13

CHEMICAL EQUILIBRIUM

When reactants are mixed in exact stoichiometric proportion to perform a chemical reaction, it is believed that all the reactants would be converted into products with the release or absorption of energy. This is not true in all cases. Many chemical reactions proceed only to a certain extent and stop. When analysed, the resulting mixture contains both the reactants and products. It is because when reactants combine to form products, the products also start combining to give back the reactants.

When such opposing processes take place at equal rates, no reaction appears to take place and it is said that a state of equilibrium has reached. In this lesson, we will examine many aspects of chemical equilibrium. We shall also discuss how can we control the extent to which a reaction can proceed by changing the various conditions of the equilibrium.

Objective

After reading this lesson you will able to :

- differentiate between static and dynamic equilibrium;

- identify and differentiate between reversible and irreversible reactions;

- explain the reversible reaction occuring at the equilibrium state;

- list and explain characteristics of equilibrium state;

- apply the law of equilibrium and write expression of equilibrium constant for different types of equilibria, namely physical, chemical, homogeneous and heterogenous;

- state and derive the relation between K_c and K_p and carry out some calculations involving them and

- list the factors which affect the state of equilibrium and state and apply Le-Chatelier principle.

**Notes**

13.1 Static and Dynamic Equilibrium

The state equilibrium can be observed in physical and chemical systems. Also, equilibrium can be static or dynamic in nature. A book lying on the table is an example of static equilibrium. The forces of action and reaction cancel each other and no change takes place. Thus it is a case of static equilibrium. On the other hand, when an escalator is coming down and a passenger is going up at the same speed it is a case of dynamic equilibrium. Here, because both are moving in opposite directions and at the same speed, no net change takes place. The equilibrium established in the above examples are in physical systems.

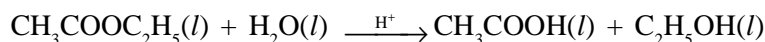## 13.2 Reversible and Irreversible Reactions

Chemical reactions can be classified as : **Reversible and Irreversible reactions.**

13.2.1 Reversible reactions

Consider the reaction between ethanol and acetic acid. When mixed in the presence of dilute sulphuric acid they react and form ethyl acetate and water.

$$C_2H_5OH(l) + CH_3COOH\ (l) \xrightarrow{\ H^+\ } CH_3COO\ C_2H_5(l) + H_2O(l)$$
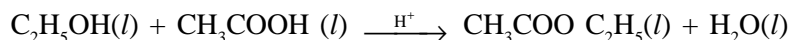
On the other hand, when ethyl acetate and water are mixed in the presence of dilute sulphuric acid the reverse reaction occurs.

$$CH_3COOC_2H_5(l) + H_2O(l) \xrightarrow{\ H^+\ } CH_3COOH(l) + C_2H_5OH(l)$$

It may be noted here that the second reaction is reverse of the first one and under the same conditions, the two reactions occur simultaneously. Such reactions which occur simultaneously in opposite directions are called reversible reactions.

A reaction is said to be reversible if under certain conditions of temperature and pressure, the forward and reverse reactions occur simultaneously.

Reversible reactions are indicated by placing two half arrows pointing in opposite directions ($\rightleftharpoons$) between the reactants and products. Thus the above reaction is more appropriately written as

$$CH_3COOH\ (l) + C_2H_5OH\ (l) \rightleftharpoons CH_3COOC_2H_5\ (l) + H_2O(l)$$
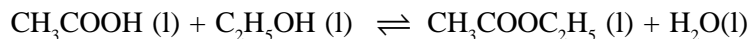
When ethyl acetate and water are formed in the forward reaction the reverse reaction also starts in which ethanol and acetic acid are formed. After some time the concentrations of all the reactants and products become constant. This happens when the rates of forward and reverse reactions become equal; and all the properties of the system become constant. It is said that the system has attained *state of equilibration*. However it may be noted that the state of equilibrium is reached only if the reaction is carried out in a closed system. At the time of equilibrium, forward and reverse reactions are taking place and it is in a state of dynamic equilibrium because no change is taking place.
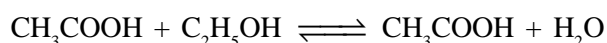
A reversible reaction is said to be in the equilibrium state when the forward and backward reaction occur simultaneously at the same rate in a closed system and the concentrations of reactants and products do not change with time

Notes

A common example of reversible reactions of the type A + B $\rightleftharpoons$ C + D

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOH + H_2O$$

The following graphs Fig. 13.1 shows the equilibrium state in a reversible reaction.
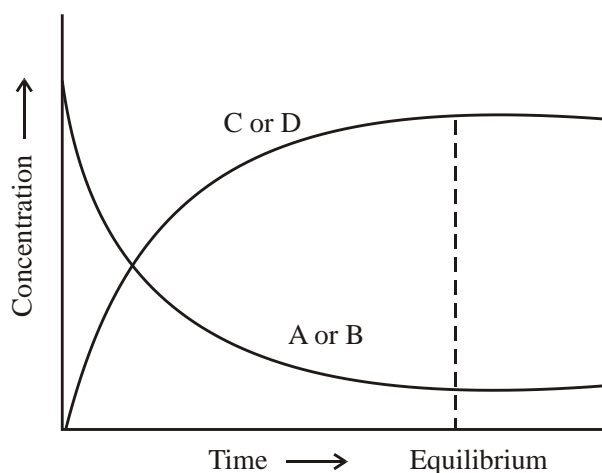

Fig. 13.1 : *Equilibrium in reversible reaction*

The graph depicts that the rate of forward reaction gradually decreases while the rate of backward reaction increase till they become constant and equal to each other.

13.2.2 Irreversible Reactions

Most of the reactions occur only in one direction. They are called *irreversible reactions*. For example when carbon is burnt in air to form carbon dioxide the reaction goes only in one direction i.e. in the direction of formation of carbon dioxide

$$C\ (s) + O_2\ (g) \longrightarrow CO_2\ (g)$$
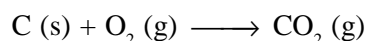
Strictly speaking all reactions are considered to be reversible. But the rate of reaction in one particular direction is extremely small compared to the other. Thus the reaction proceeds practically in one direction to near completion, leaving a negligibly small amount of reactant at the end.

When hydrochloric acid is mixed with sodium hydroxide, a base, in equimolar quantities, a neutralisation reaction takes place; with the formation of salt and water.

$$HCl\ (aq) + NaOH\ (aq) \longrightarrow NaCl\ (aq) + H_2O\ (l)$$
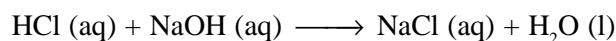
This reaction proceeds to completion in the forward direction. Similarly when a solution of silver nitrate is added to a solution of sodium chloride silver chloride is precipitated immediately.

$$NaCl\ (aq) + AgNO_3\ (aq) \longrightarrow AgCl\ (s) + NaNO_3\ (aq)$$
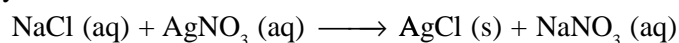
Notes

13.3 Characteristics of Equilibrium State

1. The state of chemical equilibrium is reached in a reversible reaction when;

(i) the temperature of the system attains a constant value.

