c for the following reaction using the information below:

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

Initial conc. of $H_{2(g)}$ = 10.00 mol dm^{-3}.

Initial conc. of $CO_{2(g)}$ = 10.00 mol dm^{-3}.

Equilibrium conc. of $CO_{(g)}$ = 9.47 mol dm^{-3}.

8.8.2 Units of Equilibrium Constants

- When the number of moles of reactants and products in balanced chemical equations are equal, then units are canceled out, and equilibrium constant does not have any unit. The ester formation reaction happens in solution state, and number of moles of reactants and products are equal. The K_c will have no units.

$$CH_3COOH_{(aq)} + C_2H_5OH_{(aq)} \rightleftharpoons CH_3COOC_2H_{5(aq)} + H_2O_{(\ell)}$$

$$K_c = \frac{[CH_3COOC_2H_5]\,[H_2O]}{[CH_3COOH_{(aq)}]\,[C_2H_5OH_{(aq)}]} = \frac{\text{mol dm}^{-3} \times \text{mol dm}^{-3}}{\text{mol dm}^{-3} \times \text{mol dm}^{-3}} = \text{No units}$$

- When the number of moles are unequal, then value of equilibrium constant depend upon the units of reactants and products used. In the synthesis of NH_3 by Haber's process, the units of reactants and products are not cancelled.

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

$$K_c = \frac{[NH_{3(g)}]^2}{[N_{2(g)}]\;[H_{2(g)}]^3} = \frac{[\text{mols dm}^{-3}]^2}{[\text{mol dm}^{-3}]\,[\text{mol dm}^{-3}]^3}$$

$$= \frac{1}{[\text{mol dm}^{-3}]^2}$$

$$= \text{dm}^6\ \text{mol}^{-2}$$

8.9 RELATIONSHIPS BETWEEN VARIOUS EQUILIBRIUM CONSTANTS

There are four different types of quantities which may be used to calculate the equilibrium constants of reversible reaction. Let the general reaction be,

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

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(1) When the concentrations of reactants and products are in mole dm^{-3}, then equilibrium constant is written as below:

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

Square brackets [ ] are used for mole dm^{-3}.

(2) When the concentrations are expressed in terms of partial pressures (p) for gaseous reactants and products, then

$$K_p = \frac{p_C^c \cdot p_D^d}{p_A^a \cdot p_B^b} \qquad \text{(ii)}$$

(3) When the concentrations are expressed in terms of number of moles, then

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

(4) When the concentrations are expressed in terms of mole fractions, (X) then

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

The relationships between these equilibrium constants are as follows:

$$K_p = K_c\,(RT)^{\Delta n} \qquad \text{(v)}$$

$$K_p = K_x\,(P)^{\Delta n} \qquad \text{(vi)}$$

$$K_p = K_n\,(N)^{\Delta n} \qquad \text{(vii)}$$

Where:

R = General gas constant

T = Absolute temperature of the system

P = Pressure of the system

N = Total number of moles of reactants and products

Δn = Difference of number of moles of products and reactants in the balanced chemical equation

It depends upon the value of 'Δn' that which of the equilibrium constants is bigger or smaller than the other. Anyhow, if the number of moles of reactants and products in a balanced chemical equation are equal, and all the constants have equal values.

That is, $\Delta n = 0$ then $K_p = K_c = K_x = K_n$

Hence, whichever concentration units are used, the equilibrium constants are same.

Sample Problem 8.3

$N_{2(g)}$ and $H_{2(g)}$ combine to form $NH_{3(g)}$. The value of K_c at 500°C is 6.0×10^{-2}. Calculate the numerical value of K_p for this reaction.

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Solution:

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

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

$T = 500°C + 273 = 773\ K$

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

$K_p = ?$

The formula for conversion of K_c to K_p is,

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

Δn = Number of moles of product – Number of moles of reactants

$\Delta n = 2 - 4 = -2$

Substituting these values in the expression

$K_p = 6.0 \times 10^{-2}\ (0.0821\ dm^3\ atm\ K^{-1}\ mol^{-1} \times 773\ K)^{-2}$

$= 6.0 \times 10^{-2}\ (63.5\ dm^3\ atm\ mol^{-1})^{-2}$

$$K_p = \frac{6.0 \times 10^{-2}}{(63.5)^2} = \frac{0.06}{4032.25}$$

$K_p = 1.4 \times 10^{-5}$

So, the value of K_p is less than K_c.

