

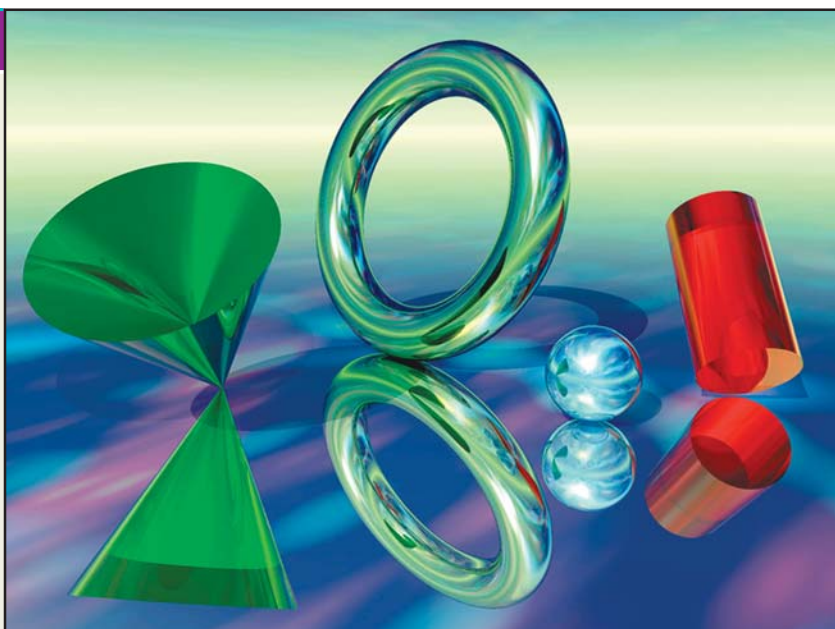
17

Chemical Equilibrium

CHAPTER

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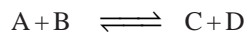


REVERSIBLE REACTIONS

Not all chemical reactions proceed to completion. In most reactions two or more substances react to form products which themselves react to give back the original substances. Thus A and B may react to form C and D which react together to reform A and B.



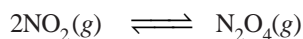
A reaction which can go in the forward and backward direction simultaneously is called a **Reversible reaction**. Such a reaction is represented by writing a pair of arrows between the reactants and products.



The arrow pointing right indicates the forward reaction, while that pointing left shows the reverse reaction.

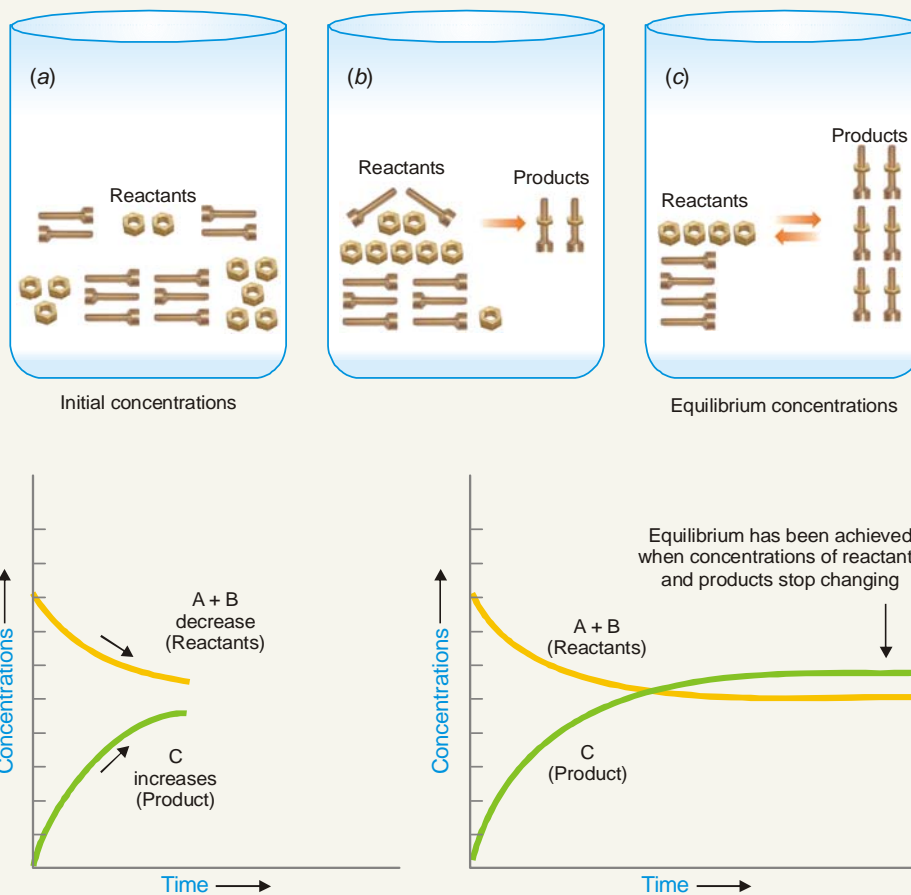
Some Examples of Reversible Reactions

A few common examples of reversible reactions are listed below :

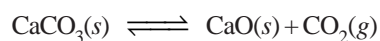
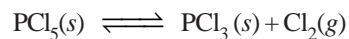
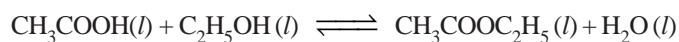
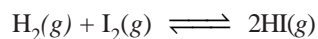


AN EQUILIBRIUM ANALOGY

Nuts and Bolts Representation of Chemical Equilibrium

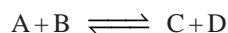


A “nuts and bolts” representation of chemical equilibrium for a reversible reaction. Initially (a) there are 100 nuts and 100 bolts in the beakers represented in the figure by 10 of each. The concentration is 100 bolts per beaker for both nuts and bolts. As time passes (b) concentrations of reactants decrease and concentrations of products - assembled units - increase. Equilibrium is established (c) when concentrations stop changing. For this equilibrium, there are 40 nuts per beaker, 40 bolts per beaker, and 60 assembled units per beaker. The rate of the forward reaction (assembling units) is equal to the rate of the reverse reaction (taking the units apart).



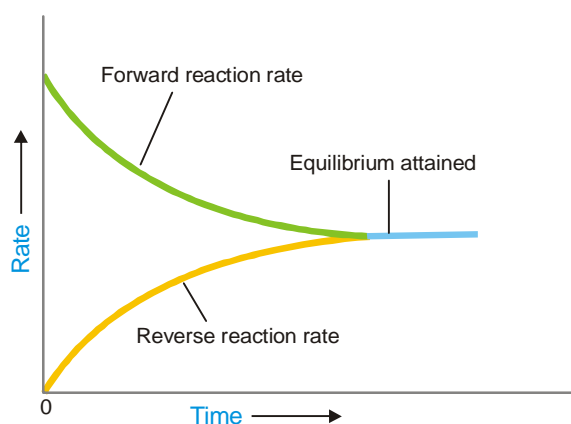
NATURE OF CHEMICAL EQUILIBRIUM : ITS DEFINITION

Let us consider the reaction



If we start with A and B in a closed vessel, the forward reaction proceeds to form C and D. The concentrations of A and B decrease and those of C and D increase continuously. As a result the rate of forward reaction also decreases and the rate of the reverse reaction increases. Eventually, the rate of the two opposing reactions equals and the system attains a *state of equilibrium*. Thus **Chemical equilibrium** may be defined as: **the state of a reversible reaction when the two opposing reactions occur at the same rate and the concentrations of reactants and products do not change with time.**

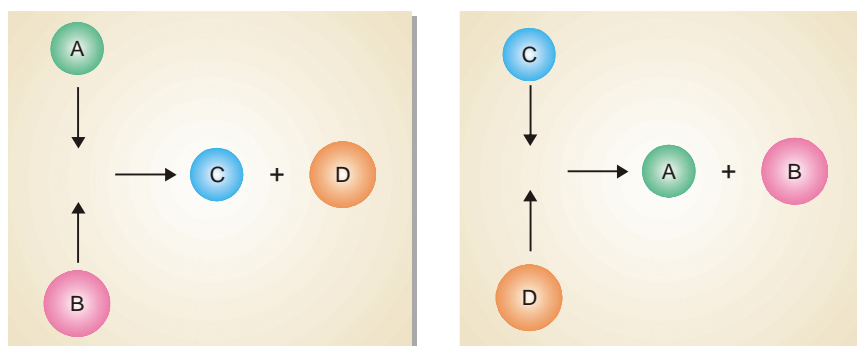
Furthermore, the true equilibrium of a reaction can be attained from both sides. Thus the equilibrium concentrations of the reactants and products are the same whether we start with A and B, or C and D.



■ **Figure 17.1**
At equilibrium the forward reaction rate equals the reverse reaction rate.

Chemical Equilibrium is Dynamic Equilibrium

We have shown above that as the reaction $A + B \rightleftharpoons C + D$ attains equilibrium, the concentrations of A and B, as also of C and D remain constant with time. Apparently it appears that the equilibrium is dead. But it is not so. The equilibrium is dynamic. Actually, the forward and the reverse reactions are taking place at equilibrium but the concentrations remain unchanged.



■ **Figure 17.2**
Molecules of A and B colliding to give C and D, and those of C and D colliding to give A and B.

The dynamic nature of chemical equilibrium can be easily understood on the basis of the kinetic molecular model. The molecules of A and B in the equilibrium mixture collide with each other to form C and D. Likewise C and D collide to give back A and B. The collisions of molecules in a closed system is a ceaseless phenomenon. Therefore collisions of A and B giving C and D (Forward reaction) and collisions of C and D giving back A and B (reverse reaction) continue to occur even at equilibrium, while concentrations remain unchanged.

CHARACTERISTICS OF CHEMICAL EQUILIBRIUM

Before we take up the mathematical study of chemical equilibria, let us understand the chemical characteristics of chemical equilibrium.

(1) Constancy of concentrations

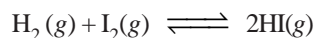
When a chemical equilibrium is established in a closed vessel at constant temperature, concentrations of the various species in the reaction mixture become constant.

The reaction mixture at equilibrium is called **Equilibrium mixture**.

The concentrations at equilibrium are called **Equilibrium concentrations**. The equilibrium concentrations are represented by square brackets with subscript *eq* or *eqm*, $[]_{eq}$. Thus $[A]_{eq}$ denotes the equilibrium concentration of substance A in moles per litre. In modern practice the subscript *eq* is not used.

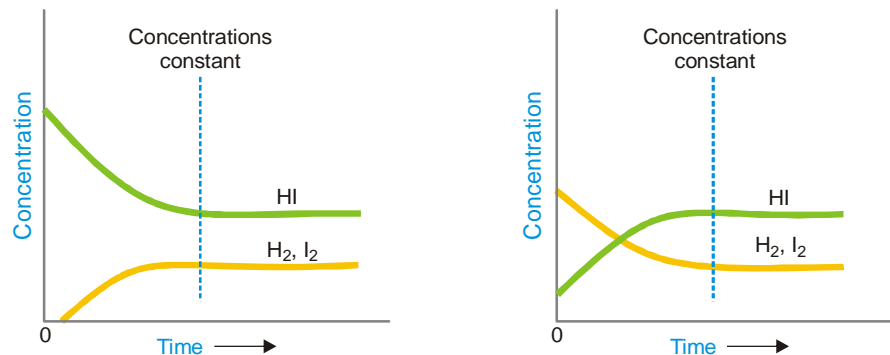
(2) Equilibrium can be initiated from either side

The state of equilibrium of a reversible reaction can be approached whether we start with reactants or products, for example, the equilibrium



is established if we start the reaction with H_2 and I_2 , or 2 HI.

Fig. 17.3. Shows whether we start with 1 mole of I_2 and 1 mole of H_2 , or with 2 moles of HI in a vessel of the same volume, the same mixture of H_2 , I_2 and HI is obtained.



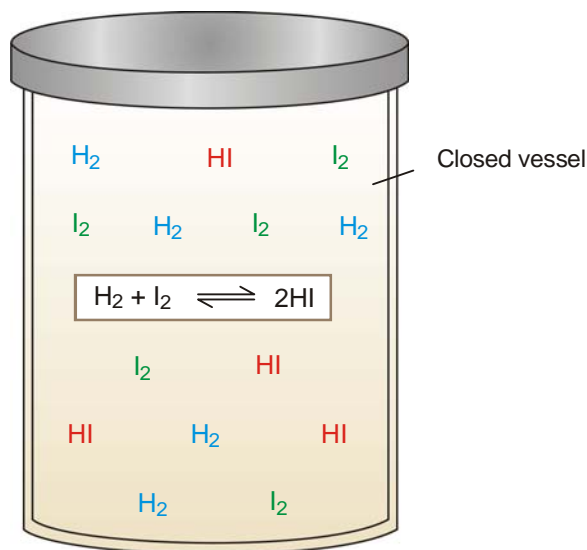
■ **Figure 17.3**

The left graph shows how equilibrium is attained for start with H_2 and I_2 .
The right graph depicts the attainment of equilibrium for start with 2HI.
Equilibrium concentrations in both cases are the same.