(ii) the pressure of the system attains a constant value.

(iii) the concentrations of all the reactants and products attain constant values.

The state of equilibrium has following characteristics properties :

(i) Chemical Equilibrium is dynamic in nature

The chemical equalibrium is the result of two equal but opposite processes occurring in the forward and reverse directions and there is no "net" change occurring in the system.

(ii) Equilibrium can be attained from either side

The same state of equilibrium (characterized by its equilibrium constant which is discussed later can be reached whether the reaction is started from the reactants or products side. For example, the same equilibrium

$$N_2O_4 \text{ (g)} \rightleftharpoons 2NO_2 \text{ (g)}$$
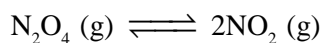
is established whether we start the reaction with N_2O_4 or NO_2.

(iii) Equilibrium can be attained only in a closed system

Equilibrium can be attained only if no substance among, reactants or products, is allowed to escape i.e. the system is a closed one. Any system consisting of gaseous phase or volatile liquids must be kept in a closed container, e.g.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$
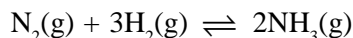
A system consisting of only non-volatile liquid and solid phases can be kept even in an open container because such substances have no tendency to escape, e.g.

$$FeCl_3(aq) + 3 \, NH_4SCN(aq) \rightleftharpoons Fe \, (SCN)_3 \, (s) + 3 \, NH_4Cl(aq)$$
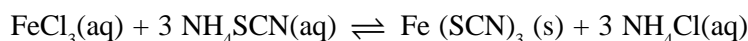
**(iv) A catalyst can not change the equilibrium state**

Addition of a catalyst speeds up the forward and reverse reactions by same extent and help in attaining the equilibrium faster. However, the equilibrium concentrations of reactants and products are not affected in any manner.

13.4 Equilibrium in Physical Processes; Phase Equilibrium

State of equilibrium can also be reached in physical processes.

13.4.1 Liquid – Vapour Equilibrium

Let us take some quantity of a liquid in an empty container and close it. Initially the vapour pressure above the liquid will be zero. The liquid will evaporate and its vapour will fill the empty space above it.
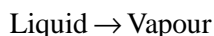
Liquid $\rightarrow$ Vapour

Notes

The rate of evaporation is maximum in beginning. As vapours build up, its pressure increases and the rate of evaporation slows down. Also the reverse process of condensation begins (Fig. 13.2).
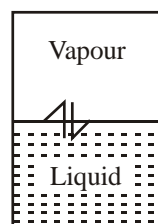
$$\text{Vapour} \rightarrow \text{Liquid}$$

Fig. 13.2 : *Liquid Vapour equilibrium*

and its rate gradually increases with the increase in the vapour pressure. After some time the two rates (of evaporation and condensation) become equal and the following equilibrium is established.

$$\text{Liquid} \rightleftharpoons \text{Vapour}$$

At equilibrium the vapour pressure reaches its maximum value and is known as the **saturated vapour pressure** or simply the vapour pressure. At a fixed temperature, each liquid has its own characteristic vapour pressure. The vapour pressure of a liquid increases with rise in temprature.

13.4.2 Solid – Vapour Equilibrium

Volatile solids sublime form vapour. The situation is just similar to the liquid vapour system. When kept in a closed container at a constant temperature the following equilibrium is established.

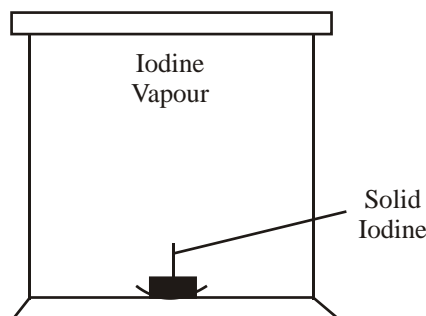$$\text{Solid} \rightleftharpoons \text{Vapour}$$

Fig. 13.3 : *Solid vapour equilibrium*

Such an equilibrium can be established by keeping some solid iodine in a gas jar covered with a lid. (Fig. 13.3). Gradually the purple coloured iodine vapours fill the jar and the following equilibrium is established.
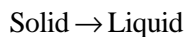
$$I_2(s) \rightleftharpoons I_2(g)$$
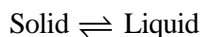
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13.4.3 Solid – Liquid Equilibrium

Below its freezing point a liquid freezes spontaneously

Liquid $\rightarrow$ Solid
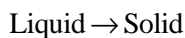
When heated above its melting point the solid melts spontaneously :

Solid $\rightarrow$ Liquid

At the melting point, the two phases are in equilibrium

Solid $\rightleftharpoons$ Liquid

because the above two processes occur simultaneously and at the same rate. Such an equilibrium is characterized by its temperature i.e. the melting point of the solid.

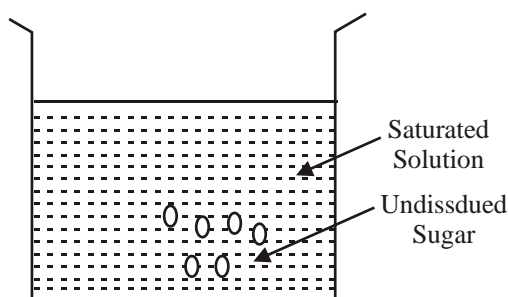### 13.4.4 Solute – Solution Equilibria

Fig. 13.4 : *Solute - Solution Equilibrium*

When sugar crystals are put in a saturated solution of sugar in water; it will appear that no change is taking place and sugar appears to remain undissolved. Actually, the undissolved sugar does dissolve in the saturated sugar solution; and an equal amount of sugar seperates out from the solution. The solid sugar and the sugar solution form an equilibrium system which is dynamic in nature.

sugar (s) $\rightleftharpoons$ sugar solution (saturated)
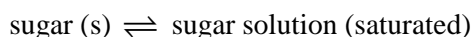
The equilibrium is established when the rate of dissolution of sugar becomes equal to the rate of crystallisation. In general such equilibrium can be represented as

solute (s) $\rightleftharpoons$ solution (saturated)

This equilibrium is known as **Solubility Equilibrium.**

13.4.5 Phase and Phase Equilibrium

You must have noticed in each of the above equilibria the system consists of two distinct parts; solid, liquid, solution or vapour. Each of these parts is called a phase.

A phase is defined as a homogenous part of a system which has uniform composition and properties throughout.

A phase is not the same as physical state. A mixture of two solids, even when powdered

finely is a two phase system. This is because particles of the two solids have different chemical compositions and physical properties. Completely miscible liquids, solutions and all gaseous mixture constitute only one phase each.

All the cases of physical equilibrium are in fact the systems in which different phases are in equilibrium; only if they contain, at least one common component. A dynamic exchange of the common component between two phases takes place. When the rates of exchange becomes equal the equilibrium is established. In solid solute and solution equilbrium the example given earlier, sugar is the common component.

13.5 Equilibrium in Homogeneous and Heterogeneous Systems

13.5.1 Homogeneous and Heterogeneous Systems

Homogeneous system is one which has one phase. It has the same chemical composition and uniform properties throughout. It is formed by particles of molecular size only. Pure solids, liquids, gases and solutions are the examples of homogeneous systems.

