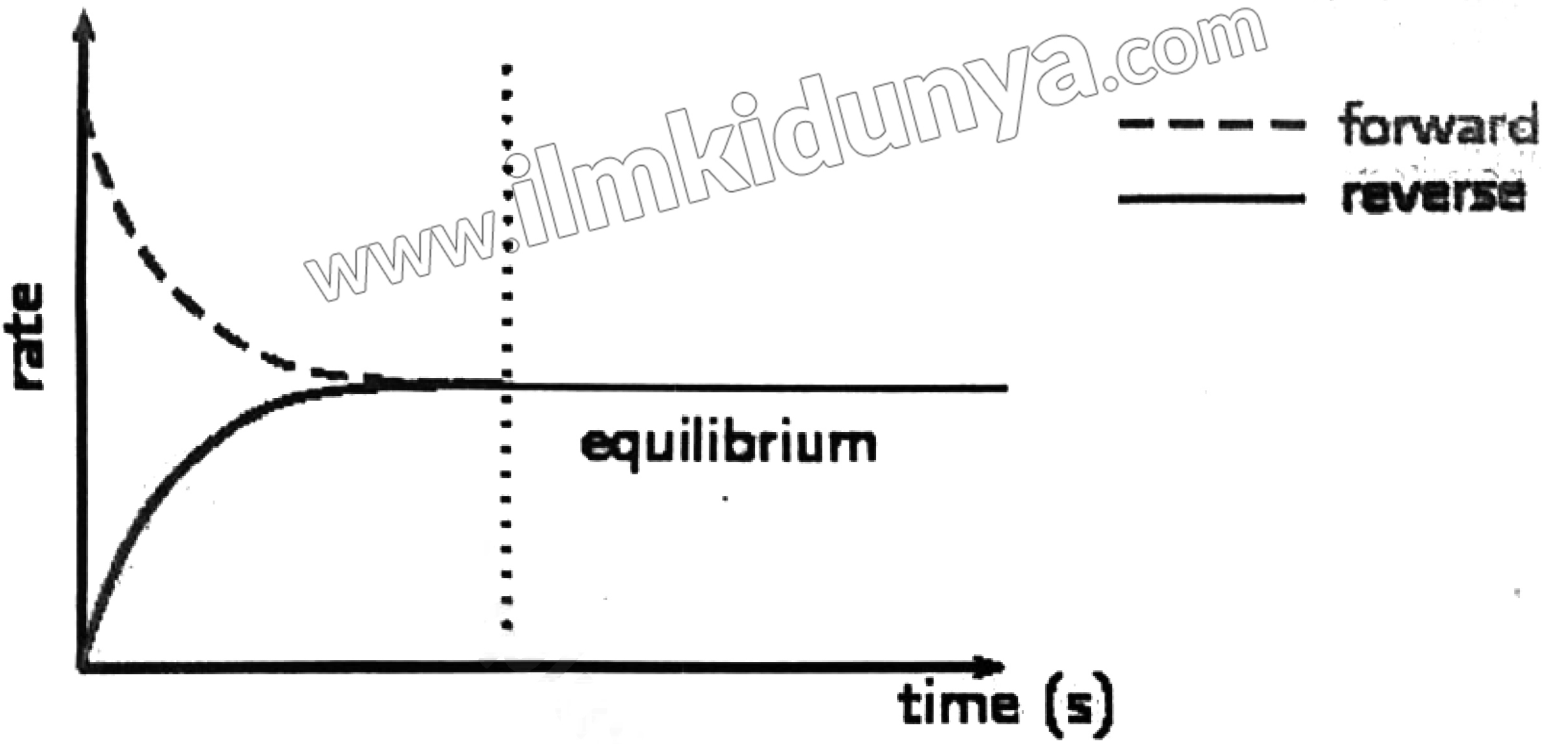

CHEMICAL EQUILIBRIUM

SLOs: After completing this lesson, the student will be able to:

1. 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.
2. Define dynamic equilibrium between two physical states.
3. State the necessary conditions for equilibrium and the ways that equilibrium can be recognized.
4. Describe the microscopic events that occur when a chemical system is in equilibrium. Define with examples.
5. Deduce the equilibrium constant expression [K_c] from an equation for homogeneous reaction.
6. Determine the relationship between different equilibrium constants (K_c) for the same reaction at the same temperature.
7. Write the equilibrium expression for a given chemical reaction in terms of concentration, Kc, partial pressure, number of moles and mole fraction.
8. Differentiate between microscopic and macroscopic events in a chemical reaction.
9. Propose microscopic that account for observed macroscopic changes that take place during a shift in equilibrium.
10. Determine if the equilibrium constant will increase or decrease when temperature is changed,given the equation for the reaction.
11. 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.
12. Explain industrial applications of Le Chatelier's Principle using Haber's process and the contact process as an example
13. Discuss the industrial applications of chemical equilibria and how it can be used to optimize chemical reactions to maximize yields and minimize waste products.
14. Use the concept of hydrolysis to explain why aqueous solutions of some salts are acidic or basic.

This reaction 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, in many reactions, the net formation of products ends before all of the limiting reactant is consumed. Such reactions actually occur in both directions, ie. forward and backward, and are called reversible reactions. These reactions reach a stage called chemical equilibrium. At this point, the concentration of reactants and products becomes constant. However, the reaction continues in both directions without changing the concentration of reactants and products under the existing conditions. Such reactions never stop and are called reversible reactions.

8.1 MACROSCOPIC EVENTS AND MICROSCOPIC EVENTS

Macroscopic events

Macroscopic events refer to phenomena that can be observed with the naked eye without considering the individual particles or molecules involved in the process. For example, a change in colour, the evolution or absorption of heat, the formation of precipitation, a change in volume or pressure, and a change in the composition of a substance in a chemical reaction.

Microscopic events

Microscopic events refer to phenomena that cannot be observed with the naked eye. For example, collisions between molecules, breaking and forming bonds, rearrangement of atoms in molecules, loss or gain of electrons, etc. Macroscopic events are the result of multiple simultaneous microscopic events. Understanding the microscopic events helps us 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 collisions and the 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.

8.2 REVERSIBLE REACTIONS AND DYNAMIC EQUILIBRIUM

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

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

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

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

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

The double arrow tells that the reaction is reversible.

Consider the reaction between steam and carbon monoxide under appropriate conditions.

On mixing **macroscopic** changes are observed (e.g, changes in concentration).

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

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

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

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

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

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

Unless the system is somehow disturbed no further changes in concentration will occur. **"The state of a reversible reaction at which composition of the reaction mixture does not change is called the state of chemical equilibrium"**. The plots of the concentrations of reactants and products versus time are shown in Fig.8.1 what do these plots show? Why have they become parallel?

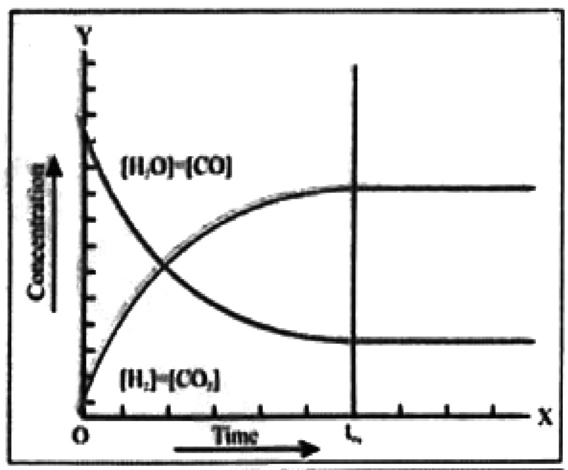

Figure.8.1: The plots of concentration of reactants and products versus time

When the concentration of reactants and products becomes constant, the reaction may appear to have stopped. But that is not true. At the microscopic level, there is intense activity. The individual molecules of the reactants continue to combine. Individual product molecules also continue to combine. But the speed of one process is exactly balanced by the speed of the other process. Therefore, it is a dynamic equilibrium. The system is dynamic because the individual molecules are constantly reacting, but the rate of forward and reverse reactions is the same. It is balanced

8.3 THE LAW OF MASS ACTION

Two chemists C.M Guldberg and P. Wage in 1864 proposed the law of mass action as a general description of the equilibrium state.

