

# EQUILIBRIUM

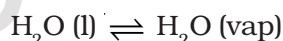
## Objectives

After studying this unit you will be able to

- identify dynamic nature of equilibrium involved in physical and chemical processes;
- state the law of equilibrium;
- explain characteristics of equilibria involved in physical and chemical processes;
- write expressions for equilibrium constants;
- establish a relationship between  $K_p$  and  $K_c$ ;
- explain various factors that affect the equilibrium state of a reaction;
- classify substances as acids or bases according to Arrhenius, Bronsted-Lowry and Lewis concepts;
- classify acids and bases as weak or strong in terms of their ionization constants;
- explain the dependence of degree of ionization on concentration of the electrolyte and that of the common ion;
- describe pH scale for representing hydrogen ion concentration;
- explain ionisation of water and its dual role as acid and base;
- describe ionic product ( $K_w$ ) and  $pK_w$  for water;
- appreciate use of buffer solutions;
- calculate solubility product constant.

Chemical equilibria are important in numerous biological and environmental processes. For example, equilibria involving  $O_2$  molecules and the protein hemoglobin play a crucial role in the transport and delivery of  $O_2$  from our lungs to our muscles. Similar equilibria involving CO molecules and hemoglobin account for the toxicity of CO.

When a liquid evaporates in a closed container, molecules with relatively higher kinetic energy escape the liquid surface into the vapour phase and number of liquid molecules from the vapour phase strike the liquid surface and are retained in the liquid phase. It gives rise to a constant vapour pressure because of an *equilibrium* in which the number of molecules leaving the liquid equals the number returning to liquid from the vapour. We say that the system has reached **equilibrium state** at this stage. However, this is not static equilibrium and there is a lot of activity at the boundary between the liquid and the vapour. Thus, at *equilibrium*, the rate of evaporation is equal to the rate of condensation. It may be represented by



The double half arrows indicate that the processes in both the directions are going on simultaneously. The mixture of reactants and products in the equilibrium state is called an **equilibrium mixture**.

Equilibrium can be established for both physical processes and chemical reactions. The reaction may be fast or slow depending on the experimental conditions and the nature of the reactants. When the reactants in a closed vessel at a particular temperature react to give products, the concentrations of the reactants keep on decreasing, while those of products keep on increasing for some time after which there is no change in the concentrations of either of the reactants or products. This stage of the system is the **dynamic equilibrium** and the rates of the forward and

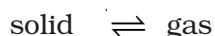
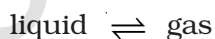
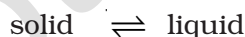
reverse reactions become equal. It is due to this dynamic equilibrium stage that there is no change in the concentrations of various species in the reaction mixture. Based on the extent to which the reactions proceed to reach the state of **chemical equilibrium**, these may be classified in three groups.

- (i) The reactions that proceed nearly to completion and only negligible concentrations of the reactants are left. In some cases, it may not be even possible to detect these experimentally.
- (ii) The reactions in which only small amounts of products are formed and most of the reactants remain unchanged at equilibrium stage.
- (iii) The reactions in which the concentrations of the reactants and products are comparable, when the system is in equilibrium.

The extent of a reaction in equilibrium varies with the experimental conditions such as concentrations of reactants, temperature, etc. Optimisation of the operational conditions is very important in industry and laboratory so that equilibrium is favorable in the direction of the desired product. Some important aspects of equilibrium involving physical and chemical processes are dealt in this unit along with the equilibrium involving ions in aqueous solutions which is called as **ionic equilibrium**.

## 7.1 EQUILIBRIUM IN PHYSICAL PROCESSES

The characteristics of system at equilibrium are better understood if we examine some physical processes. The most familiar examples are **phase transformation processes**, *e.g.*,



### 7.1.1 Solid-Liquid Equilibrium

Ice and water kept in a perfectly insulated thermos flask (no exchange of heat between its contents and the surroundings) at 273K

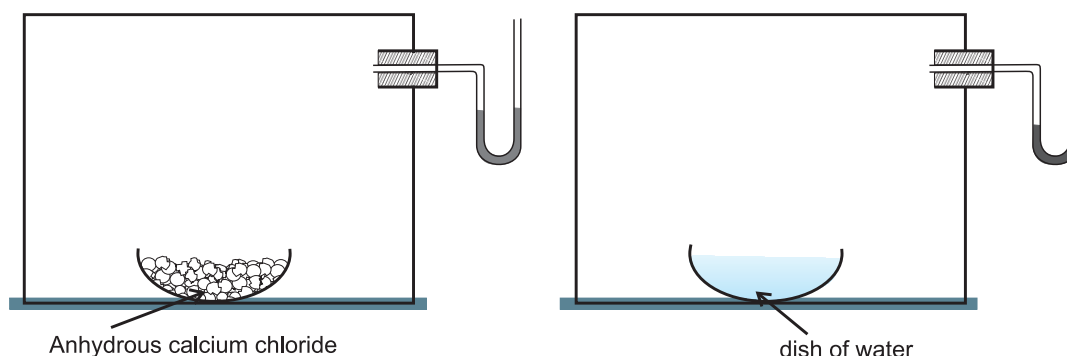
and the atmospheric pressure are in equilibrium state and the system shows interesting characteristic features. We observe that the mass of ice and water do not change with time and the temperature remains constant. However, the equilibrium is not static. The intense activity can be noticed at the boundary between ice and water. Molecules from the liquid water collide against ice and adhere to it and some molecules of ice escape into liquid phase. There is no change of mass of ice and water, as the rates of transfer of molecules from ice into water and of reverse transfer from water into ice are equal at atmospheric pressure and 273 K.

It is obvious that ice and water are in equilibrium only at particular temperature and pressure. *For any pure substance at atmospheric pressure, the temperature at which the solid and liquid phases are at equilibrium is called the normal melting point or normal freezing point of the substance.* The system here is in dynamic equilibrium and we can infer the following:

- (i) Both the opposing processes occur simultaneously.
- (ii) Both the processes occur at the same rate so that the amount of ice and water remains constant.