A system consisting of only one phase is called a homogeneous system

Heterogeneous system, on the other hand has at least two phases – a mixture of solids or immiscible liquids constitutes a heterogeneous system.

Any system consisting of two or more phases is called heterogeneous system
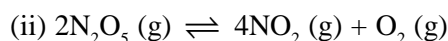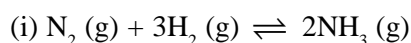
13.5.2 Homogeneous and Heterogeneous Equilibrium Systems

Equilibrium can be established in either type of systems. Since all physical equilibria involve at least two phases, therefore these are all examples of heterogeneous equilibrium. But chemical equilibrium can be homogeneous or heterogeneous in nature. It is homogeneous if both the reactants and products are present only in one phase gas or liquid and heterogeneous if present in more than one phase. In the following sections we shall study such systems.

13.5.3 Homogeneous Chemical Equilibrium System

(a) Gas – Phase homogeneous systems

Such systems contain only gaseous reactants and products. Since all gaseous mixtures are homogeneous in nature they constitute only one phase. Following are examples of this type of equilibrium:

(i) $N_2 (g) + 3H_2 (g) \rightleftharpoons 2NH_3 (g)$

(ii) $2N_2O_5 (g) \rightleftharpoons 4NO_2 (g) + O_2 (g)$

(b) Liquid – Phase homogeneous systems

These are the systems in which both the reactants and products are present in only one liquid phase (as a solution) for example :

(i) $CH_3 COOH (l) + C_2H_5OH (l) \xrightleftharpoons{H^+} CH_3COOC_2H_5(l) + H_2O (l)$

(ii) $KCN (aq) + H_2O (l) \rightleftharpoons HCN (aq) + KOH (aq)$
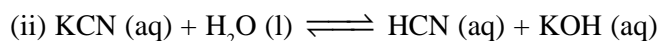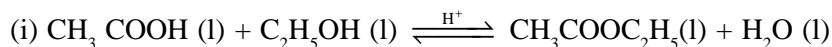
Notes

13.5.4 Heterogeneous Chemical Equilibrium Systems

The systems in which reactants and products are present in more than one phase belong to this type. For example :

(i) $Fe\ (s) + 4H_2O\ (g) \rightleftharpoons Fe_3O_4\ (s) + 4H_2\ (g)$

(ii) $CaCO_3\ (s) \rightleftharpoons CaO\ (s) + CO_2\ (g)$

Intext Questions 13.1

1. What is a reversible reaction? Give two examples.

    ....

2. When does a reaction reach equilibrium state?

    ....
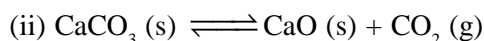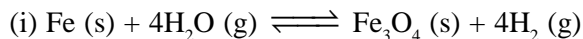
3. How would you know whether a system has reached the equilibrium state or not?

    ....

4. Give two examples of physical equilibrium.

    ....

5. Give two example each of chemical homogeneous and heterogeneous equilibria.

    ....

13.6 Quantitative Aspect of Equilibrium State

13.6.1 Law of Equilibrium and Concentration Equilibrium Constant

Consider the following equilibrium

$$H_2(g) + I_2(g) \rightleftharpoons 2HI\ (g)$$
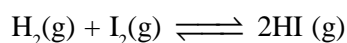
At equilibrium the concentrations of H_2, I_2 and HI become constant. Also, it has been found experimentally that irrespective of the starting concentrations of H_2 and I_2 the following ratio of concentration terms always remains constant.

$$K_c = \frac{[HI]^2}{[H_2][I_2]}$$

Here $[H_2]$, $[I_2]$ and [HI] represent the equilibrium molar concentrations of H_2, I_2 and HI respectively and K_e is called the *concentration equilibrium constant* (some times it is written as simply *K*). In general, for reversible reaction

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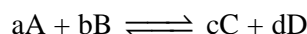
Notes

at equilibrium, the following ratio of concentration terms always remains constant at a given temperature.

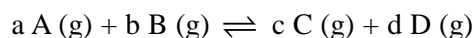$$K_c = \frac{[C]^c\ [D]^d}{[A]^a\ [B]^b}$$

The above relation is known as the **law of equilibrium.** It may be noted here that all the concentrations values in the law of equilibrium are the equilibrium concentrations of reactants and products. The numerator of the law of equilibrium is the product of equilibrium molar concentrations of products, each term being raised to the power equal to its stoichiometric coefficient in the chemical equation and the denominator contains products of similar concentration terms of reactants.

13.6.2 Pressure Equilibrium Constant K_p

In case of gases their partial pressures can also be used in place of molar concentrations (since the two are directly proportional to each other) in the law of equilibrium. The new equilibrium constant, K_p, is called the pressure equilibrium constant. For the reaction between H_2 and I_2, K_p is given by

$$K_p = \frac{p^2_{HI}}{p_{H_2} \times p_{I_2}}$$

Here p_{H_2}, p_{I_2} and p_{HI} are the **equilibrium partial pressures** of H_2, I_2 and HI respectively. For the general gas phase reaction :

$$a\,A\,(g) + b\,B\,(g) \rightleftharpoons c\,C\,(g) + d\,D\,(g)$$

it is given by :

$$k_p = \frac{p_C^c \times p_D^d}{p_A^a \times p_B^b}$$

13.6.3 Relation between K_p and K_c

For a general gas phase reaction at equilibrium
$$a\,A\,(g) + b\,B\,(g) \rightleftharpoons c\,C\,(g) + d\,D\,(g)$$
The pressure and concentration equilibrium constants Kp and Kc are
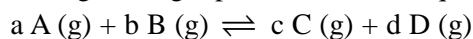
$$k_p = \frac{p_C^c \times p_D^d}{p_A^a \times p_B^b} \quad \text{and} \quad k_c = \frac{[C]^c\ [D]^d}{[A]^a\ [B]^b}$$

For a gaseous substance i, the ideal gas equation is

$$p_i V = n_i RT$$

where p_i and n_i are its partial pressure and amount in a gaseous mixture and V and T are its volume and temperature and R is the gas constant. The relation may be written as

$$p_i = \frac{n_i}{V} RT = c_i\ RT$$

Where c_i is the molar concentration or molarity of 'i' expressed in moles per litre. This relation can be used for replacing the partial pressure terms in the expression for K_p.

$$K_p = \frac{(c_C \, RT)^c \, (c_D RT)^d}{(c_A \, RT)^a \, (c_B \, RT)^b}$$

$$= \frac{c_C^c \, c_D^d}{c_A^a \, c_B^b} \, (RT)^{(c+d)-(a+b)}$$

Notes

Using the square bracket notation for molar concentration the relation can be written as

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

$$= K_c (RT)^{\Delta n_g}$$

where Δn_g is the change in the moles of gaseous substances in the reaction and is equal to the difference in the moles of gaseous products n_P and the moles of gaseous reactants, n_R. Δn_g may be zero positive or negative.

(i) In the reaction

$$H_2 \, (g) + I_2 \, (g) \rightleftharpoons 2HI \, (g)$$
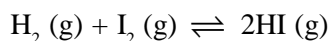
Here n_P = moles of the gaseous product is equal to 2

n_R = moles of gaseous reactant H_2 and I_2 is equal to 2 (as 1 + 1).