Sample Problem 8.4

In the reaction

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

the equilibrium partial pressures at constant temperature are $SO_2 = 1.0 \times 10^6$ Pa, $O_2 = 7.0 \times 10^6$ Pa, $SO_3 = 8.0 \times 10^6$ Pa. Calculate the value of K_p for this reaction.

Solution

Step 1 Write the equilibrium expression for the reaction in terms of partial pressures.

$$K_p = \frac{p^2_{SO_3}}{p^2_{SO_2} \times p_{O_2}}$$

Step 2 Substitute the equilibrium concentrations into the expression.

$$K_p = \frac{(8.0 \times 10^6)^2}{(1.0 \times 10^6)^2 \times (7.0 \times 10^6)} = 9.1 \times 10^{-6}\ Pa^{-1}$$

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Quick Check 8.5

a) Compare the magnitudes of K_c and K_p, for the following reversible reactions.

i) Ammonia synthesis ii) Dissociation of PCl_5

(b) Nitrogen reacts with hydrogen to form ammonia.

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

The pressure exerted by this mixture of hydrogen, nitrogen and ammonia at constant temperature is 2.0 x 10^7 Pa. Under these conditions, the partial pressure of nitrogen is 1.5 x 10^7 Pa and the partial pressure of hydrogen is 0.4 x 10^7 Pa. Calculate the value of K_p for this reaction.

8.10 POSITION OF EQUILIBRIUM AND REACTION CONDITIONS

The position of equilibrium refers to the relative amounts of products and reactants present in an equilibrium mixture. If a system in equilibrium is disturbed.

- If the concentration of products is increased relative to the reactants, we say that the position of equilibrium has shifted to the left.
- If the concentration of products is decreased relative to the reactants, we say that the position of equilibrium has shifted to the right.

8.11 LE-CHATELIER'S PRINCIPLE

Le-Chatelier's principle can be stated as follows:

"If a system in equilibrium is disturbed, it behaves in such a way as to nullify or counteract the effect of that disturbance".

Le-Chatelier's principle describes what happens to a system when something momentarily takes it away from equilibrium.

8.11.1 Applications of Le-Chatelier's Principle

Some of the most common applications of this principle with reference to certain physical and chemical equilibria are discussed below:

i) Effect of change in concentration

ii) Effect of change in pressure

iii) Effect of change in temperature.

iv) Effect of catalyst on equilibrium.

Henry-Louis Le Chatelier

(1850-1936)

A French chemist proposed the Le-Chatlier principle, a significant achievement in chemistry

8.12 THE EFFECT OF CHANGE OF CONCENTRATIONS

If the system is at the equilibrium position and a certain amount of one of the reactants or products is added or removed, the equilibrium position is disturbed.

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There are four possibilities for the change in concentration of reactants and products:

i) Adding reactant(s)
ii) Removing reactant(s)
iii) Adding product(s)
iv) Removing product(s)

8.12.1 Hydrolysis of $BiCl_3$

Consider the following reversible reaction in which $BiCl_3$ reacts with water to give a white insoluble compound, BiOCl.

$$BiCl_3 + H_2O \rightleftharpoons BiOCl + 2HCl$$

The expression for this reaction can be written as

$$K_c = \frac{[BiOCl]\,[HCl]^2}{[BiCl_3]\,[H_2O]}$$

When water is added in $BiCl_3$ solution, it becomes cloudy due to the formation of white precipitate of BiOCl. At equilibrium, a certain amount of BiOCl and HCl has been produced and certain number of moles of $BiCl_3$ are left behind. If a few moles of $BiCl_3$ are added at equilibrium, the reaction is pushed to the forward direction.

The addition of $BiCl_3$ or H_2O disturbs the equilibrium position. To re-establish the equilibrium, more BiOCl and HCl are produced. In other words, the reaction is pushed to the forward direction. K_c remains constant, but equilibrium position has changed.

The addition of BiOCl or HCl, or both disturbs the equilibrium position. To re-establish the equilibrium, more $BiCl_3$ is produced and the reaction moves in the reverse direction. The K_c remains the constant, but position of equilibrium changes.

If a certain amount of $BiCl_3$ is removed at equilibrium stage, the reaction will move in the reverse direction to compensate that change. A new equilibrium position is established, K_c being constant.

