

SUMMARY

Thermodynamics deals with energy changes in chemical or physical processes and enables us to study these changes quantitatively and to make useful predictions. For these purposes, we divide the universe into the system and the surroundings. Chemical or physical processes lead to evolution or absorption of heat (q), part of which may be converted into work (w). These quantities are related through the **first law of thermodynamics** via $\Delta U = q + w$. ΔU , change in internal energy, depends on initial and final states only and is a state function, whereas q and w depend on the path and are not the state functions. We follow sign conventions of q and w by giving the positive sign to these quantities when these are added to the system. We can measure the transfer of heat from one system to another which causes the change in temperature. The magnitude of rise in temperature depends on the heat capacity (C) of a substance. Therefore, heat absorbed or evolved is $q = C\Delta T$. Work can be measured by $w = -p_{\text{ex}}\Delta V$, in case of expansion of gases. Under reversible process, we can put $p_{\text{ex}} = p$ for infinitesimal changes in the volume making $w_{\text{rev}} = -p dV$. In this condition, we can use gas equation, $pV = nRT$.

At constant volume, $w = 0$, then $\Delta U = q_v$, heat transfer at constant volume. But in study of chemical reactions, we usually have constant pressure. We define another state function **enthalpy**. Enthalpy change, $\Delta H = \Delta U + \Delta n_g RT$, can be found directly from the heat changes at constant pressure, $\Delta H = q_p$.

There are varieties of enthalpy changes. Changes of phase such as melting, vaporization and sublimation usually occur at constant temperature and can be characterized by enthalpy changes which are always positive. Enthalpy of formation, combustion and other enthalpy changes can be calculated using **Hess's law**. Enthalpy change for chemical reactions can be determined by

$$\Delta_r H = \sum_f (a_i \Delta_f H_{\text{products}}) - \sum_i (b_i \Delta_f H_{\text{reactions}})$$

and in gaseous state by

$$\Delta_r H^\ominus = \sum \text{bond enthalpies of the reactants} - \sum \text{bond enthalpies of the products}$$

First law of thermodynamics does not guide us about the direction of chemical reactions i.e., what is the driving force of a chemical reaction. For isolated systems, $\Delta U = 0$. We define another state function, S , **entropy** for this purpose. **Entropy** is a measure of disorder or randomness. For a spontaneous change, total entropy change is positive. Therefore, for an isolated system, $\Delta U = 0$, $\Delta S > 0$, so entropy change distinguishes a spontaneous change, while energy change does not. Entropy changes can be measured by the equation

$$\Delta S = \frac{q_{\text{rev}}}{T} \text{ for a reversible process. } \frac{q_{\text{rev}}}{T} \text{ is independent of path.}$$

Chemical reactions are generally carried at constant pressure, so we define another state function **Gibbs energy**, G , which is related to entropy and enthalpy changes of the system by the equation:

$$\Delta_r G = \Delta_r H - T \Delta_r S$$

For a spontaneous change, $\Delta G_{\text{sys}} < 0$ and at equilibrium, $\Delta G_{\text{sys}} = 0$.

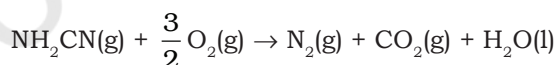
Standard Gibbs energy change is related to equilibrium constant by

$$\Delta_r G^\ominus = -RT \ln K.$$

K can be calculated from this equation, if we know $\Delta_r G^\ominus$ which can be found from $\Delta_r G^\ominus = \Delta_r H^\ominus - T \Delta_r S^\ominus$. Temperature is an important factor in the equation. Many reactions which are non-spontaneous at low temperature, are made spontaneous at high temperature for systems having positive entropy of reaction.

EXERCISES

- 5.1 Choose the correct answer. A thermodynamic state function is a quantity
(i) used to determine heat changes
(ii) whose value is independent of path
(iii) used to determine pressure volume work
(iv) whose value depends on temperature only.
- 5.2 For the process to occur under adiabatic conditions, the correct condition is:
(i) $\Delta T = 0$
(ii) $\Delta p = 0$
(iii) $q = 0$
(iv) $w = 0$
- 5.3 The enthalpies of all elements in their standard states are:
(i) unity
(ii) zero
(iii) < 0
(iv) different for each element
- 5.4 ΔU^\ominus of combustion of methane is $-X \text{ kJ mol}^{-1}$. The value of ΔH^\ominus is
(i) $= \Delta U^\ominus$
(ii) $> \Delta U^\ominus$
(iii) $< \Delta U^\ominus$
(iv) $= 0$
- 5.5 The enthalpy of combustion of methane, graphite and dihydrogen at 298 K are, $-890.3 \text{ kJ mol}^{-1}$, $-393.5 \text{ kJ mol}^{-1}$, and $-285.8 \text{ kJ mol}^{-1}$ respectively. Enthalpy of formation of $\text{CH}_4(\text{g})$ will be
(i) $-74.8 \text{ kJ mol}^{-1}$ (ii) $-52.27 \text{ kJ mol}^{-1}$
(iii) $+74.8 \text{ kJ mol}^{-1}$ (iv) $+52.26 \text{ kJ mol}^{-1}$.
- 5.6 A reaction, $\text{A} + \text{B} \rightarrow \text{C} + \text{D} + q$ is found to have a positive entropy change. The reaction will be
(i) possible at high temperature
(ii) possible only at low temperature
(iii) not possible at any temperature
(v) possible at any temperature
- 5.7 In a process, 701 J of heat is absorbed by a system and 394 J of work is done by the system. What is the change in internal energy for the process?
- 5.8 The reaction of cyanamide, $\text{NH}_2\text{CN}(\text{s})$, with dioxygen was carried out in a bomb calorimeter, and ΔU was found to be $-742.7 \text{ kJ mol}^{-1}$ at 298 K. Calculate enthalpy change for the reaction at 298 K.