Hence $\Delta n_g = n_P - n_R = 2 - 2 = 0$

$$\Delta n_g = 0$$

(ii) In the reaction

$$N_2 \, (g) + 3H_2 \, (g) \rightleftharpoons 2NH_3 \, (g)$$
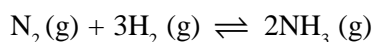
$$n_P = 2, \, n_R = 1 + 3 = 4$$

and $\Delta n_g = 2 - 4 = -2$

(iii) In the reaction involving solids and gases

$$CaCO_3 \, (s) \rightleftharpoons CaO \, (s) + CO_2 \, (g)$$
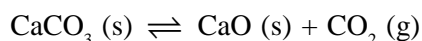
$$\Delta n_g = 1$$

13.6.4 Expressions of Equilibrium Constant for Some Reactions

The law of equilibrium can be applied to write down expressions of K_c and K_p for some reactions

13.7 Homogeneous Equilibria

(i) Decomposition of N_2O_4

$$N_2O_4 \, (g) \rightleftharpoons 2 \, NO_2 \, (g)$$

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

(ii) Oxidation of sulphur dioxide

$$2SO_2 \, (g) + O_2 \, (g) \rightleftharpoons 2SO_3 \, (g)$$

$$K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]} \; ; K_p = \frac{p_{SO_3}^2}{p_{SO_2}^2 \cdot p_{O_2}}$$

(iii) Esterification of acetic acid with ethanol

$$CH_3COOH \, (I) + C_2H_5OH \, (I) \rightleftharpoons CH_3COOC_2H_5 \, (I) + H_2O(l)$$
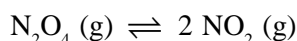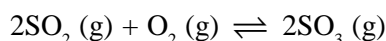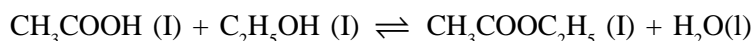
$$K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$$

In this reaction no gas is involved, therefore expression for K_p is meaningless.

13.7.1 Heterogeneous Equilibrium

Consider the following equilibrium

$$CaCO_3 \, (s) \rightleftharpoons CaO \, (s) + CO_2 \, (g)$$

According to the law of equilibrium

$$K_c = \frac{[CaO][CO_2]}{[CaCO_3]}$$

Here $CaCO_3$ and CaO are pure solids. The concentration of any solid is constant at a fixed temperature therefore these are not written in expression for equilibrium constant for hetrogenous reactions. Equilibrium constants for the reaction can be written as

$$K_c = [CO_2] \text{ and } K_p = Pco_2$$

Following are some more examples of heterogenous equilibrium

(i) Reaction between iron and steam

$$3 \, Fe \, (s) + 4H_2O \, (g) \rightleftharpoons Fe_3O_4 \, (s) + 4H_2 \, (g)$$
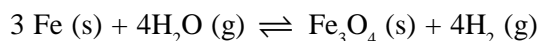
$$K_c = \frac{[H_2]^4}{[H_2O]^4} \; ; K_p = \frac{p_{H_2}^4}{p_{H_2O}^4}$$

(ii) Liquid – Vapour Equilibrium

$$H_2O(I) \rightleftharpoons H_2O \, (g)$$

$$K_c = [H_2O; g] \; ; K_p = p_{H_2O} \, .$$

Notes
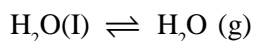
13.8 Characteristics of Equilibrium Constant

13.8.1 Equilibrium Constant and Chemical Equation

The expression of equilibrium constant depends upon the manner in which the chemical equation representing it is written. For the reaction

$$H_2 \text{ (g)} + I_2 \text{ (g)} \rightleftharpoons 2HI \text{ (g)}$$
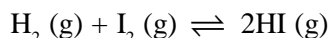
The equilibrium constant K is given by $K = \dfrac{[HI]^2}{[H_2][I_2]}$

When the same reaction is written as

(a) $\dfrac{1}{2} H_2 \text{ (g)} + \dfrac{1}{2} I_2 \text{ (g)} \rightleftharpoons HI \text{ (g)}$
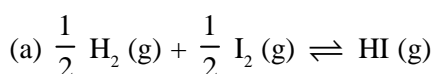
the corresponding equilibrium constant K_1 is given by

$$K_1 = \dfrac{[HI]}{[H_2]^{\frac{1}{2}}[I_2]^{\frac{1}{2}}}$$

It may be noted that equilibrium constants K and K_1 are related as $K_1 = \sqrt{K}$

(b) When the reaction is written as reverse

$$2HI \text{ (g)} \rightleftharpoons H_2 \text{ (g)} + I_2 \text{ (g)}$$
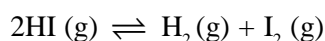
$$K_2 = \dfrac{[H_2][I_2]}{[HI]^2}$$

Here it can be seen that

$$K_2 = \dfrac{1}{K}$$

Similar relationship is also observed in the pressure equilibrium constant K_p. Thus the expression of equilibrium constant depends on how the reaction is expressed in the form of a chemical equation.

13.8.2 Units of Equilibrium Constant

Units of equilibrium constant K_c or K_p depend upon the fact whether during the reactions there is any change in the moles of substance or not.

(a) **The reactions in which there is no change** in moles of substance i.e. $\Delta n = 0$.

The equilibrium constant for such reaction has no units. For example in the reaction between H_2 and I_2

$$H_2 \text{ (g)} + I_2 \text{ (g)} \rightleftharpoons 2HI \text{ (g)}$$
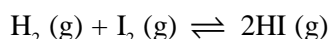
$$K_c = \frac{[HI]^2}{[H_2][I_2]} \qquad\qquad K_p = \frac{p_{HI}^2}{p_{H_2} \cdot p_{I_2}}$$

$$K_c = \frac{(mol\ L^{-1})^2}{(mol\ L^{-1})(mol\ L^{-1})} \qquad K_p = \frac{bar^2}{(bar)(bar)}$$

$\therefore$ Hence K_p and K_c have no units in such cases.

(b) The reaction where there is change in the moles of substance i.e. $\Delta n \neq 0$.

The equilibrium constant for such reactions has units which depend upon the change in moles of substances.

For example :

$$N_2\ (g) + 3H_2\ (g) \rightleftharpoons 2NH_3\ (g)$$
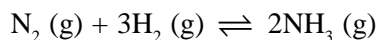
$$\Delta n = \Delta_{n_p} - \Delta_{n_R}$$

$$= 2 - 4 = -2$$

The units of K_c for this reaction would be $(mol\ L^{-1})^{-2}$ or $L^2\ mol^{-2}$ and those of K_p would be bar^{-2} as shown below :

The equilibrium constant for such reactions are

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} \qquad\qquad K_p = \frac{p_{NH_3}^2}{p_{N_2} \times p_{H_2}^3}$$

$$Kc = \frac{(mol\ L^{-1})^2}{(mol\ L^{-1})(mol\ L^{-1})^3}$$

$$= (mol\ L^{-1})^{-2}$$

$$= L^2\ mol^{-2}$$

$$Kp = \frac{pressure^2}{pressure.\ pressure^3}$$

$$= pressure^{-2}$$

$$= bar^{-2}$$

For the reaction $PCl_5\ (g) \rightleftharpoons PCl_3\ (g) + Cl_2\ (g)$

$\Delta n = 2 - 1 = 1$. Therefore,

The units for K_c and K_p are

$K_c = mol\ L^{-1}$ and $K_p = bar$

Notes

13.8.3 Significance of the Magnitude of K

The equilibrium constant of a reaction has a constant and characteristic value at a given temperature. The changes in starting concentration, pressure and the presence of a catalyst do not change the value of the equilibrium constant. However if the temperature is changed. The value of the equilibrium constant also changes.