(3) Equilibrium cannot be Attained in an Open Vessel

The equilibrium can be established only if the reaction vessel is closed and no part of the reactants or products is allowed to escape out. In an open vessel, the gaseous reactants and/or products may escape into the atmosphere leaving behind no possibility of attaining equilibrium.

However, the equilibrium can be attained when all the reactants and products are in the same phase *i.e.*, ethanol and ethanoic acid.



■ **Figure 17.4**
A chemical equilibrium between H_2 , I_2 and HI .

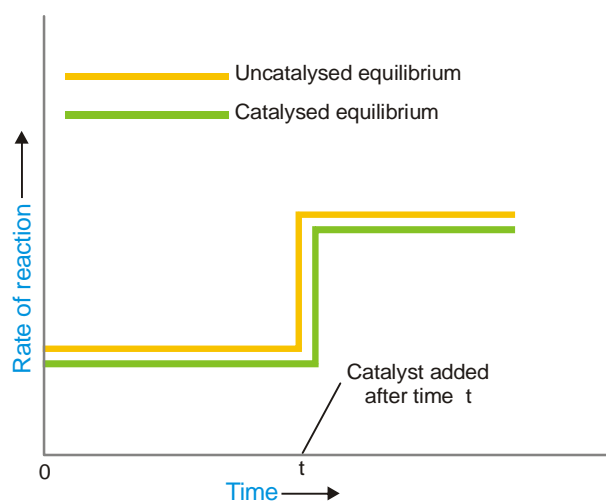
(4) A catalyst cannot change the equilibrium point

When a catalyst is added to a system in equilibrium, it speeds up the rate of both the forward and the reverse reaction to an equal extent. Therefore a catalyst cannot change the equilibrium point except that it is achieved earlier. This enhances the rate of the reaction.

The rapid increase of the rate of an equilibrium reaction on the addition of a catalyst is illustrated in Fig. 17.5.

(5) Value of Equilibrium Constant does not depend upon the initial concentration of reactants

It has been found that equilibrium constant must be the same when the concentrations of reacting species are varied over a wide range.



■ **Figure 17.5**
The vertical part of the curve indicates rapid increase of rate of reaction on addition of catalyst.

(6) At Equilibrium $\Delta G = 0$

At equilibrium the Gibbs free energy (G) is minimum and any change taking place at equilibrium proceeds without change in free energy *i.e.* $\Delta G = 0$.

LAW OF MASS ACTION

Two Norwegian chemists, Guldberg and Waage, studied experimentally a large number of equilibrium reactions. In 1864, they postulated a generalisation called the **Law of Mass action**. It states that : **the rate of a chemical reaction is proportional to the active masses of the reactants**.

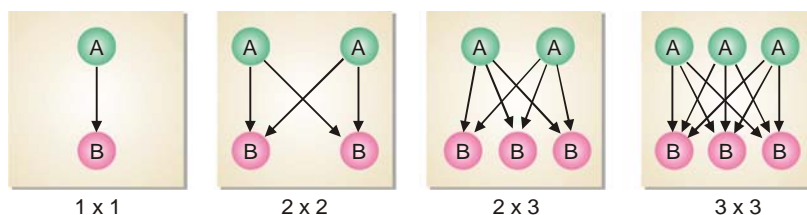
By the term ‘active mass’ is meant the molar concentration *i.e.*, number of moles per litre. It is expressed by enclosing the formula of the substance in square brackets. Thus a gas mixture containing 1 g of hydrogen (H_2) and 127 g of iodine (I_2) per litre has the concentrations

$$[H_2] = 0.5 \text{ and } [I_2] = 0.5$$

Explanation of the Law of Mass Action Based on the Molecular Collision Theory

We assume that a chemical reaction occurs as a result of the collisions between the reacting molecules. Although some of these collisions are ineffective, the chemical change produced is proportional to the number of collisions actually taking place. Thus at a fixed temperature the rate of a reaction is determined by the number of collisions between the reactant molecules present in unit volume.

Let us consider four boxes of one cubic centimetre volume; containing different number of reacting molecules A and B (Fig 17.6). They undergo collisions to form the products C and D, the rate of reaction being governed by the number of possible collisions between them.



■ **Figure 17.6**
Possible collisions between molecules of the reactants A and B.

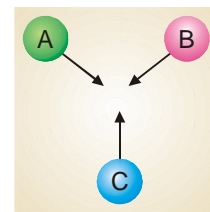
In the first box there is one molecule of A and one molecule of B, and the possibilities of collision at any instant is $1 \times 1 = 1$. In the second box, the number of molecules of A and B are two each and the possibilities of collisions are $2 \times 2 = 4$. In the third box, there are two molecules of A and three molecules of B, and the number of possibilities of collisions between A and B are increased to $3 \times 2 = 6$. In the fourth box, we have three molecules of each of A and B and the total number of collisions between them is $3 \times 3 = 9$. Thus in general, we can say that the possibilities of collisions between the reacting molecules A and B are equal to the product of the number of molecules of each species per unit volume. Since the rate of reaction is determined by molecular impacts, it is proportional to moles per unit volume *i.e.*, molar concentration. Thus we can write

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

In a reaction, $A + B + C \longrightarrow$ the number of collisions between A, B and C depends on the concentration of each reactant (Fig. 17.7). Therefore,

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

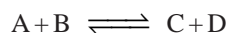
From the above considerations, it stands proved that the rate of a reaction is proportional to the molar concentrations of the reactants.



■ **Figure 17.7**

EQUILIBRIUM CONSTANT : EQUILIBRIUM LAW

Let us consider a general reaction



and let [A], [B], [C] and [D] represent the molar concentrations of A, B, C and D at the equilibrium point. According to the Law of Mass action.

$$\text{Rate of forward reaction} \propto [A][B] = k_1 [A][B]$$

$$\text{Rate of reverse reaction} \propto [C][D] = k_2 [C][D]$$

where k_1 and k_2 are rate constants for the forward and reverse reactions.

At equilibrium, rate of forward reaction = rate of reverse reaction.

Therefore,

$$k_1 [A][B] = k_2 [C][D]$$

$$\text{or} \quad \frac{k_1}{k_2} = \frac{[C][D]}{[A][B]} \quad \dots (1)$$

At any specific temperature k_1/k_2 is constant since both k_1 and k_2 are constants. The ratio k_1/k_2 is called **Equilibrium constant** and is represented by the symbol K_c or simply k . The subscript 'c' indicates that the value is in terms of concentrations of reactants and products. The equation (1) may be written as

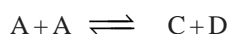
$$\text{Equilibrium constant} \quad k_c = \frac{[C][D]}{[A][B]} \quad \begin{array}{l} \text{--- Product concentrations} \\ \text{--- Reactant concentrations} \end{array}$$

This equation is known as the **Equilibrium constant expression or Equilibrium law**.

Consider the reaction



Here, the forward reaction is dependent on the collisions of each of two A molecules. Therefore, for writing the equilibrium expression, each molecule is regarded as a separate entity *i.e.*,



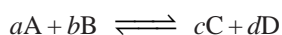
Then the equilibrium constant expression is

$$k_c = \frac{[C][D]}{[A][A]} = \frac{[C][D]}{[A]^2} \quad \text{Power equal to coefficient of A}$$

As a general rule, if there are two or more molecules of the same substance in the chemical equation, **its concentration is raised to the power equal to the numerical coefficient of the substance in the equation**.

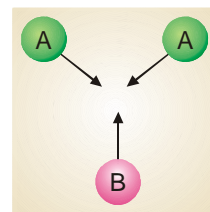
Equilibrium Constant Expression for a Reaction in General Terms

The general reaction may be written as



where a , b , c and d are numerical quotients of the substance, A, B, C and D respectively. The equilibrium constant expression is

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



■ Figure 17.8

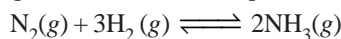
where K_c is the **Equilibrium constant**. The general definition of the equilibrium constant may thus be stated as : **the product of the equilibrium concentrations of the products divided by the product of the equilibrium concentrations of the reactants, with each concentration term raised to a power equal to the coefficient of the substance in the balanced equation.**

How to Write the Equilibrium Constant Expression?

- (1) Write the balanced chemical equation for the equilibrium reaction. By convention, the substances on the left of the equation are called the **reactants** and those on the right, the **products**.
- (2) Write the product of concentrations of the 'products' and raise the concentrations of each substance to the power of its numerical quotient in the balanced equation.
- (3) Write the product of concentrations of 'reactants' and raise the concentration of each substance to the power of its numerical quotient in the balanced equation.
- (4) Write the equilibrium expression by placing the **product concentrations in the numerator and reactant concentrations in the denominator**. That is,

$$K_c = \frac{\text{Product of concentrations of 'products' from Step (2)}}{\text{Product of concentrations of 'reactants' from Step (3)}}$$

SOLVED PROBLEM 1. Give the equilibrium constant expression for the reaction

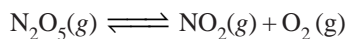


SOLUTION

- (1) The equation is already balanced. The numerical quotient of H_2 is 3 and of NH_3 is 2.
- (2) The concentration of the 'product' NH_3 is $[\text{NH}_3]^2$
- (3) The product of concentrations of the reactants is $[\text{N}_2][\text{H}_2]^3$
- (4) Therefore, the equilibrium constant expression is

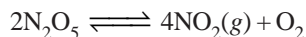
$$K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$$

SOLVED PROBLEM 2. Write the equilibrium constant expression for the reaction



SOLUTION

- (1) The equation as written is not balanced. Balancing yields



- (2) The quotient of the product NO_2 is 4 and of the reactant N_2O_5 it is 2.
- (3) The product of the concentrations of products is

$$[\text{NO}_2]^4 [\text{O}_2]$$

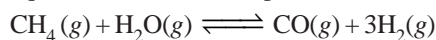
- (4) The concentration of the reactant is

$$[\text{N}_2\text{O}_5]^2$$

- (5) The equilibrium constant expression can be written as

$$K_c = \frac{[\text{NO}_2]^4 [\text{O}_2]}{[\text{N}_2\text{O}_5]^2}$$

SOLVED PROBLEM 3. What is the equilibrium constant expression of the reaction



SOLUTION

Write the product of concentrations of ‘products’ divided by the product of concentrations of ‘reactants’. The concentration of H_2 is to be raised by its quotient in the equation. Thus, the equilibrium constant expression is:

$$K_c = \frac{[\text{CO}][\text{H}_2]^3}{[\text{CH}_4][\text{H}_2\text{O}]}$$

EQUILIBRIUM CONSTANT EXPRESSION IN TERMS OF PARTIAL PRESSURES

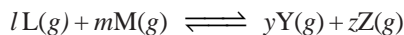
When all the reactants and products are gases, we can also formulate the equilibrium constant expression in terms of partial pressure. The relationship between the partial pressure (p) of any one gas in the equilibrium mixture and the molar concentration follows from the general ideal gas equation

$$pV = nRT \quad \text{or} \quad p = \left(\frac{n}{V}\right) RT$$

The quantity $\frac{n}{V}$ is the number of moles of the gas per unit volume and is simply the molar concentration. Thus,

$$p = (\text{Molar concentration}) \times RT$$

i.e., **the partial pressure of a gas in the equilibrium mixture is directly proportional to its molar concentration at a given temperature.** Therefore, we can write the equilibrium constant expression in terms of partial pressure instead of molar concentrations. For a general reaction

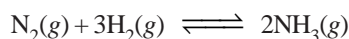


the equilibrium law or the equilibrium constant may be written as

$$K_p = \frac{(p_Y)^y (p_Z)^z}{(p_L)^l (p_M)^m}$$

Here K_p is the equilibrium constant, the subscript p referring to partial pressure. Partial pressures are expressed in atmospheres.