### 7.1.2 Liquid-Vapour Equilibrium

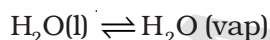
This equilibrium can be better understood if we consider the example of a transparent box carrying a U-tube with mercury (manometer). Drying agent like anhydrous calcium chloride (or phosphorus penta-oxide) is placed for a few hours in the box. After removing the drying agent by tilting the box on one side, a watch glass (or petri dish) containing water is quickly placed inside the box. It will be observed that the mercury level in the right limb of the manometer slowly increases and finally attains a constant value, that is, the pressure inside the box increases and reaches a constant value. Also the volume of water in the watch glass decreases (Fig. 7.1). Initially there was no water vapour (or very less) inside the box. As water evaporated the pressure in the box increased due to addition of water



**Fig.7.1** Measuring equilibrium vapour pressure of water at a constant temperature

molecules into the gaseous phase inside the box. The rate of evaporation is constant. However, the rate of increase in pressure decreases with time due to condensation of vapour into water. Finally it leads to an equilibrium condition when there is no net evaporation. This implies that the number of water molecules from the gaseous state into the liquid state also increases till the equilibrium is attained i.e.,

rate of evaporation = rate of condensation



At equilibrium the pressure exerted by the water molecules at a given temperature remains constant and is called the equilibrium vapour pressure of water (or just vapour pressure of water); vapour pressure of water increases with temperature. If the above experiment is repeated with methyl alcohol, acetone and ether, it is observed that different liquids have different equilibrium vapour pressures at the same temperature, and the liquid which has a higher vapour pressure is more volatile and has a lower boiling point.

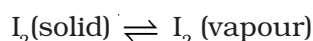
If we expose three watch glasses containing separately 1mL each of acetone, ethyl alcohol, and water to atmosphere and repeat the experiment with different volumes of the liquids in a warmer room, it is observed that in all such cases the liquid eventually disappears and the time taken for complete evaporation depends on (i) the nature of the liquid, (ii) the amount of the liquid and (iii) the temperature. When the watch glass is open to the atmosphere, the rate of evaporation remains constant but the molecules are

dispersed into large volume of the room. As a consequence the rate of condensation from vapour to liquid state is much less than the rate of evaporation. These are open systems and it is not possible to reach equilibrium in an open system.

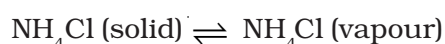
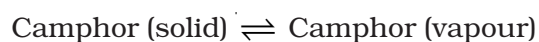
Water and water vapour are in equilibrium position at atmospheric pressure (1.013 bar) and at 100°C in a closed vessel. The boiling point of water is 100°C at 1.013 bar pressure. For any pure liquid at one atmospheric pressure (1.013 bar), the temperature at which the liquid and vapours are at equilibrium is called normal boiling point of the liquid. Boiling point of the liquid depends on the atmospheric pressure. It depends on the altitude of the place; at high altitude the boiling point decreases.

### 7.1.3 Solid – Vapour Equilibrium

Let us now consider the systems where solids sublime to vapour phase. If we place solid iodine in a closed vessel, after sometime the vessel gets filled up with violet vapour and the intensity of colour increases with time. After certain time the intensity of colour becomes constant and at this stage equilibrium is attained. Hence solid iodine sublimates to give iodine vapour and the iodine vapour condenses to give solid iodine. The equilibrium can be represented as,



Other examples showing this kind of equilibrium are,



### 7.1.4 Equilibrium Involving Dissolution of Solid or Gases in Liquids

#### Solids in liquids

We know from our experience that we can dissolve only a limited amount of salt or sugar in a given amount of water at room temperature. If we make a thick sugar syrup solution by dissolving sugar at a higher temperature, sugar crystals separate out if we cool the syrup to the room temperature. We call it a saturated solution when no more of solute can be dissolved in it at a given temperature. The concentration of the solute in a saturated solution depends upon the temperature. In a saturated solution, a dynamic equilibrium exists between the solute molecules in the solid state and in the solution:

Sugar (solution)  $\rightleftharpoons$  Sugar (solid), and

the rate of dissolution of sugar = rate of crystallisation of sugar.

Equality of the two rates and dynamic nature of equilibrium has been confirmed with the help of radioactive sugar. If we drop some radioactive sugar into saturated solution of non-radioactive sugar, then after some time radioactivity is observed both in the solution and in the solid sugar. Initially there were no radioactive sugar molecules in the solution but due to dynamic nature of equilibrium, there is exchange between the radioactive and non-radioactive sugar molecules between the two phases. The ratio of the radioactive to non-radioactive molecules in the solution increases till it attains a constant value.

#### Gases in liquids

When a soda water bottle is opened, some of the carbon dioxide gas dissolved in it fizzes out rapidly. The phenomenon arises due to difference in solubility of carbon dioxide at different pressures. There is equilibrium between the molecules in the gaseous state and the molecules dissolved in the liquid under pressure i.e.,



This equilibrium is governed by Henry's law, **which states that the mass of a gas dissolved in a given mass of a solvent at any temperature is proportional to the**

**pressure of the gas above the solvent.** This amount decreases with increase of temperature. The soda water bottle is sealed under pressure of gas when its solubility in water is high. As soon as the bottle is opened, some of the dissolved carbon dioxide gas escapes to reach a new equilibrium condition required for the lower pressure, namely its partial pressure in the atmosphere. This is how the soda water in bottle when left open to the air for some time, turns 'flat'. It can be generalised that:

- (i) For solid  $\rightleftharpoons$  liquid equilibrium, there is only one temperature (melting point) at 1 atm (1.013 bar) at which the two phases can coexist. If there is no exchange of heat with the surroundings, the mass of the two phases remains constant.
- (ii) For liquid  $\rightleftharpoons$  vapour equilibrium, the vapour pressure is constant at a given temperature.
- (iii) For dissolution of solids in liquids, the solubility is constant at a given temperature.
- (iv) For dissolution of gases in liquids, the concentration of a gas in liquid is proportional to the pressure (concentration) of the gas over the liquid. These observations are summarised in Table 7.1

**Table 7.1 Some Features of Physical Equilibria**

Process	Conclusion
Liquid $\rightleftharpoons$ Vapour $\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_2\text{O}(\text{g})$	$p_{\text{H}_2\text{O}}$ constant at given temperature
Solid $\rightleftharpoons$ Liquid $\text{H}_2\text{O}(\text{s}) \rightleftharpoons \text{H}_2\text{O}(\text{l})$	Melting point is fixed at constant pressure
Solute(s) $\rightleftharpoons$ Solute (solution) Sugar(s) $\rightleftharpoons$ Sugar (solution)	Concentration of solute in solution is constant at a given temperature
Gas(g) $\rightleftharpoons$ Gas (aq) $\text{CO}_2(\text{g}) \rightleftharpoons \text{CO}_2(\text{aq})$	$[\text{gas}(\text{aq})]/[\text{gas}(\text{g})]$ is constant at a given temperature $[\text{CO}_2(\text{aq})]/[\text{CO}_2(\text{g})]$ is constant at a given temperature



### 7.1.5 General Characteristics of Equilibria Involving Physical Processes

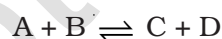
For the physical processes discussed above, following characteristics are common to the system at equilibrium:

- (i) Equilibrium is possible only in a closed system at a given temperature.
- (ii) Both the opposing processes occur at the same rate and there is a dynamic but stable condition.
- (iii) All measurable properties of the system remain constant.
- (iv) When equilibrium is attained for a physical process, it is characterised by constant value of one of its parameters at a given temperature. Table 7.1 lists such quantities.
- (v) The magnitude of such quantities at any stage indicates the extent to which the physical process has proceeded before reaching equilibrium.