The magnitude of the equilibrium constant is a measure of the extent upto which a reaction proceeds before the equilibrium is reached. The magnitude of K is large when the products are present in larger amounts than the reactants in the equilibrium mixture. For the reaction

$$H_2 \text{ (g)} + I_2 \text{ (g)} \rightleftharpoons 2 \text{ HI (g)} \qquad K_c = 90 \text{ at 298 K}$$

and for $2CO \text{ (g)} + O_2 \text{ (g)} \rightleftharpoons 2 CO_2 \text{ (g)} \qquad K_c = 2.2 \times 10^{22}$ at 1000 K.

A large value of K_c for the second reaction indicates that amount of products is much more than the reactants present at the time of equilibrium. Thus the magnitude of equilibrium constant tells us about the position of the equilibrium.

13.8.4 Calculation of Equilibrium Constants

Equilibrium constants K_c and K_p can be calculated if the equilibrium concentrations or partial pressures are known or can be obtained from the given data. The following examples illustrate the calculations.

Example 13.1 : Calculate the equilibrium constant for the reaction

$$A \text{ (g)} + B \text{ (g)} \rightleftharpoons C \text{ (g)} + D \text{ (g)}$$
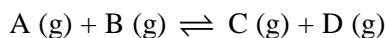
If at equilibrium 1 mol of A, 0.5 mole of B, 3.0 mole of C and 10 mol of D are present in a one litre vessel.

Solution : From the law of equilibrium

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

Since the volume of the vessel is one litre, the number of moles of A, B, C and D are equal to their concentrations. Thus

$[A] = 1 \text{ mol L}^{-1}$, $[B] = 0.5 \text{ mol L}^{-1}$, $[C] = 3.0 \text{ mol L}^{-1}$ and $[D] = 10 \text{ mol L}^{-1}$ and

$$K_c = \frac{(3.0 \text{ mol L}^{-1})(10 \text{ mol L}^{-1})}{(1 \text{ mol L}^{-1})(0.5 \text{ mol L}^{-1})}$$

$$= \frac{3.0 \times 10}{1 \times 0.5} = 60$$

Example 13.2 In an experiment carried out at 298 K, 4.0 mol of NOCl were placed in a 2 litre flask and after the equilibrium was reached 1.32 mol of NO were formed. Calculate K_c at 298 K for the reaction

$$2NOCl \text{ (g)} \rightleftharpoons 2 NO \text{ (g)} + Cl_2 \text{ (g)}$$
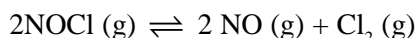
Notes

Solution Calculation of equilibrium concentrations

(i) $[NO] = \dfrac{\text{No. of moles of NO}}{\text{Volume}} = \dfrac{1.32 \text{ mol}}{2L} = 0.66 \text{ mol L}^{-1}$

(ii) $[Cl_2] = \dfrac{\text{No. of moles of Cl}_2}{\text{Volume}} = \dfrac{\frac{1}{2}(\text{No. of moles of NO})}{\text{Volume}} = \dfrac{1.32 \text{ mol}}{2 \times 2L} = 0.33 \text{ mol L}^{-1}$

(iii) $[NOCl] = \dfrac{\text{No. of moles of NOCl}}{\text{Volume}} = \dfrac{(\text{Initial moles - moles decomposed})}{\text{Volume}}$

$= \dfrac{(4.0 - 1.32) \text{ mol}}{2 \text{ L}} = \dfrac{2.68 \text{ mol}}{2 \text{ L}} = 1.34 \text{ mol L}^{-1}$

For the reaction

$$2NOCl \text{ (g)} \rightleftharpoons 2NO \text{ (g)} + Cl_2 \text{ (g)}$$
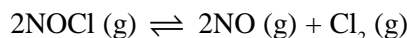
$K_c = \dfrac{[NO]^2 [Cl_2]}{[NOCl]^2} = \dfrac{(0.66 \text{ mol L}^{-1})^2 (0.33 \text{ mol L}^{-1})}{(1.34 \text{ mol L}^{-1})^2} = \dfrac{(0.66)^2 \times 0.33}{(1.34)^2}$

$= 0.080 \text{ mol L}^{-1}$

$K_c = 0.080 \text{ mol L}^{-1}$

Example 13.3 : 2 moles of HI were heated in a vessel of one litre capacity at 713 K till the equilibrium was reached. At equilibrium HI was found to be 25% dissociated. Calculated K_c and K_p for the reaction.

Solution Initial moles of HI = 2

Moles of HI dissociated $= \dfrac{25 \times 2}{100} = 0.5 \text{ mol}$

Moles of HI at equilibrium $= 2.0 - 0.5 = 1.5 \text{ mol}$

The dissociation of HI occurs as

	2HI (g) $\rightleftharpoons$	H$_2$ (g) +	I$_2$ (g)
Initial moles	2	0	0
Equilibrium moles	(2 – 0.5)	0.25	0.25
	1.5 mol	0.25 mol	0.25 mol
Volume of reaction vessel	1L	1L	1L
Equilibrium concentration	1.5 mol L^{-1}	0.25 mol L^{-1}	0.25 mol L^{-1}

For the reaction

Notes

$$K_c = \frac{[H_2][I_2]}{[HI]^2} = \frac{(0.25 \text{ mol L}^{-1})(0.25 \text{ mol L}^{-1})}{(1.5 \text{ mol L}^{-1})^2}$$

$$= \frac{(0.25)^2}{(1.5)^2} = 0.028$$

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

For this reaction $\Delta n_g = n_p - n_R = 2 - 2 = 0$

$\therefore K_p = K_c = 0.028$

Example 13.4 : Calculate K_p for the reaction $COCl_2 \rightleftharpoons CO + Cl_2$ in atm and Nm^{-2}. The equilibrium partial pressures of $COCl_2$, CO and Cl_2 are 0.20, 0.16 and 0.26 atm respectively.