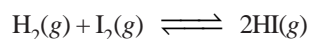
SOLVED PROBLEM 1. Write the equilibrium constant expression for the synthesis of ammonia,



SOLUTION

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

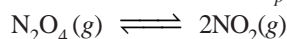
SOLVED PROBLEM 2. Using partial pressures, write the equilibrium law for the reaction



SOLUTION

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

SOLVED PROBLEM 3. What is the expression K_p for the reaction



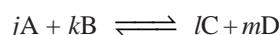
SOLUTION

For K_p we use the partial pressure in the equilibrium constant expression. Therefore,

$$K_p = \frac{(p_{\text{NO}_2})^2}{(p_{\text{N}_2\text{O}_4})}$$

HOW K_c AND K_p ARE RELATED?

Let us consider a general reaction



where all reactants and products are gases. We can write the equilibrium constant expression in terms of partial pressures as

$$K_p = \frac{(p_C)^l (p_D)^m}{(p_A)^j (p_B)^k} \quad \dots(1)$$

Assuming that all these gases constituting the equilibrium mixture obey the ideal gas equation, the partial pressure (p) of a gas is

$$p = \left(\frac{n}{V}\right)RT$$

Where $\frac{n}{V}$ is the molar concentration. Thus the partial pressures of individual gases, A, B, C and D are:

$$P_A = [\text{A}]RT; p_B = [\text{B}]RT; p_C = [\text{C}]RT; p_D = [\text{D}]RT$$

Substituting these values in equation (1), we have

$$K_p = \frac{[\text{C}]^l (RT)^l [\text{D}]^m (RT)^m}{[\text{A}]^j (RT)^j [\text{B}]^k (RT)^k}$$

$$\text{or} \quad K_p = \frac{[\text{C}]^l [\text{D}]^m}{[\text{A}]^j [\text{B}]^k} \times \frac{(RT)^{l+m}}{(RT)^{j+k}}$$

$$K_p = K_c \times (RT)^{(l+m)-(j+k)}$$

$$\therefore K_p = K_c \times (RT)^{\Delta n} \quad \dots(2)$$

where $\Delta n = (l+m) - (j+k)$, the difference in the sums of the coefficients for the gaseous products and reactants.

From the expression (2) it is clear that when $\Delta n = 0$, $K_p = K_c$.

SOLVED PROBLEM 1. At 500°C , the reaction between N_2 and H_2 to form ammonia has $K_c = 6.0 \times 10^{-2}$. What is the numerical value of K_p for the reaction?

SOLUTION

Here, we will use the general expression

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

For the reaction $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$

we have $\Delta n = (\text{sum of quotients of products}) - (\text{sum of quotients of reactants})$

$$= 2 - 4 = -2$$

$$K_c = 6.0 \times 10^{-2}$$

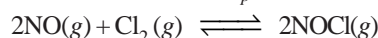
$$T = 500 + 273 = 773 \text{ K}$$

$$R = 0.0821$$

Substituting the value of R , T , K_c and Δn in the general expression, we have

$$\begin{aligned} K_p &= (6.0 \times 10^{-2}) [(0.0821) \times (773)]^{-2} \\ &= \mathbf{1.5 \times 10^{-5}} \end{aligned}$$

SOLVED PROBLEM 2. The value of K_p at 25°C for the reaction



is $1.9 \times 10^3 \text{ atm}^{-1}$. Calculate the value of K_c at the same temperature.

SOLUTION

We can write the general expression as

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

Here,

$$T = 25 + 273 = 298 \text{ K}$$

$$R = 0.0821$$

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

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

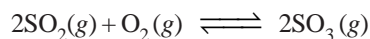
Substituting these values in the general expression

$$\begin{aligned} K_c &= \frac{1.9 \times 10^3}{(0.0821 \times 298)^{-1}} \\ &= \mathbf{4.6 \times 10^4} \end{aligned}$$

Calculation of K_c from Experimental Information

To determine the value of K_c of a reaction, write the balanced equation. Then write the equilibrium constant expression. Substitute in it the equilibrium concentrations of the reactants and products found experimentally. Thus calculate the value of K_c .

SOLVED PROBLEM 1. At equilibrium for the reaction



the concentrations of reactants and products at 727°C were found to be : $\text{SO}_2 = 0.27 \text{ mol L}^{-1}$; $\text{O}_2 = 0.40 \text{ mol L}^{-1}$; and $\text{SO}_3 = 0.33 \text{ mol L}^{-1}$. What is the value of the equilibrium constant, K_c , at this temperature?

SOLUTION

Write the equilibrium constant expression for the reaction

$$K_c = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2 [\text{O}_2]}$$

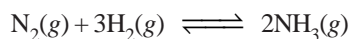
We know that:

$$[\text{SO}_3] = 0.33 \text{ mol L}^{-1}; [\text{SO}_2] = 0.27 \text{ mol L}^{-1}; [\text{O}_2] = 0.40 \text{ mol L}^{-1}$$

Substituting these values in the equilibrium constant expression, we have

$$K_c = \frac{(0.33)^2}{(0.27)^2 \times (0.40)} = \mathbf{3.7 \text{ mol l}^{-1}} \text{ or simply } \mathbf{3.7}$$

SOLVED PROBLEM 2. Some nitrogen and hydrogen gases are pumped into an empty five-litre glass bulb at 500°C. When equilibrium is established, 3.00 moles of N₂, 2.10 moles of H₂ and 0.298 mole of NH₃ are found to be present. Find the value of K_c for the reaction



at 500°C.

SOLUTION

The equilibrium concentrations are obtained by dividing the number of moles of each reactant and product by the volume, 5.00 litres. Thus,

$$[\text{N}_2] = 3.00 \text{ mole}/5.00 \text{ L} = 0.600 \text{ M}$$

$$[\text{H}_2] = 2.10 \text{ mole}/5.00 \text{ L} = 0.420 \text{ M}$$

$$[\text{NH}_3] = 0.298 \text{ mole}/5.00 \text{ L} = 0.0596 \text{ M}$$

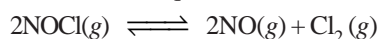
Substituting these concentrations (not number of moles) in the equilibrium constant expression, we get the value of K_c.

$$K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{(0.0596)^2}{(0.600)(0.420)^3} = 0.080$$

Thus, for the reaction of H₂ and N₂ to form NH₃ at 500°C, we can write

$$K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \mathbf{0.080}$$

SOLVED PROBLEM 3. Calculate the equilibrium constant at 25°C for the reaction



In an experiment, 2.00 moles of NOCl were placed in a one-litre flask and the concentration of NO after equilibrium achieved was 0.66 mole/litre.

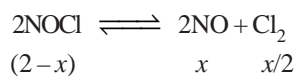
SOLUTION

Let us write the equilibrium constant expression for the balanced chemical equation.

$$K_c = \frac{[\text{NO}]^2[\text{Cl}_2]}{[\text{NOCl}]^2}$$

Next we proceed to find the equilibrium concentrations of NOCl, NO and Cl₂. Since the volume of the reaction vessel is one litre, the moles of various reagents also represent their molar concentrations.

The initial amount of NOCl is 2.00 moles. Let us assume that *x* moles of it have reacted to achieve the equilibrium. The moles of different reagents at equilibrium are indicated in the equation



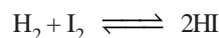
According to this equation, one mole of NOCl gives one mole of NO and half a mole of Cl₂.

The experimental value of equilibrium concentration of NO is 0.66 mole/litre. Therefore, the

equilibrium concentration Cl_2 is half of it *i.e.* 0.33 mole/litre. Since $x = 0.66$, the equilibrium concentration of $\text{NOCl} = (2 - 0.66) = 1.34$. To find K_c , these values of equilibrium concentrations are substituted in the equilibrium constant expression.

$$K_c = \frac{[\text{NO}]^2 [\text{Cl}_2]}{[\text{NOCl}]^2} = \frac{(0.66)^2 (0.33)}{(1.34)^2} = \mathbf{0.080}$$

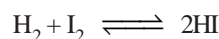
SOLVED PROBLEM 4. At a certain temperature, 0.100 mole of H_2 and 0.100 mole of I_2 were placed in a one-litre flask. The purple colour of iodine vapour was used to monitor the reaction. After a time, the equilibrium



was established and it was found that the concentration of I_2 decreased to 0.020 mole/litre. Calculate the value of K_c for the reaction at the given temperature.

SOLUTION

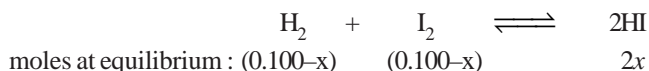
The equilibrium constant expression for the reaction



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

Let us proceed to find the equilibrium concentrations of the various species.

The initial moles of H_2 , I_2 and HI present at equilibrium are



Since the volume of the reaction vessel is one litre, the moles at equilibrium also represent the equilibrium concentrations. Thus,

$$[\text{I}_2] = 0.100 - x = 0.020 \text{ (given)}$$

or
$$\begin{aligned} x &= 0.100 - 0.020 \\ &= 0.080 \end{aligned}$$

Knowing the value of x , we can give the equilibrium concentrations of H_2 , I_2 and HI.

$$[\text{H}_2] = 0.100 - x = 0.100 - 0.080 = 0.020$$

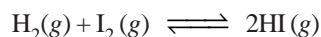
$$[\text{I}_2] = 0.020 \text{ (given)}$$

$$[\text{HI}] = 2x = 0.160$$

Substituting these values in the equilibrium constant expression, we get the value of K_c .

$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(0.160)^2}{0.02 \times 0.02} = \mathbf{64}$$

SOLVED PROBLEM 5. 13.5 ml of HI are produced by the interaction of 8.1 ml of hydrogen and 9.3 ml of iodine vapour at 444°C . Calculate the equilibrium constant at this temperature of the reaction.



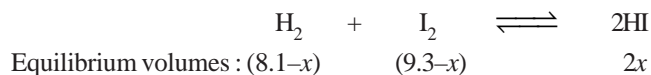
SOLUTION

The equilibrium constant expression for the reaction is

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

Let us proceed to find the equilibrium concentrations.

Since the number of moles in a gas under the same conditions of temperature and pressure are proportional to volumes, ml of a gas may be used instead of molar concentrations. Thus,



The experimental volume of HI = 13.5 ml (given)

$$\therefore 2x = 13.5 \text{ ml}$$

$$\text{or } x = 6.75 \text{ ml}$$

Thus, the equilibrium concentrations are:

$$[\text{H}_2] = (8.1 - x) = 8.1 - 6.75 = 1.35$$

$$[\text{I}_2] = (9.3 - x) = 9.3 - 6.75 = 2.55$$

$$[\text{HI}] = 13.5$$

Substituting these values in the equilibrium constant expression, we have

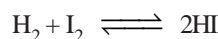
$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(13.5)^2}{1.35 \times 2.55} = 52.94$$

Calculation of Equilibrium Concentrations

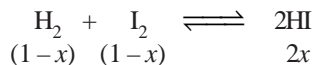
SOLVED PROBLEM 1. One mole of H_2 and one mole of I_2 were heated in a 1 litre sealed glass box at 490°C till the equilibrium was reached. Assuming that the equilibrium constant is 45.9, find the final concentrations of H_2 , I_2 and HI.

SOLUTION

The equation for the reaction is



If x mole of H_2 has reacted on attainment of equilibrium, the moles of components are



Since the reaction vessel is a 1 litre box, the concentrations at equilibrium are the same as the moles. Thus,

$$[\text{H}_2] = 1 - x$$

$$[\text{I}_2] = 1 - x$$

$$[\text{HI}] = 2x$$

Substituting the values in the equilibrium constant expression

$$K = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(2x)^2}{(1-x)(1-x)} = 45.9$$

$$\text{or } \frac{4x^2}{1 - 2x + x^2} = 45.9$$

$$\text{or } 41.9x^2 - 91.8x + 45.9 = 0$$

Using the quadratic formula $x = 0.79$. Hence the equilibrium concentrations are

$$[\text{H}_2] = 1 - 0.79 = 0.21 \text{ mole per litre}$$

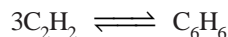
$$[\text{I}_2] = 1 - 0.79 = 0.21 \text{ mole per litre}$$

$$[\text{HI}] = 2x = 2(0.79) = 1.58 \text{ mole per litre}$$

SOLVED PROBLEM 2. At a certain temperature, K for the reaction $3\text{C}_2\text{H}_2(\text{g}) \rightleftharpoons \text{C}_6\text{H}_6(\text{g})$ is 4. If the equilibrium concentration of C_2H_2 is 0.5 mole/litre, what is the concentration of C_6H_6 ?