## 7.2 EQUILIBRIUM IN CHEMICAL PROCESSES – DYNAMIC EQUILIBRIUM

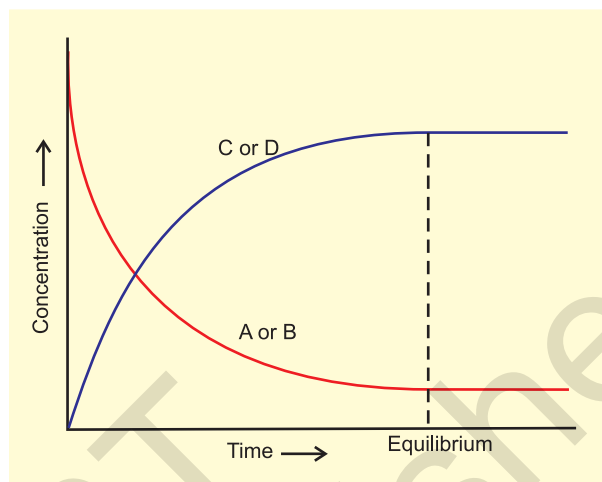
Analogous to the physical systems chemical reactions also attain a state of equilibrium. These reactions can occur both in forward and backward directions. When the rates of the forward and reverse reactions become equal, the concentrations of the reactants and the products remain constant. This is the stage of chemical equilibrium. This equilibrium is *dynamic* in nature as it consists of a *forward* reaction in which the reactants give product(s) and *reverse* reaction in which product(s) gives the original reactants.

For a better comprehension, let us consider a general case of a reversible reaction,



With passage of time, there is accumulation of the products C and D and depletion of the reactants A and B (Fig. 7.2). This leads to a decrease in the rate of forward reaction and an increase in the rate of the reverse reaction,

Eventually, the two reactions occur at the



**Fig. 7.2** Attainment of chemical equilibrium.

same rate and the system reaches a state of equilibrium.

Similarly, the reaction can reach the state of equilibrium even if we start with only C and D; that is, no A and B being present initially, as the equilibrium can be reached from either direction.

The dynamic nature of chemical equilibrium can be demonstrated in the synthesis of ammonia by Haber's process. In a series of experiments, Haber started with known amounts of dinitrogen and dihydrogen maintained at high temperature and pressure and at regular intervals determined the amount of ammonia present. He was successful in determining also the concentration of unreacted dihydrogen and dinitrogen. Fig. 7.4 (page 191) shows that after a certain time the composition of the mixture remains the same even though some of the reactants are still present. This constancy in composition indicates that the reaction has reached equilibrium. In order to understand the dynamic nature of the reaction, synthesis of ammonia is carried out with exactly the same starting conditions (of partial pressure and temperature) but using  $D_2$  (deuterium) in place of  $H_2$ . The reaction mixtures starting either with  $H_2$  or  $D_2$  reach equilibrium with the same composition, except that  $D_2$  and  $ND_3$  are present instead of  $H_2$  and  $NH_3$ . After equilibrium is attained, these two mixtures

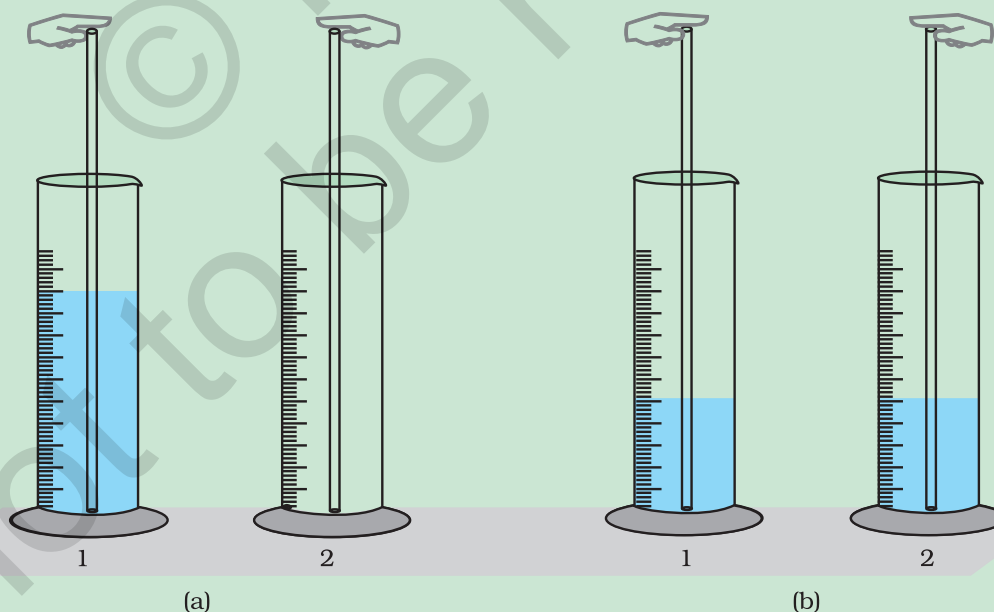
### Dynamic Equilibrium – A Student's Activity

Equilibrium whether in a physical or in a chemical system, is always of dynamic nature. This can be demonstrated by the use of radioactive isotopes. This is not feasible in a school laboratory. However this concept can be easily comprehended by performing the following activity. The activity can be performed in a group of 5 or 6 students.

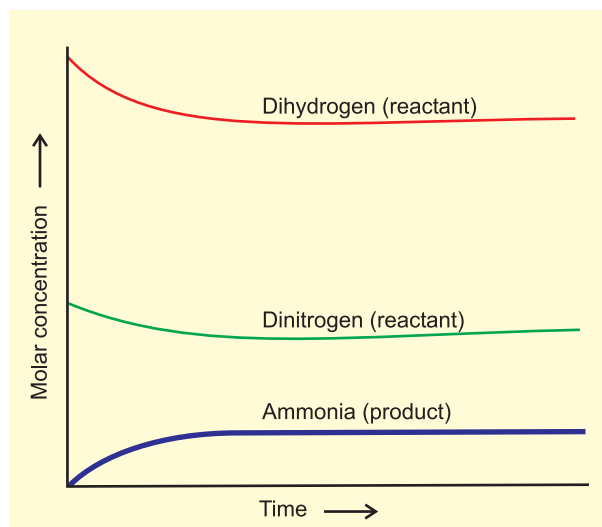
Take two 100mL measuring cylinders (marked as 1 and 2) and two glass tubes each of 30 cm length. Diameter of the tubes may be same or different in the range of 3-5mm. Fill nearly half of the measuring cylinder-1 with coloured water (for this purpose add a crystal of potassium permanganate to water) and keep second cylinder (number 2) empty.

