That is,

$$\Delta H^{\circ} = \begin{bmatrix} \text{Total standard heat} \\ \text{of formation of products} \end{bmatrix} - \begin{bmatrix} \text{Total standard heat} \\ \text{of formation of reactants} \end{bmatrix}$$

$$\Delta H^{\circ} = \Delta H_f^{o} \text{ (products)} - \Delta H_f^{o} \text{ (reactants)}$$

Let us consider a general reaction

$$aA + bB \longrightarrow cC + dD$$

The standard heat of reaction is given by

$$\Delta H^{o} = \Delta H_f^{o} \text{ (products)} - \Delta H_f^{o} \text{ (reactants)}$$

$$= [c \times \Delta H_f^{o} \text{ (C)} + d \times H_f^{o} \text{ (D)}] - [a \times \Delta H_f^{o} \text{ (A)} + b \times \Delta H_f^{o} \text{ (B)}]$$

SOLVED PROBLEM 1. Calculate ΔH^{o} for the reaction

$$CO_2(g) + H_2(g) \longrightarrow CO(g) + H_2O(g)$$

given that ΔH_f^{o} for $CO_2(g)$, $CO(g)$ and $H_2O(g)$ are -393.5, -111.31 and -241.80 kJ mol^{-1} respectively.

SOLUTION

Here we have

$$CO_2(g) + H_2(g) \longrightarrow CO(g) + H_2O(g)$$

$$\Delta H^{o} = \Delta H_f^{o} \text{ (products)} - \Delta H_f^{o} \text{ (reactants)}$$

$$= [\Delta H_f^{o} [CO(g)] + \Delta H_f^{o} [H_2O(g)]] - [\Delta H_f^{o} [CO_2(g)] + \Delta H_f^{o} [H_2(g)]]$$

$$= [-111.3 + (-241.8)] - [-393.5 + 0]$$

$$= -353.1 + 393.5$$

$$= \textbf{40.4 kJ}$$

SOLVED PROBLEM 2. The standard heats of formation of $C_2H_5OH(l)$, $CO_2(g)$ and $H_2O(l)$ are -277.0, -393.5 and -285.5 kJ mol^{-1} respectively. Calculate the standard heat change for the reaction

$$C_2H_5OH(l) + 3O_2(l) \longrightarrow 2CO_2(g) + 3H_2O(l)$$

SOLUTION

We know that :

$$\Delta H^{o} = \Delta H_f^{o} \text{ (products)} - \Delta H_f^{o} \text{ (reactants)}$$

In the present case

$$\Delta H^{o} = [2 \times \Delta H_f^{o} [CO_2(g)] + 3 \times \Delta H_f^{o} [H_2O(l)]$$

$$- \Delta H_f^{o} [C_2H_5OH(l)] + 3 \times \Delta H_f^{o} [O_2(g)]$$

$$= [2 \times (-393.5) + 3 \times -285.5] - [-277.0 - 0]$$

$$= -1643.5 - (-277)$$

$$= \textbf{-1366.5 kJ}$$

HEAT OF COMBUSTION

The heat of combustion of a substance is defined as : **the change in enthalpy of a system when one mole of the substance is completely burnt in excess of air or oxygen.**

It is denoted by ΔH_c. As for example, heat of combustion of methane is -21.0 kcal $(= 87.78$ kJ$)$ as shown by the equation

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l) \qquad \Delta H_c = -21.0 \, kcal$$
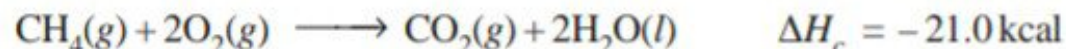
Now consider the chemical equations

$$C(s) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H = -94.3 \, kcal$$

$$C(s) + \tfrac{1}{2}O_2(g) \longrightarrow CO(g) \qquad \Delta H = -26.0 \, kcal$$

It may be noted that -94.3 kcal and not -26.0 kcal is the heat of combustion of carbon as the combustion is complete only in the first reaction. In the second case, oxidation has converted carbon to carbon monoxide and is by no means complete as carbon monoxide can be further oxidised to carbon dioxide.

It should be noted clearly that the **heat of combustion of a substance (ΔH_c) is always negative.** Heat energy is evolved during the process of combustion *i.e.*, $\Delta H_c = -$ ve.

SOLVED PROBLEM. Calculate the standard heat of formation of propane (C_3H_8) if its heat of combustion is -2220.2 kJ mol^{-1}. The heats of formation of $CO_2(g)$ and $H_2O(l)$ are -393.5 and -285.8 kJ mol^{-1} respectively.

SOLUTION

We are given

(i) $\quad C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(l)$ $\qquad\qquad \Delta H_c = -2220.2$ kJ

(ii) $\qquad C(s) + O_2(g) \longrightarrow CO_2(g)$ $\qquad\qquad\qquad\qquad \Delta H = -393.5$ kJ

(iii) $\quad H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$ $\qquad\qquad\qquad\qquad \Delta H = -285.8$ kJ

We should manipulate these equations in a way so as to get the required equation

$\qquad 3C(s) + 4H_2(g) \longrightarrow C_3H_8(g)$ $\qquad\qquad\qquad \Delta H = ?$
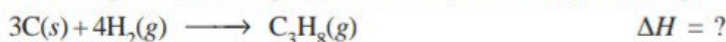
Multiplying equation (ii) by 3 and equation (iii) by 4 and adding up we get

$\qquad 3C(s) + 3O_2(g) \longrightarrow 3CO_2(g)$ $\qquad\qquad\qquad \Delta H = -1180.5$ kJ

$\qquad 4H_2(g) + 2O_2(g) \longrightarrow 4H_2O(l)$ $\qquad\qquad\qquad \Delta H = -1143.2$ kJ

(iv) $\quad 3C(s) + 4H_2(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(l)$ $\qquad \Delta H = -2323.7$ kJ

Subtracting equation (i) from equation (iv), we have

$\qquad 3C(s) + 4H_2(g) + 5O_2(g) - 5O_2(g) \longrightarrow C_3H_8(g)$ $\qquad \Delta H = -103.5$ kJ
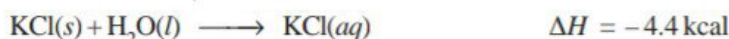
$\therefore$ The heat of formation of propane is $-$**103.5 kJ mol^{-1}**.

HEAT OF SOLUTION

Heat changes are usually observed when a substance is dissolved in a solvent. When a reaction takes place in solution, the heat of solution of reactants and products must be taken into consideration. The heat of solution is defined as : **the change in enthalpy when one mole of a substance is dissolved in a specified quantity of solvent at a given temperature.**

For example, when one mole of copper sulphate is dissolved in water so that we get one molar solution, the heat absorbed is 78.5 kJ. If the solution so obtained is further diluted, there will again be a change in enthalpy. If we go on diluting the solution, a stage will come when further dilution produces no thermal effect. This state is called the state of infinite dilution. To avoid the quantity of the solvent, we have to incorporate the idea of infinite dilution in our definition which may be stated as : **the heat of solution is the change in enthalpy when one mole of a substance is dissolved in a solvent so that further dilution does not give any change in enthalpy.**

The heat of solution can also be expressed as :

$$KCl(s) + H_2O(l) \longrightarrow KCl(aq) \qquad\qquad \Delta H = -4.4 \text{ kcal}$$

$$MgSO_4(s) + H_2O(l) \longrightarrow MgSO_4(aq) \qquad\qquad \Delta H = -20.28 \text{ kcal}$$

The heat of solution of an electrolyte may be due to energy change involved during ionisation or some hydrate formation as in case of sulphuric acid. Usually heat is absorbed when ions are torn apart from each other in the process of solution and heat is evolved during hydrate formation. With a salt as sodium chloride the heat of separation of ions just equals the heat of hydration and there is very little heat effect.
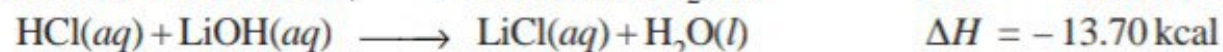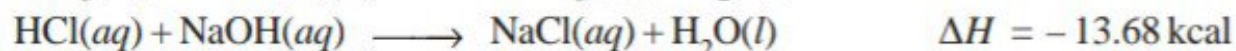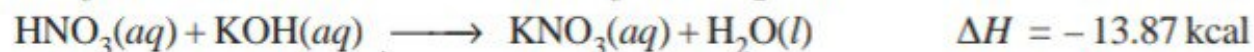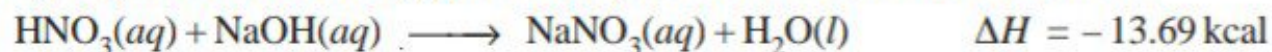
HEAT OF NEUTRALISATION

The heat of neutralisation is defined as : **the change in heat content (enthalpy) of the system when one gram equivalent of an acid is neutralised by one gram equivalent of a base or *vice versa* in dilute solution.**

HEAT OF NEUTRALISATION

The heat of neutralisation is defined as : **the change in heat content (enthalpy) of the system when one gram equivalent of an acid is neutralised by one gram equivalent of a base or *vice versa* in dilute solution.**

The following may be considered as typical examples of the heat of neutralisation.

$$HNO_3(aq) + NaOH(aq) \longrightarrow NaNO_3(aq) + H_2O(l) \qquad \Delta H = -13.69 \text{ kcal}$$

$$HNO_3(aq) + KOH(aq) \longrightarrow KNO_3(aq) + H_2O(l) \qquad \Delta H = -13.87 \text{ kcal}$$

$$HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(l) \qquad \Delta H = -13.68 \text{ kcal}$$

$$HCl(aq) + LiOH(aq) \longrightarrow LiCl(aq) + H_2O(l) \qquad \Delta H = -13.70 \text{ kcal}$$

HEAT OF FUSION

It is defined as : **the heat change (or enthalpy change) when one mole of a solid substance is converted into the liquid state at its melting point.**

As an example, we can take the melting of one mole of ice at its melting point, 0°C or 273 K. The process can be represented as

$$H_2O(s) \longrightarrow H_2O(l) \qquad \Delta H = +1.43 \, kcal$$
$$\text{ice} \qquad\qquad \text{water}$$

and is accompanied by the absorption of 1.43 kcal of heat. From the values of fusion of various substances we can compare their magnitudes of intermolecular forces. **Greater the heat of fusion of a substance higher the magnitude of intermolecular forces.**

HEAT OF VAPOURISATION

The heat of vapourisation is defined as : **the heat change (or enthalpy change) when one mole of liquid is converted into vapour or gaseous state at its boiling point.**

For example, when one mole of water is converted into steam at 100°C or 373 K, the heat absorbed is 9.71 kcal which is the heat of vaporisation of water. The change can be represented as :

$$H_2O(l) \longrightarrow H_2O(g) \qquad \Delta H = +9.71 \, kcal$$
$$\text{water} \qquad\qquad \text{steam}$$

The heats of vaporisation of ethyl alcohol (C_2H_5OH) and benzene (C_6H_6) are 7.29 kcal mol^{-1} and 7.36 kcal mol^{-1} respectively. The values of heats of vaporisation can also be used for the comparison of the magnitude of intermolecular forces of attraction in liquids.

HEAT OF SUBLIMATION

Sublimation is a process when a solid changes directly into gaseous state without changing into liquid state. It occurs at a temperature below the melting point of the solid. Heat of sublimation is defined as : **the heat change (or enthalpy change) when one mole of a solid is directly converted into the gaseous state at a temperature below its melting point.**

For example, the heat of sublimation of iodine is 14.92 kcal mol^{-1}. It can be represented as

$$I_2(s) \longrightarrow I_2(g) \qquad \Delta H = +14.92 \, kcal$$

HEAT OF TRANSITION

The heat of transition is defined as : **the change in enthalpy which occurs when one mole of an element changes from one allotropic form to another.**

For example, the transition of diamond into amorphous carbon may be represented as

$$C_{diamond} \longrightarrow C_{amorphous} \qquad \Delta H = +3.3 \, kcal$$

Similarly,

$$S_{monoclinic} \longrightarrow S_{rhombic} \qquad \Delta H = -0.016 \, kcal$$

and

$$P_{white} \longrightarrow P_{red} \qquad \Delta H = -1.028 \, kcal$$

where – 0.016 kcal and – 1.028 kcal are heats of transition of monoclinic sulphur to rhombic sulphur and white phosphorus to red phosphorus respectively.

HESS'S LAW OF CONSTANT HEAT SUMMATION

We have already seen that heat changes in chemical reactions are equal to the difference in internal energy (ΔE) or heat content (ΔH) of the products and reactants, depending upon whether the reaction is studied at constant volume or constant pressure. Since ΔE and ΔH are functions of the state of the system, the heat evolved or absorbed in a given reaction must be independent of the manner in which the reaction is brought about. Thus it depends only on the initial state and final

states of the system and not the manner or the steps in which the change takes place. This generalisation is known as **Hess's Law** and may be stated as : **If a chemical change can be made to take place in two or more different ways whether in one step or two or more steps, the amount of total heat change is same no matter by which method the change is brought about.**

The law also follows as a mere consequence of the first law of thermodynamics. Let us suppose that a substance A can be changed to Z directly.

$$A \longrightarrow Z + Q_1 \qquad\qquad \Delta H_1 = -Q_1$$

where Q_1 is the heat evolved in the direct change. When the same change is brought about in stages :

$$A \longrightarrow B + q_1 \qquad\qquad \Delta H_2 = -q_1$$
$$B \longrightarrow C + q_2 \qquad\qquad \Delta H_2 = -q_2$$
$$C \longrightarrow Z + q_3 \qquad\qquad \Delta H_2 = -q_3$$

the total evolution of heat $= q_1 + q_2 + q_3 = Q_2$

According to Hess's law $Q_1 = Q_2$. If it be not so, let $Q_2 > Q_1$. Then by transforming A to Z through stages and retransforming directly back to A, there would be gain of heat energy $= Q_2 - Q_1$. By repeating the process again and again an unlimited heat energy will be developed in an isolated system. This goes against the first law of thermodynamics. Hence Q_1 must be equal to Q_2.
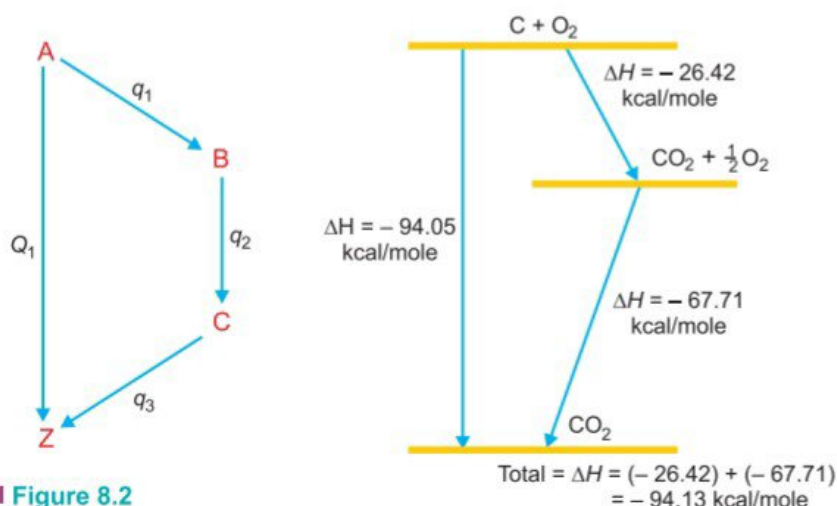
■ Figure 8.2
Illustration of Hess's Law.

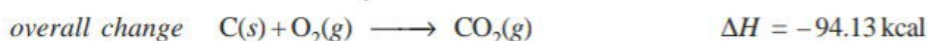Hess's law has been tested experimentally and shown to be true.

Illustrations of Hess's Law

(1) **Burning of carbon to CO_2.** Carbon can be burnt to carbon dioxide directly or it may first be changed to carbon monoxide which may then be oxidised to carbon dioxide.
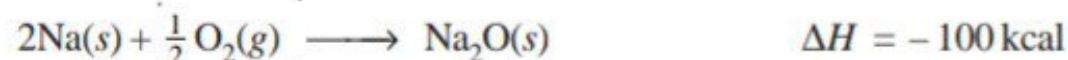
1st way :

$$C(s) + O_2(g) \longrightarrow CO_2(g) \qquad\qquad \Delta H = -94.05 \, \text{kcal}$$

2nd way :

$$C(s) + \tfrac{1}{2} O(g) \longrightarrow CO_2(g) \qquad\qquad \Delta H = -26.42 \, \text{kcal}$$
$$CO(g) + \tfrac{1}{2} O_2(g) \longrightarrow CO(g) \qquad\qquad \Delta H = -67.71 \, \text{kcal}$$

overall change $\quad C(s) + O_2(g) \longrightarrow CO_2(g) \qquad\qquad \Delta H = -94.13 \, \text{kcal}$
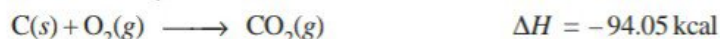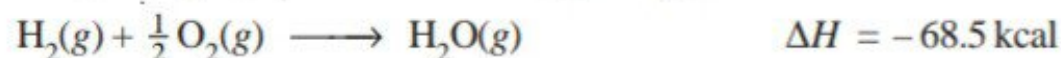
It is evident from above that the total heat energy evolved is the same in the two cases (Fig. 8.2)

(2) **Formation of Sodium hydroxide from Na.** The formation of sodium hydroxide from metallic sodium presents another example of Hess's law. The process can be carried out in two ways.

1st way :

$$2Na(s) + \tfrac{1}{2}O_2(g) \longrightarrow Na_2O(s) \qquad\qquad \Delta H = -100 \, \text{kcal}$$

$$Na_2O(s) + H_2O(l) \longrightarrow 2NaOH(aq) \qquad\qquad \Delta H = -56 \, \text{kcal}$$

$$\overline{2Na(s) + H_2O(l) + \tfrac{1}{2}O_2(g) \longrightarrow 2NaOH(aq) \qquad\qquad \Delta H = -156 \, \text{kcal}}$$

2nd way :

$$2Na(s) + 2H_2O(l) \longrightarrow 2NaOH(aq) + H_2(g) \qquad \Delta H = -88 \, \text{kcal}$$

$$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(g) \qquad\qquad \Delta H = -68.5 \, \text{kcal}$$

$$\overline{2Na(s) + H_2O(l) + \tfrac{1}{2}O_2(g) \longrightarrow 2NaOH(aq) \qquad\qquad \Delta H = -156.5 \, \text{kcal}}$$

It may be observed that the total heat evolved in carrying the reaction in two different ways is the same. The difference of 0.5 kcal is within the experimental error.

It is obvious from the above examples that by the addition of a series of chemical equations we can obtain not only the resultant products of this series of reactions but also the net heat effect. It is, therefore, clear that : **thermochemical equations may be multiplied, added or subtracted like ordinary algebraic equations.** For this reason, Hess's law has been of great service in the indirect determination of heats of formation.

17

CHAPTER

Chemical Equilibrium

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.

$$A + B \longrightarrow C + D \qquad \text{(Forward reaction)}$$
$$A + B \longleftarrow C + D \qquad \text{(Reverse reaction)}$$

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.

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

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

Some Examples of Reversible Reactions

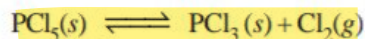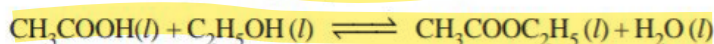A few common examples of reversible reactions are listed below :

$$2NO_2(g) \rightleftharpoons N_2O_4(g)$$
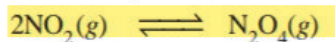
AN EQUILIBRIUM ANOLOGY

Nuts and Bolts Representation of Chemical Equilibrium
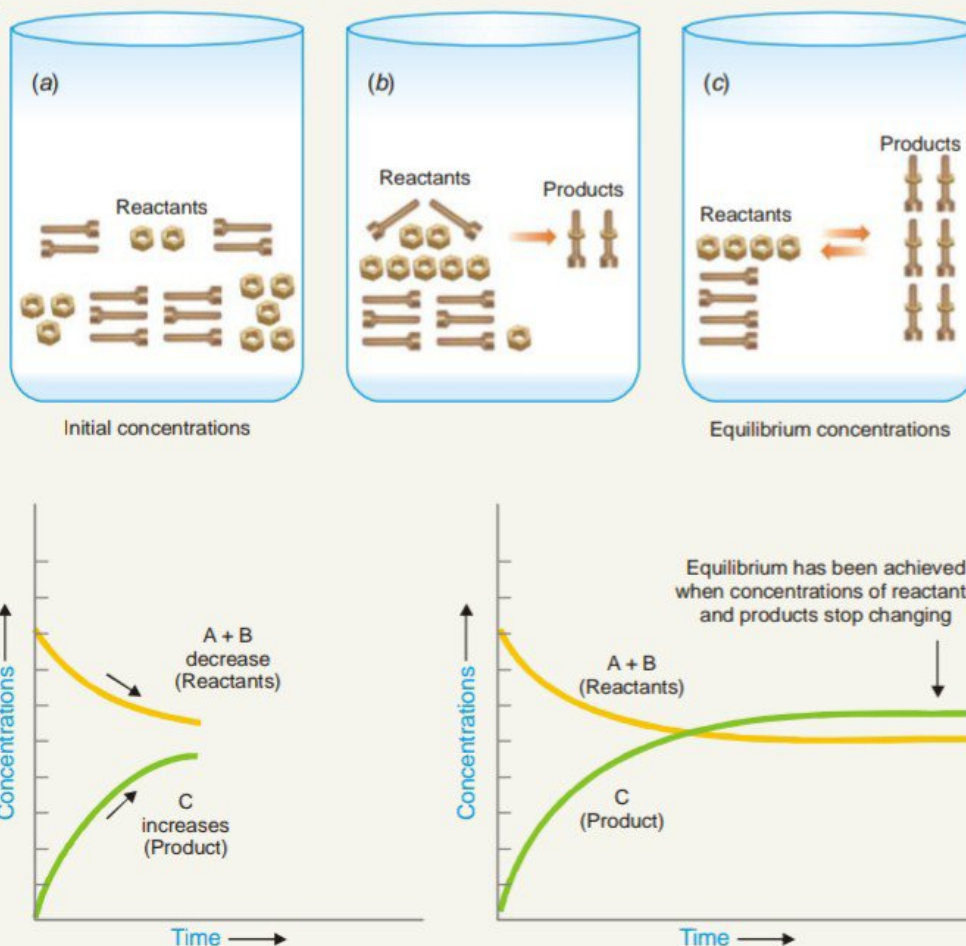
A "nuts and bolts" representation of chemical equilibrium for a reversible reaction. Initially (a) there are 100 nuts and 100 bolts in the beakers represented in the figure by 10 of each. The concentration is 100 bolts per beaker for both nuts and bolts. As time passes (b) concentrations of reactants 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).

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

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

$$PCl_5(s) \rightleftharpoons PCl_3(s) + Cl_2(g)$$

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$
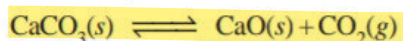
NATURE OF CHEMICAL EQUILIBRIUM : ITS DEFINITION

Let us consider the reaction

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

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.
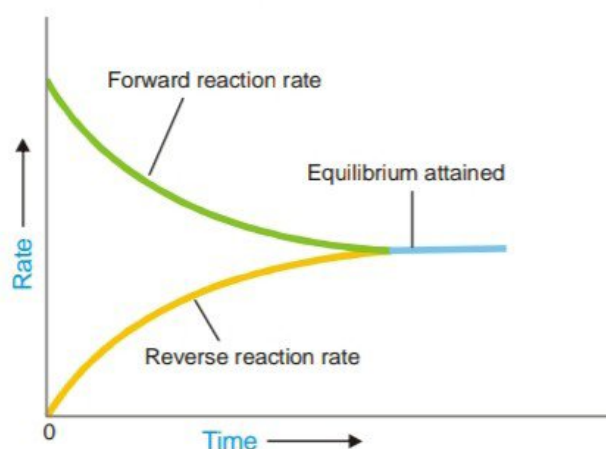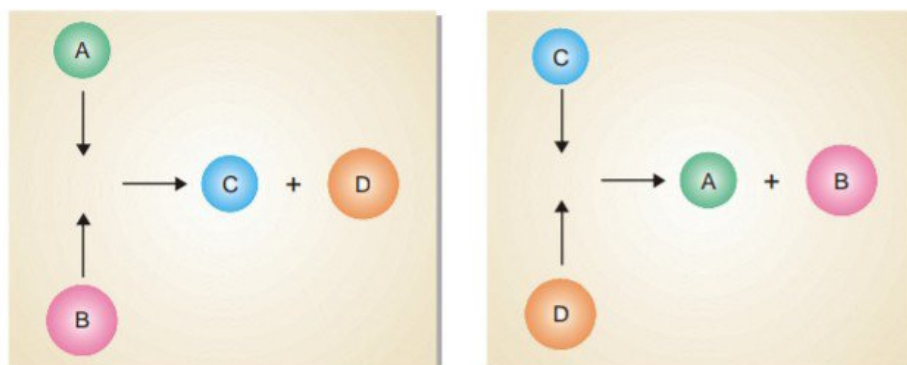

■ Figure 17.1
At equilibrium the forward reaction rate equals the reverse reaction rate.

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.

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

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

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.
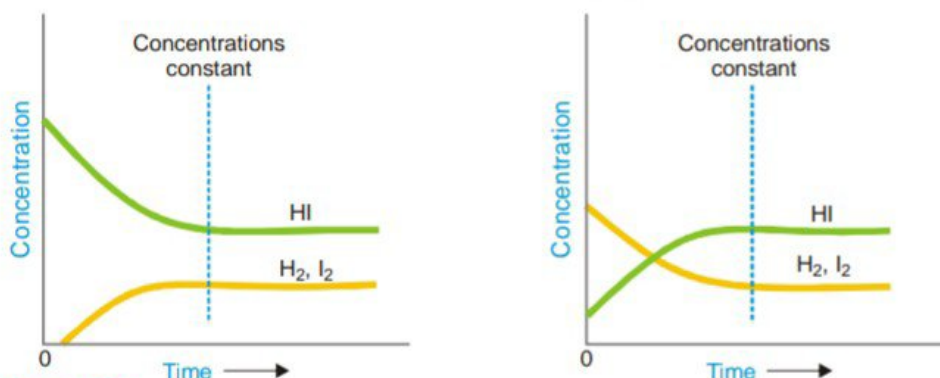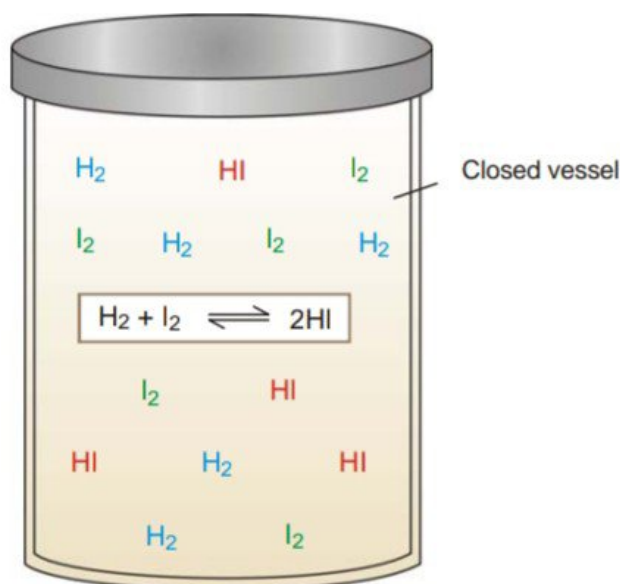

■ **Figure 17.3**
The left graph shows how equilibrium is attained for start with H_2 and I_2.
The right graph depicts the attainment of equilibrium for start with 2HI.
Equilibrium concentrations in both cases are the same.

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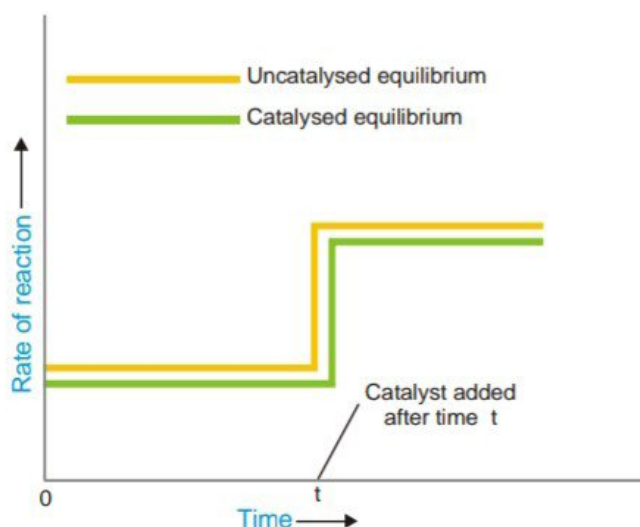
Figure 17.5
The vertical part of the curve indicates rapid increase of rate of reaction on addition of catalyst.

(6) At Equilibrium ΔG = 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.
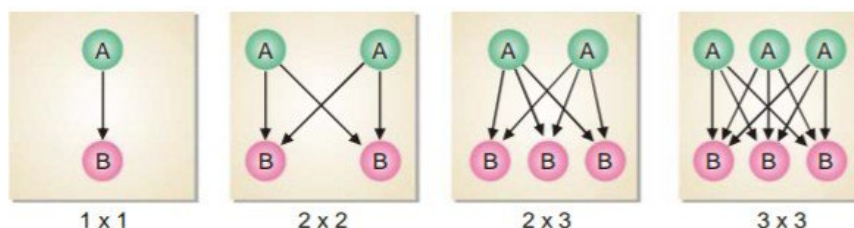
■ Figure 17.6

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

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

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.
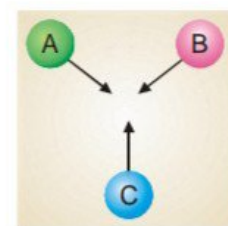
■ Figure 17.7

EQUILIBRIUM CONSTANT : EQUILIBRIUM LAW

Let us consider a general reaction

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

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,

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

or $\qquad \dfrac{k_1}{k_2} = \dfrac{[C][D]}{[A][B]} \qquad \qquad \text{...(1)}$

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

Equilibrium constant $\qquad k_c = \dfrac{[C][D]}{[A][B]}$ ── Product concentrations ── Reactant concentrations

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

Consider the reaction

Coefficient of A $\qquad 2A \rightleftharpoons C + D$

■ **Figure 17.8**

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.*,

$$A + A \rightleftharpoons C + D$$

Then the equilibrium constant expression is

$$k_c = \dfrac{[C][D]}{[A][A]} = \dfrac{[C][D]}{[A]^2} \quad \text{── Power equal to coefficent of A}$$

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

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

where a, b, c and d are numerical quotients of the substance, A, B, C and D respectively. The equilibrium constant expression is
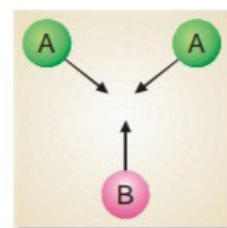
$$K_c = \dfrac{[C]^c[D]^d}{[A]^a[B]^b}$$

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,

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

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

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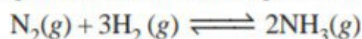
SOLUTION

(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 $[NH_3]^2$

(3) The product of concnentrations of the reactants is $[N_2][H_2]^3$

(4) Therefore, the equilibrium constant expression is

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

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

$$N_2O_5(g) \rightleftharpoons NO_2(g) + O_2(g)$$

SOLUTION

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

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

(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

$$[NO_2]^4[O_2]$$

(4) The concentration of the reactant is

$$[N_2O_5]^2$$

(5) The equilibrium constant expression can be written as

$$K_c = \frac{[NO_2]^4[O_2]}{[N_2O_5]^2}$$