(1 atm = 101300 Nm^{-2})

Solution : (i) K_p **in atmospheres**

$COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$

$$K_p = \frac{p_{co} \times p_{Cl_2}}{p_{COCl_2}} = \frac{(0.16 \text{ atm})(0.26 \text{ atm})}{(0.20 \text{ atm})} = \frac{0.16 \times 0.26}{0.20} \text{ atm}$$

$$= 0.21 \text{ atm}.$$

(ii) **Kp in Nm^{-2}**

$K_p = 0.21$ atm and 1 atm = 101300 Nm^{-2}

$\therefore K_p = (0.21 \text{ atm})(101300 \text{ Nm}^{-2} \text{ atm}^{-1}) = 21273 \text{ Nm}^{-2}$

Example 13.5 : When equal number of moles of ethanol and acetic acid were mixed at 300 K, two-third of each had reacted when the equilibrium was reached. What is the equilibrium constant for the reaction?

$$CH_3COOH (l) + C_2H_5OH (l) \rightleftharpoons CH_3COOC_2H_5 (l) + H_2O (l)$$
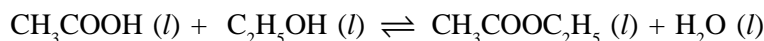
Solution : Let n moles each of acetic acid and ethanol be mixed initially. Then the

number of moles each reacted $= \dfrac{2}{3} n$.

Let V be the volume of the reaction mixture in litres.
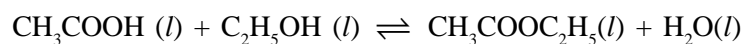
	$CH_3COOH (l)$	$+ C_2H_5OH (l)$	$\rightleftharpoons CH_3COOC_2H_5(l)$	$+ H_2O(l)$
Initial mole	n	n	0	0
Equilibrium concentration in moles	$(n - \dfrac{2}{3}n)$	$(n - \dfrac{2}{3}n)$	$\dfrac{2}{3}n$	$\dfrac{2}{3}n$
	$\dfrac{1}{3}n$	$\dfrac{1}{3}n$	$\dfrac{2}{3}n$	$\dfrac{2}{3}n$
Equilibrium concentration	$\dfrac{n}{3V}$	$\dfrac{n}{3V}$	$\dfrac{2n}{3V}$	$\dfrac{2n}{3V}$

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

$$= \frac{\left(\dfrac{2n}{3V}\right)\left(\dfrac{2n}{3V}\right)}{\left(\dfrac{n}{3V}\right)\left(\dfrac{n}{3V}\right)} = 2 \times 2 = 4$$

$$K_c = 4$$

Intext Questions 13.2

1. For a reversible reaction

   $$2A + B \rightleftharpoons 3C + 3D$$

   Write the expression for the equilibrium constant

   ....

2. What is the relation between K_p and K_c.

   ....

3. (i) Apply the law of equilibrium to the following and write the expression for K_p and K_c.

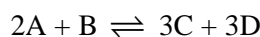   (a) CO_2 (g) + H_2 (g) $\rightleftharpoons$ CO (g) + H_2O (g)

   (b) I_2 (s) $\rightleftharpoons$ I_2 (g)
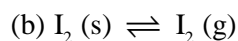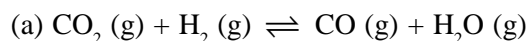
   (ii) For the above reaction write equation for K_p and K_c.

   ....

4. The equilibrium constant for the reactions
   (i) N_2 (g) + $3H_2$ (g) $\rightleftharpoons$ $2NH_3$ (g)

   (ii) $\dfrac{1}{3}N_2(g) + H_2(g) \rightleftharpoons \dfrac{2}{3}NH_3$
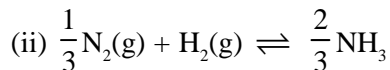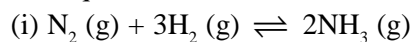
   are K_1 and K_2 respectively. What is the relation between them.

   ....

5. What is the significance of the magnitude of equilibrium constant?

   ....

13.9 Factors Affecting Equilibrium State

Supposing a reaction has reached the equilibrium state and then some conditions like concentrations, temperature, pressure etc. are changed, would it be affecting the equilibrium state. If yes how?

In this section, we shall discuss these questions.

The state of equilibrium is in a dynamic balance between forward and backward reaction. This balance can be disturbed by changing concentration, temperature or pressure. If done so a certain net change occurs in the system. The direction of change can be predicted with the help of Le-Chatelier principle.

13.9.1 Le Chatelier Principles

It states that when a system in equilibrium is disturbed by a change in concentration, pressure or temperature, a 'net' change occurs in it in a direction that tends to decrease the disturbing factor.

The prinicple can be applied to various situations.

13.9.2 Change in Concentration

Consider the state of equilibrium for the formation of ammonia from nitrogen and hydrogen.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g), \ \Delta H = -92.4 \text{ kJ/mol}$$

The concentration of nitrogen, hydrogen and ammonia become constant at the point of equilibrium. Now if any amount of reactants or ammonia is added or removed their concentration will change and the equilibrium will get disturbed.

(i) **Increase concentration of reactant :** When the concentration of either nitrogen or hydrogen is increased; a net forward reaction will take place which consumes the added reactant.

(ii) Increase in the concentration of any product : If the concentration of product ammonia is increased, a net backward reaction would take place to utilise the added ammonia.

13.9.3 Change in Pressure

Change in pressure affects equilibrium involving gaseous phase either in a homogeneous or hetrogeneons system.

Le Chatelier prinicple for systems involving gases can be studied as follows :

(i) When the number of moles of products is more than the total number of moles of reactants as in the following system

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$
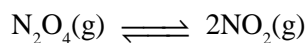
Increase in total pressure keeping the temperature constant, will cause a decrease in volume. This means that the number of moles per unit volume will increase. A net change will take place in the equilibrium in the direction where the number of moles decrease i.e. backward direction.

(ii) When the number of moles of products is less than reactants. As in the following case

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$
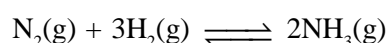
According to Le Chatelier's principle increase in total pressure will bring a net change to the equilibrium in the direction where the total number of moles is decreasing i.e. to the product side as $\Delta n_g = 2$. Decrease in total pressure will bring the net change to equilibrium in the direction where the total number of moles is increasing i.e. backward direction.

(iii) When there is no change in the total number of moles of reactant and product as in the following state of equilibrium.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI$$

There is no net change in equilibrium state when pressure is changed.

13.9.4 Change of Temperature

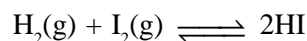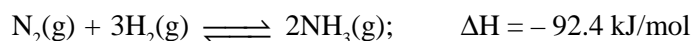According to Le Chatelier prinicple when the temperature is changed (increased or decreased) the equilibrium system reacts to nullify the change in heat content. However, the net change in equilibrium is directed by the exothermic or endothermic nature of reaction.

(i) Exothermic equilibrium : For the following system of equilibrium of exothermic nature :

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g); \qquad \Delta H = -92.4 \text{ kJ/mol}$$

according to Le Chatelier prinicple increase in temperature brings a net change in the equilibrium state in that direction where this extra heat is consumed. The net change is in the backward direction and some ammonia will decompose producing nitrogen and hydrogen. Similarly if the temperature is decreased the equilibrium shifts to the forward direction.

(ii) **Endohermic equilibrium**

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g); \qquad \Delta H = +180.7 \text{ kJ/mol}^{-1}$$
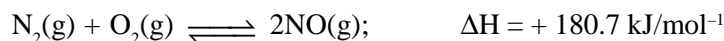
If the temperature is increased the added heat will be absorbed by the reactant and the net change takes place to the equilibrium in the forward direction. If the temperature in decreased it will bring a 'net' change to equilibrium in the backward direction i.e. direction in which it is exothermic.