Put one tube in cylinder 1 and second in cylinder 2. Immerse one tube in cylinder 1, close its upper tip with a finger and transfer the coloured water contained in its lower portion to cylinder 2. Using second tube, kept in 2<sup>nd</sup> cylinder, transfer the coloured water in a similar manner from cylinder 2 to cylinder 1. In this way keep on transferring coloured water using the two glass tubes from cylinder 1 to 2 and from 2 to 1 till you notice that the level of coloured water in both the cylinders becomes constant.

If you continue intertransferring coloured solution between the cylinders, there will not be any further change in the levels of coloured water in two cylinders. If we take analogy of 'level' of coloured water with 'concentration' of reactants and products in the two cylinders, we can say the process of transfer, which continues even after the constancy of level, is indicative of dynamic nature of the process. If we repeat the experiment taking two tubes of different diameters we find that at equilibrium the level of coloured water in two cylinders is different. How far diameters are responsible for change in levels in two cylinders? Empty cylinder (2) is an indicator of no product in it at the beginning.



**Fig.7.3** Demonstrating dynamic nature of equilibrium. (a) initial stage (b) final stage after the equilibrium is attained.



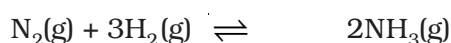
**Fig 7.4** Depiction of equilibrium for the reaction  

$$\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$$

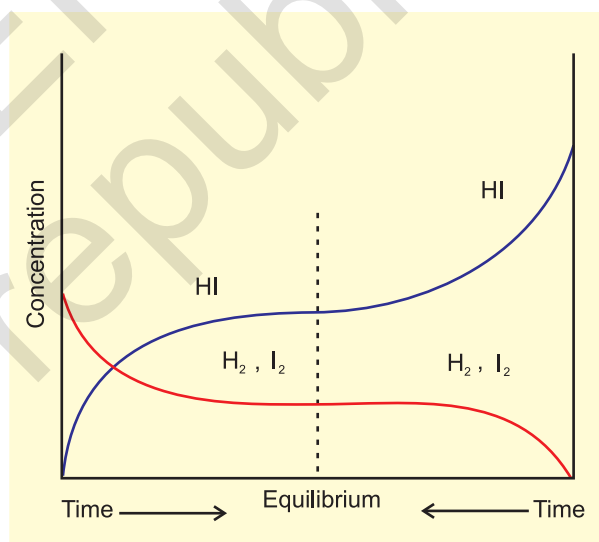
( $\text{H}_2$ ,  $\text{N}_2$ ,  $\text{NH}_3$  and  $\text{D}_2$ ,  $\text{N}_2$ ,  $\text{ND}_3$ ) are mixed together and left for a while. Later, when this mixture is analysed, it is found that the concentration of ammonia is just the same as before. However, when this mixture is analysed by a mass spectrometer, it is found that ammonia and all deuterium containing forms of ammonia ( $\text{NH}_3$ ,  $\text{NH}_2\text{D}$ ,  $\text{NHD}_2$  and  $\text{ND}_3$ ) and dihydrogen and its deuterated forms ( $\text{H}_2$ ,  $\text{HD}$  and  $\text{D}_2$ ) are present. Thus one can conclude that scrambling of H and D atoms in the molecules must result from a continuation of the forward and reverse reactions in the mixture. If the reaction had simply stopped when they reached equilibrium, then there would have been no mixing of isotopes in this way.

Use of isotope (deuterium) in the formation of ammonia clearly indicates that **chemical reactions reach a state of dynamic equilibrium in which the rates of forward and reverse reactions are equal and there is no net change in composition.**

Equilibrium can be attained from both sides, whether we start reaction by taking,  $\text{H}_2(\text{g})$  and  $\text{N}_2(\text{g})$  and get  $\text{NH}_3(\text{g})$  or by taking  $\text{NH}_3(\text{g})$  and decomposing it into  $\text{N}_2(\text{g})$  and  $\text{H}_2(\text{g})$ .



Similarly let us consider the reaction,  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$ . If we start with equal initial concentration of  $\text{H}_2$  and  $\text{I}_2$ , the reaction proceeds in the forward direction and the concentration of  $\text{H}_2$  and  $\text{I}_2$  decreases while that of  $\text{HI}$  increases, until all of these become constant at equilibrium (Fig. 7.5). We can also start with  $\text{HI}$  alone and make the reaction to proceed in the reverse direction; the concentration of  $\text{HI}$  will decrease and concentration of  $\text{H}_2$  and  $\text{I}_2$  will increase until they all become constant when equilibrium is reached (Fig. 7.5). If total number of H and I atoms are same in a given volume, the same equilibrium mixture is obtained whether we start it from pure reactants or pure product.



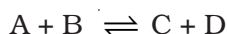
**Fig. 7.5** Chemical equilibrium in the reaction  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$  can be attained from either direction

### 7.3 LAW OF CHEMICAL EQUILIBRIUM AND EQUILIBRIUM CONSTANT

A mixture of reactants and products in the equilibrium state is called an equilibrium mixture. In this section we shall address a number of important questions about the composition of equilibrium mixtures: What is the relationship between the concentrations of reactants and products in an equilibrium mixture? How can we determine equilibrium concentrations from initial concentrations?

What factors can be exploited to alter the composition of an equilibrium mixture? The last question in particular is important when choosing conditions for synthesis of industrial chemicals such as  $H_2$ ,  $NH_3$ ,  $CaO$  etc.

To answer these questions, let us consider a general reversible reaction:

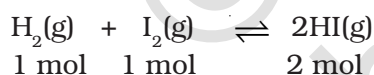


where A and B are the reactants, C and D are the products in the balanced chemical equation. On the basis of experimental studies of many reversible reactions, the Norwegian chemists Cato Maximillian Guldberg and Peter Waage proposed in 1864 that the concentrations in an equilibrium mixture are related by the following **equilibrium equation**,

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

where  $K_c$  is the *equilibrium constant* and the expression on the right side is called the *equilibrium constant expression*.

The equilibrium equation is also known as the *law of mass action* because in the early days of chemistry, concentration was called "active mass". In order to appreciate their work better, let us consider reaction between gaseous  $H_2$  and  $I_2$  carried out in a sealed vessel at 731K.



Six sets of experiments with varying initial conditions were performed, starting with only gaseous  $H_2$  and  $I_2$  in a sealed reaction vessel in first four experiments (1, 2, 3 and 4) and only HI in other two experiments (5 and 6). Experiment 1, 2, 3 and 4 were performed taking different concentrations of  $H_2$  and / or  $I_2$ , and with time it was observed that intensity of the purple colour remained constant and equilibrium was attained. Similarly, for experiments 5 and 6, the equilibrium was attained from the opposite direction.

