

Chemical Equilibrium



C11CH7



Learning Objectives

Upon completion of this topic, learners will:

- Discuss the general principles of equilibrium
- Explain the Le Chatelier's Principle as it relates to factors influencing equilibrium
- Explain the nature of equilibrium constant, performing simple related calculations and
- Demonstrate the mathematical relationship between K_p and K_c .

It is generally observed that many of the chemical reactions do not proceed to completion when they are carried out in a closed container. This implies that the reactants are not completely converted into the products. Instead, after some time *concentrations* of the reactants do not undergo further decrease and the reaction appears to have stopped. This state of the system in which no further net change occurs is called a **state of equilibrium**.

Equilibrium can be attained for both physical and chemical processes. The equilibrium achieved in physical processes such as dissolution of salt, evaporation of water, etc., is called **physical equilibrium**, whereas the equilibrium achieved in chemical processes such as decomposition of calcium carbonate or reaction between hydrogen and iodine is called **chemical equilibrium**.

The equilibrium situation raises many interesting questions such as:

- (a) What is the equilibrium state and how is it recognised?

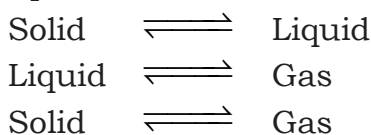
(b) What is the molecular behaviour when state of equilibrium is reached?

(c) What are the factors which alter the state of equilibrium?

In this unit, we shall seek answers to these questions.

7.1. EQUILIBRIUM IN PHYSICAL PROCESSES

In order to understand the characteristics of systems in equilibrium state let us study some physical changes in a state of equilibrium. Some common physical equilibria are:



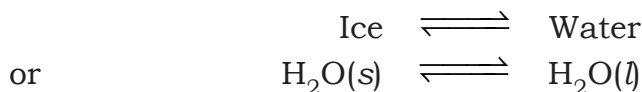
Solid-Liquid Equilibrium

When a pure solid substance is heated, it starts changing into liquid at a certain temperature. At this temperature, the solid and liquid states of the substance coexist under the given conditions of pressure.

For any pure substance, at atmospheric pressure, the temperature at which the solid and liquid states can coexist is called the normal melting point or the normal freezing point of the substance.

At melting point the solid substance is in equilibrium with liquid state of the substance. If heat energy is added to a mixture of solid and liquid at equilibrium, the solid is gradually converted to liquid while the temperature remains constant. If a solid-liquid system at melting point is taken in a well-insulated container then this constitutes a system in which solid is in dynamic equilibrium with liquid.

For example, let us consider ice and water at 273 K (melting point of ice), taken in a perfectly insulated thermos flask. It may be noted that the temperature as well as the masses of ice and water remain constant. This represents a dynamic equilibrium between ice and water.



Since there is no change in mass of ice and water the number of molecules going from ice into water is equal to the number of molecules of water going into ice. Thus, at equilibrium,

$$\text{Rate of melting} = \text{Rate of freezing.}$$

Liquid-Vapour Equilibrium

In order to illustrate the liquid-vapour equilibrium, let us consider evaporation of water in a closed vessel. When a small amount of water is taken in an evacuated vessel at room temperature it starts evaporating. A pressure is built up gradually within the vessel due to the formation of water vapours. This process continues for some time as indicated by the *gradually increasing pressure* recorded on the manometer attached to the vessel (Fig. 7.1).

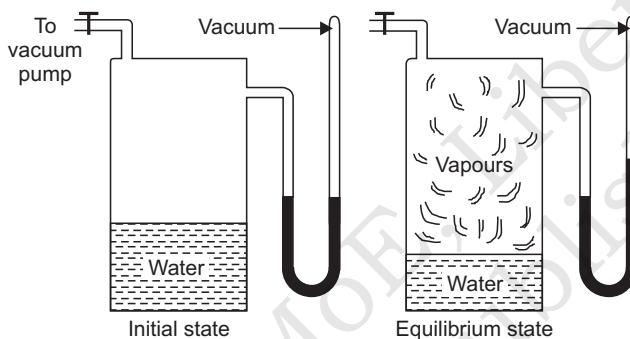
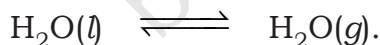


Fig. 7.1. Evaporation of water in a closed vessel.

After some time it is observed that *pressure becomes constant* indicating that no more water is evaporating, although liquid water is still present in the vessel. This indicates that a *state of equilibrium has been attained* between water and water vapour.



Equilibrium from Molecular Point of View

Now let us examine this equilibrium state from **molecular point of view**. In the evaporation of water in a closed evacuated vessel, at first the pressure inside the vessel increases. As the number of molecules in the gas phase increases the molecules of water in gas phase may strike the liquid surface and may be captured by the liquid. This process is called **condensation** and it acts in a direction opposite to evaporation. The rate of condensation is less than rate of evaporation in the beginning (Fig. 7.2) but with increase in population of molecules in gas phase the rate of condensation continues to increase and eventually the two rates become equal. At this state the equilibrium is said to be established. Thus, *at equilibrium the number of molecules entering the gas phase at any time is equal to the number of molecules returning to the liquid*

phase i.e., evaporation and condensation occur at the same rate. Thus, at equilibrium,

$$\text{Rate of evaporation} = \text{Rate of condensation.}$$

The pressure exerted by the vapours in equilibrium with the liquid at a particular temperature is called the equilibrium vapour pressure or just vapour pressure of the liquid.

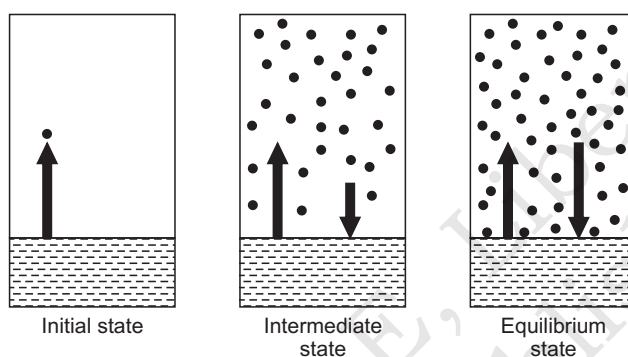


Fig. 7.2. Equilibrium state in evaporation: a dynamic balance between evaporation and condensation.

The vapour pressure of a liquid is constant at a given temperature. It does not depend upon the amount of the liquid or size of the vessel.

The vapour pressure of a liquid increases with increase in temperature. The vapour pressure of a liquid also depends on nature of the liquid. A liquid having weaker interparticle forces has higher vapour pressure. For example, acetone has higher vapour pressure than water. A liquid having greater vapour pressure is more volatile.

A liquid having greater vapour pressure has lower boiling point because for such a liquid vapour pressure becomes equal to atmospheric pressure at lower temperature. For example, consider the two liquids, water and ethanol. Vapour pressures of water and ethanol at 293 K are 2.34 kPa and 5.85 kPa respectively. This indicates that ethanol is more volatile than water. Water will have higher boiling point than ethanol because it has lower vapour pressure. Vapour pressure of water will become equal to atmospheric pressure at higher temperature.

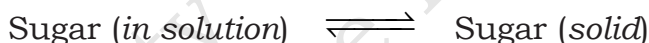
It may be emphasized that **the equilibrium between the vapours and the liquid is attained only in a closed vessel**. If the vessel is open, the vapours leave the vessel and get dispersed. As a result, the rate of condensation can never become equal to the rate of evaporation.

Dissolution of Solids in Liquids

We know that it is not possible to dissolve just any amount of a solute in a given amount of solvent. **For example**, when we add sugar to water, the crystals of sugar keep on going into solution in the beginning. But after some time no more of sugar dissolves.

A solution in which no more solute can be dissolved is called a saturated solution. The amount of solute required to prepare a saturated solution in a given quantity of solvent is known as solubility of the solute at a particular temperature.

The saturated solution corresponds to the *state of equilibrium*. Now let us see how equilibrium is established in this case. When we add sugar crystals to water, molecular vibration tends to dislodge molecules from the surface of the crystals. The molecules of sugar which go into solution are free to move through the water. In the beginning, the rate at which molecules leave the crystal is much greater than the rate of their return. As the number of molecules in solution increases, the rate at which molecules return to the crystal also increases. Soon a balance between the two rates *i.e.*, the rate of dissolution and the rate of precipitation, is established and this corresponds to the state of equilibrium. Thus, in a saturated solution, a dynamic equilibrium exists between the molecules of sugar in the solid state and the molecules of sugar in the solution.



The **dynamic nature of equilibrium** can be demonstrated by adding radioactive sugar into a saturated solution of non-radioactive sugar (Fig. 7.3). It is observed that the solution and the rest of the non-radioactive sugar also becomes radioactive. This shows that even at equilibrium, the processes of dissolution and precipitation are taking place. This means that equilibrium is dynamic in nature. Thus, at equilibrium,

$$\text{Rate of dissolution} = \text{Rate of precipitation.}$$

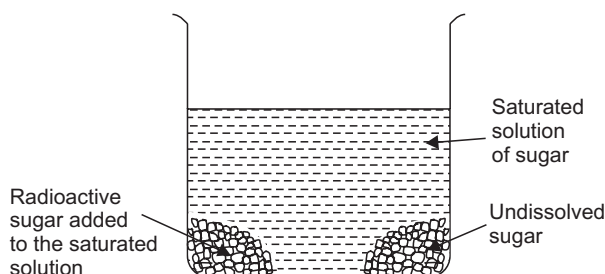
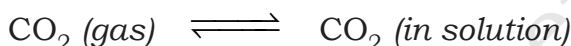


Fig. 7.3. Demonstration of dynamic nature of physical equilibrium.

Solubility of a solid in any liquid depends upon temperature. Pressure does not have any significant effect on the solubilities of solid in liquids.

Dissolution of Gases in Liquids

We know that when a **soda water** bottle is opened, the carbon dioxide dissolved in it fizzes out rapidly. At a given pressure, there is an equilibrium between the molecules of the carbon dioxide (solute) in gaseous state and the molecules dissolved in the liquid. This may be expressed as:



Effect of pressure on the solubility of a gas in a liquid is given by **Henry's Law**. This law states that:

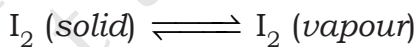
The mass of a gas dissolved in a given mass of a solvent, at a given temperature, is directly proportional to the pressure of the gas above the solvent.

$$m \propto p$$

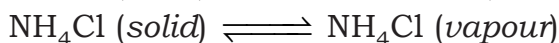
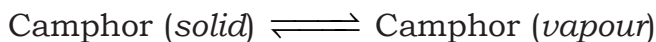
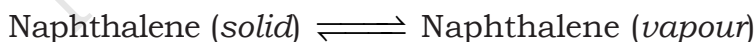
$$m = kp$$

Solid-Vapour Equilibrium

In case of a solid which undergoes sublimation at room temperature, a solid-vapour equilibrium exists when such a solid is enclosed in a closed vessel. For example, when solid iodine crystals are placed in a closed vessel, it is observed that the vessel gets filled up with violet vapours of iodine. The intensity of colour increases for sometime and then becomes constant. At this stage vapours of iodine are in dynamic equilibrium with solid iodine. The equilibrium may be represented as:



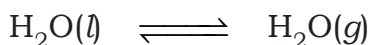
Some more examples showing solid-vapour equilibrium are,



General Characteristics of Equilibria Involving Physical Processes

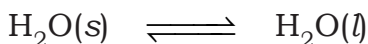
In the physical equilibria discussed above, it may be noted that:

1. In the case of *liquid* \rightleftharpoons *gas equilibrium*, the vapour pressure of the liquid is constant at equilibrium at a particular temperature. **For example**, for the equilibrium,

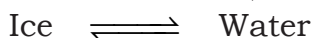


vapour pressure of water, $p_{\text{H}_2\text{O}}$, is constant at a given temperature.

2. For *solid* \rightleftharpoons *liquid equilibrium*, there is only one temperature at which the two phases can co-exist at a particular pressure. This temperature is known as melting point. For example, the equilibrium



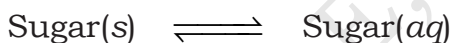
or



exists at 273 K at 1.0 atm pressure. At the melting point the masses of the two phases remain constant provided no exchange of heat takes place between the system and the surroundings.

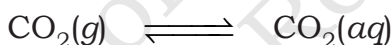
3. For dissolution of solids in liquids, the solubility (concentration of solid solute in solution) is constant at a given temperature.

For example, for the equilibrium,



concentration of sugar in solution is constant at a given temperature.

4. For dissolution of gases in liquids, the concentration of a gas in liquid, at a given temperature, is directly proportional to the pressure of the gas over the liquid. For example, for the equilibrium,



or $\frac{[\text{CO}_2(aq)]}{[\text{CO}_2(g)]}$ is constant at a given temperature.

From the physical equilibria discussed above the **general characteristics of the equilibria involving physical processes** may be stated as follows:

1. At equilibrium, the measurable properties of the system become constant.

For example, in case of evaporation of water, the vapour pressure of liquid becomes constant at equilibrium.

2. At equilibrium, there is a dynamic balance between the two opposite processes.

For example, in case of evaporation of water, the rate of evaporation is equal to the rate of condensation at equilibrium.

3. The equilibrium is attained only in a system which cannot gain matter from the surroundings or lose matter to the surroundings (*i.e.*, a closed system).

For example, if evaporation of water takes in an open vessel, no equilibrium is attained and whole of the water evaporates.

4. When equilibrium is attained, there exists an expression involving the concentration of substances involved in equilibrium which reaches a constant value at a given temperature.

For example, for the dissolution of CO_2 in water, $\frac{[\text{CO}_2(aq)]}{[\text{CO}_2(g)]}$ is

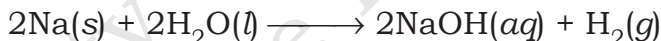
constant at a given temperature. Similarly, for the dissolution of sugar in water, concentration of sugar in water (solubility of sugar) is constant at a given temperature.

5. The magnitude of the constant value of the concentration-related expression indicates the extent to which the process proceeds before reaching equilibrium.

For example, for the dissolution of CO_2 in water greater the value of $\frac{[\text{CO}_2(aq)]}{[\text{CO}_2(g)]}$, greater is the extent to which CO_2 dissolves in water.

Equilibrium in Chemical Processes

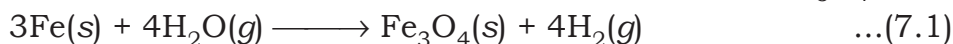
When a piece of sodium is dropped into water, a violent reaction occurs resulting in the formation of sodium hydroxide and hydrogen gas.



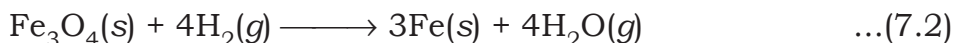
However, it is not possible to carry out the reverse reaction under any known experimental conditions, *i.e.*, reduction of aqueous sodium hydroxide by hydrogen to form sodium and water cannot be achieved.

The reactions in which the products do not react under any condition to give back reactants are called irreversible reactions.

On the other hand, let us consider the reaction between metallic iron and steam. Again, hydrogen gas is formed but at much slower rate than in the case of sodium. The iron is converted into iron oxide Fe_3O_4 .



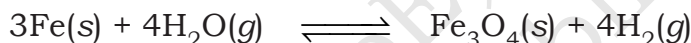
If this reaction is carried out in an open vessel, then the hydrogen gas escapes and the reaction proceeds to completion provided the sufficient amount of steam is supplied. The reverse of this reaction, *i.e.*, reduction of iron oxide (Fe_3O_4) to iron by hydrogen gas can also be achieved rather easily in the laboratory.



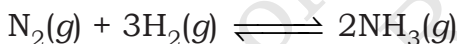
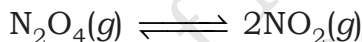
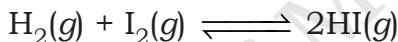
To carry out this reaction hydrogen gas is passed over heated iron oxide. Again, if this reaction is carried out in an open vessel the whole of Fe_3O_4 is reduced to iron because one of the products, *i.e.*, water escapes as steam. Now if we combine the reactants of equation (7.1) in stoichiometric ratio in a *closed vessel* at constant temperature, Fe_3O_4 and hydrogen are formed. As the products accumulate, occasional collisions of these species are effective and the reduction of Fe_3O_4 begins to occur. Eventually, a stage is reached at which no further net change occurs. This state is called *equilibrium state*.

The reactions in which products under suitable conditions react to give back reactants are called reversible reactions.

A reversible reaction is represented by putting two arrows pointing in opposite directions between the formulae of the reactants and the products as shown below:



Some more examples of reversible reactions are



Since, in a reversible reaction both forward as well as backward reactions are feasible, therefore, if such a reaction is carried in a closed vessel then both the reactions occur simultaneously and before whole of the reactants are converted into products a state of equilibrium is established. In the state of equilibrium, the reaction appears to be stopped even though the reactants are still present. Therefore, reversible reactions do not proceed to completion. On the other hand, irreversible reactions are feasible only in one direction and hence, go to completion.

Let us illustrate the state of equilibrium in some reversible processes and see how it is recognised.

1. Decomposition of Calcium Carbonate. Calcium carbonate when heated to 1073 K in a closed evacuated vessel, starts decomposing to yield calcium oxide and carbon dioxide gas. Carbon dioxide builds up pressure within the vessel which can be recorded on a manometer, as shown in Fig. 7.4. The pressure goes on increasing as the reaction proceeds and *finally becomes constant* and remains so *as long as the*

temperature remains constant. It appears as if the reaction has come to a stop although CaCO_3 is still present. This indicates that the system has attained the equilibrium state.

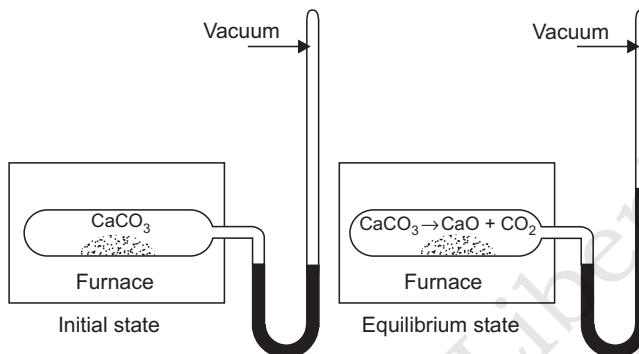


Fig. 7.4. Attainment of equilibrium in the thermal decomposition of CaCO_3 .

2. Reaction between Hydrogen and Iodine. When hydrogen and iodine are heated in a closed vessel at 717 K, they react to form hydrogen iodide. The colour of the reaction mixture is deep violet in the beginning due to the presence of iodine. As the reaction progresses the intensity of colour decreases due to the formation of hydrogen iodide which is colourless.

After sometime, it is observed that *intensity of colour becomes constant* indicating that the reaction has stopped although hydrogen and iodine are still present. Actually the system acquires a state of equilibrium.

Concept of Equilibrium State

From the study of the reversible processes discussed earlier, it may be noticed that when such a process is carried out in a closed container, it appears to stop after sometime although the reactants are not completely consumed. This state of the system is referred to as *state of equilibrium*. The attainment of equilibrium is recognised by constancy of *certain observable properties*. **For example**, in the case of dissociation of calcium carbonate, we recognised the attainment of equilibrium by observing that pressure of carbon dioxide had become constant. In this case, *attainment of equilibrium has been recognised by observing constancy of pressure*. In case of reaction between hydrogen and iodine the attainment of equilibrium is recognised by observing *constancy of intensity of colour* of the reaction mixture.

Sometimes, concentration of one of the reactants or products is measured to recognise the state of equilibrium. Thus:

The state of equilibrium is a state in which the measurable properties of the system do not undergo any noticeable change under a particular set of conditions.

EXPERIMENT 1

Aim: Perform an experiment to demonstrate reversible and irreversible chemical reactions

Theory:
$$\text{PCl}_5 \longrightarrow \frac{\text{PCl}_3 + \text{Cl}_2}{\text{Product}}$$

Reactant Product

$$\frac{\text{PCl}_3 + \text{Cl}_2}{\text{Products}} \longrightarrow \frac{\text{PCl}_5}{\text{Reactants}}$$

Reversible reactions are those reactions where products react again under suitable conditions to form reactants again. For example, if we heat PCl_5 it decomposes to PCl_3 and Cl_2 . If PCl_3 and Cl_2 are given suitable conditions of temperature and pressure, they react to form PCl_5 again. Such reactions are reversible reactions.

If products are not able to form reactants again the reaction is called irreversible.

Requirements: Beaker, Water, Common salt (NaCl), Paper, Raw egg, Burner, Stirrer, Wire gauge.

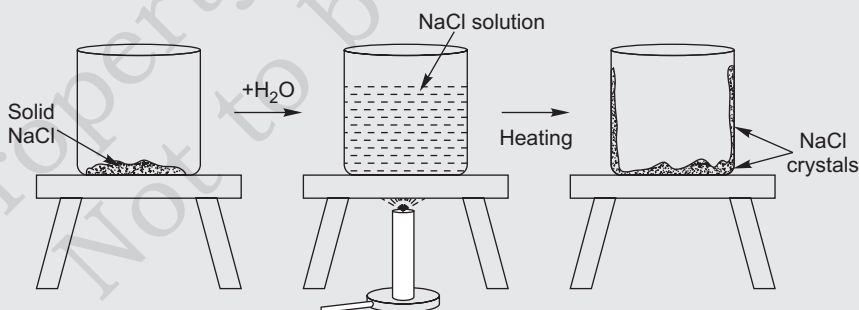


Fig. 7.5. Reversible reaction showing solid NaCl \rightarrow NaCl solution \rightarrow NaCl Crystals evaporation

Procedure: Reversible Reaction:

1. Take a beaker and pour 100 ml of water in it.
2. Now add 35 gm of common salt and dissolve it with a stirrer.
3. Heat the aqueous solution of NaCl to evaporate water.

4. We get crystals of NaCl again.
5. Hence this is a reversible reaction.

Other examples:

1. Same experiment can be done with copper sulphate solution
2. Freezing of water to ice, then melting of ice water again.
3. $2\text{KClO}_3 \rightleftharpoons 2\text{KCl} + 3\text{O}_2$. This is a reversible reaction.
4. Take copper sulphate in a test tube, heat the test tube. the blue copper sulphate loses water and becomes white. Now left the test tube cool again. The anhydrous copper sulphate absorbs water vapours from the air and turns blue again.

Irreversible reaction:

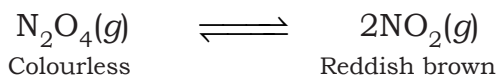
1. Here reactants change to product permanently and do not give back the reactants again.
2. Take flour, egg, and sugar. Mix them and add water to it. Now take it in an oven. It becomes a cake. This cake can not be changed again to initial ingredients (Reactants) e.g. flour, egg, sugar and water.

Other Characteristics of Chemical Equilibrium

It has already been discussed that chemical equilibrium is dynamic in nature. In addition to this, other characteristics of chemical equilibrium are:

1. **The observable properties of the system, such as pressure, colour, concentration, etc., become constant at equilibrium and remain unchanged thereafter.** For example, for the reaction between hydrogen and iodine to form hydrogen iodide, the colour of the reaction mixture becomes constant at equilibrium.

2. **The equilibrium can be approached from either direction.** This can be proved with the help of a very simple experiment of the equilibrium between dinitrogen tetroxide, N_2O_4 (colourless gas) and nitrogen dioxide, NO_2 (a reddish brown gas).



It is observed that at ordinary temperature, say 298 K, two gases exist as equilibrium mixture having pale brown colour. At very low temperature (273 K), N_2O_4 is stable and exists almost as pure N_2O_4 (colourless gas). When temperature is increased, it decomposes to NO_2 . At 373 K, it decomposes almost completely to NO_2 , which is dark brown in colour.

Let us take two identical flasks A and B. Fill both of them with nitrogen dioxide and seal them. Place the flask A in an ice bath and the flask B in boiling water as shown in Fig. 7.6.

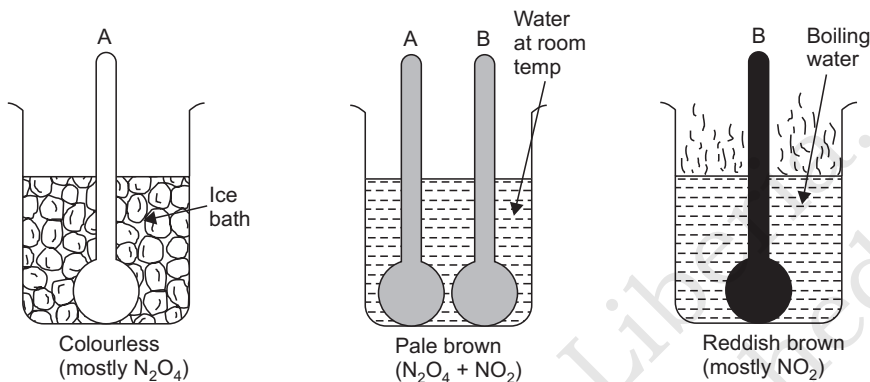


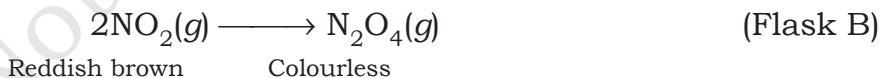
Fig. 7.6. Study of the equilibrium, $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$.

The gas in a flask A becomes almost colourless and consists of mostly N_2O_4 molecules. On the other hand, the gas in flask B becomes reddish brown and consists of mainly NO_2 molecules.

Now transfer both the flasks into a bath maintained at 298 K and observe the change in colour. The colour of the gas in flask A starts changing into brown colour indicating the gradual conversion of N_2O_4 into NO_2 .



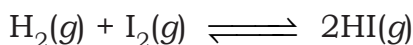
On the other hand, the reddish brown colour in flask B begins to fade and becomes pale brown indicating the gradual decomposition of N_2O_4 . This may be represented as:



After some time, when both the flasks attain the temperature of the bath, the colour in the two flasks becomes identical and no further change in colour occurs. This constancy of colour indicates that equilibrium has been attained in both the flasks and both contain mixture of NO_2 and N_2O_4 of the same composition.

This experiment clearly demonstrates that the equilibrium can be approached from either direction.

Similarly, let us consider the reaction between hydrogen and iodine to form hydrogen iodide.



Suppose 1 mol each of H_2 and I_2 is taken in a closed container and heated to 730 K. The forward reaction starts. As a result concentrations of H_2 and I_2 start decreasing while that of HI starts increasing. Finally, all the concentrations become constant and the reaction attains equilibrium. The colour of the reaction mixture becomes constant at this stage. Now take 2 mol of HI in the closed container of the same size and heat to 730 K. The backward reaction starts taking place. As a result, concentration of HI starts decreasing while that of H_2 and I_2 start increasing and finally become constant when the equilibrium is attained.

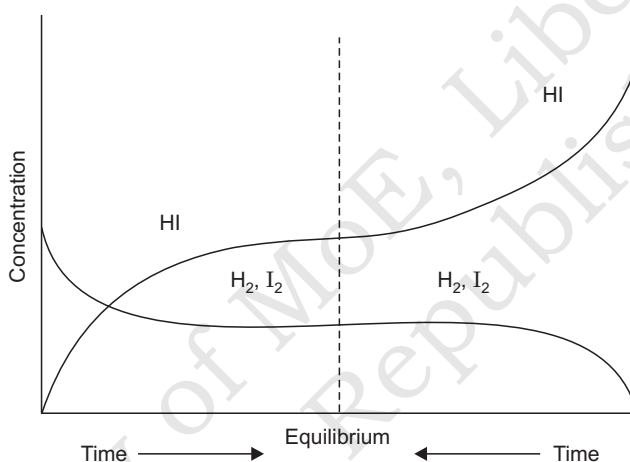


Fig. 7.7. Chemical equilibrium can be attained from either direction.

If we compare the intensity of purple colour in the two containers we find that it is identical. It indicates that same equilibrium is attained in both cases, in one case starting with H_2 and I_2 and in the other case starting with HI . It shows that equilibrium can be attained from either direction.

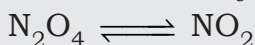
3. The equilibrium can be attained only if the system is closed.

For the establishment of equilibrium, it is necessary that the system should be close one. If the system is not closed, the products may escape from the container and, therefore, backward reaction may not take place.

4. A catalyst does not alter the equilibrium point. In a reversible reaction, catalyst increases the rate of forward as well as backward reaction to the same extent. Therefore, equilibrium point is not altered. However, the equilibrium is attained earlier in the presence of a catalyst.

EXPERIMENT 2

Aim: Demonstrate an experiment by heating $\text{Pb}(\text{NO}_3)_2$ and dinitrogen tetra oxide to explain the variation of K_c/K_p .



Theory: The $K_c = \frac{[\text{CNO}_2]^1}{[\text{N}_2\text{O}_4]^1}$ when temperature increases number of molecules/moles of NO_2 increase as a result K_c will increase.

Same way $K_p = \frac{[\text{PNO}_2]^1}{[\text{PN}_2\text{O}_4]^1}$ on increasing of temperature pressure created by NO_2 molecules will increase hence K_p will increase on increase of temperature.

Requirements: Beaker, ice, water, flask, N_2O_4 , burner, tripod stand.

Procedure:

1. Take a flask containing N_2O_4 (dinitrogen)tetra oxide at low temperature (273 K). The N_2O_4 gas is colourless.
2. Now put the flask in another beaker at 298 K. At this temperature, the flask contains a mixture of N_2O_4 and NO_2 . Hence the flask shows a pale brown colour.
3. Now heat the flask upto 373 K. At this temperature the whole of N_2O_4 changes to NO_2 resulting in change of colour to pure brown as NO_2 is brown in colour.
4. Hence it is observed that on increasing the temperature both K_c and K_p will increase.

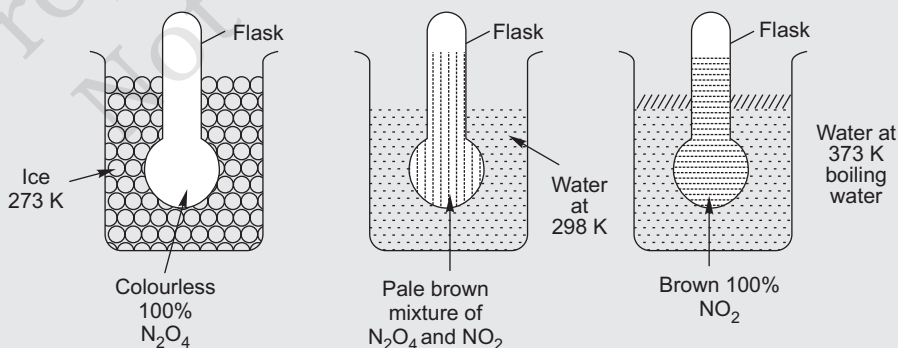


Fig. 7.8

Observation:

1. At 273 K (0°C) the flask contains only N_2O_4 which is colourless. The formation of NO_2 .
2. At 298 K (20°C) the flask contains a mixture of N_2O_4 and NO_2 resulting in pale brown colour in the flask.
3. At 373 K (100°C) whole of N_2O_4 changes to NO_2 showing 100% brown colour in the brown.

Result: K_p and K_c increases with increase in temperature.

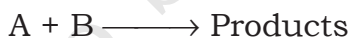
7.2. LAW OF CHEMICAL EQUILIBRIUM AND EQUILIBRIUM CONSTANT

Law of Mass Action

On the basis of observations of many equilibrium reactions, two Norwegian chemists Cato Guldberg and Peter Waage (1864) suggested a qualitative relationship between rates of reaction and the concentration of the reacting species. The relationship is known as **Law of Mass Action**. This law states that:

At constant temperature the rate of a chemical reaction is directly proportional to the product of the molar concentrations of reacting species with each concentration term raised to the power equal to the numerical co-efficient of that species in the chemical equation.

Let us apply mass action to a hypothetical reaction.

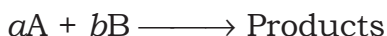


According to law of mass action,

$$\text{Rate of reaction, } r \propto [\text{A}][\text{B}] = k [\text{A}][\text{B}]$$

where $[\text{A}]$ and $[\text{B}]$ are the molar concentrations of the reactants A and B respectively, k is a constant of proportionality called rate constant.

For any general reaction,



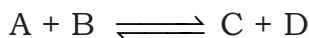
The law of mass action may be written as

$$\text{Rate} = k [\text{A}]^a [\text{B}]^b$$

Application of Law of Mass Action to Chemical Equilibrium

By applying law of mass action to a reversible reaction, at equilibrium, it is possible to derive a simple mathematical expression known as **law of chemical equilibrium**.

Let us consider a simple reversible reaction,



in which an equilibrium exists between the reactants A and B and the products C and D. According to law of mass action:

$$\begin{aligned} \text{Rate of forward reaction} &\propto [A][B] \\ &= k_f [A][B] \end{aligned}$$

where k_f is the rate constant for the forward reaction. [A] and [B] are molar concentrations of reactants A and B respectively.

$$\begin{aligned} \text{Similarly, the rate of backward reaction} \\ &\propto [C][D] \\ &= k_b [C][D] \end{aligned}$$

where k_b is the rate constant for the backward reaction and [C] and [D] are molar concentrations of products C and D respectively.

At equilibrium the rates of two opposing reactions become equal. Therefore, at equilibrium,

$$\text{Rate of forward reaction} = \text{Rate of backward reaction}$$

$$\therefore k_f [A][B] = k_b [C][D]$$

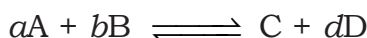
$$\text{or } \frac{k_f}{k_b} = \frac{[C][D]}{[A][B]}$$

Since k_f and k_b are constants, therefore, the ratio k_f/k_b is also constant and is represented by K_c .

$$K_c = \frac{k_f}{k_b} = \frac{[C][D]}{[A][B]} \quad \dots(7.3)$$

The constant K_c is called **equilibrium constant**. The subscript 'c' indicates that K_c is expressed in terms of concentrations (mol L^{-1}) of reactants and products. The concentrations in the expression 7.3 are the equilibrium concentrations.

For a general reaction of the type:



The expression of equilibrium constant can be written as:

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

The equilibrium constant, K_c , may be defined as the ratio of product of the equilibrium concentrations of the products to that of the reactants with each concentration term raised to the power equal to the stoichiometric co-efficient of the substance in the balanced chemical equation.

Equations (7.3) and (7.4) are the expressions for law of chemical equilibrium.

Law of chemical equilibrium may be stated as :

At a given temperature, the ratio of product of equilibrium concentrations of the products to that of the reactants with each concentration term raised to the power equal to the respective stoichiometric co-efficients in the balanced chemical has a constant value.

$$\text{The concentration ratio} = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

is called **concentration quotient** and is denoted by Q_c . According to law of chemical equilibrium,

$$Q_c = K_c, \text{ at equilibrium.}$$

Equilibrium Constant in Gaseous Systems

If an equilibrium involves gaseous species, then the concentrations in the concentration quotient may be replaced by partial pressures because at a given temperature the partial pressure of a gaseous component is proportional to its concentration. If the above mentioned reaction has all the gaseous species, then

$$Q_p = \frac{[p_C]^c [p_D]^d}{[p_A]^a [p_B]^b} = K_p$$

The equilibrium constant, K_p , defined in terms of partial pressures is not the same as the equilibrium constant, K_c , defined in terms of concentrations.

7.3. RELATIONSHIP BETWEEN K_p AND K_c

K_p	K_p is the equilibrium constant in terms of partial pressure of gaseous reactants and products.
K_c	K_c is the equilibrium constant in terms of concentration of reactants and products.

For an ideal gas,

$$PV = nRT$$

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

∴

$$p_A = C_A RT$$

$$p_B = C_B RT$$

$$p_C = C_C RT$$

$$p_D = C_D RT$$

$$K_p = \frac{[C_C RT]^c [C_D RT]^d}{[C_A RT]^a [C_B RT]^b}$$

$$= \frac{[C_C]^c [C_D]^d}{[C_A]^a [C_B]^b} \cdot (RT)^{(c+d) - (a+b)}$$

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

where

$$\Delta n = \left(\begin{array}{l} \text{Sum of the exponents in} \\ \text{the numerator of } Q_c \end{array} \right) - \left(\begin{array}{l} \text{Sum of the exponents in} \\ \text{the denominator of } Q_c \end{array} \right)$$

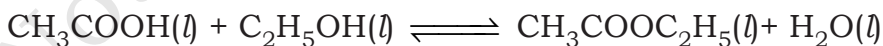
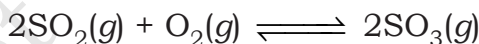
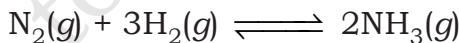
For the reactions such as $\text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2\text{HI}(g)$ and $\text{N}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{NO}(g)$ for which $\Delta n = 0$, the value of $K_p = K_c$. However, this is not true for all equilibria.

It is necessary that while calculating the value of K_p , pressures should be expressed in bar because standard state is 1 bar. The value of R in the relation $K_p = K_c (RT)^{\Delta n}$ is 0.083 bar litre/mol K.

Homogeneous and Heterogeneous Equilibria

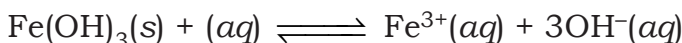
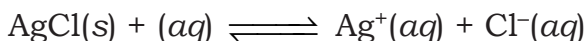
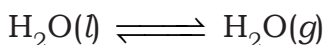
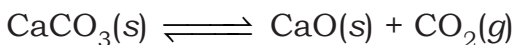
The equilibrium in which all the substances are present in the same phase is known as homogeneous equilibrium.

For example,



The equilibrium in which the substances involved are present in different phases is called heterogeneous equilibrium.

For example,

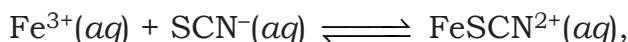


Characteristics of Equilibrium Constant (K)

Some important characteristics of equilibrium constant are as follows:

1. The equilibrium constant has a definite value for every chemical reaction at a particular temperature. The value of equilibrium constant is independent of initial concentrations of the reacting species.

For example, the equilibrium constant for the reaction,



at 298 K is

$$K = \frac{[\text{FeSCN}^{2+}]}{[\text{Fe}^{3+}][\text{SCN}^{-}]} = 138.0$$

Whatever may be the initial concentrations of the reactants, Fe^{3+} and SCN^{-} ions, the value of K comes out to be 138.0 at 298 K.

2. The value of equilibrium constant, K changes with change in temperature.

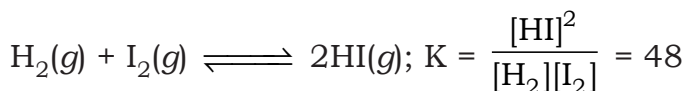
The value of K may increase or decrease with increase in temperature depending upon whether the reaction is endothermic or exothermic in nature. The values of K_p at different temperatures for an endothermic reaction $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$ and for an exothermic reaction ($\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$) are given in Table 7.1.

Table 7.1. Variation of K_p with Temperature for Some Reactions

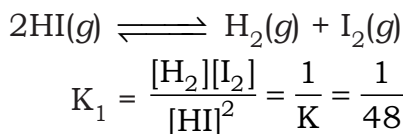
Reactions	Temperature (K)	K_p
$\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$	298	0.98
	400	47.9
	500	1700
$\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$	298	6.8×10^5
	400	41
	500	3.6×10^{-2}

3. For a reversible reaction, the equilibrium constant for the backward reaction is inverse of the equilibrium constant for the forward reaction.

For example, equilibrium constant, K, for the reaction of combination between hydrogen and iodine at 717 K is 48.



The equilibrium constant for the decomposition of hydrogen iodide at the same temperature is the inverse of the above equilibrium constant.



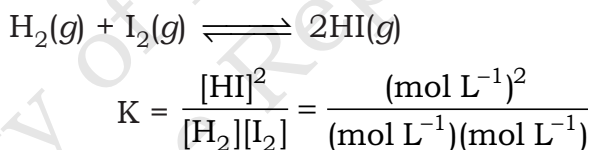
4. *The equilibrium constant is independent of the presence of catalyst.*

This is so because the catalyst does not affect the equilibrium state, at a particular temperature.

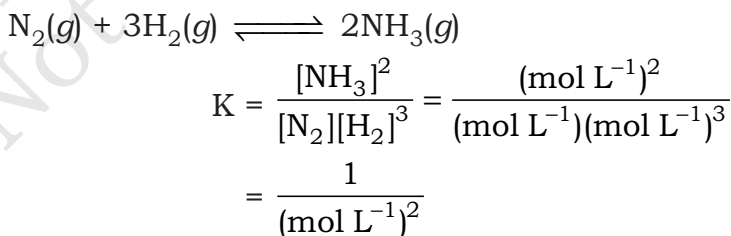
5. *If the equilibrium constant is expressed in terms of concentration, it has different units for different reactions.*

This can be illustrated by following examples:

(a) If the number of moles of the product is same as the number of moles of reactants, K has no units (*i.e.*, it is dimensionless). Thus, in the reaction between hydrogen and iodine to form hydrogen iodide, K has no units as illustrated below:



(b) If the number of moles of the products is *not the same* as that of reactants, K will have certain units depending upon the change in the number of moles. Thus, for the reaction between nitrogen and hydrogen to form ammonia, K would have the units $L^2 \text{ mol}^{-2}$ as shown below:



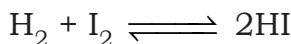
Thus, K will have the units $L^2 \text{ mol}^{-2}$.

Similarly, K_p for this reaction has units bar^{-2} .

Equilibrium Constants for a General Reaction and its Multiples

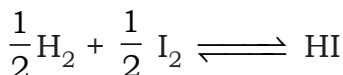
It may be noted that the value of K changes if the co-efficients of various species in the equation representing equilibrium are multiplied by some

number. For example, equilibrium constant for the equation



$$K_1 = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = 49 \text{ at } 711 \text{ K}$$

is different from the equilibrium constant for the equation



$$K_2 = \frac{[\text{HI}]}{[\text{H}_2]^{1/2} [\text{I}_2]^{1/2}} = \sqrt{K_1} = 7 \text{ at } 711 \text{ K}$$

In general, if K_1 is the equilibrium constant for a particular equation then equilibrium constant K_2 for some new equation which is obtained by multiplying the first equation by n is given by the following relation:

$$K_2 = (K_1)^n$$

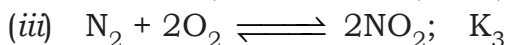
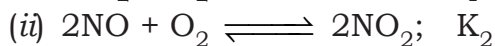
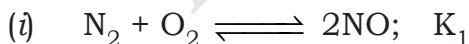
Thus, when the equation for an equilibrium is multiplied by a factor, the equilibrium constant must be raised to the power equal to the factor.

Table 7.2. 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
$c\text{C} + d\text{D} \rightleftharpoons a\text{A} + b\text{B}$	$K'_c = (1/K_c)$
$na\text{A} + nb\text{B} \rightleftharpoons nc\text{C} + nd\text{D}$	$K''_c = (K_c)^n$

6. When addition of two equilibria leads to another equilibrium then, the product of their equilibrium constants gives the equilibrium constant of the resultant equilibrium.

For example, consider the following three equilibria:



Now, addition of (i) and (ii) gives (iii), then

$$K_1 \times K_2 = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]} \times \frac{[\text{NO}_2]^2}{[\text{NO}]^2[\text{O}_2]}$$

$$= \frac{[\text{NO}_2]^2}{[\text{N}_2][\text{O}_2]^2} = K_3$$

Thus, $K_1 \times K_2 = K_3$.

Temperature Dependence of Equilibrium Constant

At equilibrium the rates of forward and backward reactions are equal. On increasing the temperature, the rates of reactions, in general, increase. However, the extents of increase in rates of forward and backward reactions are different. This is because of different values of activation energies for forward and backward reactions. In other words, the values of k_f and k_b will change with the increase in temperature but to a different extent. Consequently, the ratio k_f/k_b i.e., equilibrium constant will change with the rise in temperature. Some important facts to be noted are :

- K for endothermic reaction increases with rise in temperature.
- K for exothermic reaction decreases with rise in temperature.

If K_1 and K_2 are equilibrium constants of the reactions at two temperatures T_1 and T_2 and ΔH is the enthalpy change of the reaction, then

$$\log \frac{K_2}{K_1} = \frac{\Delta H}{2.303R} \left[\frac{T_2 - T_1}{T_2 T_1} \right]$$

7.4. APPLICATIONS OF EQUILIBRIUM CONSTANT

The knowledge of equilibrium constant helps us in

1. Predicting the extent of a reaction.
2. Predicting the direction in which the net reaction is taking place.
3. Calculation of equilibrium concentrations and equilibrium pressures.

1. Prediction of Extent of Reaction

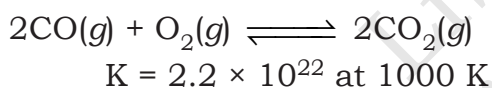
The magnitude of equilibrium constant tells us about the extent to which the reactants are converted into the products before the equilibrium is attained.

Larger the value of K , greater is the extent to which the reactants are converted into the products. On the other hand, if the value of K is small

it indicates that equilibrium is mainly in favour of reactants and that only a small fraction of the reactants is converted into products.

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

- If $K_c > 10^3$, products predominate over reactants. If K_c is very large, the reaction proceeds nearly to completion.
- If $K_c < 10^{-3}$, reactants predominate over products. If K_c is very small, the reaction hardly proceeds.
- If K_c is in the range of 10^{-3} to 10^3 , appreciable concentrations of both reactants and products are present.
- For example, consider the following reaction:

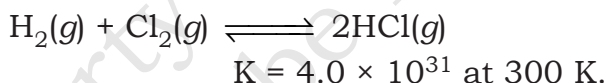


K for this reaction is given by the expression:

$$K = \frac{[\text{CO}_2]^2}{[\text{CO}]^2 [\text{O}_2]}$$

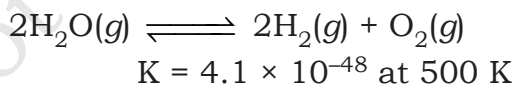
Large value of K in this indicates that at equilibrium, concentration of CO_2 is quite high. In other words, this indicates that the reaction between CO and O_2 to form CO_2 is almost complete under the given conditions.

Similarly, the value of K is very large for the reaction:



This indicates that the formation of HCl from H_2 and Cl_2 goes to almost completion at 300 K.

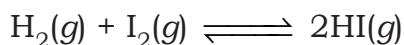
Let us now consider another reaction:



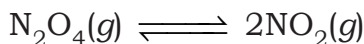
The expression for equilibrium constant of this reaction is

$$K = \frac{[\text{H}_2]^2 [\text{O}_2]}{[\text{H}_2\text{O}]^2}$$

Since the value of K in this case is very small, it indicates that at equilibrium, the concentrations of H_2 and O_2 are very small. In other words, under the given conditions only a small fraction of H_2O dissociates into H_2 and O_2 . Now let us consider some reactions in which the value of K_c is neither too small nor too large. In such reactions there are appreciable concentrations of both reactants and products at equilibrium. The two such equilibria are given as follows:



$$K_c = 57 \text{ at } 700 \text{ K}$$



$$K_c = 4.64 \times 10^{-3} \text{ at } 298 \text{ K}$$

Relationship between K_c and the extent of reaction is illustrated in Fig. 7.9.

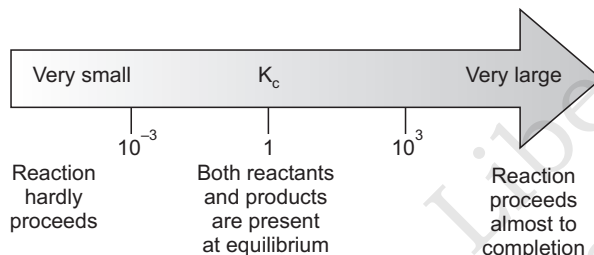


Fig. 7.9. Relationship between K_c and the extent of reaction.

The value of K also gives us an idea about the relative stabilities of reactants and products. If value of K is large, the products are more stable whereas if K is small, the reactants are more stable.

2. Predicting the Direction of the Net Reaction

From the knowledge of equilibrium constant, it is possible to predict the direction in which the net reaction is taking place at a given concentrations or partial pressures of reactions and products.

From the given concentrations, the concentration quotient Q_c for the reaction is calculated. By comparing the value of Q_c with the equilibrium constant, K_c the direction of reaction can be predicted.

- If $Q_c > K_c$, the net reaction is taking place in backward direction *i.e.*, direction of reactants.
- If $Q_c < K_c$, the net reaction is taking place in forward direction *i.e.*, direction of products.
- If $Q_c = K_c$, the reaction is at equilibrium *i.e.*, no net reaction is taking place.

For example, for the reaction, $\text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2\text{HI}(g)$, the value of K_c at 717 K is 48. If at a particular instant, the concentrations of H_2 , I_2 and HI are 0.2 mol L^{-1} , 0.3 mol L^{-1} and 0.6 mol L^{-1} respectively then the concentration quotient of the reaction at this stage would be

$$Q_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(0.6)^2}{(0.2)(0.3)} = 6$$

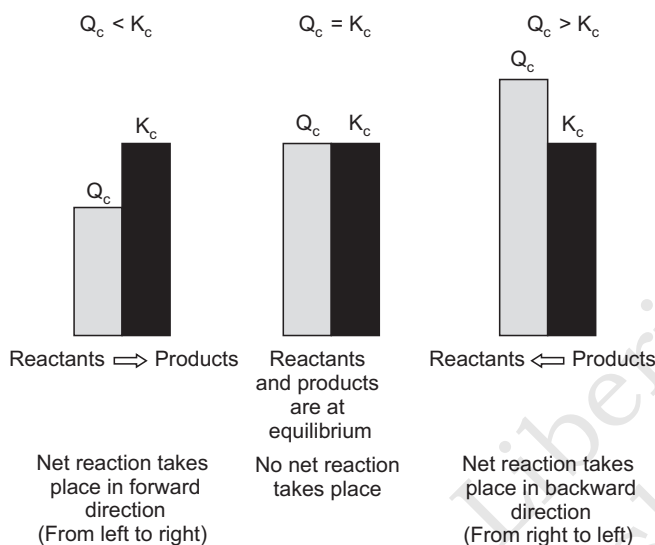


Fig. 7.10. Relation between Q_c , K_c and the direction of net reaction.

At this stage Q_c is less than K_c , therefore the net reaction will occur in the forward direction, resulting in the formation of more of HI.

3. Calculation of Equilibrium Concentrations and Equilibrium Pressures

If the equilibrium concentrations of various reactants and products are known in a reaction, the equilibrium constant can be calculated. On the other hand, if the equilibrium constant is known, then equilibrium concentration can be calculated.

Steps for Calculating Equilibrium Concentrations and Equilibrium Pressures

- Step I.** Write chemical equation for the equilibrium.
- Step II.** Write equilibrium constant expression for the reaction.
- Step III.** Express all unknown concentrations or partial pressures in terms of a single variable x .
- Step IV.** Substitute the equilibrium concentrations or partial pressures (in terms of x) in the equilibrium constant expression.
- Step V.** Solve the equation for x .
- Step VI.** Substitute the value obtained for x in the expressions in step III to calculate equilibrium concentrations or equilibrium partial pressures.

7.5. FACTORS AFFECTING EQUILIBRIA—Le Chatelier's Principle

Le Chatelier, a French chemist, made a generalization to explain the effect of changes in concentration, temperature or pressure on the state of system in equilibrium. The generalization is known as **Le Chatelier's Principle**. It states that:

If a system in equilibrium is subjected to a change of concentration, pressure or temperature, the equilibrium shifts in the direction that tends to undo the effect of the change.

Let us consider the effect of these variables in the light of Le Chatelier's principle, in the case of a few well known equilibria.

Effect of Change of Concentration

According to Le Chatelier's principle, when the concentration of one of the substance in a system at equilibrium is increased, then the equilibrium will shift so as to use up the substance added. Suppose at equilibrium one of the reactants is added, the equilibrium will shift in the direction that consumes reactants, *i.e.*, the forward direction. In other words, more of the reactants would be converted into products. On the other hand, if one of the products is added, the equilibrium will shift in the backward direction because it consumes the products.

In order to understand the effect of change of concentration on equilibrium, let us consider the reaction,



If H_2 is added to the reaction mixture at equilibrium, then the equilibrium of the reaction is disturbed. In order to restore it, the reaction proceeds in a directions wherein H_2 is consumed, *i.e.*, more of H_2 and I_2 react to form HI and finally the equilibrium is re-established. Thus, addition of H_2 shifts the equilibrium in forward direction. In the new equilibrium mixture, the concentration of H_2 would be less than it was after addition of H_2 but more than what it was in the original equilibrium has been shown Fig. 7.11.

The same point can be understood in terms of the reaction quotient, Q_c .

$$Q_c = [\text{HI}]^2 / [\text{H}_2] [\text{I}_2]$$

If concentration of H_2 is increased, the value of Q_c decreases and it is no longer equal to K_c . In order to attain new equilibrium, the reaction proceeds in forward direction resulting in decrease in concentrations of H_2 and I_2 and increase in concentration of HI. Finally, new equilibrium is attained.

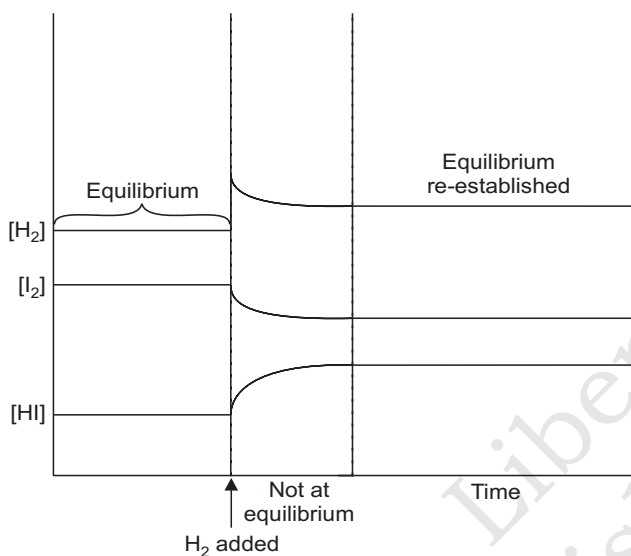
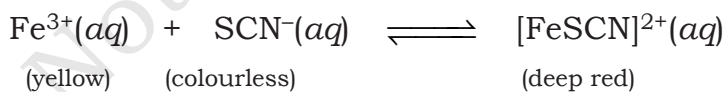


Fig. 7.11. Effect of addition of H_2 on change of concentration for the reactants and products in the reaction, $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$.

Similarly, we can say that removal of a product also favours the forward reaction and increases the concentration of the products. **For example**, in the manufacture of NH_3 by Haber's process, ammonia is liquefied and removed from the reaction mixture so that reaction keeps moving in forward direction. Similarly, in the large scale production of CaO , by calcination of lime stone (CaCO_3), CO_2 is continuously removed from the kiln to shift the reaction in forward direction. Continuous removal of one of the products maintains Q_c at a value less than K_c and thus reaction keeps on proceeding in the forward direction.

The effect of concentration on equilibrium can be demonstrated with the help of the following reaction:



$$K_c = \frac{[\text{Fe}(\text{SCN})^{2+}(\text{aq})]}{[\text{Fe}^{3+}(\text{aq})][\text{SCN}^{-}(\text{aq})]}$$

A reddish colour appears on adding 2 – 3 drops of 0.002 M potassium thiocyanate solution to 5 mL of 0.2 M iron (III) nitrate solution due to the formation of $[\text{Fe}(\text{SCN})]^{2+}$. The intensity of the red colour becomes constant when equilibrium is attained. This equilibrium can be shifted in either forward or backward directions depending on our choice of adding a reactant or a product.

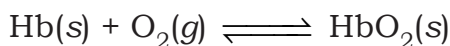
Suppose, some ferric salt (say, ferric chloride) is added to this equilibrium. The colour of the solution deepens immediately showing that there is increase in the concentration of the coloured complex ion $[\text{FeSCN}]^{2+}$. This change is in accordance with Le-Chatelier's principle. Addition of more of Fe^{3+} ions has resulted in increasing the concentration of the complex $[\text{FeSCN}]^{2+}$ ions. The change imposed on the system meant to raise the concentration of one of the *reactants* (Fe^{3+} ions) but it has resulted in raising the concentration of the *product*. Similarly, if some potassium thiocyanate is added at the equilibrium, the colour deepens again due to the formation of more of the $[\text{FeSCN}]^{2+}$ ions. Here again the addition of one of the *reactants* had led to the formation of more of the *products*.

The above equilibrium can be shifted in the backward direction by adding reagents that remove Fe^{3+} or SCN^- ions. For example, oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$), reacts with Fe^{3+} ions to form the stable complex ion $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$, thus decreasing the concentration of Fe^{3+} ions. In accordance with the Le Chatelier's principle, the decrease in the concentration of Fe^{3+} ions, leads to the decrease in concentration of $[\text{FeSCN}]^{2+}$ ions which is indicated by the fact that colour of the solution becomes lighter.

Addition of HgCl_2 solution also decreases red colour because Hg^{2+} ions reacts with SCN^- ions to form stable complex ion $[\text{Hg}(\text{SCN})_4]^{2-}$. Removal of free SCN^- ions shifts the equilibrium in backward direction to increase the concentration of SCN^- ions. The colour again becomes lighter due to decrease in concentration of $[\text{Fe}(\text{SCN})]^{2+}$ ions.

Let us study some **examples** illustrating the effect of change of concentration on equilibrium.

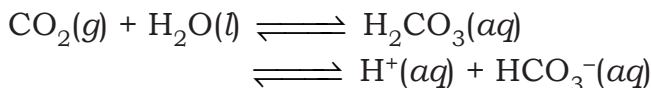
- (i) **Clothes dry quicker when there is breeze.** Clothes get dried quickly in breeze or by shaking them in air. It is because, the water vapours of nearby air are removed and the clothes lose water vapours to re-establish the equilibrium with surrounding air.
- (ii) **On a humid day we sweat more.** The sweating on a humid day is more because surrounding air has large amount of water vapours and our body cannot lose water as water vapours.
- (iii) **Transport of oxygen by haemoglobin in blood.** The haemoglobin, Hb, in the red corpuscles of our blood carries oxygen to the tissues. The equilibrium may be represented as



The blood that is in equilibrium with the oxygen of the air in the lungs finds a situation in the tissues where partial pressure of oxygen is low

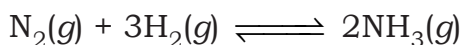
and hence the equilibrium readjusts itself by some of the oxyhaemoglobin releasing the oxygen. When the blood returns to the lungs the partial pressure of the oxygen is higher and more oxyhaemoglobin is formed.

(iv) **Removal of CO₂ from tissues by blood.** The blood removes the CO₂ from the tissues in the similar way. The equilibrium is :



Here, CO₂ dissolves in the blood in the tissues since its partial pressure is high; in the lungs where the partial pressure of CO₂ is low, it is released from the blood.

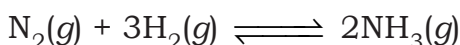
(v) **Formation of ammonia.** The reaction involving formation of ammonia is :



If at equilibrium more H₂ or N₂ is added to the above reaction, equilibrium shifts in the forward direction resulting in the formation of more NH₃. The equilibrium can also be shifted in forward direction by removing ammonia by liquifying. In general, it may be concluded that if concentration of one or all the reactant species is increased, the equilibrium shifts in the forward direction and more of the products are formed. Alternatively, if the concentration of one or all the product species is increased, the equilibrium shifts in the backward direction forming more of the reactants.

Effect of Change in Pressure

The change of pressure has effect only on those equilibria which involve gaseous substances and proceed with a change in the number of moles of the gases. According to Le Chatelier's principle, increase of external pressure should affect the equilibrium in such a way as to reduce the pressure. This implies that the equilibrium will shift in the direction which has smaller number of moles of the gaseous substances. This can be easily understood from the following equilibrium representing the formation of ammonia.



On increasing the pressure, the volume occupied by the system will decrease. As such there will be greater number of moles per unit volume. The effect of this change can be counteracted if the equilibrium shifts in the direction involving a decrease in the number of moles. This can happen only if nitrogen and hydrogen combine to form ammonia. Thus, increase in pressure in this case will favour the forward reaction.

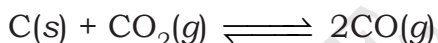
This can also be understood in terms of reaction quotient Q_c . Suppose pressure of the reaction mixture is doubled and volume is reduced to half. The partial pressures and concentrations of various species in the reaction mixture would become double. We obtain Q_c by replacing each equilibrium concentration by double its value.

$$K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{(a)^2}{(b)(c)^3} = \frac{a^2}{bc^3}$$

$$Q_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{(2a)^2}{(2b)(2c)^3} = \frac{a^2}{4bc^3}.$$

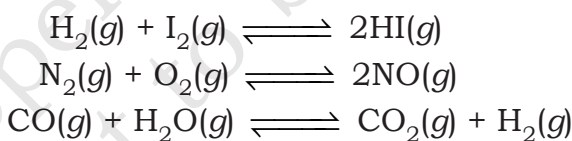
As the value of Q_c is less than K_c , the reaction proceeds in the forward direction.

Let us now consider the equilibrium in the following reaction :



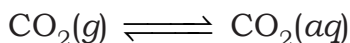
Here backward reaction takes place with a decrease in the number of moles of gaseous species. As the pressure is increased, the volume decreases and the number of moles per unit volume increases. Therefore, the equilibrium shifts in the backward direction. In this way, the number of moles of gases decreases and the effect of increase of pressure is counteracted to some extent. On the other hand, decrease in pressure shifts the equilibrium in the favour of forward reaction.

Now, let us consider some reactions which do not involve any change in number of moles of gaseous species :



In such reactions pressure does not have any effect on equilibrium.

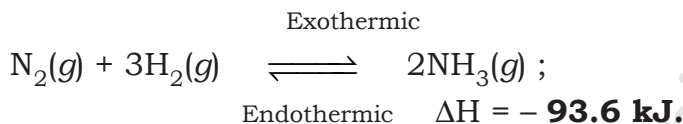
Let us explain the effect of pressure on solubility of gases in liquid solvents on the basis of **Le Chatelier's principle**. As an example, let us study the equilibrium involving dissolution of CO_2 in water. The equilibrium may be represented as :



On increasing the pressure of CO_2 the equilibrium shifts in the direction which results in the decrease in pressure of CO_2 . The pressure of CO_2 will be lowered only if $\text{CO}_2(g)$ dissolves in water to form $\text{CO}_2(aq)$. Thus, *solubility of a gas in some liquid is directly proportional to the pressure of the gas in equilibrium with the solution.*

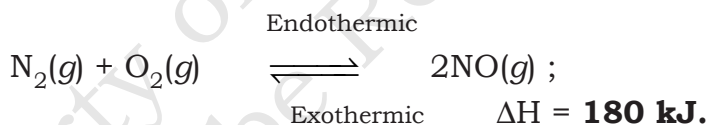
Effect of Temperature

A chemical equilibrium involves two opposing reactions, one favouring the products and the other favouring the reactants. If one of the reactions is exothermic the other must be endothermic. **For example**, let us consider the equilibrium representing the formation of ammonia:



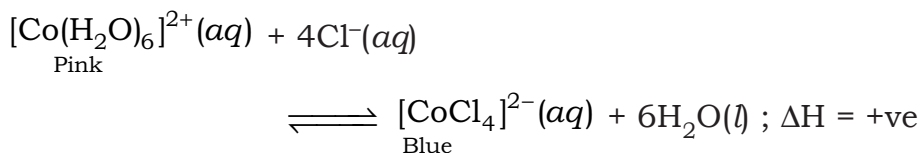
In this equilibrium, the forward reaction is exothermic while the backward reaction is endothermic. Now, if the temperature is increased, the equilibrium will shift in the direction of endothermic reaction, which tends to undo the effect of added heat. Since the backward reaction is endothermic, so the equilibrium shifts in favour of backward reaction. In other words, it will result into lesser amount of ammonia. On the other hand, if temperature is decreased, the equilibrium will shift towards exothermic reaction. So low temperature favours the formation of ammonia.

In the case of reaction between nitrogen and oxygen, the forward reaction is endothermic while the backward reaction is exothermic.



According to **Le Chatelier's principle**, the increase in temperature will favour the forward (endothermic) reaction. This is because, the equilibrium shifts towards the direction in which heat is absorbed to relieve the system of the stress of added heat. On the other hand, decrease in temperature shifts the equilibrium in the direction of exothermic reaction, *i.e.*, in favour of reactants in the above **example**.

The effect of temperature on equilibrium can be demonstrated with the help of a simple endothermic reaction.



At room temperature, the above equilibrium mixture is blue in colour due to the presence of $[\text{CoCl}_4]^{2-}$. When the reaction mixture is cooled in a freezing mixture the colour becomes pink due to formation of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$,

indicating that equilibrium has shifted in favour of reactants. On heating, the colour again becomes blue indicating that the equilibrium has shifted in favour of products.

It may be emphasized here that whenever an equilibrium is disturbed by a change in the concentration or pressure or volume, the reaction quotient, Q_c changes and no longer equals the equilibrium constant, K_c . However, when a change in temperature occurs, the value of equilibrium constant, K_c changes and Q_c is no longer equal to K_c .

In general, the temperature dependence of the K_c depends on whether the reaction is exothermic or endothermic.

- The equilibrium constant for an exothermic reaction decreases as the temperature increases.
- The equilibrium constant for an endothermic reaction increases as the temperature increases.

Effect of Temperature on Solubility of the Substances

We can also explain the effect of temperature on solubility of solids in liquids with the help of Le-Chatelier's principle. If during the dissolution **heat is absorbed**, the solubility **increases** with increase in temperature. NH_4Cl and NaNO_3 are examples of such substances. On the other hand, substances such as CaCl_2 , Li_2CO_3 , Li_2SO_4 and NaI **liberate heat** during dissolution. The solubility of such substances **decreases** with increase in temperature.

Dissolution of **gases in liquids** is always **exothermic**. Therefore, solubility of gases in liquids decreases with increase in temperature.

Effect of Catalyst

The presence of catalyst does not disturb the state of equilibrium because it increases the rate of forward as well as backward reaction to the same extent. It simply hastens the attainment of equilibrium by providing a new pathway having low activation energy. Catalyst does not disturb the equilibrium composition of the reaction mixture.

Certain reactions such as formation of ammonia from nitrogen and hydrogen cannot be carried out at high temperatures because high temperature favours the backward reaction. So such reactions give poor yields at high temperatures and therefore, have to be carried out at low temperature. But at low temperature the rate of reaction becomes very slow and it takes very long time to attain the equilibrium. In order to increase the rates of such reactions, generally, catalysts are used so

that equilibrium is attained early. For example, in case of formation of ammonia, a catalyst consisting of iron to catalyse the reaction is used.

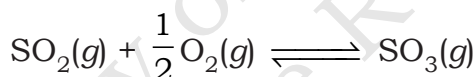
Effect of Addition of Inert Gas

The effect of addition of inert gas (*i.e.*, a gas which does not react with any of species involved in equilibrium) can be discussed under different conditions as described below :

(a) **Addition of inert gas at constant volume.** When inert gas is added to the equilibrium system at constant volume, it will cause the increase in the total pressure of the system. But the partial pressure of each of the reactant as well as product species will not be affected and will remain the same. Hence, under these conditions, *there will be no effect on the equilibrium.*

(b) **Addition of inert gas at constant pressure.** When inert gas is added to the system at constant pressure, it will result in the increase in volume. As a consequence of this, the number of moles per unit volume of various reactants and products will decrease. To counterbalance this stress, *the equilibrium will shift to the side where number of moles are increased.*

For example, for an equilibrium,



the addition of inert gas at constant pressure will push the equilibrium to the backward direction.

Similarly, for an equilibrium,



the addition of inert gas at constant pressure will push the equilibrium to the forward direction.

The effect of change of concentration, pressure and temperature has been summed up in the following table :

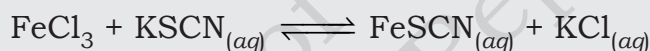
Stress	Direction in which Equilibrium Shifts
• Increase in the concentration of one or more reactants	Forward direction
• Increase in the concentration of one or more products	Backward direction
• Increase in temperature	Towards endothermic reaction

• Decrease in temperature	Towards exothermic reaction
• Increase of pressure	Towards lesser number of gaseous moles
• Decrease of pressure	Towards large number of gaseous moles
• Addition of catalyst	No effect
• Addition of inert gas : (a) at constant volume (b) at constant pressure	No effect Towards larger number of gaseous moles.

EXPERIMENT 3

Aim: Explain Le Chaterlier's principle using the reaction of FeCl_3 , KCN and H_2O .

Theory: According to Le Chaterlier's principle the equilibrium is subjected to change of concentration, pressure or temperature, the equilibrium shifts in the dirrection that tends to undo the effect of change.



$$K_c = \frac{[\text{Fe}(\text{SCN})_{\text{aq}}^{2+}]}{[\text{FeCl}_3] + [\text{KSCN}]}$$

Procedure: Take 25 ml 0.2 m FeCl_3 solution in a beaker, now add few drops of KSCN (pottassium thiocynate). The colour of the solution starts becoming dark red because of the formation of potassium thiocynate. Soon the stage of equilibrium comes. Now if we add any of the reactants like FeCl_3 or KSCN, it will lead to shift of equilibrium in forward direction resulting in formation of more feric thiocynate hence deepening of red colour. If we add water to the solution. The H_2O will react with Fe^{3+} ions decreasing the concentration of FeCl_2 in the solution resulting is lightening of red colour. It means decrease in concentration of Fe^{3+} ions result in decrease of product concentration also (FeSCN). Means equilibrium is shifting to left in order to undo the change of concentration.

Observation:

1. Adding of potassium thiosulphate causes increasing of concentration of reactant resulting in formation of more feric thiocynate due to shifting of equilibrium towards product side.

2. Adding of water causes decreases in concentration of reactant resulting in shifting of equilibrium towards reactant side hence decreasing the concentration of product (ferric thiocynate) which is visibly seen as lightening of colour. This experiment proves the Le Chaterlier's principle.

Precautions:

1. Can should be taken that temperature and pressure should remain constant.

SUMMARY

- **Equilibrium State.** A state of the system when its observable properties do not change at a given set of conditions. At equilibrium, the forward and backward reactions proceed at same rate.
- **Physical Equilibrium.** Equilibrium achieved in physical processes.
- **Chemical Equilibrium.** Equilibrium achieved in chemical processes.
- **Homogeneous Equilibrium.** Equilibrium in which reactants and products are in same phase.
- **Heterogeneous Equilibrium.** Equilibrium in which various substances involved have different phases.
- **Law of Mass Action.** A theoretical concept which states that rate of reaction is directly proportional to the product of molar concentrations of reactants with each concentration term raised to the power equal to stoichiometric co-efficient of that species in the balanced equation.
- **Velocity Constant or Rate Constant.** It is the rate of reaction when concentration of each of reacting species is unity.
- **Equilibrium Constant (K).** It is the ratio of the velocity constants of forward reaction to that of backward reaction.
- **Applications of Equilibrium Constant**
 - To predict the extent of a reaction on the basis of its magnitude.
 - To predict the direction of the reaction.
 - To calculate equilibrium concentrations.
- If $K_c > 10^3$, products predominate over reactants, and the reaction proceeds nearly to completion.
If $K_c < 10^{-3}$, reactants predominate over products, and the reaction proceeds rarely.

If K_c is in the range 10^3 to 10^{-3} appreciable concentrations of both the reactants and products are present.

- **Le Chatelier's Principle.** When an equilibrium is subjected to any kind of stress (change in concentration, temperature or pressure) it shifts in a direction so as to undo the effect of stress.

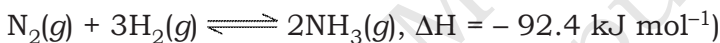


EVALUATION

I. Multiple Choice Questions

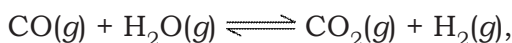
- In a chemical reaction, equilibrium is established when:
 - opposing reaction ceases
 - concentrations of reactants and products are equal
 - velocity of the opposing reaction is same as that of forward reaction
 - forward reaction ceases.

- Application of Le Chatelier's principle indicates that synthesis of ammonia (represented by



is favoured by

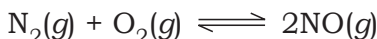
- low pressure
 - high temperature
 - presence of catalyst
 - removal of ammonia.
- According to Le Chatelier's principle, adding heat to a solid and liquid in equilibrium will cause the
 - amount of solid to decrease
 - amount of liquid to decrease
 - temperature to rise
 - temperature to fall.
 - Which of the following is not a general characteristic of equilibria involving physical processes?
 - All the physical processes stop at equilibrium.
 - Equilibrium is possible only in a closed system at a given temperature.
 - All measurable properties of the system become constant.
 - The opposing processes occur at the same rate.
 - Which of the following equilibria will have the same values for K_p and K_c ?
 - $\text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g)$
 - $\text{PCl}_5(g) \rightleftharpoons \text{PCl}_3(g) + \text{Cl}_2(g)$
 - $\text{A}(s) + 2\text{B}(g) \rightleftharpoons 2\text{C}(g)$
 - $\text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g)$.
 - For the reaction,



at a given temperature, the equilibrium amount of $\text{CO}_2(g)$ can be increased by

- (a) adding a suitable catalyst
- (b) adding an inert gas
- (c) decreasing the volume of container
- (d) increasing the amount of $\text{CO}(g)$.

7. The equilibrium constant for the reaction,



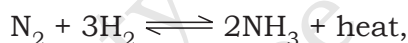
is 4×10^{-4} at 2000 K. In presence of a catalyst, equilibrium is attained ten times faster. Therefore, the equilibrium constant, in presence of the catalyst, at 2000 K is

- (a) 40×10^{-4}
- (b) 4×10^{-4}
- (c) 4×10^{-3}
- (d) difficult to compute without more data.

8. Which of the following statements is correct about the equilibrium constant?

- (a) Its value increases by increase in temperature
- (b) Its value decreases by decrease in temperature
- (c) Its value may increase or decrease with increase in temperature
- (d) Its value is constant at all temperatures.

9. The units of equilibrium constant for the reaction



will be

- (a) $\text{mol}^{-2} \text{L}^2$
- (b) mol L^{-1}
- (c) $\text{mol}^2 \text{L}^{-2}$
- (d) L mol^{-1} .

10. In which of the following equilibria K_c and K_p are not equal?

- (a) $2\text{NO}(g) \rightleftharpoons \text{N}_2(g) + \text{O}_2(g)$
- (b) $\text{SO}_2(g) + \text{NO}_2(g) \rightleftharpoons \text{SO}_3(g) + \text{NO}(g)$
- (c) $\text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2\text{HI}(g)$
- (d) $2\text{C}(s) + \text{O}_2(g) \rightleftharpoons 2\text{CO}_2(g) + \text{O}_2(g)$.

II. Fill in the Blanks

1. An equilibrium can be achieved only in _____ reactions.
2. For the reaction,

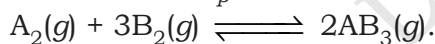


the increase in temperature shifts the equilibrium in _____ direction.

3. For a certain equilibrium reaction $K_p = K_c$. It indicates the equilibrium is _____ pressure variation.
4. The temperature at which solid \rightleftharpoons liquid equilibrium exist is known as _____ of the substance.
5. With increase in concentrations of the reactants, the value of equilibrium constant _____ .

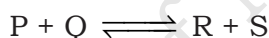
III. Descriptive Questions

1. What is the meaning of notation $[A]^x$ as used in the expression of equilibrium?
2. What is meant by concentration quotient of chemical reaction? Under what conditions, it is equal to equilibria constant?
3. Write expression and units of K_p for the reaction



4. Equilibrium constants for certain reactions for certain reactions at two temperatures 20°C and 50°C are respectively 1×10^{-2} and 1×10^{-3} , can it help in predicting the exothermic and endothermic nature of the forward reaction?

5. Two equilibria $A + B \rightleftharpoons C + D$



have values of K at 25°C as 1×10^{-2} and 1×10^{20} . What do they tells us about reaction?

6. For reaction $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ the value of equilibrium constant is 80 atm at 100°C . What is the behaviour of the mixture of NO_2 and N_2O_4 with respective partial pressure as 4×10^{-3} atm each?
7. Can equilibrium be achieved between water and its vapours in an open beaker?
8. On dissolving ammonium chloride in water cooling effect is caused. Predict on the basis of Le Chatelier's principle the effect of temperature on the solubility of ammonium chloride.
9. Why do we sweat more on humid day?
10. Name the factors on which equilibrium constant depends.
11. Why solubility of CO_2 decreases with rise in temperature?
12. What is the effect of catalyst on equilibrium state?
13. Explain the following:
 - (i) Normal freezing point
 - (ii) Vapour pressure of a liquid.
 - (iii) Henery's Law.

14. What is the effect of temperature and pressure on the solubility of
- (i) a solid in liquid
 - (ii) a gas in liquid.

IV. Numerical Questions

1. For reaction $\text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g)$ the value of K_p is 3.6×10^{-3} at 500 K. Calculate the value of K_c for the reaction at the same temperature.

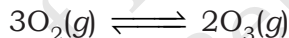
2. At 700 K, the equilibrium constant K_p of the reaction



is 1.8×10^{-3} kPa. What is the numerical value in moles per litre K_c for this reaction at the same temperature.

3. A gaseous reaction $e + f \rightleftharpoons g$ at 373 K, the partial pressure of e, f, g at equilibrium are 0.30 atm and 0.60 atm respectively. Calculate K_p and K_c for the reaction.
4. Consider the reaction $\text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g)$ at 373 K. Suppose at a particular moment concentration of N_2O_4 and NO_2 are 1 mol L^{-1} each. In which direction the reaction will proceed to establish equilibrium? K for the reaction is 0.36.

5. The value of K_c for the reaction



is 2.0×10^{-50} at 25°C . If the equilibrium concentration of O_2 in air at 25°C is 1.6×10^{-2} . What is the concentration of O_3 ?