Addition of a Catalyst : It does not affect the equilibrium. However it helps to achieve the equilibrium faster.

13.9.5 Applications of Le Chatelier's Principle

It can be applied to physical as well as chemical equilibria

(A) Physical Equilibria

(1) Melting of Ice

$$\text{Ice} \rightleftharpoons \text{Water} ; \qquad \Delta H = +6 \text{ kJ/mol}^{-1}$$

The change of ice to water is endothermic process. According to Le Chatelier principle if the temperature is increased the net change will take place in the forward direction some ice will melt into water.

Notes

When the pressure is increased on the equilibrium system, then the volume should decrease; according to Le Chatelier principle the net change in equilibrium takes place in the forward direction and ice melts. Therefore, ice melts on increasing the pressure.

(2) Vaporization of Water

$$\text{Water(l)} \rightleftharpoons \text{Water vapour;} \quad \Delta H = + \text{ve}$$
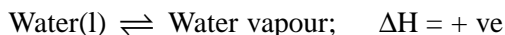
This process occurs with a large increase in volume since $\Delta n_g = 1 - 0 = + 1$, and it occurs with absorption of heat.

Increasing the temperature results in more vapour formation (endothermic process). Since $\Delta n_g = + 1$, increase in pressure results in a net change in equilibrium in the backward direction as the volume of water vapours is more than that of liquid water for a given mass of water.

(3) Solubility Equilibrium

The equilibrium is

Solute (s) $\rightleftharpoons$ Solute (solution)

The process of dissolution can be endothermic or exothermic. In case of solutes like KCl, KNO_3 and NH_4Cl, ΔH is positive (endothermic) and more solute will dissolve on heating. Thus, the solubility increases with rise in temperature. In case of solutes like KOH and NaOH the ΔH is negative (exothermic) and their solubility decreases on heating.

(B) Chemical Equilibra

(1) Favourable Conditions for Synthesis of Ammonia : This reaction is of great industrial importance. During the synthesis of ammonia such conditions are maintained which favour the 'net' forward reaction namely low temperature and high pressure. Addition of catalyst makes the reaction occur fast. Besides, nitrogen and hydrogen gases are continuously fed into the reaction chamber and ammonia is continuously removed. All this keeps the system under stress and equilibrium is never permitted to be attained, so that the synthesis of ammonia continues to occur.

In industry the reaction is carried out at 450^0C and 200 atm pressure in the presence of finely divided iron (catalyst) and molybdenum (promotor)

(2) Formation of SO_3

The reaction

$$2SO_2 (g) + O_2 (g) \rightleftharpoons 2SO_3 (g) ; \Delta H = - \text{ve}$$
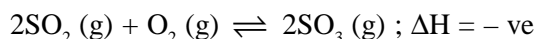
is extothermic and $\Delta n_g = 2 - 3 = - 1$. Formation of SO_3 will be favoured by high pressure and low temperature in the presence of a catalyst.

(3) Formation of NO

The reaction

$$N_2 (g) + O_2 (g) \rightleftharpoons 2NO (g) ; \quad \Delta H = + \text{ve}$$

is endothermic and $\Delta n_g = 2 - 2 = 0$. The reaction is not affected by pressure changes and is favoured at high temperature. Presence of a suitable catalyst would be helpful.

Intext Questions 13.3

1. What is Le Chatelier' principle?

    ....

2. What are the factors that can affect a system at equilibrium?

    ....

3. What will happen to solid-vapour equilibrium when the temperature and pressure are decreased.

    ....

4. (a) Which of the following will result in 'net' forward reaction in case of

    $A (g) + 2B (g) \rightleftharpoons C (s) + D (g)$; $\Delta H = +$ ve

    (i) addition of C

    (ii) addition of A

    (iii) decrease in pressure

    (iv) increase in temperature

    ....

    (b) What are the most favourable conditions for the formation of C and D?

    ....

What You Have Learnt

*   A chemical reaction is said to be reversible under certain conditions, if along with the reactants forming the products, the products also react and form back the reactants simultaneously.

*   Reversible reactions do not reach completion stage and result in a state of equilibrium which is reached when two opposite processes occur at the same rate.

*   The macroscopic properties of the system do not change once the equilibrium has been established.

*   Irreversible reactions are in fact the reversible reactions in which the equilibrium is reached only when a negligible amount of the reactants is left unreacted.

*   Chemical equilibrium is dynamic in nature. It can be attained by starting the reaction from any side and only in a closed system.

*   When equilibrium is reached as a result of two opposite physical changes, it is called physical equilibrium and when as a result of two opposite chemical changes it is called chemical equilibrium.

Notes

- A phase is a homogeneous system or a part of a system which has same composition and uniform properties throughout. It is not same as physical state.

- A system with only one phase is called a homogeneous system and the one with more than one phases is called heterogeneous system.

- Chemical equilibrium can be homogeneous or heterogeneous while physical equilibrium is always heterogeneous.

- For a general reaction $aA + bB \rightleftharpoons cC + dD$ according to the law of equilibrium, the equilibrium constant K is given by the expression

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

- Concentration equilibrium constant K_c is obtained when molar concentration are used for calculating K. Concentrations of pure solids and liquids are constant and are not included in the expression of K_c.

- In case of gaseous systems, the concentration of gases are expressed in terms of their partial pressures. The equilibrium constant thus obtained is called the pressure equilibrium constant, K_p.

- The relation between K_p and K_c is $= K_c \, (RT)^{\Delta n_g}$ where Δn_g is the change in the number of moles of gaseous substances during the reaction.

- Expression of equilibrium constant depends upon how the chemical equation is written for the reaction.

- Magnitude of the equilibrium constant is a measure of how close the reaction is to the completion stage.

- Units of K depends upon the change in the number of moles of the substances during the reaction.

- Concentration, pressure and temperature can affect the equilibrium systems and the affect can be qualitatively predicted by Le Chatelier's principle which states that when a system at equilibrium is disturbed by changing concentration, pressure or temperature, a 'net' change occurs in the direction that tends to neutralize the effect of the disturbing factor.

- Changes in concentration and pressure do result in some chemical reaction, but the value of the equilibrium constant is not changed.

- A catalyst does not change the equilibrium constant. It only helps in reaching the equilibrium state quicker.

- A change in temperature change the value of the equilibrium constant.

Notes

Terminal Exercise

1. What do you understand by reversible and irreversible reactions? Give one example of each.

    ....

2. What is physical equilibrium? Give one example?

    ....

3. Give characteristics of equilibrium state.

    ....

4. Is the phase same as physical state? Illustrate your answer with one example of each.

    ....

5. How do homogeneous and heterogeneous systems differ from each other? Which of the following are homogeneous systems?

    (a) Liquid $\rightleftharpoons$ Vapour

    (b) N_2O_4 (g) $\rightleftharpoons$ $2NO_2$ (g)

    (c) NH_4Cl (s) $\rightleftharpoons$ NH_3 (g) + HCl (g)

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

    ....

6. What are K_p and K_c? Derive a relation between them.

    ....