Data obtained from all six sets of experiments are given in Table 7.2.

It is evident from the experiments 1, 2, 3 and 4 that number of moles of dihydrogen reacted = number of moles of iodine reacted =  $\frac{1}{2}$  (number of moles of HI formed). Also, experiments 5 and 6 indicate that,

$$[H_2(g)]_{eq} = [I_2(g)]_{eq}$$

Knowing the above facts, in order to establish a relationship between concentrations of the reactants and products, several combinations can be tried. Let us consider the simple expression,

$$[HI(g)]_{eq} / [H_2(g)]_{eq} [I_2(g)]_{eq}$$

It can be seen from Table 7.3 that if we put the equilibrium concentrations of the reactants and products, the above expression

**Table 7.2 Initial and Equilibrium Concentrations of  $H_2$ ,  $I_2$  and HI**

Experiment number	Initial concentration/mol L <sup>-1</sup>			Equilibrium concentration/mol L <sup>-1</sup>		
	[ H <sub>2</sub> (g) ]	[ I <sub>2</sub> (g) ]	[ HI (g) ]	[ H <sub>2</sub> (g) ]	[ I <sub>2</sub> (g) ]	[ HI (g) ]
1	$2.4 \times 10^{-2}$	$1.38 \times 10^{-2}$	0	$1.14 \times 10^{-2}$	$0.12 \times 10^{-2}$	$2.52 \times 10^{-2}$
2	$2.4 \times 10^{-2}$	$1.68 \times 10^{-2}$	0	$0.92 \times 10^{-2}$	$0.20 \times 10^{-2}$	$2.96 \times 10^{-2}$
3	$2.44 \times 10^{-2}$	$1.98 \times 10^{-2}$	0	$0.77 \times 10^{-2}$	$0.31 \times 10^{-2}$	$3.34 \times 10^{-2}$
4	$2.46 \times 10^{-2}$	$1.76 \times 10^{-2}$	0	$0.92 \times 10^{-2}$	$0.22 \times 10^{-2}$	$3.08 \times 10^{-2}$
5	0	0	$3.04 \times 10^{-2}$	$0.345 \times 10^{-2}$	$0.345 \times 10^{-2}$	$2.35 \times 10^{-2}$
6	0	0	$7.58 \times 10^{-2}$	$0.86 \times 10^{-2}$	$0.86 \times 10^{-2}$	$5.86 \times 10^{-2}$



**Table 7.3 Expression Involving the Equilibrium Concentration of Reactants**



Experiments Number	$\frac{[\text{HI}(\text{g})]_{\text{eq}}}{[\text{H}_2(\text{g})]_{\text{eq}} [\text{I}_2(\text{g})]_{\text{eq}}}$	$\frac{[\text{HI}(\text{g})]_{\text{eq}}^2}{[\text{H}_2(\text{g})]_{\text{eq}} [\text{I}_2(\text{g})]_{\text{eq}}}$
1	1840	46.4
2	1610	47.6
3	1400	46.7
4	1520	46.9
5	1970	46.4
6	790	46.4

is far from constant. However, if we consider the expression,

$$\frac{[\text{HI}(\text{g})]_{\text{eq}}^2}{[\text{H}_2(\text{g})]_{\text{eq}} [\text{I}_2(\text{g})]_{\text{eq}}}$$

we find that this expression gives constant value (as shown in Table 7.3) in all the six cases. It can be seen that in this expression the power of the concentration for reactants and products are actually the stoichiometric coefficients in the equation for the chemical reaction. Thus, for the reaction  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$ , following equation 7.1, the equilibrium constant  $K_c$  is written as,

$$K_c = \frac{[\text{HI}(\text{g})]_{\text{eq}}^2}{[\text{H}_2(\text{g})]_{\text{eq}} [\text{I}_2(\text{g})]_{\text{eq}}} \quad (7.2)$$

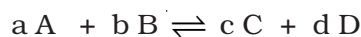
Generally the subscript 'eq' (used for equilibrium) is omitted from the concentration terms. It is taken for granted that the concentrations in the expression for  $K_c$  are equilibrium values. We, therefore, write,

$$K_c = \frac{[\text{HI}(\text{g})]^2}{[\text{H}_2(\text{g})] [\text{I}_2(\text{g})]} \quad (7.3)$$

The subscript 'c' indicates that  $K_c$  is expressed in concentrations of mol L<sup>-1</sup>.

**At a given temperature, the product of concentrations of the reaction products raised to the respective stoichiometric coefficient in the balanced chemical equation divided by the product of concentrations of the reactants raised to their individual stoichiometric coefficients has a constant value. This is known as the Equilibrium Law or Law of Chemical Equilibrium.**

The equilibrium constant for a general reaction,

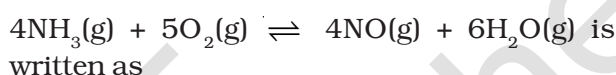


is expressed as,

$$K_c = \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b} \quad (7.4)$$

where [A], [B], [C] and [D] are the equilibrium concentrations of the reactants and products.

Equilibrium constant for the reaction,



$$K_c = \frac{[\text{NO}]^4 [\text{H}_2\text{O}]^6}{[\text{NH}_3]^4 [\text{O}_2]^5}$$

Molar concentration of different species is indicated by enclosing these in square bracket and, as mentioned above, it is implied that these are equilibrium concentrations. While writing expression for equilibrium constant, symbol for phases (s, l, g) are generally ignored.

Let us write equilibrium constant for the reaction,  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$  (7.5)

$$\text{as, } K_c = \frac{[\text{HI}]^2}{[\text{H}_2] [\text{I}_2]} = x \quad (7.6)$$

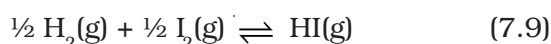
The equilibrium constant for the reverse reaction,  $2\text{HI}(\text{g}) \rightleftharpoons \text{H}_2(\text{g}) + \text{I}_2(\text{g})$ , at the same temperature is,

$$K'_c = \frac{[\text{H}_2] [\text{I}_2]}{[\text{HI}]^2} = 1/x = 1/K_c \quad (7.7)$$

$$\text{Thus, } K'_c = 1/K_c \quad (7.8)$$

**Equilibrium constant for the reverse reaction is the inverse of the equilibrium constant for the reaction in the forward direction.**

If we change the stoichiometric coefficients in a chemical equation by multiplying throughout by a factor then we must make sure that the expression for equilibrium constant also reflects that change. For example, if the reaction (7.5) is written as,



the equilibrium constant for the above reaction is given by

$$\begin{aligned} K''_c &= \frac{[\text{HI}]}{[\text{H}_2]^{1/2} [\text{I}_2]^{1/2}} = \left\{ \frac{[\text{HI}]^2}{[\text{H}_2] [\text{I}_2]} \right\}^{1/2} \\ &= x^{1/2} = K_c^{1/2} \quad (7.10) \end{aligned}$$

On multiplying the equation (7.5) by n, we get



Therefore, equilibrium constant for the reaction is equal to  $K_c^n$ . These findings are summarised in Table 7.4. It should be noted that because the equilibrium constants  $K_c$  and  $K'_c$  have different numerical values, it is important to specify the form of the balanced chemical equation when quoting the value of an equilibrium constant.