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

Consider the following general reversible reaction.

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

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

According to the law of mass action.

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

$$= k_f\,[A]^a\,[B]^b \qquad \text{................ (1)}$$

Where k_f is the rate constant for the forward reaction.

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

$$= k_r[C]^c\,[D]^d \qquad \text{................ (2)}$$

Where k_r is the rate constant for the reverse reaction.

At equilibrium state

Rate of forward reaction = Rate of reverse reaction

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

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

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

Where $K_c = \dfrac{k_f}{k_r}$ and is known as **equilibrium constant**, and the equation (3) is known as **equilibrium constant expression.** The square brackets indicate the concentration of the chemical species at equilibrium.

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

Conditions for Equilibrium

Important features of equilibrium constant expression are as follows:

- K_c applies only at the equilibrium state. The subscript c indicates the concentration of reactants and products in moles per dm^3 at equilibrium state.
- K_c does not depend on the initial concentration of reactants and products but, depends upon temperature. It has only one value at a given temperature. Whether we start the reaction with pure reactants or pure products or any composition in between, the value of K_c remains the same.
- K_c is related to the coefficients of the balanced chemical equation. The concentration of the products is placed in the numerator and those of reactants in the denominator. Each concentration is raised to a power equal to its coefficient in the balanced chemical equation.
- The magnitude of K_c indicates the position of equilibrium. When K_c is less than 1, the denominator is greater in magnitude than the numerator. This means the concentration of the reactants is greater than those of products when the equilibrium is established. Whereas, when K_c is greater than 1, the numerator is greater in magnitude than the denominator. This means the concentration of the products is greater than those of the reactants at equilibrium.

Examples of Equilibrium Constant Expression

Problem solving strategy

1. Write the products in the numerator and the reactants in the denominator within square brackets.
2. Raise each concentration to the power that corresponds to the co-efficient of each species in the balanced chemical equation.

Example 8.1

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

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

Example 8.2

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

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

Concept Assessment Exercise 8.1

1. The following equations represent various industrial reactions at equilibrium. Write K_c expression for each of these reactions. Do not forget to balance the equations:

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

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

(iii) $CH_{4(g)} + H_2O_{(g)} \rightleftharpoons CO_{(g)} + H_{2(g)}$

2. Give the balanced equations that correspond to following equilibrium expressions.

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

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

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

Example 8.3

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

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

[A] = 0.399M, [B] = 1.197M, [AB] = 0.203M.Calculate K_c

Solution

Here $[A_2] = 0.399\ mol\ dm^{-3}[B_2]=1.197\ mol\ dm^{-3}[AB]=0.203\ mol\ dm^{-3}$

$$K_c = \frac{[AB]^2}{[A_2][B_2]}$$

$$K_c = \frac{(0.203\ mol\ dm^{-3})^2}{(0.399 mole\ dm^{-3})(1.197\ mol\ dm^{-3})}$$

$$K_c = 0.086$$

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

Consider the general gaseous reversible reaction.

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

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

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

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

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

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

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

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

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

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

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

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

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

$$K_x = \frac{x_C^c \cdot x_D^d}{x_A^a \cdot x_B^b}$$

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

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

Where P is the pressure of the equilibrium mixture.

Example 8.4

Following reaction was studied at 25°C. Calculate its K_p and K_c.

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

The partial pressures at equilibrium were found to be

$$P_{NOCl} = 1.2 \text{ atm}$$

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

$$PCl_2 = 3.0 \times 10^{-1} atm$$

Problem Solving Strategy

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

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

$$K_P = \frac{(1.2)^2}{(5.0 \times 10^{-2})^2 (3.0 \times 10^{-1})}$$

$$K_P = 1.9 \times 10^3$$

Now

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

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

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

$T = 25°C + 273 = 298K$

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

$$1.9 \times 10^3 = K_C (0.0821 \times 298)^{-1}$$

$$1.9 \times 10^3 = \frac{K_C}{(0.0821 \times 298)}$$

$$K_C = 1.9 \times 10^3 \times 0.0821 \times 298$$

$$K_C = 4.65 \times 10^4$$

Concept Assessment Exercise 8.2

The contact process prepares purest sulphuric acid commercially. Following reaction takes place in the contact chamber in the presence of V_2O_5 at 450°C.