If a certain amount of BiOCl or HCl or both is removed at equilibrium stage, the reaction will move in the forward direction to compensate that change. A new equilibrium position is established; however, K_c remains constant.

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8.13 THE EFFECT OF CHANGE IN PRESSURE OR VOLUME

The effect of change of volume or pressure is not applicable when

(a) The system does not involve gaseous components.

(b) The number of moles of reactants and products are equal in gaseous phase homogeneous equilibrium.

$$n_{\text{reactants}} = n_{\text{products}}$$

This effect can only be discussed if the gaseous moles of reactants and products are unequal.

$$n_{\text{reactants}} \neq n_{\text{products}}$$

In order to explain this effect, let us consider the synthesis of ammonia by Haber's process.

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

a) Increase in pressure or decrease in volume:

For the forward reaction, the number of moles and hence volume decreases. At equilibrium stage the volume occupied by the mixture is less than the volume at the initial stage under the given conditions. So, if pressure is increased at equilibrium, more ammonia is produced. It means, that reaction is shifted to the forward direction.

b) Decrease in pressure or increase in volume:

If the pressure is decreased or volume is increased, the reaction will move to that side, where the reaction occupies greater volume. Ammonia synthesis is shifted to the reverse direction.

Quick Check 8.6

The change of volume or pressure for the following reactions only changes the equilibrium position but not the equilibrium constant. How the direction of reaction changes for each of the following reactions.

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

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

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

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

8.14 THE EFFECT OF CHANGE IN TEMPERATURE

Le Chatelier's Principle can be used to predict the direction of a reaction with a change in temperature. Temperature is the only factor that also affects the value of equilibrium constant (K_c).

For an exothermic reaction, an increase in temperature (adding heat) favours the reverse reaction. A decrease in temperature (removing heat) favours the forward reaction.

The equation for the conversion of SO_2 to SO_3 is given below:

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

According to the *Le-Chatelier's principle,* an increase in temperature will shift the reaction from right to left.

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

As a result of this change, the concentration of SO_3 will decrease and concentration of SO_2 and O_2 will increase. Therefore, the value of the equilibrium constant will decrease. The equilibrium will shift towards left. The decrease in temperature will favour the forward reaction and the formation of the product. The production of SO_3 is favoured at a lower temperature. On the other hand, an increase in temperature will shift the reaction from left to right.

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

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Due to this change, the concentration of SO_3 will increase and concentration of SO_2 and O_2 will decrease. Therefore, the value of the equilibrium constant will increase.

The equilibrium will shift towards right. The increase in temperature will favour the reverse reaction and the formation of the reactants. The production of SO_3 is not favoured at a higher temperature. K_c for this reaction is 2.8 x 10^2 at 1000 K; whereas, at 298 K the value of K_c is 1 x 10^{26}.

For an endothermic reaction, an increase in temperature (adding heat) favours the forward reaction. A decrease in temperature (removing heat) favours the reverse reaction.

The equation for the conversion of N_2O_4 to NO_2 is given below:

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

According to the *Le-Chatelier's Principle,* an increase in temperature will shift the reaction from left to right.

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

As a result of this change, the concentration of N_2O_4 will decrease and concentration of NO_2 will increase. Therefore, the value of the equilibrium constant (K_c) will increase. The equilibrium will shift towards right. The increase in temperature will favour the forward reaction and the formation of the product.

On the other hand, a decrease in temperature will shift the reaction from right to left. The decrease in temperature will favour the reverse reaction and the formation of the reactant.

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

K_c for this reaction is 7.7 x 10^{-5} at 273 K, whereas 0.4 at 373 K.

8.15 EFFECT OF CATALYST ON EQUILIBRIUM

A catalyst is that substance which increases the rate of a chemical reaction without itself being consumed in the reaction. The catalyst does not change the equilibrium position and the equilibrium constant of a chemical reaction. It speeds up the rate at which equilibrium is attained. It means that the yield of the chemical reaction remains the same.

A catalyst provides new path of lower activation energy for a reaction. If we plot a graph between reaction coordinate on x-axis and potential energy of the chemical reaction on y-axis, then the maxima of the curve become lower in the presence of a catalyst as shown in **Figure 8.4.**

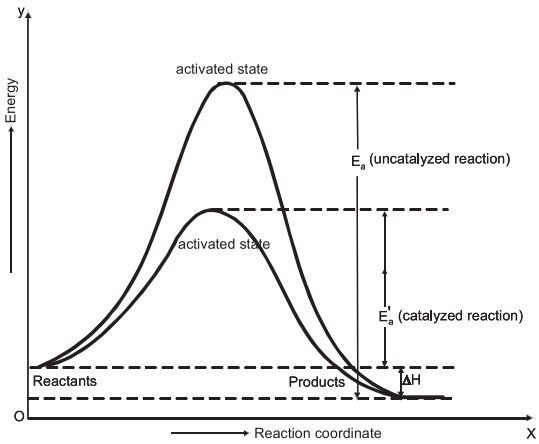

Figure 8.4 Effect of a catalyst on Reversible Reactions.

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8.16 INDUSTRIAL APPLICATIONS OF CHEMICAL EQUILIBRIUM

8.16.1 Synthesis Of Ammonia By Haber's Process

It is one of the basic needs of industry to have maximum yield of the product. We can apply the concept of equilibrium in order to have the maximum yield from the industrial synthesis of ammonia.

Ammonia synthesis from nitrogen and hydrogen is a reversible process.

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \quad \Delta H = -46.11 \text{ kJ mol}^{-1}$$

The maximum yield of ammonia can be achieved by the following ways:

1. Decrease the concentration of ammonia by removing it from the reaction vessel from time to time. Equilibrium will shift to the forward direction in accordance with Le-*Chatelier's principle*.
2. Since, four moles of reactants combine to give two moles of products, reaction happens with the decreasing volume. High pressure will shift the equilibrium position to the right to give more and more ammonia.
3. This is an exothermic reaction. By decreasing temperature, it will shift to the forward direction according to *Le-Chatelier's principle*.

When we look at the **Table 8.1** given below and the **Figure 8.5**, then it becomes clear that the effect of pressure and temperature on the yield of ammonia is very prominent. The most complete conversion is 98.3% at 473 K (200°C) and 1000 atmospheric pressure.

Table 8.1 Effect of Temperature on K_c for Ammonia Synthesis.

T(K)	K_c
200	7.15×10^{15}
300	2.69×10^{8}
400	3.94×10^{1}
500	1.72×10^{2}
600	4.53×10^{0}
700	2.96×10^{-1}
800	3.96×10^{-2}

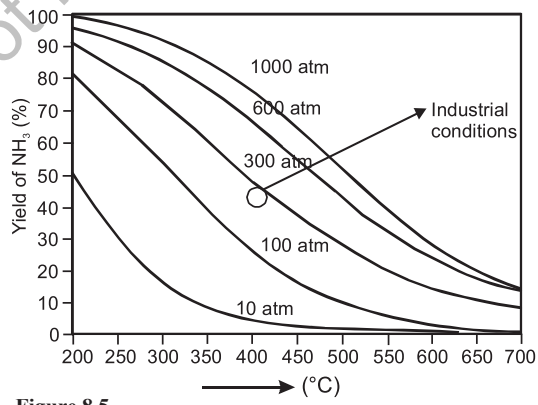

Figure 8.5 Percent yield of ammonia vs. Temperature(°C) at five different operating pressures. At very high pressure and low temperature (top left), the yield is high, but the rate of formation is low. Industrial conditions (circle) are between 200 and 300 atm at about 400°C

At 200°C, the yield is being favoured but the rate of reaction becomes very slow and the process becomes uneconomical. So, the temperature is raised to a moderate level i.e. 400 ºC and a catalyst is used to increase the rate. If we want to achieve the same rate without a

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catalyst then we require much higher temperature, which lowers the yield.

Optimum conditions to get best yield of ammonia

The most suitable conditions to get maximum yield of ammonia are:

a) Pressure between 200-300 atmospheres

b) Temperature around 673 K (400°C)

c) Pieces of iron crystals present in a fused mixture of MgO, Al_2O_3 and SiO_2 as catalyst

8.16.2 Preparation of Sulphur Trioxide

To manufacture H_2SO_4, sulphur trioxide gas is produced from SO_2 and O_2 in a reversible process.

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)} \quad \Delta H = -97.9 \text{ kJ mol}^{-1}$$

According to Le-Chatelier's principle, a high pressure and low temperature are the essential conditions to have better yield of SO_3. At low temperature, the equilibrium constant for the formation of SO_3 is large but equilibrium is achieved very slowly. As the temperature is raised, the rate increases but the yield of SO_3 drops off.