**Table 7.4 Relations between Equilibrium Constants for a General Reaction and its Multiples.**

Chemical equation	Equilibrium constant
$a\text{A} + b\text{B} \rightleftharpoons c\text{C} + d\text{D}$	$K$
$c\text{C} + d\text{D} \rightleftharpoons a\text{A} + b\text{B}$	$K'_c = (1/K_c)$
$na\text{A} + nb\text{B} \rightleftharpoons nc\text{C} + nd\text{D}$	$K''_c = (K_c^n)$

### Problem 7.1

The following concentrations were obtained for the formation of  $\text{NH}_3$  from  $\text{N}_2$  and  $\text{H}_2$  at equilibrium at 500K.  $[\text{N}_2] = 1.5 \times 10^{-2}\text{M}$ ,  $[\text{H}_2] = 3.0 \times 10^{-2}\text{M}$  and  $[\text{NH}_3] = 1.2 \times 10^{-2}\text{M}$ . Calculate equilibrium constant.

### Solution

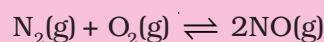
The equilibrium constant for the reaction,  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$  can be written as,

$$\begin{aligned} K_c &= \frac{[\text{NH}_3(\text{g})]^2}{[\text{N}_2(\text{g})][\text{H}_2(\text{g})]^3} \\ &= \frac{(1.2 \times 10^{-2})^2}{(1.5 \times 10^{-2})(3.0 \times 10^{-2})^3} \\ &= 0.106 \times 10^4 = 1.06 \times 10^3 \end{aligned}$$

### Problem 7.2

At equilibrium, the concentrations of  $\text{N}_2 = 3.0 \times 10^{-3}\text{M}$ ,  $\text{O}_2 = 4.2 \times 10^{-3}\text{M}$  and  $\text{NO} = 2.8 \times 10^{-3}\text{M}$  in a sealed vessel at

800K. What will be  $K_c$  for the reaction



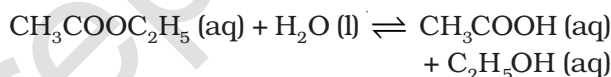
### Solution

For the reaction equilibrium constant,  $K_c$  can be written as,

$$\begin{aligned} K_c &= \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]} \\ &= \frac{(2.8 \times 10^{-3}\text{M})^2}{(3.0 \times 10^{-3}\text{M})(4.2 \times 10^{-3}\text{M})} \\ &= 0.622 \end{aligned}$$

## 7.4 HOMOGENEOUS EQUILIBRIA

In a homogeneous system, all the reactants and products are in the same phase. For example, in the gaseous reaction,  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$ , reactants and products are in the homogeneous phase. Similarly, for the reactions,



all the reactants and products are in homogeneous solution phase. We shall now consider equilibrium constant for some homogeneous reactions.

### 7.4.1 Equilibrium Constant in Gaseous Systems

So far we have expressed equilibrium constant of the reactions in terms of molar concentration of the reactants and products, and used symbol,  $K_c$  for it. For reactions involving gases, however, it is usually more convenient to express the equilibrium constant in terms of partial pressure.

The ideal gas equation is written as,

$$pV = nRT$$

$$\Rightarrow p = \frac{n}{V}RT$$

Here,  $p$  is the pressure in Pa,  $n$  is the number of moles of the gas,  $V$  is the volume in  $\text{m}^3$  and

$T$  is the temperature in Kelvin

Therefore,

$n/V$  is concentration expressed in mol/m<sup>3</sup>

If concentration  $c$ , is in mol/L or mol/dm<sup>3</sup>, and  $p$  is in bar then

$$p = cRT,$$

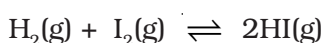
We can also write  $p = [\text{gas}]RT$ .

Here,  $R = 0.0831$  bar litre/mol K

At constant temperature, the pressure of the gas is proportional to its concentration i.e.,

$$p \propto [\text{gas}]$$

For reaction in equilibrium



We can write either

$$K_c = \frac{[\text{HI}(\text{g})]^2}{[\text{H}_2(\text{g})][\text{I}_2(\text{g})]}$$

$$\text{or } K_c = \frac{(p_{\text{HI}})^2}{(p_{\text{H}_2})(p_{\text{I}_2})} \quad (7.12)$$

Further, since  $p_{\text{HI}} = [\text{HI}(\text{g})]RT$

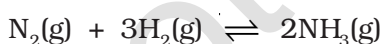
$$p_{\text{I}_2} = [\text{I}_2(\text{g})]RT$$

$$p_{\text{H}_2} = [\text{H}_2(\text{g})]RT$$

Therefore,

$$\begin{aligned} K_p &= \frac{(p_{\text{HI}})^2}{(p_{\text{H}_2})(p_{\text{I}_2})} = \frac{[\text{HI}(\text{g})]^2 [RT]^2}{[\text{H}_2(\text{g})]RT \cdot [\text{I}_2(\text{g})]RT} \\ &= \frac{[\text{HI}(\text{g})]^2}{[\text{H}_2(\text{g})][\text{I}_2(\text{g})]} = K_c \end{aligned} \quad (7.13)$$

In this example,  $K_p = K_c$  i.e., both equilibrium constants are equal. However, this is not always the case. For example in reaction

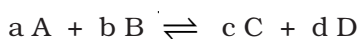


$$\begin{aligned} K_p &= \frac{(p_{\text{NH}_3})^2}{(p_{\text{N}_2})(p_{\text{H}_2})^3} \\ &= \frac{[\text{NH}_3(\text{g})]^2 [RT]^2}{[\text{N}_2(\text{g})]RT \cdot [\text{H}_2(\text{g})]^3 (RT)^3} \end{aligned}$$

$$= \frac{[\text{NH}_3(\text{g})]^2 [RT]^{-2}}{[\text{N}_2(\text{g})][\text{H}_2(\text{g})]^3} = K_c (RT)^{-2}$$

$$\text{or } K_p = K_c (RT)^{-2} \quad (7.14)$$

Similarly, for a general reaction



$$\begin{aligned} K_p &= \frac{(p_c^c)(p_d^d)}{(p_a^a)(p_b^b)} = \frac{[\text{C}]^c [\text{D}]^d (RT)^{(c+d)}}{[\text{A}]^a [\text{B}]^b (RT)^{(a+b)}} \\ &= \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b} (RT)^{(c+d)-(a+b)} \\ &= \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b} (RT)^{\Delta n} = K_c (RT)^{\Delta n} \end{aligned} \quad (7.15)$$

where  $\Delta n =$  (number of moles of gaseous products) – (number of moles of gaseous reactants) in the balanced chemical equation.