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

Calculate K_p if the following concentrations are found at equilibrium.

$[SO_2] = 0.59M$, $[O_2] = 0.05M$ & $[SO_3] = 0.259M$ (Ans: 0.0649 atm^{-1})

8.4 TYPES OF EQUILIBRIUM

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

i. Homogeneous Equilibria

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

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

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

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

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

ii. Heterogeneous Equilibria

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

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

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

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

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

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

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

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

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

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

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

Concept Assessment Exercise 8.3

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

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

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

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

8.5 WAYS TO RECOGNIZE EQUILIBRIUM

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

a) Physical Method (spectrometric method)

This method is based on measuring the physical properties of the reaction mixture. This physical property is measured during the reaction without removing the sample from the reaction mixture. Let's discuss the spectrometric method. This method can be applied when the reactant or product absorbs ultraviolet, visible or infrared radiation. The concentration can be determined by measuring the amount of radiation absorbed.

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

(Colourless) (Reddish brown)

N_2O_4 is a colourless gas whereas NO_2 is reddish brown gas. The progress of the reaction can be studied by measuring the absorbance at regular Intervals. Absorbance is proportional to the concentration of NO_2. At equilibrium spectrometer will show constant value of absorbance.

b) Chemical Method

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

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

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

The progress of the reaction can be studieu by determining the concentration of acetic acid after regular intervals. For this purpose, a small portion of mixture is withdrawn. The concentration of acetic acid is determined by titrating it against a standard solution of NaOH using phenolphthalein as an indicator. The concentration of acetic acid will decrease until equilibrium is attained. At equilibrium the concentration of acetic acid will become constant, indicating that equilibrium has been reached.

8.6 FACTORS AFFECTING EQUILIBRIUM (THE LE CHATELIER'S PRINCIPLE)

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

At equilibrium, the forward and reverse reactions are driven by molecular collisions, When we change temperature, pressure, and concentration, the frequency and energy of collisions between reacting molecules increase or decrease. This in terns changes the reaction rates and causes a shift in the equilibrium position.

8.6.1 The Effect of a Change in Concentration

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

Consider the following gas phase equilibrium:

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

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

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

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

Example 8.5

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

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

1.6 moles of ICl, 0.05 mole of I_2 and 0.05 mole of Cl_2 is present in the equilibrium mixture in 2dm³ container at 230°C. Determine the equilibrium concentrations of I_2, Cl_2 and ICl when the equilibrium is restored after the addition of another mole of ICl.

Solution

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

	$2ICl_{(g)}$ $\rightleftharpoons$	$Cl_{2(g)}$ +	$I_{2(g)}$
Initial Conc. (in moles)	1.6 + 1 = 2.6	0.05	0.05
Conc. at new Equilibrium (in moles)	2.6 - 2x	0.05 + x	0.05 + x
Eq.Conc in moles dm⁻³	$\frac{2.6-2x}{2}$	$\frac{0.05+x}{2}$	$\frac{0.5+x}{2}$

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

$$1.0\times 10^{-3} = \frac{\left(\frac{0.05+x}{2}\right)\left(\frac{0.05+x}{2}\right)}{\left(\frac{2.6-2x}{2}\right)^2}$$

Taking square root of both the sides

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

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

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

$[ICl] = 2.6 - 2x$

$= 2.6 - (2\times 0.029)$

$= 2.571$ moles dm^{-3}

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

$= 0.05 + 0.029$

$= 0.079$ moles dm^{-3}

Concept Assessment Exercise 8.4

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

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

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

8.6.2 The Effect of Pressure Change

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

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

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

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

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

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

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

When the pressure is changed in such a system, neither the forward nor the reverse reaction is favoured because the number of molecules is the same on both sides. Changes in pressure or volume do not affect such equilibriums.