The following **Table 8.2** helps us to understand the parameters, when pressure is maintained at 1 atmosphere.

Table 8.2 Effect of temperature on equilibrium position of SO_3 formation

1. Temperature (°C)	200	300	400	500	600	700
2. K_c	5500	690	160	55	25	13
3. Mole % of SO_3	98	91	75	61	46	31

Optimum conditions

In order to have a best yield of SO_3, within a reasonable time, a mixture of $SO_{2(g)}$ and $O_{2(g)}$ (air) at one atmospheric pressure is passed over a solid catalyst, such as V_2O_5, But due to the exothermic reaction, the temperature of the gas increases to 600 °C. The equilibrium mixture is recycled at low temperature of 400-500 °C to increase the yield of $SO_{3(g)}$.

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Quick Check 8.7

Look at the information given in the table below:

$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$		$N_2O_{4(g)} \rightleftharpoons 2NH_{2(g)}$		$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$	
$\Delta H^o = -92$ kJ mol^{-1}		$\Delta H^o = +57$ kJ mol^{-1}		$\Delta H^o = -197$ kJ mol^{-1}	
	$K_P = \frac{(P_{NH3})^2}{P_{N2}(P_{H2})^3}$		$K_P = \frac{(P_{NO2})^2}{P_{N2}O_4}$		$K_P = \frac{(P_{SO3})^2}{(P_{SO2})^2 P_{O2}}$
T/K	**K_P / atm^{-2}**	**T/K**	**K_P / atm**	**T/K**	**K_P / atm^{-1}**
400	1.0×10^2	200	1.9×10^{-6}	600	3.2×10^3
500	1.6×10^{-1}	300	1.7×10^{-1}	700	2.0×10^2
600	3.1×10^{-3}	400	5.1×10	800	3.2×10
700	6.3×10^{-5}	500	1.5×10^3	900	6.3
800	7.9×10^{-6}	600	$1A \times 10^4$	1000	2.0

i) How does the proportion of products in the above systems change as the temperature increases?

ii) Calculate the values of K_c for the reactions at 600 K?

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EXERCISE

MULTIPLE CHOICE QUESTIONS

Q.1 Four choices are given for each question. Select the correct choice.

I. For which system, does the equilibrium constant, K_c has units of (concentration)$^{-1}$?

a) $N_2 + 3H_2 \rightleftharpoons 2NH_3$ b) $H_2 + I_2 \rightleftharpoons 2HI$

c) $2NO_2 \rightleftharpoons N_2O_4$ d) $2HF \rightleftharpoons H_2 + F_2$

II. Which statement about the following equilibrium is correct?

$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$ $\Delta H = -197.9$ kJmol^{-1}

a) The value of K_p falls with a rise in temperature.

b) The value of K_p falls with increasing pressure.

c) Adding V_2O_5 catalyst increase the equilibrium yield of sulphur trioxide.

d) The value of K_p is equal to K_c.

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

The conventional equilibrium constant expression (K_c) for the system as described by the above equation is:

a) $[SO_2]^2/[SO_3]$ b) $[SO_2]^2[O_2]/[SO_3]^2$

c) $[SO_3]^2/[SO_3]^2[O_2]$ d) $[SO_2][O_2]$

IV. A saturated solution represents a dynamic equilibrium. Macroscopically, the concentration of dissolved solute is constant. Microscopically, this occurs because:

a) No more solute particles are dissolving.

b) The rate of dissolution of solute is zero.

c) Solute particles are dissolving and precipitating at the same rate.

d) All solute particles have dissolved.

V. Which of the following statements correctly describes the effect of temperature on the equilibrium constant?

a) K_c is directly proportional to temperature.

b) K_c is inversely proportional to temperature.

c) K_c depends on the enthalpy change of the reaction.

d) Temperature has no effect on the value of K_c.