It is necessary that while calculating the value of  $K_p$ , pressure should be expressed in bar because standard state for pressure is 1 bar. We know from Unit 1 that :

$$1 \text{ pascal, Pa} = 1 \text{ Nm}^{-2}, \text{ and } 1 \text{ bar} = 10^5 \text{ Pa}$$

$K_p$  values for a few selected reactions at different temperatures are given in Table 7.5

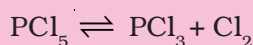
**Table 7.5 Equilibrium Constants,  $K_p$  for a Few Selected Reactions**

Reaction	Temperature/K	$K_p$
$\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3$	298	$6.8 \times 10^5$
	400	41
	500	$3.6 \times 10^{-2}$
$2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$	298	$4.0 \times 10^{24}$
	500	$2.5 \times 10^{10}$
	700	$3.0 \times 10^4$
$\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$	298	0.98
	400	47.9
	500	1700

### Problem 7.3

$\text{PCl}_5$ ,  $\text{PCl}_3$  and  $\text{Cl}_2$  are at equilibrium at 500 K and having concentration 1.59M  $\text{PCl}_5$ , 1.59M  $\text{Cl}_2$  and 1.41 M  $\text{PCl}_3$ .

Calculate  $K_c$  for the reaction,



### Solution

The equilibrium constant  $K_c$  for the above reaction can be written as,

$$K_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} = \frac{(1.59)^2}{(1.41)} = 1.79$$

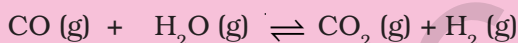
### Problem 7.4

The value of  $K_c = 4.24$  at 800K for the reaction,  
 $\text{CO (g)} + \text{H}_2\text{O (g)} \rightleftharpoons \text{CO}_2\text{ (g)} + \text{H}_2\text{ (g)}$

Calculate equilibrium concentrations of  $\text{CO}_2$ ,  $\text{H}_2$ ,  $\text{CO}$  and  $\text{H}_2\text{O}$  at 800 K, if only  $\text{CO}$  and  $\text{H}_2\text{O}$  are present initially at concentrations of 0.10M each.

### Solution

For the reaction,



Initial concentration:

$$0.1\text{M} \quad 0.1\text{M} \quad 0 \quad 0$$

Let  $x$  mole per litre of each of the product be formed.

At equilibrium:

$$(0.1-x)\text{M} \quad (0.1-x)\text{M} \quad x\text{M} \quad x\text{M}$$

where  $x$  is the amount of  $\text{CO}_2$  and  $\text{H}_2$  at equilibrium.

Hence, equilibrium constant can be written as,

$$K_c = x^2 / (0.1-x)^2 = 4.24$$

$$x^2 = 4.24(0.01 + x^2 - 0.2x)$$

$$x^2 = 0.0424 + 4.24x^2 - 0.848x$$

$$3.24x^2 - 0.848x + 0.0424 = 0$$

$$a = 3.24, b = -0.848, c = 0.0424$$

(for quadratic equation  $ax^2 + bx + c = 0$ ,

$$x = \frac{(-b \pm \sqrt{b^2 - 4ac})}{2a}$$

$$x = \frac{0.848 \pm \sqrt{(0.848)^2 - 4(3.24)(0.0424)}}{(3.24 \times 2)}$$

$$x = (0.848 \pm 0.4118) / 6.48$$

$$x_1 = (0.848 - 0.4118) / 6.48 = 0.067$$

$$x_2 = (0.848 + 0.4118) / 6.48 = 0.194$$

the value 0.194 should be neglected because it will give concentration of the reactant which is more than initial concentration.

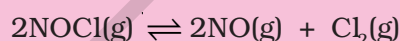
Hence the equilibrium concentrations are,

$$[\text{CO}_2] = [\text{H}_2] = x = 0.067\text{M}$$

$$[\text{CO}] = [\text{H}_2\text{O}] = 0.1 - 0.067 = 0.033\text{M}$$

### Problem 7.5

For the equilibrium,



the value of the equilibrium constant,  $K_c$  is  $3.75 \times 10^{-6}$  at 1069 K. Calculate the  $K_p$  for the reaction at this temperature?

### Solution

We know that,

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

For the above reaction,

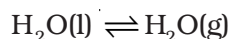
$$\Delta n = (2+1) - 2 = 1$$

$$K_p = 3.75 \times 10^{-6} (0.0831 \times 1069)$$

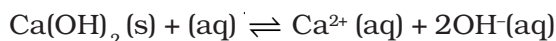
$$K_p = 0.033$$

## 7.5 HETEROGENEOUS EQUILIBRIA

Equilibrium in a system having more than one phase is called heterogeneous equilibrium. The equilibrium between water vapour and liquid water in a closed container is an example of heterogeneous equilibrium.



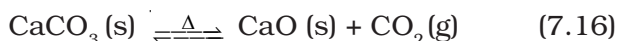
In this example, there is a gas phase and a liquid phase. In the same way, equilibrium between a solid and its saturated solution,



is a heterogeneous equilibrium.

Heterogeneous equilibria often involve pure solids or liquids. We can simplify equilibrium expressions for the heterogeneous equilibria involving a pure liquid or a pure solid, as the molar concentration of a pure solid or liquid is constant (i.e., independent of the amount present). In other words if a substance 'X' is involved, then  $[\text{X(s)}]$  and  $[\text{X(l)}]$  are constant, whatever the amount of 'X' is taken. Contrary

to this,  $[X(g)]$  and  $[X(aq)]$  will vary as the amount of X in a given volume varies. Let us take thermal dissociation of calcium carbonate which is an interesting and important example of heterogeneous chemical equilibrium.