SOLUTION

The reaction can be written as



The equilibrium constant expression is

$$K = \frac{[\text{C}_6\text{H}_6]}{[\text{C}_2\text{H}_2]^3}$$

It is given that:

$$K = 4$$

$$[\text{C}_2\text{H}_2] = 0.5 \text{ mole/litre}$$

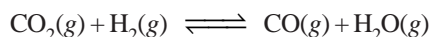
Substituting these values,

$$4 = \frac{[\text{C}_6\text{H}_6]}{[0.5]^3}$$

\therefore

$$[\text{C}_6\text{H}_6] = 4 \times (0.5)^3 = \mathbf{0.5 \text{ moles/litre}}$$

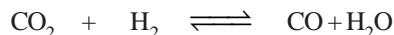
SOLVED PROBLEM 3. For the reaction



the value of K at 552°C is 0.137. If 5 moles of CO_2 , 5.0 moles of H_2 , 1.0 mole of CO and 1.0 mole of H_2O are initially present, what are the actual concentrations of CO_2 , H_2 , CO and H_2O at equilibrium?

SOLUTION

If x moles of CO_2 has reacted at equilibrium, x mole of CO and x mole of H_2O will be produced. The moles at equilibrium due to the reaction will be



$$\text{Moles at equilibrium: } \begin{array}{cccc} 5-x & 5-x & x & x \end{array}$$

But 1 mole each of CO and H_2O were present initially. Therefore the actual moles at equilibrium would be

$$\text{CO}_2 = 5 - x$$

$$\text{H}_2 = 5 - x$$

$$\text{CO} = 1 + x$$

$$\text{H}_2\text{O} = 1 + x$$

If V litres be the volume of the reaction vessel, the concentration of the various species are:

$$[\text{CO}_2] = (5 - x)/V$$

$$[\text{H}_2] = (5 - x)/V$$

$$[\text{CO}] = (1 + x)/V$$

$$[\text{H}_2\text{O}] = (1 + x)/V$$

Substituting the values in the equilibrium constant expression, we have

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

$$0.137 = \frac{[(1 + x)/V][(1 + x)/V]}{[(5 - x)/V][(5 - x)/V]} = \frac{(1 + x)^2 V^2}{(5 - x)^2 V^2}$$

$$0.137 = \frac{(1+x)^2}{(5-x)^2} = \frac{1+2x+x^2}{25-10x+x^2}$$

or

$$0.137(25) - 0.137(10)x + 0.137x^2 = 1 + 2x + x^2$$

$$0.863x^2 + 3.370x - 2.425 = 0$$

Solving for x using the quadratic formula

$$x = 0.62$$

Thus the final equilibrium concentrations are:

$$[\text{CO}] = 1 + x = 1 + 0.62 = 1.62 \text{ mole l}^{-1}$$

$$[\text{H}_2\text{O}] = 1 + x = 1 + 0.62 = 1.62 \text{ mole l}^{-1}$$

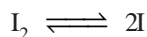
$$[\text{CO}_2] = 5 - x = 5 - 0.62 = 4.38 \text{ mole l}^{-1}$$

$$[\text{H}_2] = 5 - x = 5 - 0.62 = \mathbf{4.38 \text{ mole l}^{-1}}$$

SOLVED PROBLEM 4. For the reaction $\text{I}_2(\text{g}) \rightleftharpoons 2\text{I}(\text{g})$, $K = 3.76 \times 10^{-5}$ at 727°C . Let 1 mole of I_2 be injected into a 2-litre glass box at 727°C . What will be the concentrations of I_2 and I when the equilibrium is attained?

SOLUTION

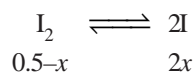
The balanced equation for the reaction is



1 mole of I_2 is injected in a 2-litre box. Thus the initial concentration of I_2 is

$$\frac{1 \text{ mole}}{2 \text{ litre}} = 0.5 \text{ M}$$

Let x moles of I_2 decompose at equilibrium. Then the moles of the two species are:



Therefore the equilibrium concentrations are:

$$[\text{I}_2] = 0.5 - x$$

$$[\text{I}] = 2x$$

and

$$K = 3.76 \times 10^{-5}$$

Substituting the values in the equilibrium constant expression, we have

$$K = \frac{[\text{I}]^2}{[\text{I}_2]} = 3.76 \times 10^{-5}$$

or

$$\frac{(2x)^2}{(0.5-x)} = 3.76 \times 10^{-5}$$

Solving for x , using the quadratic equation formula,

$$x = 2.17 \times 10^{-3}$$

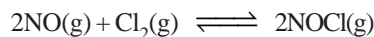
Thus the concentrations of I and I_2 at equilibrium are:

$$[\text{I}] = 2x = \mathbf{4.34 \times 10^{-3} \text{ mole l}^{-1}}$$

$$[\text{I}_2] = 0.5 - x = \mathbf{0.498 \text{ mole l}^{-1}}$$

CALCULATIONS INVOLVING K_p

It may be noted that the value of K_p depends on the units used to express pressures, which are usually atmospheres.

Calculation of K_p **SOLVED PROBLEM 1.** The reaction

was studied at 25°C. The partial pressures at equilibrium were found to be

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

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

$$p_{\text{Cl}_2} = 3.0 \times 10^{-1} \text{ atm}$$

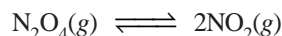
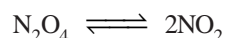
Calculate K_p for the reaction at 25°C.**SOLUTION**

The equilibrium constant expression in terms of partial pressures is

$$K_p = \frac{(p_{\text{NOCl}})^2}{(p_{\text{NO}})^2 (p_{\text{Cl}_2})}$$

Substituting the values of partial pressures

$$K_p = \frac{(1.2)^2}{(5.0 \times 10^{-2})^2 \times (3.0 \times 10^{-1})} = \mathbf{1.92 \times 10^3}$$

SOLVED PROBLEM 2. At 60°C and a total pressure of 1 atmosphere dinitrogen tetroxide, N_2O_4 , is 50% dissociated into nitrogen dioxide, NO_2 .Calculate the value of K_p at this temperature.**SOLUTION**Let us have 1 mole of N_2O_4 to start with of which x mole dissociates at equilibrium. Then the moles of N_2O_4 and NO_2 at equilibrium are:moles at equilibrium : $(1-x)$ $2x$ Since N_2O_4 is 50% dissociated, $x = 0.5$ mole and the equilibrium mixture contains

$$\text{NO}_2 = 2x = 2 \times 0.5 = 1 \text{ mole}$$

$$\text{N}_2\text{O}_4 = (1-x) = (1-0.5) = 0.5 \text{ mole}$$

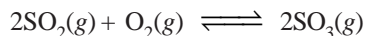
That is, the moles of N_2O_4 and NO_2 are present in the ratio 1 : 2∴ The partial pressure of $\text{N}_2\text{O}_4 = \frac{1}{3}$ atmThe partial pressure of $\text{NO}_2 = \frac{2}{3}$ atm

Substituting these values in the equilibrium constant expression, we have

$$K_p = \frac{(p_{\text{NO}_2})^2}{p_{\text{N}_2\text{O}_4}} = \frac{(2/3)^2}{1/3} = \frac{4}{3} = \mathbf{1.33}$$

Calculation of Equilibrium Partial Pressures

SOLVED PROBLEM 1. At 727°C the equilibrium constant for the reaction



is $K_p = 3.50 \text{ atm}^{-1}$. If the total pressure in the reaction flask is 1.00 atm, and the partial pressure of O_2 at equilibrium is 0.10 atm, calculate the partial pressures of SO_2 and SO_3 .

SOLUTION

Let the partial pressure of $\text{SO}_2 = x \text{ atm}$

Then the partial pressure of $\text{SO}_3 = 1.00 - p_{\text{O}_2} - x$
 $= (0.90 - x) \text{ atm}$

the partial pressure of $\text{O}_2 = 0.10 \text{ atm}$

Substituting these values in the equilibrium constant expression, we have

$$K_p = \frac{(p_{\text{SO}_3})^2}{(p_{\text{SO}_2})^2 (p_{\text{O}_2})} = \frac{(0.90 - x)^2}{x^2 \times 0.1} = 3.5 \text{ atm}^{-1}$$

Taking the square root, we have

$$\frac{0.9 - x}{x} = (0.35)^{\frac{1}{2}}$$

or

$$x = 0.57$$

$$p_{\text{SO}_2} = \mathbf{0.57 \text{ atm}}$$

$$p_{\text{SO}_3} = \mathbf{0.33 \text{ atm}}$$

Calculation of Degree of Dissociation

Case 1. By determining equilibrium concentrations. The equilibrium constant (K) for the combination reaction is first calculated using equilibrium concentrations. The equilibrium law is then applied to the reverse (dissociation) reaction when the equilibrium constant is $1/K$.

SOLVED PROBLEM 1. 25 ml of H_2 and 18 ml of I_2 vapour were heated in a sealed glass bulb at 465°C when at equilibrium 30.8 ml of HI was formed. Calculate the degree of dissociation of pure HI at 465°C.

SOLUTION

Step 1. Calculation of K

The combination of H_2 and I_2 to form HI can be written as



ml at equilibrium: $(a - x)$ $(b - x)$ $2x$

At equilibrium, HI formed is $2x \text{ ml}$

or $2x = 30.8$ (given)

$$x = 15.4$$

\therefore Concentrations at equilibrium are:

$$[\text{H}_2] = (a - x) = 25 - 15.4 = 9.6 \text{ mole l}^{-1}$$

$$[\text{I}_2] = (b - x) = 18 - 15.4 = 2.6 \text{ mole l}^{-1}$$

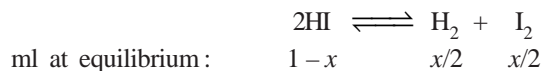
$$[\text{HI}] = 30.8 \text{ mole l}^{-1}$$

Substituting the values in the equilibrium constant expression

$$K = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{30.8 \times 30.8}{9.6 \times 2.6} = 38$$

Step 2. Calculation of Degree of dissociation, x

If we inject one ml of HI in a sealed glass bulb at 465°C, x ml of it will decompose at equilibrium, where x represents the degree of dissociation.



Substituting the values in the equilibrium constant expression

$$K' = \frac{[x/2]^2}{(1-x)^2} = \frac{x^2}{4(1-x)^2}$$

Since $K' = 1/K$, we have

$$\frac{x^2}{4(1-x)^2} = \frac{1}{38}$$

Hence $x = 0.245$

Thus the degree of dissociation of pure HI at 465°C is **0.245**.

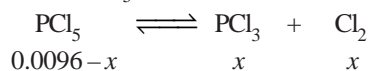
SOLVED PROBLEM 2. For the reaction $\text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{Cl}_2$, $K = 33.3$ at 760 K. 1.00 g of PCl_5 is injected into a 500 ml evacuated flask and allowed to come to equilibrium. What per cent of the PCl_5 will dissociate at equilibrium? Molecular mass of $\text{PCl}_5 = 208.235$.

SOLUTION

$$\text{Initial moles of } \text{PCl}_5 = \frac{\text{grams (mass)}}{\text{mol. mass}} = \frac{1}{208.235} = 0.0048 \text{ mole}$$

$$\text{Initial concentration of } \text{PCl}_5 = \frac{0.0048 \text{ mole}}{0.5 \text{ litre}} = 0.0096 \text{ mol l}^{-1}$$

At equilibrium if x mole of PCl_5 is dissociated, the equilibrium concentrations are:



Substituting values in the equilibrium constant expression,

$$\frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} = 33.3$$

$$\frac{(x)(x)}{(0.0096-x)} = 33.3$$

Solving for x using the quadratic equation obtained by you, we have

$$x = 9.597 \times 10^{-3}$$

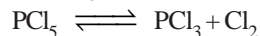
\therefore The initial concentration of $\text{PCl}_5 = 0.0096 \text{ mol l}^{-1}$

$$\begin{aligned} \text{The final concentration of } \text{PCl}_5 &= 0.0096 - x \\ &= 0.0096 - 9.597 \times 10^{-3} \\ &= 3 \times 10^{-6} \text{ mol l}^{-1} \end{aligned}$$

Thus the amount of PCl_5 dissociated at equilibrium is

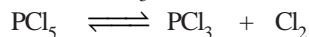
$$100 \times \frac{0.0096 - 3 \times 10^{-6}}{0.0096} = \mathbf{99.9\%}$$

Case 2. By density measurements. This method is used for the determination of the degree of dissociation of gases in which one molecule produces two or more molecules. For example, PCl_5 dissociates to give two molecules PCl_3 and Cl_2 .



Thus at constant temperature and pressure the volume increases. The density at constant pressure then decreases. The degree of dissociation can be calculated from the difference between the density of the undissociated gas and that of the partially dissociated gas at equilibrium.

If we start with one mole of gas (PCl_5) and the degree of dissociation is x , we have



moles at equilibrium : $(1-x)$ x x

Thus the total number of moles at equilibrium

$$= (1-x) + x + x = 1 + x$$

The density of an ideal gas at constant temperature and pressure is inversely proportional to the number of moles for a given weight.

Hence the ratio of density ρ_1 of the undissociated gas to the density ρ_2 of the dissociated gas at equilibrium is given as

$$\frac{\rho_1}{\rho_2} = \frac{1+x}{1}$$

whence

$$\rho_1 = \rho_2 + x\rho_2$$

or

$$x = \frac{\rho_1 - \rho_2}{\rho_2}$$

Substituting the values of ρ_1 and ρ_2 the value of x , the degree of dissociation, can be calculated.

SOLVED PROBLEM 1. When PCl_5 is heated it gasifies and dissociates into PCl_3 and Cl_2 . The density of the gas mixture at 200°C is 70.2. Find the degree of dissociation of PCl_5 at 200°C .

SOLUTION

We will use the expression $x = \frac{\rho_1 - \rho_2}{\rho_2}$

where

x = degree of dissociation

ρ_1 = density of undissociated PCl_5

ρ_2 = density of gas mixture at equilibrium (partially dissociated)

The density (ρ_1) of undissociated PCl_5 would be

$$\text{VD} = \frac{\text{mol mass}}{2} = \frac{31 + 177.5}{2} = 104.25$$

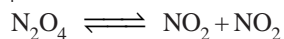
$$\text{Observed density } \rho_2 = 70.2$$

$$\therefore x = \frac{\rho_1 - \rho_2}{\rho_2} = \frac{104.25 - 70.2}{70.2} = \mathbf{0.485}$$

SOLVED PROBLEM 2. At 90°C the vapour density of nitrogen tetroxide (N_2O_4) is 24.8. Calculate the percentage dissociation into NO_2 molecules at this temperature.

SOLUTION

The dissociation of N_2O_4 can be represented by the equation



Since the number of molecules on the two sides of the equation is different, we can calculate the degree of dissociation by using the expression

$$x = \frac{\rho_1 - \rho_2}{\rho_2}$$

The density of undissociated N_2O_4 is given by

$$\rho_1 = \frac{\text{mol mass}}{2} = \frac{28 + 64}{2} = \frac{92}{2} = 46$$

$$\rho_2 = 24.8 \text{ (given)}$$

$$\therefore x = \frac{46 - 24.8}{24.8} = 0.8547$$

Hence, percentage dissociation = $100 \times x = 85.47$

Case 3. By molecular mass determination. Molecular masses are proportional at constant temperature and pressure to the gas densities. Therefore, we can substitute molecular masses for the densities in the expression

$$x = \frac{\rho_1 - \rho_2}{\rho_2}$$

which gives

$$x = \frac{M_1 - M_2}{M_2}$$

where M_1 is the molecular mass of the undissociated gas and M_2 is the average molecular mass of the gases at the equilibrium.

SOLVED PROBLEM. 1.588 g of nitrogen tetroxide gives a total pressure of 1 atm when partially dissociated at equilibrium in a 500 ml glass vessel at 25°C . What is the degree of dissociation at this temperature.

SOLUTION

$$\begin{aligned} M_1, \text{ molecular mass of undissociated } \text{N}_2\text{O}_4 \text{ gas} \\ = 14 \times 2 + 16 \times 4 = 92.0 \end{aligned}$$

M_2 , molecular mass of partially dissociated gas at equilibrium can be determined by using the general gas equation.

$$PV = nRT$$

$$\text{where } n = \frac{\text{mass of substance}}{M_2} = \frac{m}{M_2}$$

$$\text{or } PV = \frac{m}{M_2} RT \quad \dots (1)$$

Rearranging the expression (1), we have

$$M_2 = \frac{RT}{P} \times \frac{m}{V} \quad \dots (2)$$

$$\begin{aligned} \text{Here, } R &= 0.082; T = 273 + 25 = 298 \text{ K} \\ P &= 1 \text{ atm}; V = 0.500 \text{ litre}; m = 1.588 \text{ g} \end{aligned}$$

Substituting the values in the expression (2)

$$M_2 = \frac{0.082 \times 298 \times 1.588}{(1 \text{ atm}) (0.500 \text{ litre})} = 77.68$$

$$\begin{aligned} \text{Therefore, } x &= \frac{M_1 - M_2}{M_2} = \frac{92.0 - 77.68}{77.68} \\ &= \mathbf{0.1846} \end{aligned}$$

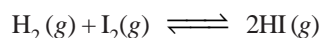
UNITS OF EQUILIBRIUM CONSTANT

In the equilibrium expression for a particular reaction, the concentrations are given in units of moles/litre or mol/L, and the partial pressure are given in atmospheres (atm). The units of K_c and K_p , depend on the specific reaction.

(1) When the total number of moles of reactants and products are equal

In the equilibrium expression of these reactions, the concentration or pressure terms in the numerator and denominator exactly cancel out. Thus K_c or K_p for such a reaction is without units.

Taking example of the reaction

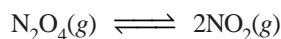


$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(\text{mol/L})^2}{(\text{mol/L})(\text{mol/L})} \quad (\text{No units})$$

$$K_p = \frac{(P_{\text{HI}})^2}{(P_{\text{H}_2})(P_{\text{I}_2})} = \frac{(\text{atm})^2}{(\text{atm})(\text{atm})} \quad (\text{No units})$$

(2) When the total number of moles of the reactants and products are unequal

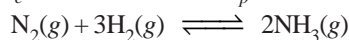
In such reactions K_c will have units (mol/litre)ⁿ and K_p will have units (atm)ⁿ, where n is equal to the total number of moles of products minus the total number of moles of reactants. Thus for the reaction



$$K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = \frac{(\text{mol/L})^2}{(\text{mol/L})} = \text{mol/L}$$

$$K_p = \frac{(P_{\text{NO}_2})^2}{(P_{\text{N}_2\text{O}_4})} = \frac{(\text{atm})^2}{(\text{atm})} = \text{atm}$$

Thus units for K_c are mol/L and for K_p units are atm. For the reaction



the units for K_c and K_p may be found as follows

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

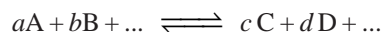
$$K_p = \frac{(P_{\text{NH}_3})^2}{(P_{\text{N}_2})(P_{\text{H}_2})^3} = \frac{(\text{atm})^2}{(\text{atm})(\text{atm})^3} = \text{atm}^{-2}$$

Thus units of K_c are mol⁻²L² and units of K_p are atm⁻².

It may be noted, however, that the units are often omitted when equilibrium constants are listed in tables.

Thermodynamic Derivation of Law of Chemical Equilibrium

Let us consider a general reaction



The chemical potential of a substance in a mixture is related to its activity by the expression

$$\mu = \mu^\circ + RT \ln a \quad \dots (i)$$

where μ° is the chemical potential of the pure substance in standard state of unit activity, R is gas constant and T the absolute temperature.

For a mole of the substance A we can write using the equation (i)

$$a\mu_A = a(\mu^\circ + RT \ln a_A)$$

and similarly

$$b\mu_B = b(\mu^\circ + RT \ln a_B)$$

$$c\mu_C = c(\mu^\circ + RT \ln a_C)$$

$$d\mu_D = d(\mu^\circ + RT \ln a_D)$$

The change in free energy for the reaction is given by

$$\Delta G = G_{\text{products}} - G_{\text{reactants}}$$

On substitution we get

$$\begin{aligned} \Delta G &= (c\mu_C + d\mu_D + \dots) - (a\mu_A + b\mu_B + \dots) \\ &= [c\{\mu_C^\circ + RT \ln a_C\} + d\{\mu_D^\circ + RT \ln a_D\}] \\ &\quad - [a\{\mu_A^\circ + RT \ln a_A\} + b\{\mu_B^\circ + RT \ln a_B\}] \\ &= [\{c\mu_C^\circ + d\mu_D^\circ + \dots\} - \{a\mu_A^\circ + b\mu_B^\circ + \dots\}] + RT \ln \frac{a_C^c \times a_D^d \times \dots}{a_A^a \times a_B^b \times \dots} \\ \Delta G &= \Delta G^\circ + RT \ln \frac{a_C^c \times a_D^d \times \dots}{a_A^a \times a_B^b \times \dots} \quad \dots (ii) \end{aligned}$$

where ΔG° is the difference in free energy of the reaction when all reactants and products are in their standard state. It is given by

$$\Delta G^\circ = \{c\mu_C^\circ + d\mu_D^\circ + \dots\} - \{a\mu_A^\circ + b\mu_B^\circ + \dots\}$$

In equation (ii) the factor A given by

$$\frac{a_C^c \times a_D^d \times \dots}{a_A^a \times a_B^b \times \dots}$$

stands for the reaction quotient of activities of the product and reactants. It may be denoted by J . The equation (ii) becomes

$$\Delta G = \Delta G^\circ + RT \ln J \quad \dots (iii)$$

The equation (iii) is called **van't Hoff reaction isotherm**

For the reaction at equilibrium

$$\Delta G = 0$$

therefore,

$$\Delta G^\circ = -RT \ln J$$

or

$$\Delta G^\circ = -RT \ln \frac{a_C^c \times a_D^d \times \dots}{a_A^a \times a_B^b \times \dots}$$

As ΔG° is the free energy of the reaction in the standard state and is constant at a given temperature.

Also, the gas constant R and T are constant, the factor

$$\frac{a_C^c \times a_D^d \times \dots}{a_A^a \times a_B^b \times \dots}$$

is a constant i.e.

$$\frac{a_C^c \times a_D^d \times \dots}{a_A^a \times a_B^b \times \dots} = \text{a constant} = K$$

It is nothing but the law of chemical equilibrium. Therefore, from equation (iii) we have

$$\Delta G^\circ = -RT \ln K \quad \dots (iv)$$

or
$$\Delta G^\circ = -2.303 RT \log K \quad \dots (v)$$

The equation (iv) is also called van't Hoff Isotherm. It may be used to calculate the change in free energy of a reaction in the standard (ΔG°) from the equilibrium constant and vice-versa.

The sign of ΔG° indicates whether the forward or reverse reaction is spontaneous. Considering the equation (iv), we can have three possibilities depending on the sign of ΔG° for the reaction.

- (1) If ΔG° is negative, $\log K$ must be positive and the reaction proceeds spontaneously in the forward reaction.
- (2) If ΔG° is positive, $\log K$ must be negative and K is less than one. The reverse reaction is then spontaneous.
- (3) If $\Delta G^\circ = 0$, $\log K = 0$ and $K = 1$. The reaction is at equilibrium.

Meaning of the Magnitude of the Free Energy Change

If ΔG° is a large negative number, K will be much greater than one and the forward reaction will proceed nearly to completion. On the other hand if ΔG° is a large positive number, K will be a small fraction. Then the reverse reaction will proceed almost to completion.

SOLVED PROBLEM 1. Calculate K for reaction which has ΔG° value -20 kcal at 25°C .

SOLUTION

We know that

$$\Delta G^\circ = -2.303 RT \log K \quad \dots (a)$$

where ΔG° is standard free energy; R is gas constant; T is absolute temperature; and K is equilibrium constant. It must be remembered that the same units of ΔG° , R and T are to be used in a given problem.

If ΔG° is given in calories

$$R = 1.99$$

$$T = 25 + 273 = 298 \text{ K}$$

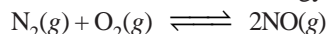
The value of K from expression (a) may be calculated as

$$\begin{aligned} -\log K &= \frac{-\Delta G^\circ}{(2.303)(1.99)(298)} \\ &= \frac{(20,000)}{1365.75} = 14.7 \end{aligned}$$

Taking antilogs, $\log K = 0.7 + 14.0$

Thus $K = 5 \times 10^{14}$

SOLVED PROBLEM 2. The standard free energy change for the reaction



is $+173.1$ kJ. Calculate K_p for the reaction at 25°C .

SOLUTION

Here, we will use the expression

$$\Delta G^\circ = -2.303 RT \log K_p$$

or
$$\log K_p = -\frac{\Delta G^\circ}{2.303 RT}$$

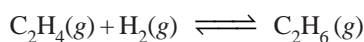
Substituting the values

$$\log K_p = \frac{1.73 \times 10^5}{(2.303)(8.314)(298)}$$

Taking antilogs

$$\begin{aligned} &= -30.34 \\ K_p &= 10^{0.66} \times 10^{-31} \\ &= 4.6 \times 10^{-31} \end{aligned}$$

SOLVED PROBLEM 3. The equilibrium constant, K_p for the reaction



is $5.04 \times 10^{17} \text{ atm}^{-1}$ at 25°C . Calculate ΔG° .

SOLUTION

$$\Delta G^\circ = -2.303 RT \log K_p \quad \dots(a)$$

Here, $R = 8.314$; $T = 25 + 273 = 298 \text{ K}$; $K_p = 5.04 \times 10^{17} \text{ atm}^{-1}$

Substituting the values in the expression (a)

$$\begin{aligned} \Delta G^\circ &= -2.303 (8.314) (298) \log (5.04 \times 10^{17}) \\ &= -5706 \times \log (5.04 \times 10^{17}) \\ &= -5706 \times (17.702) \\ &= -1.010 \times 10^5 \text{ J} \end{aligned}$$

Thus $\Delta G^\circ = -101 \text{ kJ}$

Temperature Dependence of Equilibrium Constant (van't Hoff's Equation)

There is appreciable change in the value of equilibrium constant with change in temperature. It can be determined thermodynamically using the relation

$$\Delta G^\circ = -RT \ln K_p \quad \dots(i)$$

where ΔG° is the change in standard free energy of the reaction.

Differentiating equation (i) w.r.t. at constant pressure P , we get

$$\left(\frac{\delta(\Delta G^\circ)}{\delta T} \right)_p = -R \ln K_p - RT \left(\frac{\delta \ln K_p}{\delta T} \right)_p$$

Multiplying both sides by T , we get

$$T \left(\frac{\delta(\Delta G^\circ)}{\delta T} \right)_p = -RT \ln K_p - RT^2 \left(\frac{\delta \ln K_p}{\delta T} \right)_p$$

From equation (i) we get

$$T \left(\frac{\delta(\Delta G^\circ)}{\delta T} \right)_p = \Delta G^\circ - RT^2 \left(\frac{\delta(\ln K_p)}{\delta T} \right)_p \quad \dots(ii)$$

We know that Gibb's Helmholtz equation for a reaction in the standard state can be written as

$$\Delta G^\circ = \Delta H^\circ + T \left(\frac{\delta(\Delta G^\circ)}{\delta T} \right)_p$$

$$\text{or} \quad T \left(\frac{\delta(\Delta G)}{\delta T} \right)_p = \Delta G^\circ - \Delta H^\circ \quad \dots(iii)$$

Comparing (ii) and (iii) we get

$$\Delta G^\circ = RT^2 \left(\frac{\delta(\ln K_p)}{\delta T} \right)_p$$

$$\text{or} \quad \frac{\Delta H^\circ}{RT^2} = \frac{\delta(\ln K_p)}{\delta T} \quad \dots (iv)$$

This equation is known as **van't Hoff equation**, where ΔH° is the enthalpy change of the reaction at constant pressure when all reactants and products are in their standard state. It has been found that the enthalpy change does not vary much with change in partial pressures of the reactants or products.

Therefore, ΔH° may be replaced by ΔH . The equation (iv) becomes

$$\frac{\Delta H}{RT^2} = \frac{d(\ln K_p)}{dT} \quad \dots (v)$$

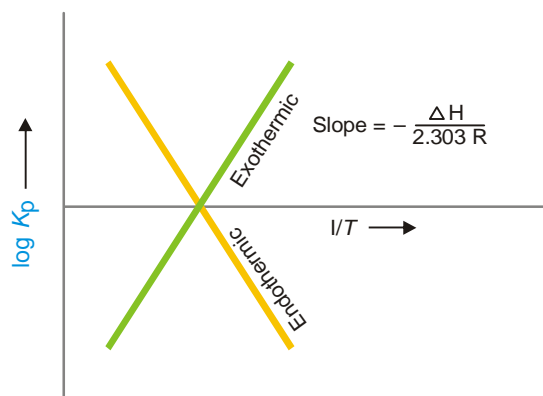
Integrating equation (v) we get

$$\ln K_p = -\frac{\Delta H}{RT} + C$$

$$\text{or} \quad \log K_p = -\frac{\Delta H}{2.303RT} + C \quad \dots (vi)$$

where C is a constant of integration. When a graph of $\log K_p$ against $1/T$ is plotted we get straight line

having slope equal to $-\frac{\Delta H}{2.303R}$ (Fig 17.9).



■ **Figure 17.9**
Graph between $\log K_p$ and $1/T$.

From the graph it is clear that

- (a) For exothermic reaction ΔH is negative and K_p decreases with increase in temperature
- (b) For endothermic reaction ΔH is positive and K_p increases with increase in temperature.

Integrating equation (v) within the limits K_{p2} at temperature T_2 and K_{p1} at temperature T_1

$$\int_{K_{p1}}^{K_{p2}} d \ln K_p = \int_{T_1}^{T_2} \frac{\Delta H}{RT^2} dT$$

$$\text{or} \quad \ln \frac{K_{p2}}{K_{p1}} = -\frac{\Delta H}{R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right]$$

$$= \frac{\Delta H}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

$$\ln \frac{K_{p2}}{K_{p1}} = \frac{\Delta H}{R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

$$\text{or} \quad \log \frac{K_{p2}}{K_{p1}} = \frac{\Delta H}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

From this equation the heat of reaction can be determined if the values of equilibrium constant K_{p2} and K_{p1} at temperature T_2 and T_1 are known and vice-versa.

van't Hoff Equation in Terms of K

We know that equilibrium constant in terms of partial pressure (K_p) and in terms of concentration (K_c) are related to each other by the relation

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

Taking logarithms we get

$$\ln K_p = \ln K_c + \Delta n \ln RT$$

Differentiating w.r.t. temperature, we get

$$\frac{d(\ln K_p)}{dT} = \frac{d(\ln K_c)}{dT} + \frac{\Delta n}{T}$$

$$\text{or} \quad \frac{d(\ln K_c)}{dT} = \frac{d(\ln K_p)}{dT} - \frac{\Delta n}{T}$$

From equation (v) we have

$$\begin{aligned} \frac{d(\ln K_c)}{dT} &= \frac{\Delta H}{RT^2} - \frac{\Delta n}{T} \\ &= \frac{\Delta H}{RT^2} - \frac{\Delta n RT}{TRT} \end{aligned}$$

$$\text{or} \quad \frac{d(\ln K_c)}{dT} = \frac{\Delta H - \Delta n RT}{RT^2}$$

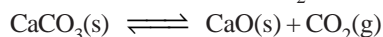
But we know

$$\Delta H = \Delta E + \Delta n RT$$

$$\therefore \frac{d(\ln K_c)}{dT} = \frac{\Delta E}{RT^2}$$

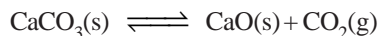
where ΔE is the heat of the reaction at constant volume.

SOLVED PROBLEM 1. The partial pressure of CO_2 in the reaction



is 0.773 mm at 500°C . Calculate K_p at 600°C for the above reaction. ΔH of the reaction is 43.2 kcal per mole and does not change in the given range of temperatures.

SOLUTION



$$K_p = P_{\text{CO}_2}$$

Given

$$K_{p1} = 0.773 \text{ mm at } 500^\circ\text{C}$$

$$\Delta H = 43.2 \text{ kcal mol}^{-1}$$

$$= 43200 \text{ cal mol}^{-1}$$

$$T_2 = 873 \text{ K}; K_{p2} = ?$$

using the relation

$$\log \frac{K_{p2}}{K_{p1}} = \frac{\Delta H}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

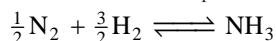
Substituting the values we get

$$\log \frac{K_{p2}}{K_{p1}} = \frac{43200}{2.303 \times 1.987} \left[\frac{873 - 773}{873 \times 773} \right]$$

$$K_{p2} = 12.06 \text{ mm}$$

∴ Equilibrium constant for the given reaction at 600°C is **12.06 mm**

SOLVED PROBLEM 2. The value of K_p at 298 K for the reaction



is found to be 826.0, partial pressures being measured in atmospheric units. Calculate ΔG° at 298 K.

SOLUTION. We know

$$\Delta G^\circ = -2.303 RT \log K_p$$

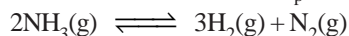
Here $R = 1.987 \text{ cal mol}^{-1} \text{ K}^{-1}$; $T = 298 \text{ K}$

$$K_p = 826; \Delta G^\circ = ?$$

Substituting the values we get

$$\begin{aligned} \Delta G^\circ &= -2.303 \times 1.987 \times 298 \times \log 826 \\ &= \mathbf{3977.78 \text{ cal}} \end{aligned}$$

SOLVED PROBLEM 3. The equilibrium constant K_p for the reaction



is 1.22×10^{-3} at 298 K and 2.16 at 498 K. Calculate ΔH° for the reaction.

SOLUTION. We know

$$\log \frac{K_{p2}}{K_{p1}} = \frac{\Delta H^\circ}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

Here $K_{p2} = 2.16$; $K_{p1} = 1.22 \times 10^{-3}$

$$T_2 = 498 \text{ K}; T_1 = 298 \text{ K}$$

$$R = 1.987 \text{ cal K}^{-1} \text{ mol}^{-1}$$

Substituting the values we get

$$\log \frac{2.16}{1.22 \times 10^{-3}} = \frac{\Delta H^\circ}{2.303 \times 1.987} \left[\frac{498 - 298}{498 \times 298} \right]$$

$$\log \frac{2.16}{1.22 \times 10^{-3}} = \frac{\Delta H^\circ}{2.303 \times 1.987} \frac{200}{498 \times 298}$$

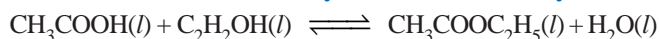
or $\Delta H^\circ = 11028.9 \text{ cal}$

$$= \mathbf{11.0289 \text{ kcals}}$$

LIQUID SYSTEMS

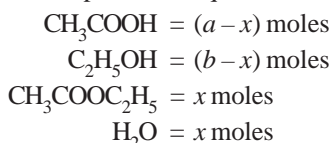
The chemical equilibrium in which all the reactants and products are in the liquid phase, are referred to as the **liquid equilibria**. Like the gas-phase equilibria, the liquid equilibria are also called **homogeneous equilibria**. For example, alcohols and acids react to form esters and water.

Reaction between Acetic acid and Ethyl alcohol to form Ethyl acetate



Let us start with a moles of acetic acid and b moles of alcohol. If x moles of acetic acid react with

x moles of ethyl alcohol, x moles of ester and x moles of water are produced when the equilibrium is established. Now the moles present at equilibrium are:



If V litre be the total volume of the equilibrium mixture, the concentrations of the various species are:

$$\begin{aligned}[\text{CH}_3\text{COOH}] &= \frac{a-x}{V} \\ [\text{C}_2\text{H}_5\text{OH}] &= \frac{b-x}{V} \\ [\text{CH}_3\text{COOC}_2\text{H}_5] &= \frac{x}{V} \\ [\text{H}_2\text{O}] &= \frac{x}{V}\end{aligned}$$

The equilibrium constant expression may be written as

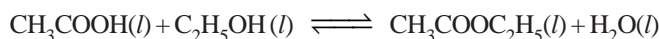
$$K = \frac{\frac{x}{V} \times \frac{x}{V}}{\frac{a-x}{V} \times \frac{b-x}{V}} \quad \text{or} \quad \frac{x^2}{(a-x)(b-x)}$$

It may be noted that the volume terms V in the numerator and denominator cancel out. **In liquid systems when there is a change in the number of moles as a result of the reaction, it is necessary to consider the volume V while calculating the equilibrium constant K .**

SOLVED PROBLEM 1. At 25°C one mole of acetic acid was allowed to react with one mole of ethyl alcohol until equilibrium was established. The equilibrium mixture was found to contain 0.333 mole of unused acid. Calculate the equilibrium constant of the reaction at the same temperature.

SOLUTION

The equation for the reaction is



The moles of unused acid = 0.333

\therefore moles reacted at equilibrium = $1 - 0.333 = 0.666$

One mole of acid reacts with one mole of alcohol to form one mole of ester and one mole of water. Therefore, moles of the various species present at equilibrium are:



Since volume term V cancels out, moles may be taken instead of concentrations and the equilibrium constant expression may be written as

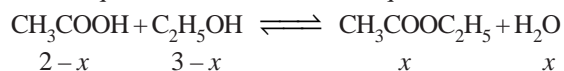
$$\begin{aligned}K &= \frac{[\text{CH}_3\text{COOC}_2\text{H}_5][\text{H}_2\text{O}]}{[\text{CH}_3\text{COOH}][\text{C}_2\text{H}_5\text{OH}]} \\ &= \frac{0.666 \times 0.666}{0.333 \times 0.333} = 4\end{aligned}$$

Thus K for the reaction between acetic acid and ethyl alcohol at 25°C is **4**.