7. Write down the expression of K_c for the following. Also give units in each case.

    (a) N_2O_5 (g) $\rightleftharpoons$ $2NO_2$ (g) + $\dfrac{1}{2}$ O_2 (g)

    (b) CH_4 (g) + H_2O (l) $\rightleftharpoons$ CO (g) + $3H_2$ (g)

    (c) $FeCl_3$ (aq) + $3NH_4SCN$ (aq) $\rightleftharpoons$ Fe $(SCN)_3$(aq) + $3NH_4Cl$ (aq)

    ....

8. Write down the expression of K_p for the following and give its units (in terms of atmosphere) in each case

    (a) CO_2 (g) + H_2 (g) $\rightleftharpoons$ CO (g) + H_2O (l)

    (b) $3Fe(s)$ + $4H_2O(l)$ $\rightleftharpoons$ Fe_3O_4 (s) + $4H_2$ (g)

    (c) $2SO_3$ (g) $\rightleftharpoons$ $2SO_2$ (g) + O_2 (g)

9. Give the relation between K_c and K_p for the reaction.

   $CaCO_3$ (s) $\rightleftharpoons$ CaO (s) + CO_2 (g)

   ....
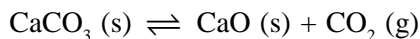
10. Using the relaction between K_p and K_c write the expression of

    (i) K_p for the reactions given in Q. No.7

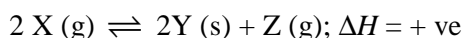   (ii) K_c for the reactions given in Q. No.8

    ....

11. List the factors that can affect

    (i) a system at equilibrium and

    (ii) equilibrium constant of a system

    ....

12. State the Le Chatelier's Principle.

    ....

13. What will be the effect of the following factors on the following systems at equilibrium?

    $2 X$ (g) $\rightleftharpoons$ 2Y (s) + Z (g); $\Delta H = +$ ve
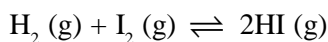
    (i) Addition of X,

    (ii) removal of Z

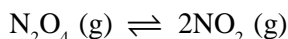   (iii) addition of a catalyst

    (iv) increasing the pressure and

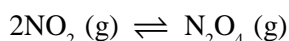   (v) increasing the temperature.

14. 5 moles of HI were produced by the reaction between 7.5 moles of H_2 and 2.6 moles of I_2 vapours at 444⁰C. What is the equilibrium constant of the reaction

    H_2 (g) + I_2 (g) $\rightleftharpoons$ 2HI (g)

15. The equilibrium constant K_p for the reaction

    N_2O_4 (g) $\rightleftharpoons$ $2NO_2$ (g)

    at 333 K is found to be 1.33 atm under a total pressure of 1 atm. Calculate K_p for the reaction

 $2NO_2$ (g) $\rightleftharpoons$ N_2O_4 (g)

    at 333 K and under 1 atm pressure.

16. At 444⁰C, 0.30 mole of H_2 and 0.30 mole of I_2 were taken in a one litre flask. After some time the equilibrium H_2 (g) + I_2 (g) $\rightleftharpoons$ 2HI (g) was established and it was found that the concentration of I_2 decreased to 0.06 mol L^{-1}. Calculate the value of K_c for the reaction at this temperature.
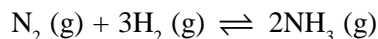
17. The equilibrium constant for the reaction.

$$CH_3COOH(l) + C_2H_5OH (l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l) \text{ is } 4.0.$$
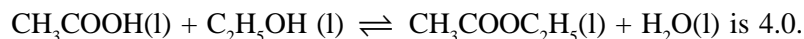
What will be the composition of the equilibrium mixture if 1 mole of acetic acid is taken with 8 moles of ethanol?

18. K_c for the reaction

$$N_2 (g) + 3H_2 (g) \rightleftharpoons 2NH_3 (g)$$

at 400^0C was found to be $0.5 \text{ L}^2 \text{ mol}^{-2}$. Calculate K_p of this reaction in atm.
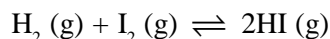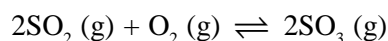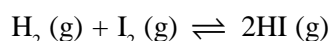
Answers to Intext Questions

13.1

1. A chemical reaction is said to be reversible, if under certain conditions its products also react and form back the reactants.
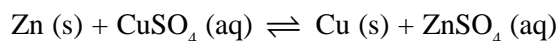
Examples :

$$H_2 (g) + I_2 (g) \rightleftharpoons 2HI (g)$$
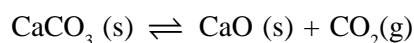
$$2SO_2 (g) + O_2 (g) \rightleftharpoons 2SO_3 (g)$$
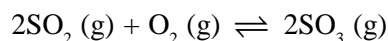
2. A reaction reaches an equilibrium state when two opposing reactions occur at the same rate and balance each other at a particular temperature.

3. When a system reaches the equilibrium state, its temperature, pressure and concentrations of all the reactants and products do not change any further with time.

4. (i) Water-vapour system in a closed container at a constant temperature.

(ii) A saturated solution containing some undissolved solute at a constant temperature.

5. (i) Homogeneous systems :

$$H_2 (g) + I_2 (g) \rightleftharpoons 2HI (g)$$

$$2SO_2 (g) + O_2 (g) \rightleftharpoons 2SO_3 (g)$$

(ii) Heterogeneous systems :

$$CaCO_3 (s) \rightleftharpoons CaO (s) + CO_2(g)$$

$$Zn (s) + CuSO_4 (aq) \rightleftharpoons Cu (s) + ZnSO_4 (aq)$$

13.2

1. $K = \dfrac{[C]^3 [D]^3}{[A]^2 [B]}$

2. $K_p = K_c (RT)^{\Delta n_g}$

3.   (i) (a) $K_c = \dfrac{[CO][H_2O]}{[CO_2][H_2]}$; $K_p = \dfrac{p_{CO} \times p_{H_2O}}{p_{CO_2} \times p_{H_2}}$

   (b) $K_c = [I_2]$; $K_p = P_{I_2}$

   (ii) For the first reaction $\Delta n_g = (1 + 1) - (1 - 1) = 0$, hence $K_c = K_p$ while for the second   reaction
   $\Delta n_g = 1 - 0 = + 1$

   $\therefore K_p = K_c\,(RT)$ or $K_c = \dfrac{K_p}{RT}$ or $K_c < K_p$.

4. $K_1 = \dfrac{[NH_3]^2}{[N_2][H_2]^3}$ and $K_2 = \dfrac{[NH_3]^{2/3}}{[N_2]^{1/3}\,[H_2]}$

   $\therefore K_1 = [K_2]^3$.

5.   It is a measure of the extent up to which a reaction proceeds before the equilibrium is reached.

13.3

1.   Le Chatelier's principle states that when a system at equilibrium is disturbed by changing concentration, pressure or temperature, a 'net' change occurs in a direction that tends to neutralize the effect of the disturbing factor.

2.   Changes in pressure, temperature and concentrations of reactants or products.

3.   When the temperature is decreased some vapour will condense and when the pressure is decreased some solid will sublime.

4.   (a) (ii) and (iv)

   (b) High temperature, increase in pressure, presence of a catalyst and continuous removal of D.