On the basis of the stoichiometric equation, we can write,

$$K_c = \frac{[\text{CaO}(s)][\text{CO}_2(g)]}{[\text{CaCO}_3(s)]}$$

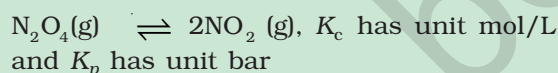
Since  $[\text{CaCO}_3(s)]$  and  $[\text{CaO}(s)]$  are both constant, therefore modified equilibrium constant for the thermal decomposition of calcium carbonate will be

$$K'_c = [\text{CO}_2(g)] \quad (7.17)$$

$$\text{or } K_p = p_{\text{CO}_2} \quad (7.18)$$

#### Units of Equilibrium Constant

The value of equilibrium constant  $K_c$  can be calculated by substituting the concentration terms in mol/L and for  $K_p$  partial pressure is substituted in Pa, kPa, bar or atm. This results in units of equilibrium constant based on molarity or pressure, unless the exponents of both the numerator and denominator are same. For the reactions,

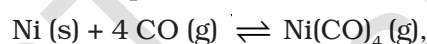


Equilibrium constants can also be expressed as dimensionless quantities if the standard state of reactants and products are specified. For a pure gas, the standard state is 1 bar. Therefore a pressure of 4 bar in standard state can be expressed as  $4 \text{ bar}/1 \text{ bar} = 4$ , which is a dimensionless number. Standard state ( $c_0$ ) for a solute is 1 molar solution and all concentrations can be measured with respect to it. The numerical value of equilibrium constant depends on the standard state chosen. Thus, in this system both  $K_p$  and  $K_c$  are dimensionless quantities but have different numerical values due to different standard states.

This shows that at a particular temperature, there is a constant concentration or pressure of  $\text{CO}_2$  in equilibrium with  $\text{CaO}(s)$  and  $\text{CaCO}_3(s)$ . Experimentally it has been found that at 1100 K, the pressure of  $\text{CO}_2$  in equilibrium with  $\text{CaCO}_3(s)$  and  $\text{CaO}(s)$ , is  $2.0 \times 10^5 \text{ Pa}$ . Therefore, equilibrium constant at 1100K for the above reaction is:

$$K_p = p_{\text{CO}_2} = 2 \times 10^5 \text{ Pa} / 10^5 \text{ Pa} = 2.00$$

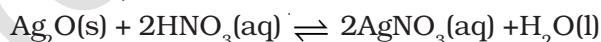
Similarly, in the equilibrium between nickel, carbon monoxide and nickel carbonyl (used in the purification of nickel),



the equilibrium constant is written as

$$K_c = \frac{[\text{Ni}(\text{CO})_4]}{[\text{CO}]^4}$$

It must be remembered that for the existence of heterogeneous equilibrium pure solids or liquids must also be present (however small the amount may be) at equilibrium, but their concentrations or partial pressures do not appear in the expression of the equilibrium constant. In the reaction,



$$K_c = \frac{[\text{AgNO}_3]^2}{[\text{HNO}_3]^2}$$

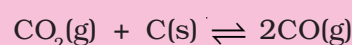
#### Problem 7.6

The value of  $K_p$  for the reaction,  $\text{CO}_2(g) + \text{C}(s) \rightleftharpoons 2\text{CO}(g)$  is 3.0 at 1000 K. If initially  $p_{\text{CO}_2} = 0.48 \text{ bar}$  and  $p_{\text{CO}} = 0 \text{ bar}$  and pure graphite is present, calculate the equilibrium partial pressures of CO and  $\text{CO}_2$ .

#### Solution

For the reaction,

let 'x' be the decrease in pressure of  $\text{CO}_2$ , then



Initial

pressure: 0.48 bar

0



At equilibrium:

$$(0.48 - x)\text{bar} \quad 2x \text{ bar}$$

$$K_p = \frac{p_{\text{CO}}^2}{p_{\text{CO}_2}}$$

$$K_p = (2x)^2 / (0.48 - x) = 3$$

$$4x^2 = 3(0.48 - x)$$

$$4x^2 = 1.44 - x$$

$$4x^2 + 3x - 1.44 = 0$$

$$a = 4, b = 3, c = -1.44$$

$$x = \frac{(-b \pm \sqrt{b^2 - 4ac})}{2a}$$

$$= [-3 \pm \sqrt{(3)^2 - 4(4)(-1.44)}] / 2 \times 4$$

$$= (-3 \pm 5.66) / 8$$

$$= (-3 + 5.66) / 8 \quad (\text{as value of } x \text{ cannot be negative hence we neglect that value})$$

$$x = 2.66 / 8 = 0.33$$

The equilibrium partial pressures are,

$$p_{\text{CO}} = 2x = 2 \times 0.33 = 0.66 \text{ bar}$$

$$p_{\text{CO}_2} = 0.48 - x = 0.48 - 0.33 = 0.15 \text{ bar}$$

## 7.6 APPLICATIONS OF EQUILIBRIUM CONSTANTS

Before considering the applications of equilibrium constants, let us summarise the important features of equilibrium constants as follows:

- Expression for equilibrium constant is applicable only when concentrations of the reactants and products have attained constant value at equilibrium state.
- The value of equilibrium constant is independent of initial concentrations of the reactants and products.
- Equilibrium constant is temperature dependent having one unique value for a particular reaction represented by a balanced equation at a given temperature.
- The equilibrium constant for the reverse reaction is equal to the inverse of the equilibrium constant for the forward reaction.

5. The equilibrium constant  $K$  for a reaction is related to the equilibrium constant of the corresponding reaction, whose equation is obtained by multiplying or dividing the equation for the original reaction by a small integer.

Let us consider applications of equilibrium constant to:

- predict the extent of a reaction on the basis of its magnitude,
- predict the direction of the reaction, and
- calculate equilibrium concentrations.

### 7.6.1 Predicting the Extent of a Reaction

The numerical value of the equilibrium constant for a reaction indicates the extent of the reaction. But it is important to note that an equilibrium constant does not give any information about the *rate* at which the equilibrium is reached. The magnitude of  $K_c$  or  $K_p$  is directly proportional to the concentrations of products (as these appear in the numerator of equilibrium constant expression) and inversely proportional to the concentrations of the reactants (these appear in the denominator). This implies that a high value of  $K$  is suggestive of a high concentration of products and vice-versa.

We can make the following generalisations concerning the composition of equilibrium mixtures:

- If  $K_c > 10^3$ , products predominate over reactants, i.e., if  $K_c$  is very large, the reaction proceeds nearly to completion. Consider the following examples:
  - The reaction of  $\text{H}_2$  with  $\text{O}_2$  at 500 K has a very large equilibrium constant,  $K_c = 2.4 \times 10^{47}$ .
  - $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons 2\text{HCl}(\text{g})$  at 300K has  $K_c = 4.0 \times 10^{31}$ .
  - $\text{H}_2(\text{g}) + \text{Br}_2(\text{g}) \rightleftharpoons 2\text{HBr}(\text{g})$  at 300 K,  $K_c = 5.4 \times 10^{18}$
- If  $K_c < 10^{-3}$ , reactants predominate over products, i.e., if  $K_c$  is very small, the reaction proceeds rarely. Consider the following examples: