

## 12. Chemical Equilibrium



### Can you recall?

What are the types of the following changes? Natural waterfall, spreading of smoke from burning incense stick, diffusion of fragrance of flowers. Can the above changes take place in the opposite direction?

**12.1 Introduction :** You have learnt earlier that changes can be physical or chemical and reversible or irreversible. All the changes listed above are **irreversible physical changes**. You have also learnt earlier that chemical changes can be represented by chemical reactions when the exact chemical composition of reactants and products is known. In this chapter we are going to look at **reversible chemical reactions**.

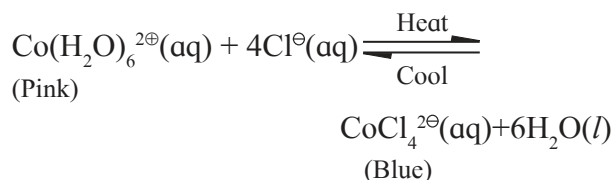
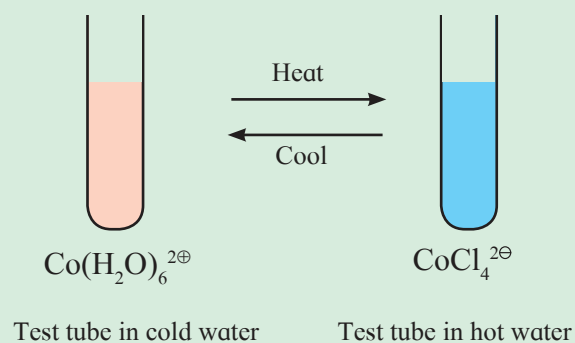
### 12.1.1 Reversible reaction

In the above activity, the change in colour of the solution is caused by the chemical reaction which reverses its direction with change of temperature.



### Try this

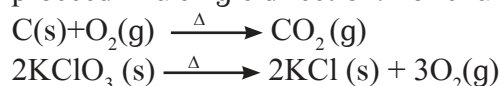
Dissolve 4 g cobalt chloride in 40 ml water. It forms a redish pink solution. Add 60 ml concentrated HCl to this. It will turn violet. Take 5 ml of this solution in a test tube and place it in a beaker containing ice water mixture. The colour of solution will become pink. Place the same test tube in a beaker containing water at 90°C. The colour of the solution turns blue.



### Can you tell?

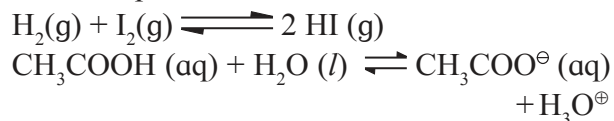
What does violet colour of the solution in above indicate?

The reaction in the above activity is an example of a **reversible reaction**. There are many chemical reactions which appear to proceed in a single direction. For example:



These are called **irreversible reactions**. They proceed only in single direction until one of the reactants is exhausted. Their direction is indicated by an arrow ( $\longrightarrow$ ) pointing towards the products in the chemical equation. On the contrary, reversible reactions proceed in both directions. The direction from reactants to products is the **forward reaction**, whereas the opposite reaction from products to reactants is called the **reverse or backward reaction**. A reversible reaction is denoted by drawing two arrows, such that one arrow points in the forward direction and other in the reverse direction ( $\rightleftharpoons$  or  $\rightleftarrows$ ). These two arrows are also referred to as double arrow.

For example :



Consider an example of decomposition of calcium carbonate. Calcium carbonate when heated strongly, decomposes to form calcium oxide and carbon dioxide. Let us consider what happens if this reaction is carried out in a closed container/system or open container/system.

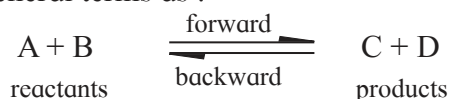


### Remember

In a closed system, there is no exchange of matter with the surroundings but exchange of heat can occur. In an open system, exchange of both matter and heat occurs with the surroundings. An isolated system does not exchange heat nor matter with surroundings.

If we perform the above reaction at high temperature in a closed system, we find that after certain time, we have some calcium carbonate present along with calcium oxide and carbon dioxide. If we continue the experiment over a longer period of time at the same temperature, we find the concentrations of calcium carbonate, calcium oxide and carbon dioxide are unchanged. The reaction thus appears to have stopped and we say the system has attained the equilibrium. Actually, the reaction does not stop but proceeds in both the directions with equal rates. In other words calcium carbonate decomposes to give calcium oxide and carbon dioxide at a particular rate. Exactly at the same rate the calcium oxide and carbon dioxide recombine and form calcium carbonate.

Such reactions which do not go to completion and occur in both the directions simultaneously are **reversible reactions**. A reversible reaction may be represented in general terms as :



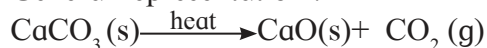
The double arrow indicates that the reaction is reversible.

Consider the reaction of decomposition of calcium carbonate occurring in an open system or container. It is seen that during decomposition of calcium carbonate in an open vessel, carbon dioxide can escape away. Hence calcium carbonate cannot be obtained back.

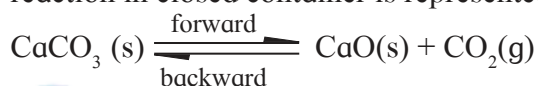
Such a reaction is **irreversible reaction** which occurs only in one direction, namely, from reactants to products.

Reactions are chemically represented as follows

General representation :



represents the irreversible reaction in an open container. On the other hand the reversible reaction in closed container is represented as



### Do you know ?

Calcium oxide is also known as quicklime or lime. When heated strongly it glows bright white. In old times this was used in theatre lighting, which gave rise to the phrase '*in the limelight*'.



### Internet my friend

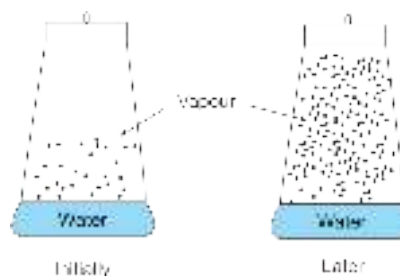
Find out the information :

1. Equilibrium existing in the formation oxyhaemoglobin in human body.
2. Refrigeration system in equilibrium.

## 12.2 Equilibrium in physical processes

### (a) Liquid - Vapour equilibrium

Let us now look at a reversible physical process of evaporation of liquid water into water vapour in a closed vessel (see Fig. 12.1).



**Fig. 12.1 : Water in a closed flask**

Initially there is practically no vapour in the vessel. When a liquid evaporates in a closed container, the liquid molecules escape from the liquid surface into vapour phase building up vapour pressure. They also condense back into liquid state because the container is closed. In the beginning the rate of evaporation is high and the rate of condensation is low. But with time, as more and more vapour is formed, the rate of evaporation goes down and the rate

of condensation increases. Eventually the two rates become equal. This gives rise to a constant vapour pressure. This state is known as an '**equilibrium state**'. In this state, the number of molecules leaving the liquid surface equals the number of molecules returning to the liquid from the vapour state. Across the interface, there is a lot of activity between the liquid and the vapour. This state, when the rate of evaporation is equal to the rate of condensation is called equilibrium state. It may be represented as :



At equilibrium, the pressure exerted by the gaseous water molecules at a given temperature remains constant, known as the equilibrium vapour pressure of water (or **saturated vapour pressure** of water or **aqueous tension**). The saturated vapour pressure increases with increase of temperature. In the case of water, the saturated vapour pressure is 1.013 bar (1atm) at 100 °C. Therefore, water boils at 100 °C when exposed to 1 atm pressure. For any pure liquid at 1 atm pressure the temperature at which its saturated vapour pressure equals to atmospheric pressure is called the normal boiling point of that liquid. The boiling point of water is 100° C at 1.013 bar pressure, whereas the boiling point of ethyl alcohol is 78 °C.

### (b) Solid - liquid equilibrium

Consider a mixture of ice and water in a perfectly insulated thermos flask at 273 K. This is an isolated system. It is an example of solid-liquid equilibrium. Ice and water are at constant temperature. They remain in what is called solid-liquid equilibrium.

### (c) Solid - vapour equilibrium :



#### Try this

1. Place some iodine crystals in a closed vessel. Observe the change in colour intensity in it. After some time the vessel gets filled up with violet coloured vapour.

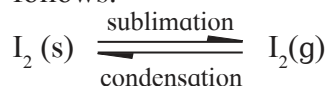
The intensity of violet colour becomes stable after certain time.

What do you see in the flask (see Fig. 12.2)?



**Fig. 12.2 Solid iodine in equilibrium with its vapour**

We see both, that is, solid iodine and iodine vapour in the closed vessel. It means solid iodine sublimates to give iodine vapour and the iodine vapour condenses to form solid iodine. The stable intensity of the colour indicates a state of equilibrium between solid and vapour iodine. We can write the same as follows:



Other examples showing this kind of equilibrium are :

1. Camphor (s)  $\rightleftharpoons$  Camphor (g)
2. Ammonium chloride (s)  $\rightleftharpoons$  Ammonium chloride (g).



#### Try this

- i. Dissolve a given amount of sugar in minimum amount of water at room temperature
- ii. Increase the temperature and dissolve more amount of sugar in the same amount of water to make a thick sugar syrup solution.
- iii. Cool the syrup to the room temperature.

**Note the observation :** Sugar crystals separate out.

In a saturated solution there exists dynamic equilibrium between the solute molecules in the solid state and in dissolved state.



The rate of dissolution of sugar

= The rate of crystallization of sugar



### Remember

A saturated solution is the solution when additional solute can not be dissolved in it at the given temperature. The concentration of solute in a saturated solution depends on temperature.

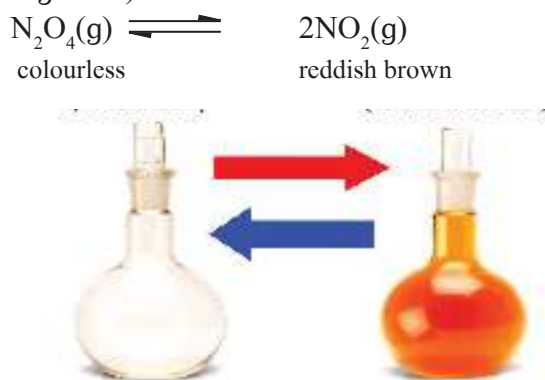
### 12.3 Equilibrium in chemical process :

If a reaction takes place in a closed system so that the products and reactants cannot escape, we often find that reaction does not give a 100 % yield of products. Instead some reactants remain after the concentrations stop changing. **When there is no further change in concentration of reactant and product, we say that the reaction has attained equilibrium, with the rates of forward and reverse reactions being equal.** Chemical equilibrium at a given temperature is characterized by constancy of measurable properties such as pressure, concentration, density etc. Chemical equilibrium can be approached from either side.



### Observe and Discuss

**I.** Colourless  $\text{N}_2\text{O}_4$  taken in a closed flask is converted to  $\text{NO}_2$  (a reddish brown gas) (See Fig. 12.3)



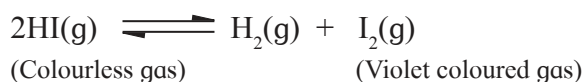
**Figure 12.3 :  $\text{N}_2\text{O}_4$  conversion to  $\text{NO}_2$**

The colour becomes light brown indicating the presence of  $\text{NO}_2$  in the mixture. The formation of  $\text{NO}_2$  from  $\text{N}_2\text{O}_4$  is reversible. In such reaction the reactants react to form the

products and the products react to give back reactants.

As soon as the forward reaction produces any  $\text{NO}_2$ , the reverse reaction begins and  $\text{NO}_2$  starts combining back to form  $\text{N}_2\text{O}_4$ . At equilibrium, the concentrations of  $\text{N}_2\text{O}_4$  and  $\text{NO}_2$  remain unchanged and do not vary with time, because the rate of formation of  $\text{N}_2\text{O}_4$  is equal to the rate of formation of  $\text{NO}_2$  as shown in Fig. 12.4. b.

**II.** Consider the following dissociation reaction

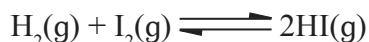


The reaction is carried out in a closed vessel starting with hydrogen iodide. The following observations are noted :

1. At first, there is an increase in the intensity of violet colour.
2. After certain time the increase in the intensity of violet colour stops.
3. When contents in the closed vessel are analysed at this stage, it is observed that reaction mixture contains hydrogen iodide, hydrogen and iodine with their concentrations remaining constant over time.

The rate of decomposition of HI becomes equal to the rate of combination of  $\text{H}_2$  and  $\text{I}_2$ . At equilibrium, no net change is observed and both reactions continue to occur.

Let us now see what happens if we start with hydrogen and iodine vapour in a closed container at a certain temperature.



1. At first, the violet colour if  $\text{I}_2$  is deep.
2. The intensity of violet colour starts decreasing.
3. After certain time the decrease in the intensity of colour stops.
4. Analysis of the reaction mixture at this stage shows that it contains HI,  $\text{H}_2$  and  $\text{I}_2$  with their concentrations remaining constant over time. In other words, the same equilibrium can be attained by starting from any side.



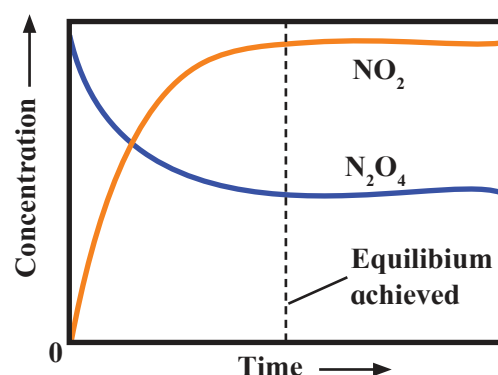


Fig. 12.4 (a) : Graph of forward and reverse reaction rates versus time for conversion of  $\text{N}_2\text{O}_4$  to  $\text{NO}_2$

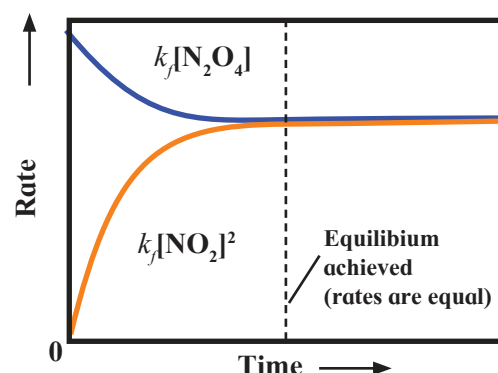


Fig. 12.4 (b) : Changes in reaction rates during a reversible reaction attaining a chemical equilibrium. (Forward rate represented by upper curve in blue and reverse reaction rate lower curve in yellow)



#### Remember

For any reversible reaction in a closed system the rate of forward reaction is high in the beginning, while the rate of reverse reaction is very slow. As the forward reaction proceeds and products accumulate, rate of forward reaction slows down while rate of reverse reaction increases. Finally the rates become equal and equilibrium is established.

**12.4 Law of mass action and equilibrium constant :** The chemical equilibrium is mathematically described in terms of what is called the **equilibrium constant ( $K_c$ )**. We noted earlier that an equilibrium state is attained when the rate of the forward and reverse reactions become equal (refer Fig.

12.4).

**12.4.1 Rate of chemical reaction :** As any reaction proceeds the concentration of the reactants decreases and the concentration of the products increases. The rate of reaction thus can be determined by measuring the extent to which the concentration of a reactant decreases in the given time interval, or extent to which the concentration of a product increases in the given time interval. Mathematically, the rate of reaction is expressed as:

$$\text{Rate} = - \frac{d[\text{Reactant}]}{dT} = \frac{d[\text{Product}]}{dT}$$

Where  $d[\text{reactant}]$  and  $d[\text{product}]$  are the small change in concentration during the small time interval  $dT$ .

**12.4.2 Law of mass action :** The law of mass action states that **the rate of a chemical reaction at each instant is proportional to the product of concentration terms of all the reactants**. In case the balanced chemical equation shows more molecules of reactants, the concentration is raised to a power equal to the number of molecules of that reactant. A rate equation can be written for a reaction by applying the law of mass action as follows :

Consider a reaction  $\text{A} + \text{B} \longrightarrow \text{C}$

Here A and B are the reactants and C is the product. The concentrations of chemical species are expressed in  $\text{mol L}^{-1}$  and denoted by putting the formula in square brackets. By applying the law of mass action to this reaction we write a proportionality expression as :

$$\text{Rate} \propto [\text{A}] [\text{B}]$$

This proportionality expression is transformed into an equation by introducing a proportionality constant,  $k$ , as follows:

$$\text{Rate} = k [\text{A}] [\text{B}] \quad \dots(12.1)$$

The Eq. (12.1) is called the **rate equation** and the proportionality constant,  $k$ , is called the **rate constant** of the reaction.

**Problem 12.1 :** Write the rate equation for the following reaction:



**Solution :** the rate equation is written by applying the law of mass action.

i. The reactants are C and  $O_2$

$$\text{Rate} \propto [C] [O_2]$$

$$\therefore \text{Rate} = k [C] [O_2]$$

ii. The reactant is  $KClO_3$  and its 2 molecules appear in the balanced equation.

$$\therefore \text{Rate} \propto [KClO_3]^2$$

$$\therefore \text{Rate} = k [KClO_3]^2$$

**12.4.3 Equilibrium constant :** Consider a hypothetical reversible reaction  $A + B \rightleftharpoons C + D$ . As we have noted earlier, two reactions, namely forward and reverse reactions occur simultaneously in a reversible chemical reaction. We, therefore, write rate equations for the forward and reverse reactions:

$$\text{Rate}_{\text{forward}} \propto [A][B]$$

$$\therefore \text{Rate}_{\text{forward}} = k_f [A] [B] \quad \text{..... (12.2)}$$

$$\text{Rate}_{\text{reverse}} \propto [C] [D]$$

$$\therefore \text{Rate}_{\text{reverse}} = k_r [C] [D] \quad \text{..... (12.3)}$$

At equilibrium, the rates of forward and reverse reactions are equal. Thus,

$$\text{Rate}_{\text{forward}} = \text{Rate}_{\text{reverse}}$$

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

$$\therefore \frac{k_f}{k_r} = K_c = \frac{[C][D]}{[A][B]} \quad \text{..... (12.4)}$$



#### Remember

At equilibrium the ratio of product multiplicative term denoting the ratio of concentration of products to that of the reactants is unchanged and equals  $K_c$ . The value of  $K_c$  depends upon the temperature. It is interesting to note that though the concentration ratio remains unchanged, both the forward as well as reverse reactions do proceed at equilibrium, but at the same rate. Therefore the chemical equilibrium is a **dynamic equilibrium**.

$K_c$  is called the **equilibrium constant**.

The equilibrium constant depends on the form of the balanced chemical equation. Consider reversible reaction :



$$\text{The equilibrium constant } K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad \text{..... (12.5)}$$

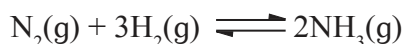
If the equilibrium is written as



$$K'_c = \frac{[A]^a [B]^b}{[C]^c [D]^d} = \frac{1}{K_c}$$

Thus equilibrium constant of the reverse chemical reaction is  $K'_c$ , is the reciprocal of the equilibrium constant  $K_c$  of the forward reaction.

Let us consider the equilibrium that occurs in the Haber process for synthesis of ammonia:



$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} \quad \begin{array}{l} \longleftarrow \text{coefficient of } NH_3 \\ \longleftarrow \text{coefficient of } H_2 \end{array}$$

and for the equilibrium reaction written as



$$K'_c = \frac{[N_2][H_2]^3}{[NH_3]^2}$$

**12.4.3 Equilibrium constant with respect to partial pressure ( $K_p$ ) :** For reactions involving gases, it is convenient to express the equilibrium constant in terms of partial pressure.

$\therefore$  For the reaction,



the equilibrium constant can be expressed using partial pressures ( $K_p$ ) as given by

$$K_p = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b} \quad \text{..... (12.6)}$$

where  $P_A$ ,  $P_B$ ,  $P_C$  and  $P_D$  are equilibrium partial pressures of A, B, C and D, respectively.



### Can you recall?

Ideal gas equation with significance of each term involved in it (refer to Chapter 10, section 10.5.5).

$PV = nRT$ , where  $P$  is pressure in pascal

$n$  is number of moles of gas

$V$  is volume in  $\text{dm}^3$  or  $\text{L}$

$R$  is molar gas constant in  $\text{Pa m}^3 \text{K}^{-1} \text{mol}^{-1}$

$T$  is absolute temperature

### 12.4.4 Relationship between partial pressure and concentration :

For a mixture of ideal gases, the partial pressure of each component is directly proportional to its concentration at constant temperature.

For component A,

$$P_A V = n_A RT$$

$$\frac{n_A}{V} \text{ is molar concentration of A in mol dm}^{-3}$$

$$P_A = \frac{n_A}{V} \times RT, \quad \text{where } \frac{n_A}{V} = [A]$$

$$\therefore P_A = [A]RT$$

Similarly for components B, C and D the partial pressures are

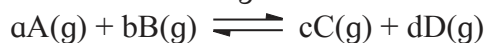
$$P_B = [B]RT$$

$$P_C = [C]RT$$

$$P_D = [D]RT$$

### 12.4.5 Relationship between $K_p$ and $K_c$

Consider a general reversible reaction:



Now substituting expressions for  $P_A, P_B, P_C, P_D$  in Eq. (12.6)

$$K_p = \frac{[P_C]^c [P_D]^d}{[P_A]^a [P_B]^b} = \frac{[C]^c (RT)^c [D]^d (RT)^d}{[A]^a (RT)^a [B]^b (RT)^b}$$

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

$$\therefore K_p = \frac{[C]^c [D]^d}{[A]^a [B]^b} \times (RT)^{(c+d)-(a+b)}$$

$$\therefore K_p = \frac{[C]^c [D]^d}{[A]^a [B]^b} \times (RT)^{\Delta n}$$

But  $K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$  from equation (12.5)

$$\therefore K_p = K_c (RT)^{\Delta n}, \quad \dots\dots (12.7)$$

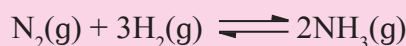
where  $\Delta n = (\text{number of moles of gaseous products}) - (\text{number of moles of gaseous reactants})$  in balanced chemical equation.

$$R = 8.314 \text{ L Pa m}^3 \text{K}^{-1} \text{mol}^{-1}$$

While calculating the value of  $K_p$ , **pressure should be expressed in bar**, because standard pressure is 1 bar.

$$[1 \text{ pascal (Pa)} = 1 \text{ Nm}^{-2} \text{ and } 1 \text{ bar} = 10^5 \text{ Pa}]$$

### Problem 12.2 :



Write expression for  $K_p$  in terms of  $K_c$ .

$$\text{Solution : } K_p = \frac{(P_{\text{NH}_3})^2}{(P_{\text{N}_2})(P_{\text{H}_2})^3}$$

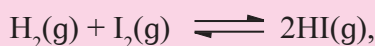
$$\therefore K_p = \frac{[\text{NH}_3(g)]^2 [RT]^2}{[\text{N}_2(g)] [RT] [\text{H}_2(g)]^3 [RT]^3}$$

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

$$\therefore K_p = K_c \times RT^{(2-4)}$$

$$\therefore K_p = K_c \times RT^{-2}$$

**Problem 12.3 :** Write an expression for  $K_p$  and relate it to  $K_c$  for the following reversible reaction.



$$\text{Solution : } K_p = \frac{(P_{\text{HI}})^2}{(P_{\text{H}_2})(P_{\text{I}_2})}$$

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

$$\therefore K_p = \frac{[\text{HI}(g)]^2}{[\text{H}_2(g)] [\text{I}_2(g)]} \times \frac{[RT]^2}{[RT] [RT]}$$

$$\therefore K_p = K_c \times RT^{2-(1+1)}$$

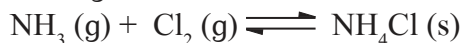
$$\therefore K_p = K_c$$

## 12.5 Homogeneous and Heterogeneous equilibria

**12.5.1 Homogeneous reactions and Heterogeneous reactions :** In a homogeneous reaction all the reactants are in the same phase. For example is a homogeneous gas phase reaction.



Reversible reaction involving reactants and products those are in different phases is called heterogeneous reaction.



Equilibria involving homogeneous or heterogeneous reactions are called homogeneous and heterogeneous equilibria respectively.

**12.5.2 Equilibrium constant for heterogeneous equilibria :** As stated earlier, equilibrium having more than one phase is called heterogeneous equilibrium. For example, if ethanol is placed in a conical flask, liquid - vapour equilibrium is established.



For a given temperature

$$K_c = \frac{[\text{C}_2\text{H}_5\text{OH(g)}]}{[\text{C}_2\text{H}_5\text{OH(l)}]}$$

At any given temperature density of liquid is constant irrespective of the amount of liquid, and, therefore, the term in the denominator is constant.  $[\text{C}_2\text{H}_5\text{OH(l)}] = \text{constant}$ .

Therefore, the modified equilibrium constant for evaporation of ethanol will be

$$K'_c = K_c \times \text{constant} = [\text{C}_2\text{H}_5\text{OH}_{(g)}]$$

For the equilibrium of sublimation of iodine  $\text{I}_2\text{(s)} \rightleftharpoons \text{I}_2\text{(g)}$  the modified equilibrium constant  $K'_c = [\text{I}_2\text{(g)}]$ .

Concentrations of pure solids do not change and thus expressions for equilibria including solids are simplified.



### Remember

While writing an equilibrium constant expression for heterogeneous reactions use only the concentrations of gases (g) and dissolved substances (aq).

### 12.5.3 Units of equilibrium constant

The unit of equilibrium constant depends upon the expression of  $K_c$  which is different for different equilibria. Therefore, the unit of  $K_c$  is also different.

**To calculate units of equilibrium constant**

Equilibrium Reaction (I)	Equilibrium Reaction (II)
$\text{H}_2\text{(g)} + \text{I}_2\text{(g)} \rightleftharpoons 2\text{HI (g)}$ $K_c = \frac{[\text{HI(g)}]^2}{[\text{H}_2\text{(g)}][\text{I}_2\text{(g)}]} \quad \dots (I)$ $\text{Unit of } K_c = \frac{[\text{mol dm}^{-3}]^2}{[\text{mol dm}^{-3}][\text{mol dm}^{-3}]}$ $= \frac{[\text{mol dm}^{-3}]^2}{[\text{mol dm}^{-3}]^2}$ <p>As all the units cancel out For (I), <math>K_c</math> has no units</p>	$\text{N}_2\text{(g)} + 3\text{H}_2\text{(g)} \rightleftharpoons 2\text{NH}_3\text{(g)}$ $K_c = \frac{[\text{NH}_3\text{(g)}]^2}{[\text{N}_2\text{(g)}][\text{H}_2\text{(g)}]^3} \quad \dots (II)$ $\text{Unit of } K_c = \frac{[\text{mol dm}^{-3}]^2}{[\text{mol dm}^{-3}][\text{mol dm}^{-3}]^3}$ $= \frac{[\text{mol dm}^{-3}]^2}{[\text{mol dm}^{-3}]^4}$ $= [\text{mol dm}^{-3}]^{-2}$ $= \text{mol}^{-2} \text{dm}^6$

**Hint :** To calculate units of  $K_c$  find out the difference between the number of moles in the numerator and the number of moles in the denominator in the expression for equilibrium constant.

The unit of  $K_c$  is  $(\text{mol dm}^{-3})^{\Delta n}$ .

With reference to expression (II) above, difference between number of moles =

$$\Delta n = 2 - (1+3)$$

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

$$\therefore \Delta n = -2$$



$\therefore$  unit of  $K_C = (\text{mol dm}^{-3})^{\Delta n}$

$\therefore$  unit of  $K_C = (\text{mol dm}^{-3})^{-2}$

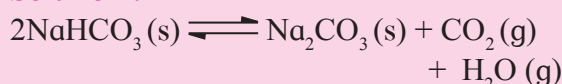
$\therefore$  unit of  $K_C = \text{mol}^{-2} \text{dm}^6$

Similarly with reference to expression (I) \ unit of  $K_C = (\text{mol dm}^{-3})^{\Delta n} = (\text{mol dm}^{-3})^0$

$\therefore K_C$  has no unit.

**Problem 12.4 :** Write the equilibrium constant expression for the decomposition of baking soda. Deduce the unit of  $K_C$  from the above expression.

**Solution :**



$$K_C = \frac{[\text{Na}_2\text{CO}_3(\text{s})][\text{CO}_2(\text{g})][\text{H}_2\text{O}(\text{g})]}{[\text{NaHCO}_3(\text{s})]^2}$$

$$\therefore K_C = [\text{CO}_2(\text{g})][\text{H}_2\text{O}(\text{g})]$$

$$\therefore \text{Unit of } K_C = (\text{mol dm}^{-3})^2 = \text{mol}^2 \text{dm}^{-6}$$

## 12.6 Characteristics of equilibrium constant

1. The value of equilibrium constant is independent of initial concentrations of either the reactants or products.
2. Equilibrium constant is temperature dependent. Hence  $K_C$ ,  $K_P$  change with change in temperature.
3. Equilibrium constant has a characteristic value for a particular reversible reaction represented by a balanced equation at the given temperature.
4. Higher value of  $K_C$  or  $K_P$  means more product is formed and the equilibrium point is more towards right hand side and vice versa.

## 12.7 Application of equilibrium constant

Some applications of equilibrium constant are discussed below.

### 12.7.1 Prediction of the direction of the reaction :

For the reversible reaction,



the equilibrium constant is

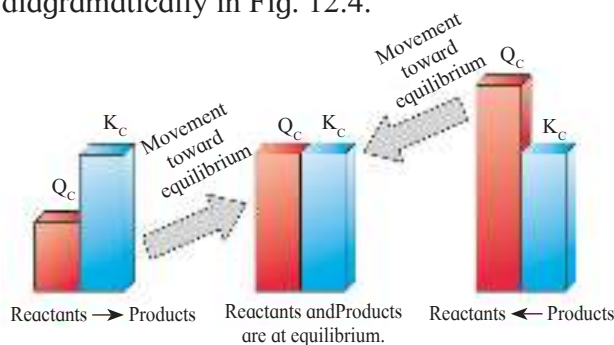
$$K_C = \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b},$$

where all concentrations are equilibrium concentrations.

The ratio is called reaction quotient,  $Q_C$ , when the concentrations are not necessarily equilibrium concentrations.

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

The reaction quotient has same form as that of equilibrium constant, but involves concentrations that are not necessarily equilibrium concentrations. Comparison of  $Q_C$  and  $K_C$  is very useful to decide whether the forward or the reverse reaction should occur to establish the equilibrium. It is shown diagrammatically in Fig. 12.4.



**Fig. 12.4 : Predicting direction of reaction**

If  $Q_C < K_C$ , the reaction will proceed from left to right, in forward direction, generating more product to attain the equilibrium.

If  $Q_C = K_C$  the reaction is at equilibrium and hence no net reaction occurs.

If  $Q_C > K_C$ , the reaction will proceed from right to left, requiring more reactants to attain equilibrium.

A comparison of  $Q_C$  with  $K_C$  indicates the direction in which net reaction proceeds as the system tends to attain the equilibrium.

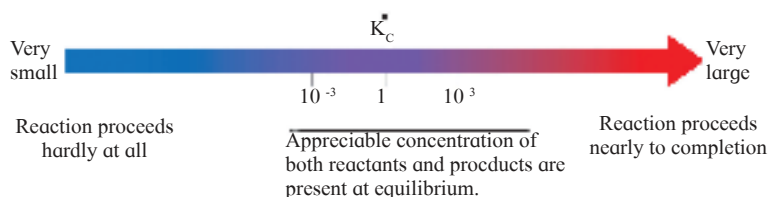
**Note :** The prediction of the direction of the reaction on the basis of  $Q_C$  and  $K_C$  values makes no comment on the time required for attaining the equilibrium.

### 12.7.2 : To know the extent of reaction :

Let us recall an expression for equilibrium constant  $K_C$ . (See Fig. 12.5). It indicates that the magnitude of  $K_C$  is

- i. directly proportional to the equilibrium concentrations of the product.
- ii. inversely proportional to the equilibrium concentrations of the reactants.

The larger the value of the equilibrium constant  $K_c$ , the farther the reaction proceeds to the right before reaching the equilibrium state :



**Fig 12.5 : Extent of reaction**

Consider, for example, the following two reversible reactions :

$2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{H}_2\text{O}(\text{g})$	$2\text{H}_2\text{O}(\text{g}) \rightleftharpoons 2\text{H}_2(\text{g}) + \text{O}_2(\text{g})$
<p>Equilibrium constant values</p> $K_c = \frac{[\text{H}_2\text{O}(\text{g})]^2}{[\text{H}_2(\text{g})]^2[\text{O}_2(\text{g})]}$ $K_c = 2.4 \times 10^{47} \text{ At } 500 \text{ K}$	$K_c = \frac{[\text{H}_2(\text{g})]^2[\text{O}_2(\text{g})]}{[\text{H}_2\text{O}(\text{g})]^2}$ $K_c = \frac{1}{K_c} = \frac{1}{2.4 \times 10^{47}}$ $K_c = 4.1 \times 10^{-48} = 0.41 \times 10^{-47} \text{ at } 500 \text{ K}$
1. Value of $K_c$ is very high ( $K_c > 10^3$ ).	1. Value of $K_c$ is very low ( $K_c < 10^{-3}$ ).
2. At equilibrium there is a high proportion of products compared to reactants.	2. At equilibrium, only a small fraction of the reactants are converted into products.
3. Forward reaction is favoured.	3. Reverse reaction is favoured.
4. Reaction is in favour of products and nearly goes to completion.	4. Reaction is in favour of reactants.
$K_c \gg 1$ . Reaction proceeds almost totally towards products.	$K_c \ll 1$ . Reaction hardly proceeds towards the products.



### Can you tell?

Comment on the extent to which the forward reaction will proceed, from the magnitude of the equilibrium constant for the following reactions :

- $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$ ,  $K_c = 20$  at 550 K
- $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons 2\text{HCl}(\text{g})$ ,  $K_c = 10^{18}$  at 550 K

**12.7.3 To calculate equilibrium concentrations :** The equilibrium constant can be used to calculate the composition of an equilibrium mixture.

Consider an equilibrium reaction,  
 $\text{CH}_3\text{COOH}(\text{aq}) + \text{C}_2\text{H}_5\text{OH}(\text{aq}) \rightleftharpoons$   
 (ethanoic acid) (ethanol)  
 $\text{CH}_3\text{COOC}_2\text{H}_5(\text{aq}) + \text{H}_2\text{O}(\text{aq})$   
 (ethyl ethanoate)

The equilibrium constant is 4.0 at a certain temperature.



### Use your brain power

The value of  $K_c$  for the dissociation reaction  $\text{H}_2(\text{g}) \rightleftharpoons 2\text{H}(\text{g})$  is  $1.2 \times 10^{-42}$  at 500 K. Does the equilibrium mixture contain mainly hydrogen molecules or hydrogen atoms ?

If we start with 2.0 mol of ethanoic acid and 2.0 mol of ethanol in 'V' litres. Let us find out the composition of equilibrium mixture. Consider x mol of ethyl ethanoate at equilibrium.



### Internet my friend

Collect information about Chemical Equilibrium.

$\text{CH}_3\text{COOH} + \text{C}_2\text{H}_5\text{OH} \rightleftharpoons \text{CH}_3\text{COOC}_2\text{H}_5 + \text{H}_2\text{O}$				
Initial (No. of moles)	2.0	2.0	0	0
At equilibrium (No. of moles)	$(2.0 - x)$	$(2.0 - x)$	$x$	$x$
Equilibrium concentrations	$\frac{(2.0 - x)}{V}$	$\frac{(2.0 - x)}{V}$	$\frac{x}{V}$	$\frac{x}{V}$

#### Equilibrium constant

$$K_c = \frac{[\text{CH}_3\text{COOC}_2\text{H}_5][\text{H}_2\text{O}]}{[\text{CH}_3\text{COOH}][\text{C}_2\text{H}_5\text{OH}]}$$

$$\therefore 4.0 = \frac{\frac{x}{V} \times \frac{x}{V}}{\frac{(2.0 - x)}{V} \times \frac{(2.0 - x)}{V}}$$

substituting the value of equilibrium concentration

$$\therefore 4.0 = \frac{x^2}{(2.0 - x)^2}$$

$$\therefore \sqrt{4} = \frac{x}{2.0 - x}$$

$$\therefore 2 = \frac{x}{2.0 - x}$$

$$\therefore 4 - 2x = x$$

$$\therefore x = \frac{4}{3}$$

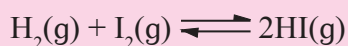
$$\therefore x = 1.33$$

$$\therefore (2.0 - x) = 0.67$$

Therefore, equilibrium concentrations are 0.67 mol of ethanoic acid, 0.67 mol of ethanol and 1.33 mol of ethyl ethanoate in  $V$  litres.

**Problem 12.5 :** Equal concentrations of hydrogen and iodine are mixed together in a closed container at 700 K and allowed to come to equilibrium. If the concentration of HI at equilibrium is  $0.85 \text{ mol dm}^{-3}$ , what are the equilibrium concentrations of  $\text{H}_2$  and  $\text{I}_2$  if  $K_c = 54$  at this temperature?

**Solution :** Balanced chemical reaction :



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

on substituting the values

$$\therefore 54 = \frac{(0.85)^2}{[\text{H}_2(\text{g})]^2}$$

as initial concentrations of  $\text{H}_2(\text{g})$  and  $\text{I}_2(\text{g})$  are equal.

(Refer to the balanced chemical equation : 1 mole of  $\text{H}_2$  reacts with 1 mole of  $\text{I}_2$ )

Equilibrium concentration of  $\text{I}_2(\text{g}) =$   
Equilibrium concentration of  $\text{H}_2(\text{g})$

$$\therefore 54 = \frac{(0.85)^2}{[\text{H}_2(\text{g})]^2},$$

$$\therefore [\text{H}_2(\text{g})] = 0.12 \text{ mol dm}^{-3}$$

Equilibrium concentrations of  $\text{H}_2$  and  $\text{I}_2$  are equal to  $0.12 \text{ mol dm}^{-3}$ .

#### 12.7.4 Link between chemical equilibrium and chemical kinetics :

We have deduced in section 12.4.3

$$K_c = \frac{k_f}{k_r} \quad \dots\dots (12.7)$$

Where  $k_f$  and  $k_r$  are velocity or **rate constants** of the forward and reverse reactions respectively.

This equation can be used to determine the composition of the reaction mixture

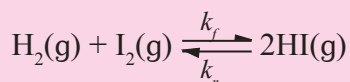
$k_f > k_r$	$k_f \approx k_r$
$\therefore K_c$ is very large.	$k_f$ and $k_r$ have comparable values $\therefore K_c$ is nearly one.
$\therefore$ Reaction goes almost to completion.	Reaction never goes to completion.
$\therefore$ If $k_f$ is much larger than $K_c$ , the reaction may be irreversible (Reverse reaction is too slow to be detected).	Comparable concentrations of reactants and products are present at equilibrium.



### Remember

The equilibrium refers to the relative amounts of reactants and products and thus a shift in equilibrium in a particular direction will imply the reaction in that direction will be favoured.

**Problem 12.6 :** The equilibrium constant  $K_C$  for the reaction of hydrogen with iodine is 54.0 at 700 K.



$K_C = 54.0$  at 700 K

a. If  $k_f$  is the rate constant for the formation of HI and  $k_r$  is the rate constant for the decomposition of HI, deduce whether  $k_f$  is larger or smaller than  $k_r$ .

**Solution :** As  $K_C = \frac{k_f}{k_r} = 54.0$ ,

$k_f$  is greater than  $k_r$  by a factor of 54.0

b. If the value of  $k_r$  at 700 K is  $1.16 \times 10^{-3}$ , what is the  $k_f$ ?

$$K_f = K_C \times k_r = 54.0 \times (1.16 \times 10^{-3}) \\ = 62.64 \times 10^{-3}$$

## 12.8 Le Chaterlier's principle and factors altering the composition at equilibrium :

We have learnt that a reaction attains a state of equilibrium under a certain set of conditions (temperature, pressure, concentration and catalyst).

In general, if we add more reactant, the system will react to remove it. If we remove a product, the system will react to replenish it. Under these changed conditions, new equilibrium will be established with different composition from the earlier equilibrium mixture.

**The principal goal of chemical synthesis is to achieve maximum conversion of reactants to products with minimum expenditure of energy.** To achieve this goal, the reaction conditions must be adjusted.

The qualitative effect of various factors on the composition of equilibrium mixture are

described through the Le Chatelier's principle.

If a stress is applied to a reaction mixture at equilibrium, reaction occurs in the direction which relieves the stress. Stress means any change in concentration, pressure, volume or temperature which disturbs the original equilibrium. The direction that the reaction takes is the one that reduces the stress. For example, if concentration of the reactants is increased, reaction goes in a direction that tends to decrease the concentration, that is, in the direction of forward reaction.

### Le Chatelier's Principle :

*It states that, when a system at equilibrium is subjected to a change in any of the factors determining the equilibrium conditions, system will respond in such a way as to minimize the effect of change.*

#### 12.8.1 Factors affecting equilibrium :

##### (a) Change of concentration

Consider reversible reaction representing production of ammonia ( $\text{NH}_3$ )



The reaction proceeds with decrease in number of moles ( $\Delta n = -2$ ) and the forward reaction is exothermic. Iron (containing a small quantity of molybdenum) is the catalyst.

$$\text{At equilibrium } Q_C = K_C = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} \dots\dots (I)$$

**Stage I :** system at equilibrium

**Stage II :** Equilibrium disturbed by making

$Q_C < K_C$  by adding  $\text{H}_2$ .

Due to addition of extra hydrogen, system is no longer at equilibrium.

The system regains its equilibrium in stage III.

**Stage III :** Added hydrogen is to be used up and converted to more  $\text{NH}_3$ . Hence forward reaction is favoured.

**Stage IV :** New state of equilibrium is established.

According to Le-Chatelier's principle, the effect of addition of  $\text{H}_2$  (or  $\text{N}_2$  or both) is reduced by shifting the equilibrium from left to right so that the added  $\text{N}_2$  or  $\text{H}_2$  is consumed.

The forward reaction occurs to a large extent than the reverse reaction until the new equilibrium is established. This results in increased yield of  $\text{NH}_3$ .



### Remember

In general, if the concentration of one of the species in equilibrium mixture is increased, the position of equilibrium shifts in the opposite direction so as to reduce the concentration of this species. However, the equilibrium constant remains unchanged.

### (b) Effect of Pressure

You know that : Ideal gas equation is

$$PV = nRT,$$

On rearranging we get,

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

$\therefore P \propto \frac{n}{V}$ , where the ratio  $\frac{n}{V}$  is an expression for the concentration of the gas in  $\text{mol dm}^{-3}$

1. An equilibrium mixture of dinitrogen tetroxide (colourless gas) and nitrogen dioxide (brown gas) is set up in a sealed flask at a particular temperature (refer to Fig. 12.3).



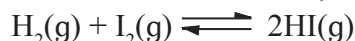
The effect of change of pressure on this gaseous equilibrium can be followed by observing the change in its colour intensity. See Table 12.1.

**Table 12.1 : Change in colour intensity**

Change in pressure	Change in colour intensity	Shift in equilibrium position
1. Decrease in pressure	The colour deepens	To the right, the side with more molecules
2. Increase in pressure	The colour lightens to almost colourless	To the left, the side with fewer molecules

In this reversible reaction, the forward reaction takes place with increase in the number of molecules, whereas reverse reaction takes place with decrease in the number of molecules.

2. Consider the reaction,



As there is the same number of molecules of gas on both sides, change of pressure has no effect on the equilibrium. Here, there is no change in value of  $K_c$  during any change in pressure of the equilibrium reaction mixture.



### Remember

A reaction in which decrease in volume takes place, reaction will be favoured by increasing pressure and the reaction with increase in volume will be favoured with lowering pressure, temperature being constant.

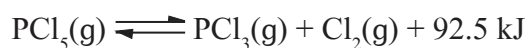


### Remember

In a reversible reaction, the reverse reaction has an energy change that is equal and opposite to that of the forward reaction.

### (c) Effect of Temperature :

Consider the equilibrium reaction,



The forward reaction is exothermic. The reverse reaction is endothermic. An endothermic reaction consumes heat. Therefore, increase in temperature results in shifting the equilibrium in the reverse direction to use up the added heat (heat energy converted to chemical energy).

Now let us study the effect of change of temperature on the equilibrium constant.

1. Consider the equilibrium reaction :



$$\Delta H = -90 \text{ kJ mol}^{-1}$$



Equilibrium constant  $K_c$  for the reaction, is given in Table 12.2.

$$K_c = \frac{[\text{CH}_3\text{OH}(\text{g})]}{[\text{CO}(\text{g})][\text{H}_2(\text{g})]^2}$$

**Table 12.2**

Temperature (K)	$K_c$
298	$1.7 \times 10^{17}$
500	$1.1 \times 10^{11}$
1000	$2.1 \times 10^6$

The forward reaction is exothermic. According to Le Chatelier's principle an increase in temperature shifts the position of equilibrium to the left. Therefore, the concentration of  $[\text{CH}_3\text{OH}(\text{g})]$  decreases and the concentration of  $\text{CO}(\text{g})$  and  $\text{H}_2(\text{g})$  increases.

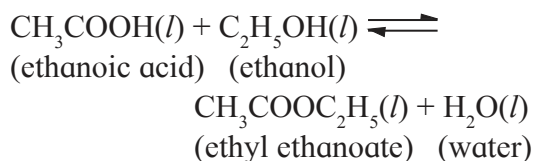
$$K_c = \frac{[\text{CH}_3\text{OH}(\text{g})]}{[\text{CO}(\text{g})][\text{H}_2(\text{g})]^2}$$

Therefore, the value of  $K_c$  decreases as the temperature is increased.

#### (d) Effect of Catalyst :

Rate of a chemical reaction, increases with the use of catalyst.

Consider an esterification reaction :



If the above reaction is carried out without catalyst, it would take many days to reach equilibrium. However, the addition of hydrogen ions ( $\text{H}^+$ ) as catalyst reduces the time only to a few hours.



#### Remember

In all the cases of change in concentration, pressure, temperature and presence of catalyst, once the equilibrium has been re-established after the change, the value of  $K_c$  will be unaltered

A catalyst does not affect equilibrium constant and equilibrium composition of a reaction mixture.



#### Do you know ?

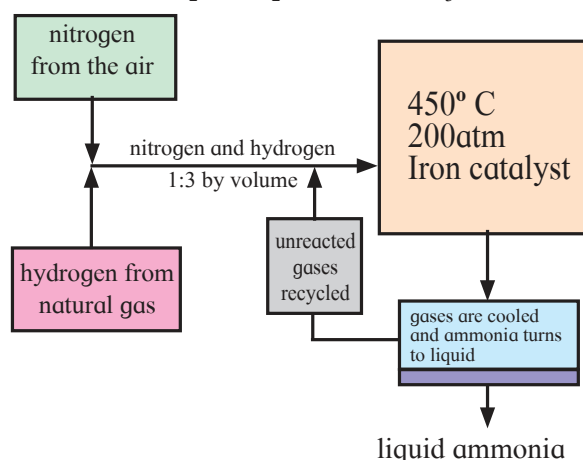
Catalyst lowers activation energy for the forward and reverse reactions by exactly the same amount.

A catalyst does not appear in the balanced chemical equation and in the equilibrium constant expression.

Let us **summarize** effects of all four factors on the position of equilibrium and value of  $K_c$ .

Effect of	Position of equilibrium	Value of $K_c$
Concentration	Changes	No change
Pressure	Changes if reaction involves change in number of gas molecules	No change
Temperature	Changes	Changes
Catalyst	No change	No change

Making ammonia The Haber process



**Fig. 12.6 The Haber process**

#### 12.9 Industrial Application :

**The Haber process :** (Industrial preparation of ammonia)

Industrial processes can be made efficient and profitable by applying ideas of rate of reaction and equilibrium.

The Haber process is the process of synthesis of ammonia gas by reacting together hydrogen gas and nitrogen gas in a particular stoichiometric ratio by volumes and at selected optimum temperature.



The reaction proceeds with a decrease in number of moles ( $\Delta n = -2$ ) and the forward reaction is exothermic. Iron (containing a small quantity of molybdenum) is used as catalyst.

We studied earlier in section 12.8.1 a. how the change in concentration of the reactants affects the yield of ammonia. Now let us consider the effect of temperature and pressure on the synthesis of ammonia.

**a. Effect of temperature :** The formation of ammonia is exothermic reaction. Hence, lowering of temperature will shift the equilibrium to right. At low temperature however, the rate of reaction is small and longer time would be required to attain the equilibrium. At high temperatures, the reaction occurs rapidly with appreciable decomposition of ammonia. Hence, the optimum temperature has to be used. The **optimum temperature** is about 773 K.

**b. Effect of pressure :** The forward reaction is favoured with high pressure as it proceeds with **decrease in number of moles**. At high pressure, the catalyst becomes inefficient. Therefore optimum pressure needs to be used. The **optimum pressure** is about 250 atm.



#### Can you tell?

1. If  $\text{NH}_3$  is added to the equilibrium system of Haber process, in which direction will the equilibrium shift to consume added  $\text{NH}_3$  so as to reduce the effect of stress?
2. In this process, out of the reverse and forward reaction, which reaction will occur to a greater extent due to this stress ?
3. What will be the effect of this stress on the yield of  $\text{NH}_3$  ?



#### Internet my friend

1. Collect information about Haber Process and Chemical Equilibrium.
2. Youtube.Freesciencelessons The Haber Process.



## Exercises

### 1. Choose the correct option

- A. The equilibrium,  $\text{H}_2\text{O}(l) \rightleftharpoons \text{H}^+(\text{aq}) + \text{OH}(\text{aq})$  is
- dynamic
  - static
  - physical
  - mechanical
- B. For the equilibrium,  $\text{A} \rightleftharpoons 2\text{B} + \text{Heat}$ , the number of 'A' molecules increases if
- volume is increased
  - temperature is increased
  - catalyst is added
  - concentration of B is decreased
- C. For the equilibrium  $\text{Cl}_2(\text{g}) + 2\text{NO}(\text{g}) \rightleftharpoons 2\text{NOCl}(\text{g})$  the concentration of NOCl will increase if the equilibrium is disturbed by
- adding  $\text{Cl}_2$
  - removing NO
  - adding NOCl
  - removal of  $\text{Cl}_2$
- D. The relation between  $K_c$  and  $K_p$  for the reaction  $\text{A}(\text{g}) + \text{B}(\text{g}) \rightleftharpoons 2\text{C}(\text{g}) + \text{D}(\text{g})$  is
- $K_c = Yk_p$
  - $K_p = K_c^2$
  - $K_c = \frac{1}{\sqrt{K_p}}$
  - $K_p/K_c = 1$
- E. When volume of the equilibrium reaction  $\text{C}(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + \text{H}_2(\text{g})$  is increased at constant temperature the equilibrium will
- shift from left to right
  - shift from right to left
  - be unaltered
  - can not be predicted

### 2. Answer the following

- A. State Law of Mass action.
- B. Write an expression for equilibrium constant with respect to concentration.
- C. Derive mathematically value of  $k_p$  for  $\text{A}(\text{g}) + \text{B}(\text{g}) \rightleftharpoons \text{C}(\text{g}) + \text{D}(\text{g})$
- D. Write expressions of  $K_c$  for following chemical reactions
- $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$
  - $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$
- E. Mention various applications of equilibrium constant.

- F. How does the change of pressure affect the value of equilibrium constant ?
- J. Differentiate irreversible and reversible reaction.
- K. Write suitable conditions of concentration, temperature and pressure used during manufacture of ammonia by Haber process.
- L. Relate the terms reversible reactions and dynamic equilibrium.
- M. For the equilibrium.  
 $\text{BaSO}_4(\text{s}) \rightleftharpoons \text{Ba}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$   
 state the effect of
- Addition of  $\text{Ba}^{2+}$  ion.
  - Removal of  $\text{SO}_4^{2-}$  ion
  - Addition of  $\text{BaSO}_4(\text{s})$  on the equilibrium.

### 3. Explain :

- A. Dynamic nature of chemical equilibrium with suitable example.
- B. Relation between  $K_c$  and  $K_p$ .
- C. State and explain Le Chatelier's principle with reference to
- change in temperature
  - change in concentration.
- D. a. Reversible reaction  
b. Rate of reaction
- E. What is the effect of adding chloride on the position of the equilibrium ?  
 $\text{AgCl}(\text{s}) \rightleftharpoons \text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq})$



### Activity :

Prepare concept maps of chemical equilibrium.