SOLVED PROBLEM 2. 2 moles of acetic acid and 3 moles of ethyl alcohol are allowed to come to equilibrium at 298 K. If the equilibrium constant of the reaction at this temperature is 4, what is the equilibrium concentration of ethyl acetate?

SOLUTION

Let x mole of acetic acid react with x mole of ethyl alcohol to form x moles of ethyl acetate and x mole of water at equilibrium. Thus moles at equilibrium are:



Since the volume terms cancel out in the equilibrium constant expression, we have

$$K = \frac{[\text{CH}_3\text{COOC}_2\text{H}_5][\text{H}_2\text{O}]}{[\text{CH}_3\text{COOH}][\text{C}_2\text{H}_5\text{OH}]} = \frac{x \times x}{(2-x)(3-x)} = 4$$

or
$$\frac{x^2}{(2-x)(3-x)} = 4$$

Rearranging gives

$$3x^2 - 20x + 24 = 0$$

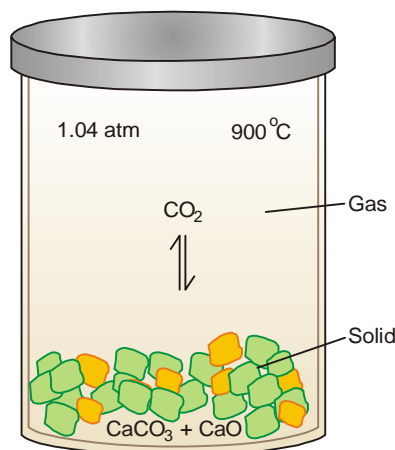
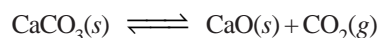
Solving this quadratic equation, we get

$$x = 1.57 \text{ or } 5.09$$

Both roots are positive of which only 1.57 is acceptable. Since 2 mole of acetic acid can yield only 2 moles of the ester, the value 5.09 is rejected. The equilibrium conc. of ethyl acetate is **1.57 mole**.

HETEROGENEOUS EQUILIBRIA

So far we have discussed chemical equilibria in which all reactants and products are either gases or liquids. Such equilibria in which the reactants and products are not all in the same phase, are called **heterogeneous equilibria**. The decomposition of calcium carbonate upon heating to form calcium oxide and carbon dioxide is an example of heterogeneous equilibrium. If the reaction is carried in a closed vessel, the following equilibrium is established.



■ **Figure 17.10**

When solid CaCO_3 is heated in a closed vessel at 900°C , equilibrium is established when the pressure of CO_2 reaches 1.04 atm.

Equilibrium Constant Expression

Straight forward application of Equilibrium law to the decomposition reaction of calcium carbonate leads to the equilibrium constant expression.

$$K = \frac{[\text{CO}_2][\text{CaO}]}{[\text{CaCO}_3]}$$

But CaCO_3 and CaO are pure solids. The concentration (moles per unit volume) of a pure solid (or liquid) is fixed and cannot vary. Thus **the concentrations of pure solids or liquids are not included in the equilibrium constant expression.**

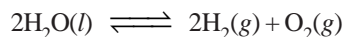
Ignoring the concentrations of CaCO_3 and CaO , the equilibrium constant expression for the decomposition of CaCO_3 may be written as

$$K_c = [\text{CO}_2]$$

In terms of partial pressures

$$K_p = p_{\text{CO}_2}$$

Similarly, the equilibrium constant expression for the decomposition of liquid water



would be

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

Ignoring the concentration of liquid water, we have

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

$$K_p = (p_{\text{H}_2})^2(p_{\text{O}_2})$$

SOLVED PROBLEM 1. Write expressions for the equilibrium constants K_c and K_p for the equilibria:



SOLUTION

Ignoring the solid and liquid species, the equilibrium constant expressions may be written as:

(a) $K_c = [\text{NH}_3][\text{HCl}]$

$$K_p = (p_{\text{NH}_3})(p_{\text{HCl}})$$

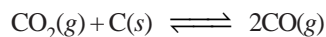
(b) $K_c = [\text{Cl}_2]$

$$K_p = p_{\text{Cl}_2}$$

(c) $K_c = \frac{[\text{H}_2]^4}{[\text{H}_2\text{O}]^4}$

$$K_p = \frac{(p_{\text{H}_2})^4}{(p_{\text{H}_2\text{O}})^4}$$

SOLVED PROBLEM 2. Carbon dioxide upon heating with carbon at high temperature is reduced to carbon monoxide:



K_p for the reaction is 1.90 atm.

In a particular experiment the total pressure at equilibrium was found to be 2.00 atm. What were the partial pressures of CO and CO_2 ?

SOLUTION

Ignoring solid carbon, the equilibrium constant expression can be written as

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

If the partial pressure of CO is x atm, partial pressure of CO_2 is $(2.00 - x)$

Substituting the values,

$$K_p = \frac{x^2}{2.00 - x} = 1.90 \text{ atm}$$

$$\therefore x^2 + 1.90x - 3.80 = 0$$

Solving the quadratic equation, $x = 1.22$

Hence

$$p_{\text{CO}} = x \text{ atm} = 1.22 \text{ atm}$$

$$p_{\text{CO}_2} = (2.00 - x) = \mathbf{0.78 \text{ atm}}$$

LE CHATELIER'S PRINCIPLE

In 1884, the French Chemist Henry Le Chatelier proposed a general principle which applies to all systems in equilibrium. This important principle called the **Le Chatelier's principle** may be stated as : **when a stress is applied on a system in equilibrium, the system tends to adjust itself so as to reduce the stress.**

There are three ways in which the stress can be caused on a chemical equilibrium:

- (1) Changing the concentration of a reactant or product.
- (2) Changing the pressure (or volume) of the system.
- (3) Changing the temperature.

Thus when applied to a chemical reaction in equilibrium, Le Chatelier's principle can be stated as: **if a change in concentration, pressure or temperature is caused to a chemical reaction in equilibrium, the equilibrium will shift to the right or the left so as to minimise the change.**

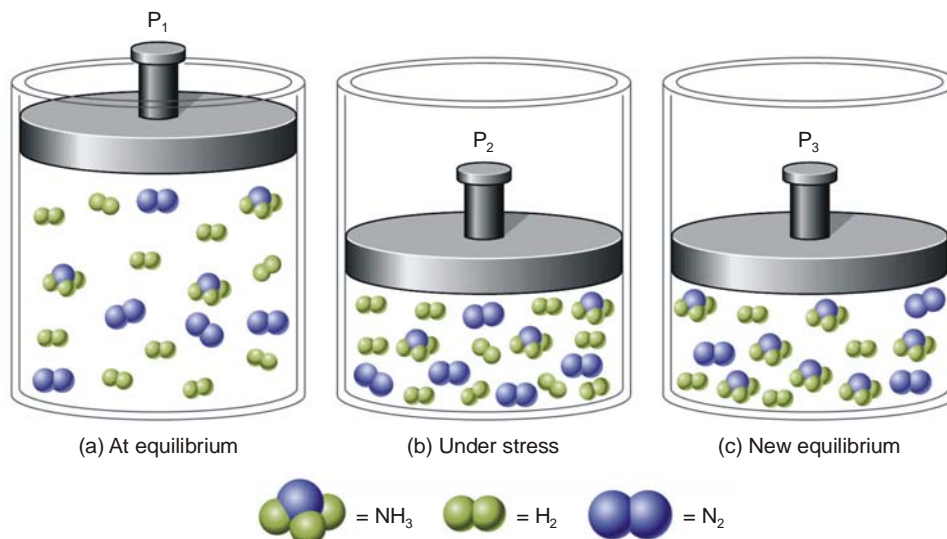
Now we proceed to illustrate the above statement by taking examples of each type of stress.

EFFECT OF A CHANGE IN CONCENTRATION

We can restate Le Chatelier's principle for the special case of concentration changes: **when concentration of any of the reactants or products is changed, the equilibrium shifts in a direction so as to reduce the change in concentration that was made.**

Addition of an inert gas

Let us add an *inert gas* to an equilibrium mixture while the volume of the reaction vessel remains the same. The addition of the inert gas increases the total pressure but the partial pressures of the reactants and products are not changed. Thus **the addition of an inert gas has no effect on the position of the equilibrium.**

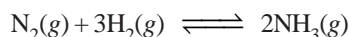


■ **Figure 17.11**

Illustration of Le Chatelier's principle. (a) System at equilibrium with 10H₂, 5N₂, and 3NH₃, for a total of 18 molecules. (b) The same molecules are forced into a smaller volume, creating a stress on the system. (c) Six H₂ and 2N₂ have been converted to 4NH₃. A new equilibrium has been established with 4H₂, 3N₂, and 7NH₃, a total of 14 molecules. The stress is partially relieved by the reduction in the total number of molecules.

Effect of change of concentration on Ammonia Synthesis reaction

Let us illustrate the effect of change of concentration on a system at equilibrium by taking example of the ammonia synthesis reaction:

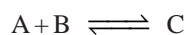


When N₂ (or H₂) is added to the equilibrium already in existence (equilibrium I), the equilibrium will shift to the right so as to reduce the concentration of N₂ (Le Chatelier's principle). The concentration of NH₃ at the equilibrium II is more than at equilibrium I. The results in a particular case after the addition of one mole/litre are given below.

Equilibrium I		Equilibrium II
[N ₂] = 0.399 M	$\xrightarrow[\text{of N}_2 \text{ added}]{1 \text{ mole/L}}$	N ₂ = 1.348 M
[H ₂] = 1.197 M		[H ₂] = 1.044 M
[NH ₃] = 0.202 M		[NH ₃] = 0.304 M

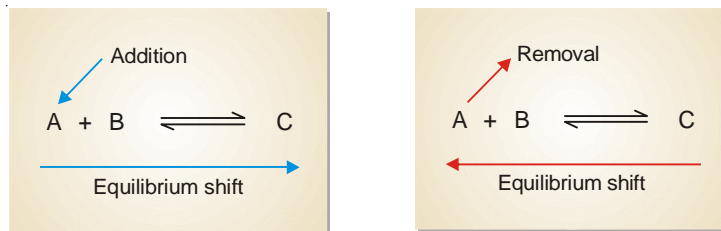
Obviously, the addition of N₂ (a reactant) increases the concentration of NH₃, while the concentration of H₂ decreases. Thus to have a better yield of NH₃, one of the reactants should be added in excess.

A change in the concentration of a reactant or product can be effected by the addition or removal of that species. Let us consider a general reaction



When a reactant, say, A is added at equilibrium, its concentration is increased. The forward reaction alone occurs momentarily. According to Le Chatelier's principle, a new equilibrium will be

established so as to reduce the concentration of A. Thus the addition of A causes the equilibrium to shift to right. This increases the concentration (yield) of the product C.



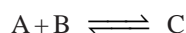
Following the same line of argument, a decrease in the concentration of A by its removal from the equilibrium mixture, will be undone by shift to the equilibrium position to the left. This reduces the concentration (yield) of the product C.

EFFECT OF A CHANGE IN PRESSURE

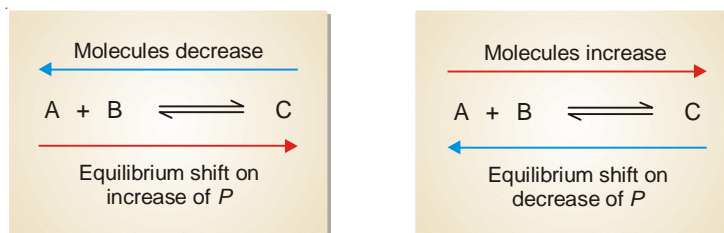
To predict the effect of a change of pressure, Le Chatelier's principle may be stated as : **when pressure is increased on a gaseous equilibrium reaction, the equilibrium will shift in a direction which tends to decrease the pressure.**

The pressure of a gaseous reaction at equilibrium is determined by the total number of molecules it contains. If the forward reaction proceeds by the reduction of molecules, it will be accompanied by a decrease of pressure of the system and *vice versa*.

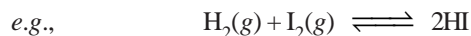
Let us consider a reaction,



The combination of A and B produces a decrease of number of molecules while the decomposition of C into A and B results in the increase of molecules. Therefore, by the increase of pressure on the equilibrium it will shift to right and give more C. A decrease in pressure will cause the opposite effect. The equilibrium will shift to the left when C will decompose to form more of A and B.



The reactions in which the number of product molecules is equal to the number of reactant molecules,



are unaffected by pressure changes. In such a case the system is unable to undo the increase or decrease of pressure.

In light of the above discussion, we can state a general rule to predict the effect of pressure changes on chemical equilibria.

The increase of pressure on a chemical equilibrium shifts it in that direction in which the number of molecules decreases and vice-versa. This rule is illustrated by the examples listed in Table 17.1.

TABLE 17.1. EFFECT OF PRESSURE ON VARIOUS GASEOUS EQUILIBRIA

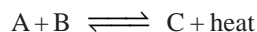
System	Pressure increased	Pressure decreased
(1) $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$	←	→
(2) $\text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{Cl}_2$	←	→
(3) $2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3$	→	←
(4) $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$	→	←
(5) $\text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI}$	No effect	No effect
(6) $\text{N}_2 + \text{O}_2 \rightleftharpoons 2\text{NO}$	No effect	No effect

EFFECT OF CHANGE OF TEMPERATURE

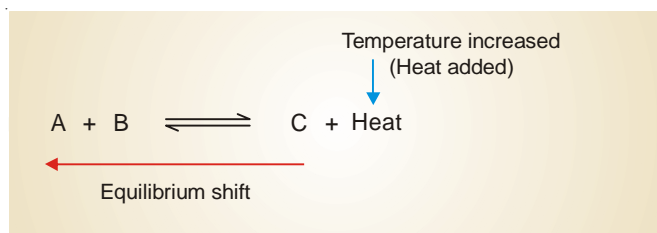
Chemical reactions consist of two opposing reactions. If the forward reaction proceeds by the evolution of heat (exothermic), the reverse reaction occurs by the absorption of heat (endothermic). Both these reactions take place at the same time and equilibrium exists between the two. If temperature of a reaction is raised, heat is added to the system. The equilibrium shifts in a direction in which heat is absorbed in an attempt to lower the temperature. Thus the effect of temperature on an equilibrium reaction can be easily predicted by the following version of the Le Chatelier's principle.

When temperature of a reaction is increased, the equilibrium shifts in a direction in which heat is absorbed.

Let us consider an exothermic reaction



When the temperature of the system is increased, heat is supplied to it from outside. According to Le Chatelier's principle, the equilibrium will shift to the left which involves the absorption of heat. This would result in the increase of the concentration of the reactants A and B.

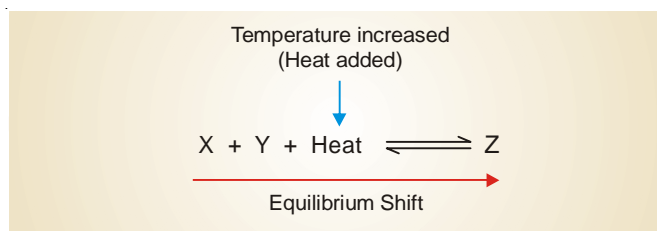


In an endothermic reaction



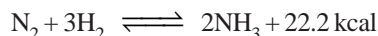
the increase of temperature will shift the equilibrium to the right as it involves the absorption of heat. This increases the concentration of the product Z.

In general, we can say that **the increase of temperature favours the reverse change in an exothermic reaction and the forward change in an endothermic reaction.**



Formation of Ammonia from N₂ and H₂

The synthesis of ammonia from nitrogen and hydrogen is an exothermic reaction.



When the temperature of the system is raised, the equilibrium will shift from right-to-left which absorbs heat (*Le Chatelier's principle*) This results in the lower yield of ammonia. On the other hand, by lowering the temperature of the system, the equilibrium will shift to the right which evolves heat in an attempt to raise the temperature. This would increase the yield of ammonia. But with decreasing temperature, the rate of reaction is slowed down considerably and the equilibrium is reached slowly. Thus in the commercial production of ammonia, it is not feasible to use temperature much lower than 500°C. At lower temperature, even in the presence of a catalyst, the reaction proceeds too slowly to be practical.

TABLE 17.2. THE DIRECTION OF EQUILIBRIUM SHIFT IN SOME REACTIONS ON INCREASE OF TEMPERATURE

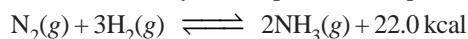
Reaction	Equilibrium Shift
$4\text{HCl} + \text{O}_2 \rightleftharpoons 2\text{H}_2\text{O} + 2\text{Cl}_2 + 284 \text{ kcal}$	←
$\text{H}_2 + \text{Cl}_2 \rightleftharpoons 2\text{HCl} + 44.2 \text{ kcal}$	←
$\text{CH}_4 + 2\text{O}_2 \rightleftharpoons \text{CO}_2 + 2\text{H}_2\text{O} + 212.8 \text{ kcal}$	←
$2\text{CO}_2 + 135.2 \text{ kcal} \rightleftharpoons 2\text{CO} + \text{O}_2$	→
$\text{N}_2\text{O}_4 + 14 \text{ kcal} \rightleftharpoons 2\text{NO}_2$	→
$\text{H}_2 + \text{I}_2 + 12.4 \text{ kcal} \rightleftharpoons 2\text{HI}$	→

CONDITIONS FOR MAXIMUM YIELD IN INDUSTRIAL PROCESSES

With the help of Le Chatelier's principle we can work out the optimum conditions for securing the maximum yield of products in industrial processes.

Synthesis of Ammonia (Haber Process)

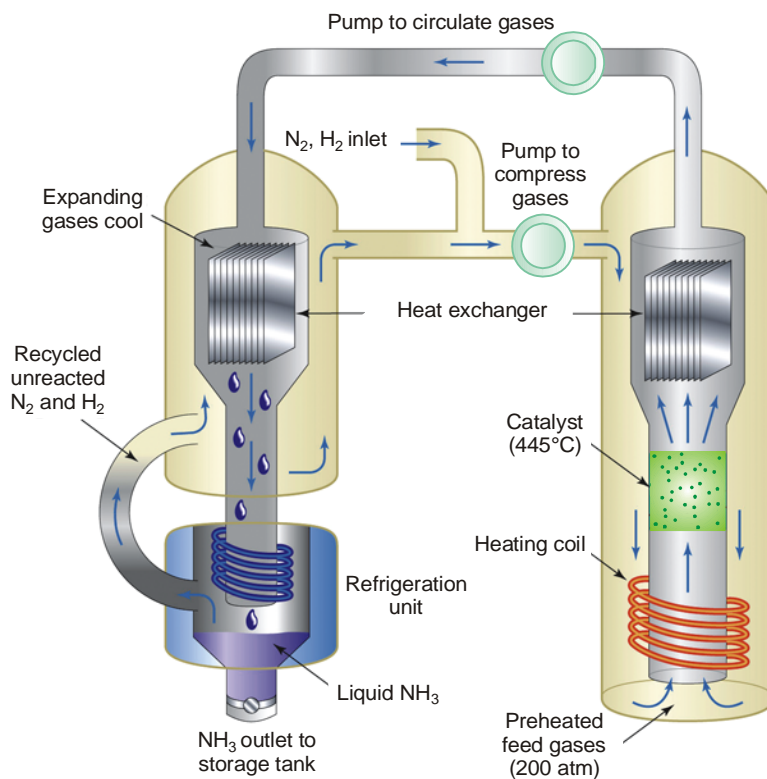
The manufacture of ammonia by Haber process is represented by the equation



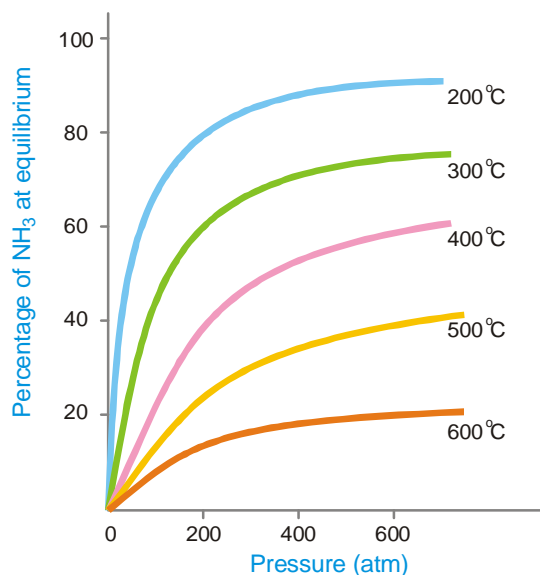
A look at the equation provides the following information:

- the reaction is exothermic
 - the reaction proceeds with a decrease in the number of moles.
- Low temperature.** By applying Le Chatelier's principle, low temperature will shift the equilibrium to the right. This gives greater yield of ammonia. In actual practice a temperature of about 450°C is used when the percentage of ammonia in the equilibrium mixture is 15.
 - High pressure.** High pressure on the reaction at equilibrium favours the shift of the equilibrium to the right. This is so because the forward reaction proceeds with a decrease in the number of moles. A pressure of about 200 atmospheres is applied in practice.
 - Catalyst.** As already stated, low temperature is necessary for higher yield of ammonia. But at relatively low temperatures, the rate of reaction is slow and the equilibrium is attained in a long time. To increase the rate of reaction and thus quicken the attainment of equilibrium, a catalyst is used. Finely divided iron containing molybdenum is employed in actual practice. Molybdenum acts as a promoter that increases the life and efficiency of the catalyst.

Pure N₂ and H₂ gases are used in the process. Any impurities in the gases would poison the catalyst and decrease its efficiency.



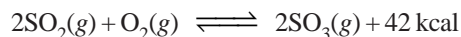
■ **Figure 17.12**
 Synthesis of ammonia by Haber process.



■ **Figure 17.13**
 Effect of temperature and pressure on the equilibrium $N_2 + 3H_2 \rightleftharpoons 2NH_3$.
 Increasing temperature decreases the percentage of NH₃ at equilibrium.
 Increasing pressure increases the percentage of NH₃ at equilibrium.

Manufacture of Sulphuric acid (Contact Process)

The chief reaction used in the process is



Following information is revealed by the above equation:

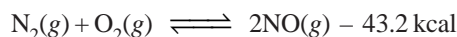
- the reaction is exothermic.
- the reaction proceeds with a decrease in number of moles.

On the basis of Le Chatelier's principle, the conditions for the maximum yield can be worked out as below:

- Low temperature.** Since the forward reaction is exothermic, the equilibrium will shift on the right at low temperature. An optimum temperature between 400-450°C is required for the maximum yield of sulphur trioxide.
- High pressure.** Since the number of moles are decreased in the forward reaction, increase of pressure will shift the equilibrium to the right. Thus for maximum yield of SO₃, 2 to 3 atmosphere pressure is used.
- Catalyst.** At the low temperature used in the reaction, the rate of reaction is slow and the equilibrium is attained slowly. A catalyst is, therefore, used to speed up the establishment of the equilibrium. Vanadium pentoxide, V₂O₅, is commonly used and it has replaced the earlier catalyst *platinum asbestos* which was easily poisoned by the impurities present in the reacting gases. All the same, SO₂ and O₂ used for the manufacture of sulphuric acid must be pure and dry.

Manufacture of Nitric acid (Birkeland-Eyde process)

Nitric acid is prepared on a large scale by making use of the reaction



The equation tells us that:

- the reaction proceeds with no change in the number of moles.
- the reaction is endothermic and proceeds by absorption of heat.

The favourable conditions for the maximum yield of NO are:

- High temperature.** Since the forward reaction is endothermic, increase of temperature will favour it (Le Chatelier's principle). Thus a high temperature of the order of 3000°C is employed to get high yield of nitric acid.
- No effect of pressure.** Since the forward reaction involves no change in the number of moles, a change in pressure has no effect on the equilibrium.
- High concentration.** The formation of nitric oxide is favoured by using high concentrations of the reactants *i.e.* N₂ and O₂.

EXAMINATION QUESTIONS

- Define or explain the following terms :
 - Chemical equilibrium
 - Equilibrium constant
 - Law of mass action
 - Heterogeneous equilibria
- One mole of PCl₅ is heated in a closed two-litre vessel. At equilibrium 40% of the PCl₅ is dissociated. Calculate the equilibrium constant of the reaction.
Answer. 0.267
- (a) Derive the law of mass action for the expression :