VI. Consider the gas-phase equilibrium system represented by the equation:

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

Given that the forward reaction is endothermic, which of the following changes will decrease the equilibrium amount of H_2O?

a) Adding more oxygen

b) Adding a solid phase catalyst

c) Decreasing the volume of the container (the total pressure increases)

d) Increasing the temperature at constant pressure

VII. K_c = 0.040 at 450 ºC for the given reaction, evaluate K_p for the reaction.

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

a) 0.40 b) 0.64

c) 2.4 d) 0.052

VIII. In which of the following gaseous equilibria, pressure has no effect on the equilibrium position?

a) $2NO_{2(g)} \rightleftharpoons N_2O_{4(g)}$ b) $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$

c) $CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2(g)} + H_{2(g)}$ d) $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$

IX. Consider the equilibrium $2H_{2(g)}+O_{2(g)} \rightleftharpoons 2H_2O_{(g)}$. If the concentration of $H_2O_{(g)}$ is increased, the concentrations of $H_{2(g)}$ and $O_{2(g)}$ will:

a) Increase b) Decrease

c) Remain the same d) Change irregularly

X. For a specific reaction, the value of the equilibrium constant, K_c:

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a) Always remains the same at different reaction conditions.

b) Increases if the concentration of one of the products is increased.

c) Changes with changes in the temperature.

d) Increases if the concentration of one of the reactants is increased.

SHORT ANSWER QUESTIONS

Q.2 Attempt the following short-answer questions:

a. What is meant by the state of chemical equilibrium?

b. Define reversible reaction. Give an example.

c. The change of volume disturbs the equilibrium position for some of the gas phase reactions but not the equilibrium constant.

d. Mention the characteristics of chemical equilibrium.

e. Reversible reaction attains the position of equilibrium which is dynamic in nature and not static. Explain it.

f. Why do the rates of forward reactions slow down when a reversible reaction approaches the equilibrium stage?

g. Why ice at 0 °C can be melted by applying pressure without supply of heat from outside?

h. Write two conditions of equilibrium constant.

i. The reversible reaction:

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

has come to equilibrium in a vessel of specific volume at a given temperature. Before the reaction began, the concentrations of the reactants were 0.060 mol/dm^3 of SO_2 and 0.050 mol/dm^3 of O_2. After equilibrium was reached, the concentration of SO_3 was 0.040 mol/ dm^3. What is the equilibrium concentration of O_2?

DESCRIPTIVE QUESTIONS

Q.3. (a) Define and explain the law of mass action and derive the expression for the equilibrium constant.

(b) Write the expressions for K_c for the following reactions:

i) $Sn^{2+}{}_{(aq)} + 2Fe^{3+}{}_{(aq)} \rightleftharpoons Sn^{4+}{}_{(aq)} + 2Fe^{2+}{}_{(aq)}$

ii) $Ag^{1+}{}_{(aq)} + Fe^{2+}{}_{(aq)} \rightleftharpoons Fe^{3+}{}_{(aq)} + Ag_{(s)}$

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

iv) $4NH_{3(g)} + 5O_{2(g)} \rightleftharpoons 4NO_{(g)} + 6H_2O_{(g)}$

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

Q.4 Write down the K_c for the following reactions. Suppose that the reaction mixture in all the case is 'V' dm^{-3}

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i) $CH_3COOH + CH_3CH_2OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$

ii) $2HI \rightleftharpoons H_2 + I_2$

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

Q.5 In the equilibrium

$$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)} \quad \Delta H = 90 \text{ kJ mol}^{-1}$$

What is the effect on the following changes? Explain your answer.

i) if temperature is increased

ii) volume of the container is decreased

iii) catalyst is added

iv) chlorine is added

Q.6 Synthesis of ammonia by Haber's process is an exothermic reaction

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

What should be the possible effect of change of temperature at equilibrium stage?

Q.7 K_c for the following reaction is 0.016 at 520ºC

$$2HI_{(g)} \rightleftharpoons H_2 + I_{2(g)}$$

The equilibrium mixture contains HI = 0.08 M; H_2 = 0.01 M and I_2 = 0.01 M. To this mixture, more HI is added. So that its new concentration is 0.096 M. What will be the concentrations of HI, H_2 and I_2 when equilibrium is re-established?

Q.8 The equilibrium constant for the reaction between acetic acid and ethyl alcohol is 4. A mixture of 3 moles of acetic acid and 1 mole of ethyl alcohol is allowed to come to equilibrium. Calculate the amount of ethyl acetate present at equilibrium.

Q.9 Study the equilibrium

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

i) Write the expression of K_p.

ii) When 1.00 mole of steam and 1.00 mole of CO are allowed to reach equilibrium, 33.3% of equilibrium mixture is hydrogen. Calculate the value of K_p. State the units of K_p.

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