Concept Assessment Exercise 8.5

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

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

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

8.6.3 The Effect of Change in Temperature

Chemical reactions that liberate heat are called exothermic and those that absorb heat are called endothermic. Heat is placed on the right side of the equation in case of exothermic reactions. In endothermic reactions, it is placed on the left side of the equation. We can use Le Chatelier's Principle to predict the direction of change. Treat energy as a reactant in the endothermic process. Predict the direction of shift in the same way as an actual reactant or product is added or removed. Therefore ,an increase in temperature adding heat favours the endothermic reaction and a decrease in temperature (removing heat) favours the exothermic reaction. Consider the following reaction. Which reaction is endothermic, forward or reverse reaction?

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

Because the reaction is exothermic, we can write

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

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

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

That is why $K_c = 2.8 \times 10^2$ at 1000K whereas at 298K the value of $K_c = 1\times10^{26}$. The equilibrium production of SO_3 is favoured at a lower temperature. This is because K_c is much larger at 298K than at 1000K.

Now consider the following reaction

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

Because the reaction is endothermic, we can write

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

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

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

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

Concept Assessment Exercise 8.6

1. Consider the following equilibrium

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

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

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

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

8.6.4 The Effect of Addition of Catalyst

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

8.7 INDUSTRIAL APPLICATION OF LECHATELIER'S PRINCIPLE

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

8.7.1 Synthesis of Ammonia by Haber's Process

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

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

This equation provides the following information.

i) The reaction is exothermic.

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

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

i. Low Temperature

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

ii. High Pressure

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

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

iii. Continual removal of ammonia

A final factor that greatly increases the production of ammonia is the continuous removal of ammonia as it is formed. This is done by liquefying ammonia. The equilibrium mixture is cooled by refrigeration coils until ammonia condenses at -33.4°C and is removed. N_2 and H_2 which do not liquefy at this temperature are recycled into the reaction chamber. The stress caused by the continual removal of ammonia shifts the equilibrium toward the production of more ammonia. In fact, the mixture need not be allowed to come to equilibrium at all. In this way practically 100% conversion of N_2 and H_2 to NH_3 is possible.

8.7.2 Synthesis of Sulphuric Acid by Contact Process

The contact process is an industrial method used to produce sulphuric acid. The manufacture of sulphuric acid is represented by the following chemical reactions.

i. Formation of sulphur dioxide

Sulphur dioxide is produced by burning sulphur.

$$S_{(s)} + O_{2(g)} \rightarrow SO_{2(g)}$$

ii. Oxidation of sulphur dioxide

SO_2 is oxidised into SO_3 using vanadium penta oxide (V_2O_5)

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

iii. Conversion of sulphur trioxide into sulphuric acid.

The oxidation of sulphur dioxide to sulphur trioxide is the most important step in the production of sulphuric acid. This reaction provides the following information.

a) The reaction is exothermic.
b) The reaction occurs with a decrease in number of moles.

Le Chatelier's principle suggests three ways to maximize the yield of sulphuric acid.

a) Low temperature
Since the forward reaction is exothermic, the low temperature favours the formation of sulphur trioxide. However, too low temperature slows down the reaction speed. So, a compromised temperature of 450 - 500 $^{\circ}C$ is used.

b) High pressure
Since forward reaction produces fewer moles, high pressure shifts the equilibrium to the right. But maintaining high pressure is very expensive. So, the compromised pressure of 2 atm. is used.

c) Adding excess oxygen
According to Le Chatelier's principle, an increase in O_2 concentration at equilibrium shifts the equilibrium to the right. However, adding too much O_2 decreases the concentration of SO_3, which slows down the reaction rate. Thus, a degraded 1:1 ratio of SO_2 and O_2 is used to obtain high yields.

Key Points

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

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

- The equilibrium equation is given by

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

Where K_c is equilibrium constant

- The equilibrium can be expressed in terms of the equilibrium partial pressure of gases as K_p.

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

References for Further Information

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

Exercise

1. Choose the correct answer

(i) K_c is independent of;

(a) Temperature
(b) Pressure
(c) Both temperature and pressure
(d) K_p

(ii) For which of the following reactions, K_c has no units of concentration?

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

(iii) For the following reaction

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

We can write?

(a) $K_c > K_p$
(b) $K_c < K_p$
(c) $K_p - K_c = 0$
(d) $K_p - K_c = -1$

(iv) What is the effect of addition of catalyst on an equilibrium mixture?

(a) Reverse reaction (b) Forward reaction

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

(v) NaCl can be purified by passing HCl gas through the _______ solution of NaCl.

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

(vi) $K_c = K_P$ when Δn is equal to;

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

(vii) Consider the following reaction:

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

Yield of sulphur trioxide can be increased by;

a) increasing pressure

b) increasing temperature

c) adding catalyst

d) increasing concentration of oxygen

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

2. Define chemical equilibrium.

3. Define and explain the following terms.

(i) Microscopic events

(ii) Dynamic equilibrium

(iii) Le Chatelier's principle

(iv) Heterogenous equilibria

(v) Homogenous equilibrium

4. Explain industrial application of Le Chatelier's principle using Haber's process as an example.

5. Propose microscopic events that account for observed macroscopic changes that take place during a shift in equilibrium.

6. Write K_c and K_p expressions for the following reactions

(i) $SO_{2(g)} + \frac{1}{2}O_{2(g)} \rightleftharpoons SO_{3(g)}$

(ii) $H_2O_{(g)} + Cl_2O_{(g)} \rightleftharpoons 2HOCl_{(g)}$

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

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

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

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

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

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

7. At a particular temperature $K_p = 0.133$ atm. Which of the following conditions corresponds to equilibrium position for the reaction?

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

(a) $P_B = 0.175$ atm, $P_A = 0.102$ atm

(b) $P_B = 0.064$ atm, $P_A = 0.0308$ atm

(c) $P_B = 0.144$ atm, $P_A = 0.156$ atm (Ans: b and c)

8. Write the expression for K_c and K_p for the following processes.

(a) Blue vitriol is deep blue solid copper (II) sulphate pentahydrate is heated to drive off water vapours to form white solid copper (II) sulphate.

(b) The decomposition of solid phosphorus pentachloride to gaseous phosphorus trichloride and chlorine gas

9. Predict the shift in equilibrium position that will occur for each of the following processes when the volume is reduced.

(i) $PCl_{3(g)} + 3NH_{3(g)} \rightleftharpoons P(NH_2)_{3(g)} + 3HCl_{(g)}$

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

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

10. For each of the following reactions, predict how the value of K_c changes as the temperature is increased.

(a) $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)} \qquad \Delta H^o = +180kJ$

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

(c) $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)} \qquad \Delta H^o = 58kJ$

(d) $CH_{4(g)} + H_2O_{(g)} \rightleftharpoons CO_{(g)} + 3H_{2(g)} \qquad \Delta H^o = 256kJ$

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

12. Describe the behaviour of the following equilibria with the stated changes

(a) Increasing pressure on;

$C_3H_{8(g)} + 5O_{2(g)} \rightleftharpoons 3CO_{2(g)} + 4H_2O_{(g)}$

(b) Adding $I_{2(g)}$ to;

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

(c) Removing heat from;

$CO_{2(g)} \rightleftharpoons CO_{(g)} + \frac{1}{2}O_{2(g)} \qquad \Delta H^o = 284kJ$

(d) Decreasing pressure on;

$C_2H_{6(g)} \rightleftharpoons C_2H_{4(g)} + H_{2(g)}$

13. Consider the following gas phase reaction

$$SO_{2(g)} + Cl_{2(g)} \rightleftharpoons SO_2Cl_{2(g)} + \text{Heat}$$

Describe four changes that would derive the equilibrium to left.

14. How would you change the volume of the following reactions to increase the yield of products.

(i) $Cl_{2(g)} + I_{2(g)} \rightleftharpoons 2ICl_{(g)}$ (ii) $2NO_{2(g)} \rightleftharpoons N_2O_{4(g)}$

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

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

What will happen if:

i) dilute Sodium hydroxide is added to this solution.

ii) dilute hydrochloric acid is added to this solution.

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

17. A propose a set of conditions (temperature, pressure and concentration) for a reversable reaction where the enthalpy change is positive.

Project:

1. Create a presentation where students explain the equilibrium concept, and discuss the factors that influence equilibrium position.
2. Investigate examples of chemical equilibrium in natural systems and prepare a report on it.