- 5.9 Calculate the number of kJ of heat necessary to raise the temperature of 60.0 g of aluminium from 35°C to 55°C. Molar heat capacity of Al is $24 \text{ J mol}^{-1} \text{ K}^{-1}$.
- 5.10 Calculate the enthalpy change on freezing of 1.0 mol of water at 10.0°C to ice at -10.0°C. $\Delta_{\text{fus}}H = 6.03 \text{ kJ mol}^{-1}$ at 0°C.
 $C_p [\text{H}_2\text{O(l)}] = 75.3 \text{ J mol}^{-1} \text{ K}^{-1}$
 $C_p [\text{H}_2\text{O(s)}] = 36.8 \text{ J mol}^{-1} \text{ K}^{-1}$
- 5.11 Enthalpy of combustion of carbon to CO_2 is $-393.5 \text{ kJ mol}^{-1}$. Calculate the heat released upon formation of 35.2 g of CO_2 from carbon and dioxygen gas.
- 5.12 Enthalpies of formation of CO(g) , $\text{CO}_2\text{(g)}$, $\text{N}_2\text{O(g)}$ and $\text{N}_2\text{O}_4\text{(g)}$ are -110, -393, 81 and 9.7 kJ mol^{-1} respectively. Find the value of Δ_rH for the reaction:
 $\text{N}_2\text{O}_4\text{(g)} + 3\text{CO(g)} \rightarrow \text{N}_2\text{O(g)} + 3\text{CO}_2\text{(g)}$
- 5.13 Given
 $\text{N}_2\text{(g)} + 3\text{H}_2\text{(g)} \rightarrow 2\text{NH}_3\text{(g)}; \Delta_rH^\ominus = -92.4 \text{ kJ mol}^{-1}$
 What is the standard enthalpy of formation of NH_3 gas?
- 5.14 Calculate the standard enthalpy of formation of $\text{CH}_3\text{OH(l)}$ from the following data:
 $\text{CH}_3\text{OH(l)} + \frac{3}{2} \text{O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)} + 2\text{H}_2\text{O(l)}; \Delta_rH^\ominus = -726 \text{ kJ mol}^{-1}$
 $\text{C(graphite)} + \text{O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)}; \Delta_cH^\ominus = -393 \text{ kJ mol}^{-1}$
 $\text{H}_2\text{(g)} + \frac{1}{2} \text{O}_2\text{(g)} \rightarrow \text{H}_2\text{O(l)}; \Delta_fH^\ominus = -286 \text{ kJ mol}^{-1}$.
- 5.15 Calculate the enthalpy change for the process
 $\text{CCl}_4\text{(g)} \rightarrow \text{C(g)} + 4 \text{Cl(g)}$
 and calculate bond enthalpy of C - Cl in $\text{CCl}_4\text{(g)}$.
 $\Delta_{\text{vap}}H^\ominus(\text{CCl}_4) = 30.5 \text{ kJ mol}^{-1}$.
 $\Delta_fH^\ominus(\text{CCl}_4) = -135.5 \text{ kJ mol}^{-1}$.
 $\Delta_aH^\ominus(\text{C}) = 715.0 \text{ kJ mol}^{-1}$, where Δ_aH^\ominus is enthalpy of atomisation
 $\Delta_aH^\ominus(\text{Cl}_2) = 242 \text{ kJ mol}^{-1}$
- 5.16 For an isolated system, $\Delta U = 0$, what will be ΔS ?
- 5.17 For the reaction at 298 K,
 $2\text{A} + \text{B} \rightarrow \text{C}$
 $\Delta H = 400 \text{ kJ mol}^{-1}$ and $\Delta S = 0.2 \text{ kJ K}^{-1} \text{ mol}^{-1}$
 At what temperature will the reaction become spontaneous considering ΔH and ΔS to be constant over the temperature range.
- 5.18 For the reaction,
 $2 \text{Cl(g)} \rightarrow \text{Cl}_2\text{(g)}$, what are the signs of ΔH and ΔS ?
- 5.19 For the reaction
 $2 \text{A(g)} + \text{B(g)} \rightarrow 2\text{D(g)}$
 $\Delta U^\ominus = -10.5 \text{ kJ}$ and $\Delta S^\ominus = -44.1 \text{ JK}^{-1}$.
 Calculate ΔG^\ominus for the reaction, and predict whether the reaction may occur spontaneously.

- 5.20 The equilibrium constant for a reaction is 10. What will be the value of ΔG^\ominus ?
 $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$, $T = 300 \text{ K}$.
- 5.21 Comment on the thermodynamic stability of NO(g) , given
$$\frac{1}{2} \text{N}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{NO(g)}; \quad \Delta_r H^\ominus = 90 \text{ kJ mol}^{-1}$$
$$\text{NO(g)} + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{NO}_2(\text{g}); \quad \Delta_r H^\ominus = -74 \text{ kJ mol}^{-1}$$
- 5.22 Calculate the entropy change in surroundings when 1.00 mol of $\text{H}_2\text{O(l)}$ is formed under standard conditions. $\Delta_f H^\ominus = -286 \text{ kJ mol}^{-1}$.



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UNIT 6

EQUILIBRIUM

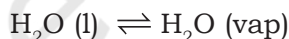
Objectives

After studying this unit you will be able to

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

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

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



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

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

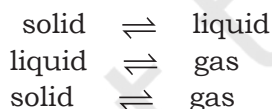
this dynamic equilibrium stage that there is no change in the concentrations of various species in the reaction mixture. Based on the extent to which the reactions proceed to reach the state of **chemical equilibrium**, these may be classified in three groups.

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

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

6.1 EQUILIBRIUM IN PHYSICAL PROCESSES

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



6.1.1 Solid-Liquid Equilibrium

Ice and water kept in a perfectly insulated thermos flask (no exchange of heat between its contents and the surroundings) at 273K and the atmospheric pressure are in equilibrium state and the system shows interesting

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

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

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

6.1.2 Liquid-Vapour Equilibrium

This equilibrium can be better understood if we consider the example of a transparent box carrying a U-tube with mercury (manometer). Drying agent like anhydrous calcium chloride (or phosphorus penta-oxide) is placed for a few hours in the box. After removing the drying agent by tilting the box on one side, a watch glass (or petri dish) containing water is quickly placed inside the box. It will be observed that the mercury level in the right limb of the manometer slowly increases and finally attains a constant value, that is, the pressure inside the box increases and reaches a constant value. Also the volume of water in the watch glass decreases (Fig. 6.1). Initially there was no water vapour (or very less) inside the box. As water evaporated the pressure in the box increased due to addition of water molecules into the gaseous phase inside the box. The rate of evaporation is constant.

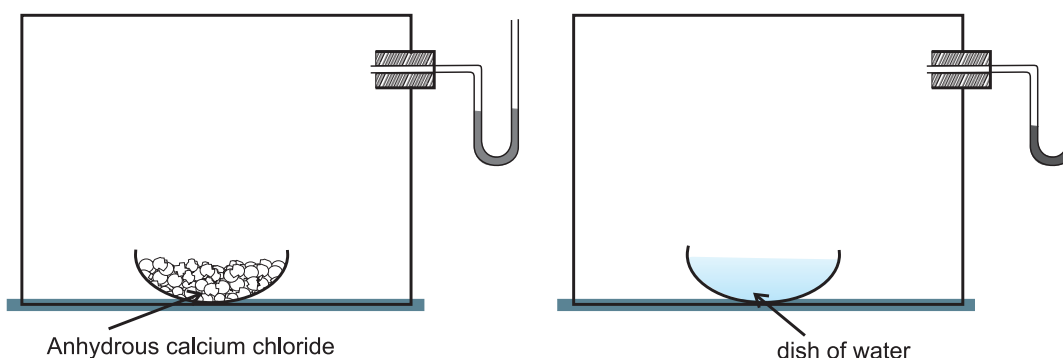
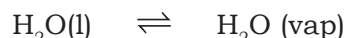


Fig. 6.1 Measuring equilibrium vapour pressure of water at a constant temperature

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

rate of evaporation = rate of condensation



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

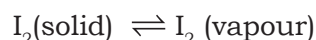
If we expose three watch glasses containing separately 1 mL each of acetone, ethyl alcohol, and water to atmosphere and repeat the experiment with different volumes of the liquids in a warmer room, it is observed that in all such cases the liquid eventually disappears and the time taken for complete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

vapour to liquid state is much less than the rate of evaporation. These are open systems and it is not possible to reach equilibrium in an open system.

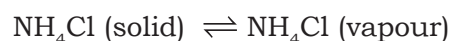
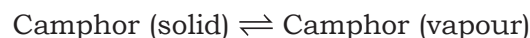
Water and water vapour are in equilibrium position at atmospheric pressure (1.013 bar) and at 100°C in a closed vessel. The boiling point of water is 100°C at 1.013 bar pressure. For any pure liquid at one atmospheric pressure (1.013 bar), the temperature at which the liquid and vapours are at equilibrium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

6.1.3 Solid – Vapour Equilibrium

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



Other examples showing this kind of equilibrium are,



6.1.4 Equilibrium Involving Dissolution of Solid or Gases in Liquids

Solids in liquids

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

Sugar (solution) \rightleftharpoons Sugar (solid), and
the rate of dissolution of sugar = rate of crystallisation of sugar.

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

Gases in liquids

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



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

pressure of the gas above the solvent.

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

- (i) For solid \rightleftharpoons liquid equilibrium, there is only one temperature (melting point) at 1 atm (1.013 bar) at which the two phases can coexist. If there is no exchange of heat with the surroundings, the mass of the two phases remains constant.
- (ii) For liquid \rightleftharpoons vapour equilibrium, the vapour pressure is constant at a given temperature.
- (iii) For dissolution of solids in liquids, the solubility is constant at a given temperature.
- (iv) For dissolution of gases in liquids, the concentration of a gas in liquid is proportional to the pressure (concentration) of the gas over the liquid. These observations are summarised in Table 6.1

Table 6.1 Some Features of Physical Equilibria

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

6.1.5 General Characteristics of Equilibria Involving Physical Processes

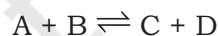
For the physical processes discussed above, following characteristics are common to the system at equilibrium:

- Equilibrium is possible only in a closed system at a given temperature.
- Both the opposing processes occur at the same rate and there is a dynamic but stable condition.
- All measurable properties of the system remain constant.
- When equilibrium is attained for a physical process, it is characterised by constant value of one of its parameters at a given temperature. Table 6.1 lists such quantities.
- The magnitude of such quantities at any stage indicates the extent to which the physical process has proceeded before reaching equilibrium.

6.2 EQUILIBRIUM IN CHEMICAL PROCESSES – DYNAMIC EQUILIBRIUM

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

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



With passage of time, there is accumulation of the products C and D and depletion of the reactants A and B (Fig. 6.2). This leads to a decrease in the rate of forward reaction and an increase in the rate of the reverse reaction,

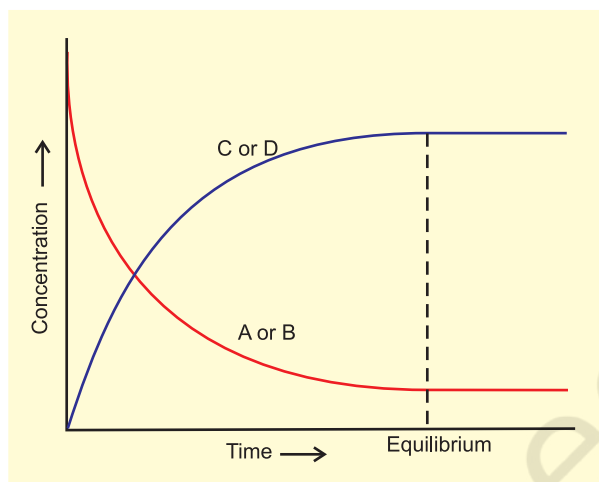


Fig. 6.2 Attainment of chemical equilibrium.

Eventually, the two reactions occur at the same rate and the system reaches a state of equilibrium.

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

The dynamic nature of chemical equilibrium can be demonstrated in the synthesis of ammonia by Haber's process. In a series of experiments, Haber started with known amounts of dinitrogen and dihydrogen maintained at high temperature and pressure and at regular intervals determined the amount of ammonia present. He was successful in determining also the concentration of unreacted dihydrogen and dinitrogen. Fig. 6.4 (page 174) shows that after a certain time the composition of the mixture remains the same even though some of the reactants are still present. This constancy in composition indicates that the reaction has reached equilibrium. In order to understand the dynamic nature of the reaction, synthesis of ammonia is carried out with exactly the same starting conditions (of partial pressure and temperature) but using D_2 (deuterium) in place of H_2 . The reaction mixtures starting either with H_2 or D_2 reach equilibrium with the same composition, except that D_2 and ND_3 are present instead of H_2 and NH_3 . After

Dynamic Equilibrium – A Student's Activity

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

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

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

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

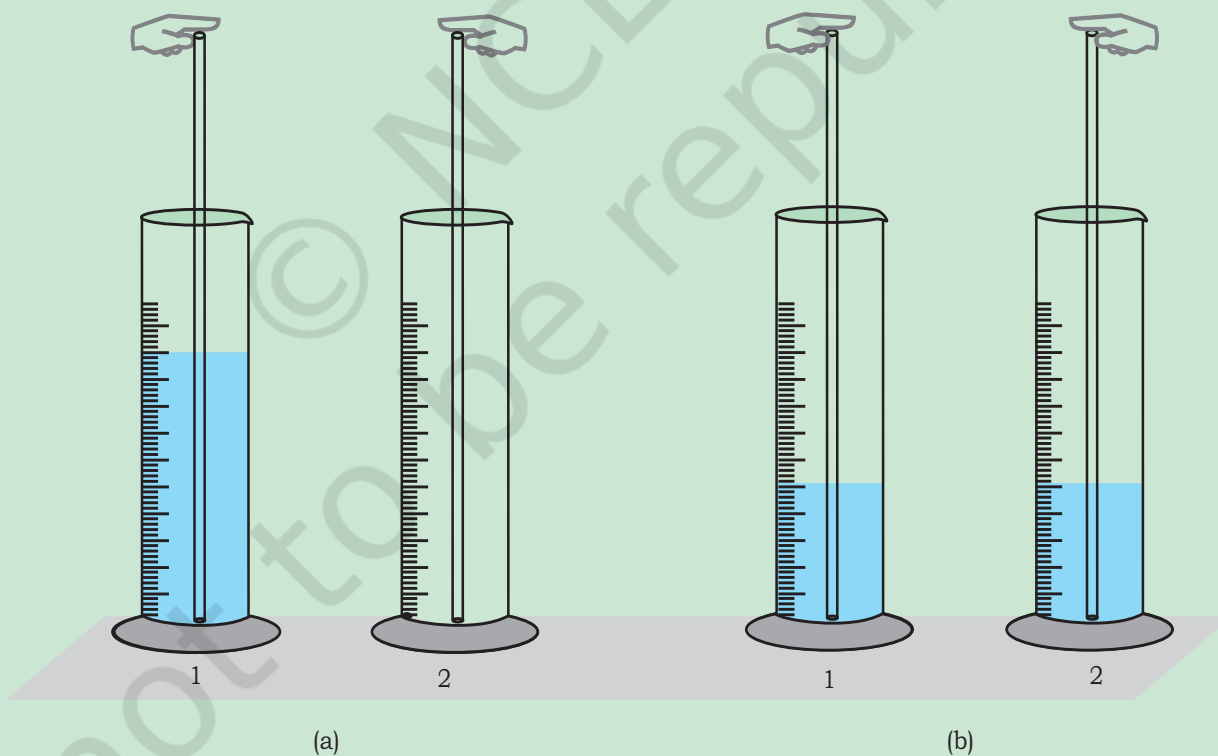


Fig.6.3 Demonstrating dynamic nature of equilibrium. (a) initial stage (b) final stage after the equilibrium is attained.

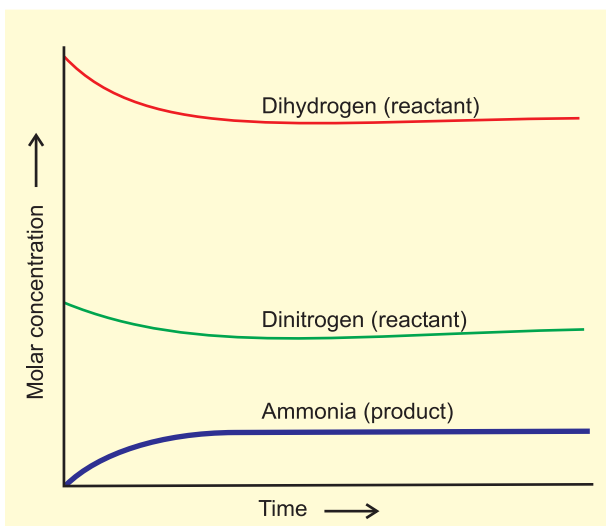
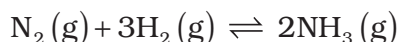


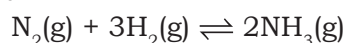
Fig. 6.4 Depiction of equilibrium for the reaction



equilibrium is attained, these two mixtures (H_2 , N_2 , NH_3 and D_2 , N_2 , ND_3) are mixed together and left for a while. Later, when this mixture is analysed, it is found that the concentration of ammonia is just the same as before. However, when this mixture is analysed by a mass spectrometer, it is found that ammonia and all deuterium containing forms of ammonia (NH_3 , NH_2D , NHD_2 and ND_3) and dihydrogen and its deuterated forms (H_2 , HD and D_2) are present. Thus one can conclude that scrambling of H and D atoms in the molecules must result from a continuation of the forward and reverse reactions in the mixture. If the reaction had simply stopped when they reached equilibrium, then there would have been no mixing of isotopes in this way.

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

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



Similarly let us consider the reaction, $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$. If we start with equal initial concentration of H_2 and I_2 , the reaction proceeds in the forward direction and the concentration of H_2 and I_2 decreases while that of HI increases, until all of these become constant at equilibrium (Fig. 6.5). We can also start with HI alone and make the reaction to proceed in the reverse direction; the concentration of HI will decrease and concentration of H_2 and I_2 will increase until they all become constant when equilibrium is reached (Fig. 6.5). If total number of H and I atoms are same in a given volume, the same equilibrium mixture is obtained whether we start it from pure reactants or pure product.

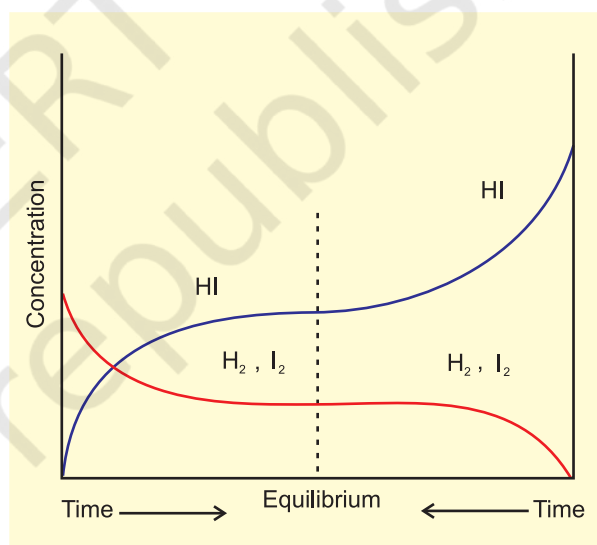


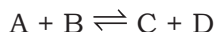
Fig. 6.5 Chemical equilibrium in the reaction $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$ can be attained from either direction

6.3 LAW OF CHEMICAL EQUILIBRIUM AND EQUILIBRIUM CONSTANT

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

composition of an equilibrium mixture? The last question in particular is important when choosing conditions for synthesis of industrial chemicals such as H_2 , NH_3 , CaO etc.

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

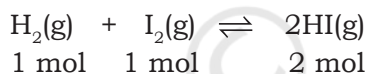


where A and B are the reactants, C and D are the products in the balanced chemical equation. On the basis of experimental studies of many reversible reactions, the Norwegian chemists Cato Maximillian Guldberg and Peter Waage proposed in 1864 that the concentrations in an equilibrium mixture are related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

$$K_c = \frac{[\text{C}][\text{D}]}{[\text{A}][\text{B}]} \quad (6.1)$$

(6.1) where K_c is the *equilibrium constant* and the expression on the right side is called the *equilibrium constant expression*.

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



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

Data obtained from all six sets of experiments are given in Table 6.2.

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

$$[\text{H}_2(\text{g})]_{\text{eq}} = [\text{I}_2(\text{g})]_{\text{eq}}$$

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

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

It can be seen from Table 6.3 that if we put the equilibrium concentrations of the reactants and products, the above expression

Table 6.2 Initial and Equilibrium Concentrations of H_2 , I_2 and HI

Experiment number	Initial concentration/mol L ⁻¹			Equilibrium concentration/mol L ⁻¹		
	[H_2 (g)]	[I_2 (g)]	[HI (g)]	[H_2 (g)]	[I_2 (g)]	[HI (g)]
1	2.4×10^{-2}	1.38×10^{-2}	0	1.14×10^{-2}	0.12×10^{-2}	2.52×10^{-2}
2	2.4×10^{-2}	1.68×10^{-2}	0	0.92×10^{-2}	0.20×10^{-2}	2.96×10^{-2}
3	2.44×10^{-2}	1.98×10^{-2}	0	0.77×10^{-2}	0.31×10^{-2}	3.34×10^{-2}
4	2.46×10^{-2}	1.76×10^{-2}	0	0.92×10^{-2}	0.22×10^{-2}	3.08×10^{-2}
5	0	0	3.04×10^{-2}	0.345×10^{-2}	0.345×10^{-2}	2.35×10^{-2}
6	0	0	7.58×10^{-2}	0.86×10^{-2}	0.86×10^{-2}	5.86×10^{-2}

Table 6.3 Expression Involving the Equilibrium Concentration of Reactants



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

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

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

we find that this expression gives constant value (as shown in Table 6.3) in all the six cases. It can be seen that in this expression the power of the concentration for reactants and products are actually the stoichiometric coefficients in the equation for the chemical reaction. Thus, for the reaction $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$, following equation 6.1, the equilibrium constant K_c is written as,

$$K_c = [\text{HI}(\text{g})]_{\text{eq}}^2 / [\text{H}_2(\text{g})]_{\text{eq}} [\text{I}_2(\text{g})]_{\text{eq}} \quad (6.2)$$

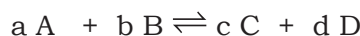
Generally the subscript 'eq' (used for equilibrium) is omitted from the concentration terms. It is taken for granted that the concentrations in the expression for K_c are equilibrium values. We, therefore, write,

$$K_c = [\text{HI}(\text{g})]^2 / [\text{H}_2(\text{g})] [\text{I}_2(\text{g})] \quad (6.3)$$

The subscript 'c' indicates that K_c is expressed in concentrations of mol L⁻¹.

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

The equilibrium constant for a general reaction,



is expressed as,

$$K_c = [\text{C}]^c [\text{D}]^d / [\text{A}]^a [\text{B}]^b \quad (6.4)$$

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

Equilibrium constant for the reaction, $4\text{NH}_3(\text{g}) + 5\text{O}_2(\text{g}) \rightleftharpoons 4\text{NO}(\text{g}) + 6\text{H}_2\text{O}(\text{g})$ is written as

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

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

Let us write equilibrium constant for the reaction, $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$ (6.5)

$$\text{as, } K_c = [\text{HI}]^2 / [\text{H}_2] [\text{I}_2] = x \quad (6.6)$$

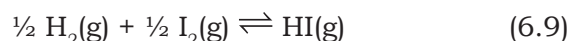
The equilibrium constant for the reverse reaction, $2\text{HI}(\text{g}) \rightleftharpoons \text{H}_2(\text{g}) + \text{I}_2(\text{g})$, at the same temperature is,

$$K_c = [\text{H}_2] [\text{I}_2] / [\text{HI}]^2 = 1 / x = 1 / K_c \quad (6.7)$$

$$\text{Thus, } K_c = 1 / K_c \quad (6.8)$$

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

If we change the stoichiometric coefficients in a chemical equation by multiplying throughout by a factor then we must make sure that the expression for equilibrium constant also reflects that change. For example, if the reaction (6.5) is written as,



the equilibrium constant for the above reaction is given by

$$\begin{aligned} K_c'' &= [\text{HI}] / [\text{H}_2]^{1/2} [\text{I}_2]^{1/2} = \{[\text{HI}]^2 / [\text{H}_2] [\text{I}_2]\}^{1/2} \\ &= x^{1/2} = K_c^{1/2} \quad (6.10) \end{aligned}$$

On multiplying the equation (6.5) by n, we get



Therefore, equilibrium constant for the reaction is equal to K_c^n . These findings are summarised in Table 6.4. It should be noted that because the equilibrium constants K_c and K_c' have different numerical values, it is important to specify the form of the balanced chemical equation when quoting the value of an equilibrium constant.

Table 6.4 Relations between Equilibrium Constants for a General Reaction and its Multiples.

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

Problem 6.1

The following concentrations were obtained for the formation of NH_3 from N_2 and H_2 at equilibrium at 500K. $[\text{N}_2] = 1.5 \times 10^{-2}\text{M}$, $[\text{H}_2] = 3.0 \times 10^{-2}\text{M}$ and $[\text{NH}_3] = 1.2 \times 10^{-2}\text{M}$. Calculate equilibrium constant.

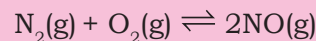
Solution

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

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

Problem 6.2

At equilibrium, the concentrations of $\text{N}_2 = 3.0 \times 10^{-3}\text{M}$, $\text{O}_2 = 4.2 \times 10^{-3}\text{M}$ and $\text{NO} = 2.8 \times 10^{-3}\text{M}$ in a sealed vessel at 800K. What will be K_c for the reaction



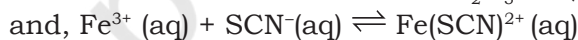
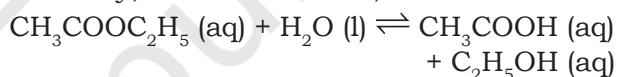
Solution

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

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

6.4 HOMOGENEOUS EQUILIBRIA

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



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

6.4.1 Equilibrium Constant in Gaseous Systems

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

The ideal gas equation is written as,
 $pV = nRT$

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

Here, p is the pressure in Pa, n is the number of moles of the gas, V is the volume in m^3 and T is the temperature in Kelvin

Therefore,

n/V is concentration expressed in mol/m^3

If concentration c , is in mol/L or mol/dm^3 , and p is in bar then

$$p = cRT,$$

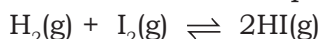
We can also write $p = [\text{gas}]RT$.

Here, $R = 0.0831 \text{ bar litre/mol K}$

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

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

For reaction in equilibrium



We can write either

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

$$\text{or } K_c = \frac{(p_{\text{HI}})^2}{(p_{\text{H}_2})(p_{\text{I}_2})} \quad (6.12)$$

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

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

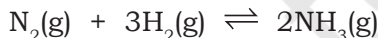
$$p_{\text{H}_2} = [\text{H}_2(\text{g})]RT$$

Therefore,

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

$$= \frac{[\text{HI}(\text{g})]^2}{[\text{H}_2(\text{g})][\text{I}_2(\text{g})]} = K_c \quad (6.13)$$

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



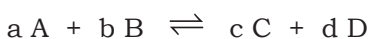
$$K_p = \frac{(p_{\text{NH}_3})^2}{(p_{\text{N}_2})(p_{\text{H}_2})^3}$$

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

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

$$\text{or } K_p = K_c (RT)^{-2} \quad (6.14)$$

Similarly, for a general reaction



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

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

$$= \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b} (RT)^{\Delta n} = K_c (RT)^{\Delta n} \quad (6.15)$$

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

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

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

K_p values for a few selected reactions at different temperatures are given in Table 6.5

Table 6.5 Equilibrium Constants, K_p for a Few Selected Reactions

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

Problem 6.3

PCl_5 , PCl_3 and Cl_2 are at equilibrium at 500 K and having concentration 1.59M PCl_3 , 1.59M Cl_2 and 1.41 M PCl_5 .

Calculate K_c for the reaction,
 $\text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{Cl}_2$

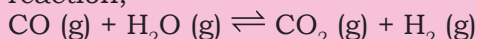
Solution

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

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

Problem 6.4

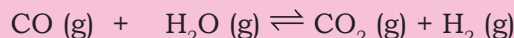
The value of $K_c = 4.24$ at 800K for the reaction,



Calculate equilibrium concentrations of CO_2 , H_2 , CO and H_2O at 800 K, if only CO and H_2O are present initially at concentrations of 0.10M each.

Solution

For the reaction,



Initial concentration:

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

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

At equilibrium:

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

where x is the amount of CO_2 and H_2 at equilibrium.

Hence, equilibrium constant can be written as,

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

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

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

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

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

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

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

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

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

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

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

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

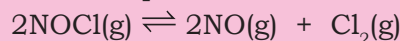
Hence the equilibrium concentrations are,

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

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

Problem 6.5

For the equilibrium,



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

Solution

We know that,

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

For the above reaction,

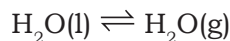
$$\Delta n = (2+1) - 2 = 1$$

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

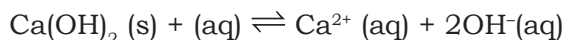
$$K_p = 0.033$$

6.5 HETEROGENEOUS EQUILIBRIA

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



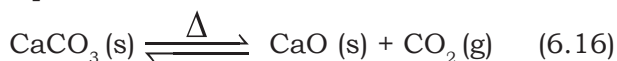
In this example, there is a gas phase and a liquid phase. In the same way, equilibrium between a solid and its saturated solution,



is a heterogeneous equilibrium.

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

vary as the amount of X in a given volume varies. Let us take thermal dissociation of calcium carbonate which is an interesting and important example of heterogeneous chemical equilibrium.



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

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

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

$$K'_c = [\text{CO}_2(\text{g})] \quad (6.17)$$

$$\text{or } K_p = p_{\text{CO}_2} \quad (6.18)$$

Units of Equilibrium Constant

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

For the reactions,

$\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}$, K_c and K_p have no unit.

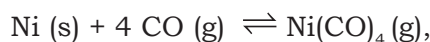
$\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$, K_c has unit mol/L and K_p has unit bar

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

This shows that at a particular temperature, there is a constant concentration or pressure of CO_2 in equilibrium with $\text{CaO}(\text{s})$ and $\text{CaCO}_3(\text{s})$. Experimentally it has been found that at 1100 K, the pressure of CO_2 in equilibrium with $\text{CaCO}_3(\text{s})$ and $\text{CaO}(\text{s})$, is 2.0×10^5 Pa. Therefore, equilibrium constant at 1100K for the above reaction is:

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

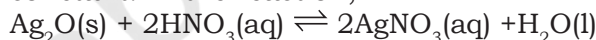
Similarly, in the equilibrium between nickel, carbon monoxide and nickel carbonyl (used in the purification of nickel),



the equilibrium constant is written as

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

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



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

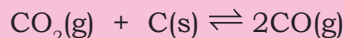
Problem 6.6

The value of K_p for the reaction, $\text{CO}_2(\text{g}) + \text{C}(\text{s}) \rightleftharpoons 2\text{CO}(\text{g})$ is 3.0 at 1000 K. If initially $P_{\text{CO}_2} = 0.48$ bar and $P_{\text{CO}} = 0$ bar and pure graphite is present, calculate the equilibrium partial pressures of CO and CO_2 .

Solution

For the reaction,

let 'x' be the decrease in pressure of CO_2 , then



Initial

pressure: 0.48 bar

0

At equilibrium:

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

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

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

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

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

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

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

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

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

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

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

$$x = 2.66 / 8 = 0.33$$

The equilibrium partial pressures are,

$$p_{\text{CO}_2} = 2x = 2 \times 0.33 = 0.66 \text{ bar}$$

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

6.6 APPLICATIONS OF EQUILIBRIUM CONSTANTS

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

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

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

Let us consider applications of equilibrium constant to:

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

6.6.1 Predicting the Extent of a Reaction

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

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

- If $K_c > 10^3$, products predominate over reactants, i.e., if K_c is very large, the reaction proceeds nearly to completion. Consider the following examples:
 - (a) The reaction of H_2 with O_2 at 500 K has a very large equilibrium constant, $K_c = 2.4 \times 10^{47}$.
 - (b) $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons 2\text{HCl}(\text{g})$ at 300K has $K_c = 4.0 \times 10^{31}$.
 - (c) $\text{H}_2(\text{g}) + \text{Br}_2(\text{g}) \rightleftharpoons 2\text{HBr}(\text{g})$ at 300 K, $K_c = 5.4 \times 10^{18}$
- If $K_c < 10^{-3}$, reactants predominate over products, i.e., if K_c is very small, the reaction proceeds rarely. Consider the following examples:

- (a) The decomposition of H_2O into H_2 and O_2 at 500 K has a very small equilibrium constant, $K_c = 4.1 \times 10^{-48}$
- (b) $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$, at 298 K has $K_c = 4.8 \times 10^{-31}$.
- If K_c is in the range of 10^{-3} to 10^3 , appreciable concentrations of both reactants and products are present. Consider the following examples:
- (a) For reaction of H_2 with I_2 to give HI , $K_c = 57.0$ at 700K.
- (b) Also, gas phase decomposition of N_2O_4 to NO_2 is another reaction with a value of $K_c = 4.64 \times 10^{-3}$ at 25°C which is neither too small nor too large. Hence, equilibrium mixtures contain appreciable concentrations of both N_2O_4 and NO_2 . These generalisations are illustrated in Fig. 6.6

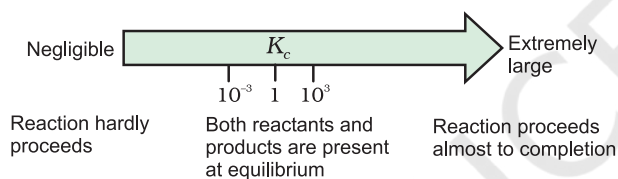


Fig. 6.6 Dependence of extent of reaction on K_c

6.6.2 Predicting the Direction of the Reaction

The equilibrium constant helps in predicting the direction in which a given reaction will proceed at any stage. For this purpose, we calculate the **reaction quotient Q** . The reaction quotient, Q (Q_c with molar concentrations and Q_p with partial pressures) is defined in the same way as the equilibrium constant K_c except that the concentrations in Q_c are not necessarily equilibrium values. For a general reaction:



$$Q_c = [\text{C}]^c[\text{D}]^d / [\text{A}]^a[\text{B}]^b \quad (6.20)$$

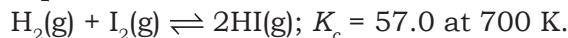
Then,

If $Q_c > K_c$, the reaction will proceed in the direction of reactants (reverse reaction).

If $Q_c < K_c$, the reaction will proceed in the direction of the products (forward reaction).

If $Q_c = K_c$, the reaction mixture is already at equilibrium.

Consider the gaseous reaction of H_2 with I_2 ,



Suppose we have molar concentrations $[\text{H}_2]_t = 0.10\text{M}$, $[\text{I}_2]_t = 0.20\text{M}$ and $[\text{HI}]_t = 0.40\text{M}$. (the subscript t on the concentration symbols means that the concentrations were measured at some arbitrary time t, not necessarily at equilibrium).

Thus, the reaction quotient, Q_c at this stage of the reaction is given by,

$$Q_c = [\text{HI}]_t^2 / [\text{H}_2]_t [\text{I}_2]_t = (0.40)^2 / (0.10)(0.20) = 8.0$$

Now, in this case, Q_c (8.0) does not equal K_c (57.0), so the mixture of $\text{H}_2(\text{g})$, $\text{I}_2(\text{g})$ and $\text{HI}(\text{g})$ is not at equilibrium; that is, more $\text{H}_2(\text{g})$ and $\text{I}_2(\text{g})$ will react to form more $\text{HI}(\text{g})$ and their concentrations will decrease till $Q_c = K_c$.

The reaction quotient, Q_c is useful in predicting the direction of reaction by comparing the values of Q_c and K_c .

Thus, we can make the following generalisations concerning the direction of the reaction (Fig. 6.7) :

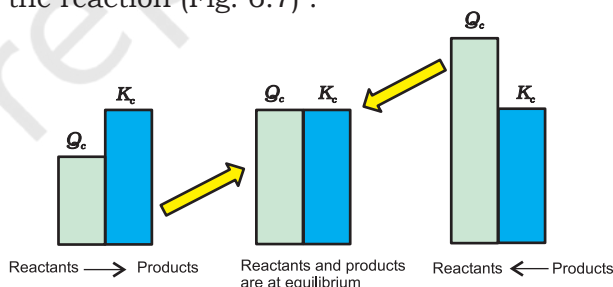


Fig. 6.7 Predicting the direction of the reaction

- If $Q_c < K_c$, net reaction goes from left to right
- If $Q_c > K_c$, net reaction goes from right to left.
- If $Q_c = K_c$, no net reaction occurs.

Problem 6.7

The value of K_c for the reaction $2\text{A} \rightleftharpoons \text{B} + \text{C}$ is 2×10^{-3} . At a given time, the composition of reaction mixture is $[\text{A}] = [\text{B}] = [\text{C}] = 3 \times 10^{-4}\text{M}$. In which direction the reaction will proceed?

Solution

For the reaction the reaction quotient Q_c is given by,

$$Q_c = [B][C] / [A]^2$$

as $[A] = [B] = [C] = 3 \times 10^{-4} \text{M}$

$$Q_c = (3 \times 10^{-4})(3 \times 10^{-4}) / (3 \times 10^{-4})^2 = 1$$

as $Q_c > K_c$ so the reaction will proceed in the reverse direction.

6.6.3 Calculating Equilibrium Concentrations

In case of a problem in which we know the initial concentrations but do not know any of the equilibrium concentrations, the following three steps shall be followed:

Step 1. Write the balanced equation for the reaction.

Step 2. Under the balanced equation, make a table that lists for each substance involved in the reaction:

- the initial concentration,
- the change in concentration on going to equilibrium, and
- the equilibrium concentration.

In constructing the table, define x as the concentration (mol/L) of one of the substances that reacts on going to equilibrium, then use the stoichiometry of the reaction to determine the concentrations of the other substances in terms of x .

Step 3. Substitute the equilibrium concentrations into the equilibrium equation for the reaction and solve for x . If you are to solve a quadratic equation choose the mathematical solution that makes chemical sense.

Step 4. Calculate the equilibrium concentrations from the calculated value of x .

Step 5. Check your results by substituting them into the equilibrium equation.

Problem 6.8

13.8g of N_2O_4 was placed in a 1L reaction vessel at 400K and allowed to attain equilibrium



The total pressure at equilibrium was found to be 9.15 bar. Calculate K_c , K_p and partial pressure at equilibrium.

Solution

We know $pV = nRT$

Total volume (V) = 1 L

Molecular mass of N_2O_4 = 92 g

Number of moles = $13.8\text{g} / 92 \text{ g} = 0.15$

of the gas (n)

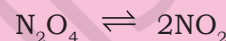
Gas constant (R) = $0.083 \text{ bar L mol}^{-1}\text{K}^{-1}$

Temperature (T) = 400 K

$$pV = nRT$$

$$p \times 1\text{L} = 0.15 \text{ mol} \times 0.083 \text{ bar L mol}^{-1}\text{K}^{-1} \times 400 \text{ K}$$

$$p = 4.98 \text{ bar}$$



Initial pressure: 4.98 bar 0

At equilibrium: $(4.98 - x)$ bar $2x$ bar

Hence,

$$p_{\text{total}} \text{ at equilibrium} = p_{\text{N}_2\text{O}_4} + p_{\text{NO}_2}$$

$$9.15 = (4.98 - x) + 2x$$

$$9.15 = 4.98 + x$$

$$x = 9.15 - 4.98 = 4.17 \text{ bar}$$

Partial pressures at equilibrium are,

$$p_{\text{N}_2\text{O}_4} = 4.98 - 4.17 = 0.81 \text{ bar}$$

$$p_{\text{NO}_2} = 2x = 2 \times 4.17 = 8.34 \text{ bar}$$

$$K_p = (p_{\text{NO}_2})^2 / p_{\text{N}_2\text{O}_4} \\ = (8.34)^2 / 0.81 = 85.87$$

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

$$85.87 = K_c(0.083 \times 400)^1$$

$$K_c = 2.586 = 2.6$$

Problem 6.9

3.00 mol of PCl_5 kept in 1L closed reaction vessel was allowed to attain equilibrium at 380K. Calculate composition of the mixture at equilibrium. $K_c = 1.80$

Solution

Initial

concentration: 3.0 0 0

Let x mol per litre of PCl_5 be dissociated,
At equilibrium:

$$\begin{array}{ccc}
 (3-x) & x & x \\
 K_c = [\text{PCl}_3][\text{Cl}_2]/[\text{PCl}_5] \\
 1.8 = x^2 / (3-x) \\
 x^2 + 1.8x - 5.4 = 0 \\
 x = [-1.8 \pm \sqrt{(1.8)^2 - 4(-5.4)}] / 2 \\
 x = [-1.8 \pm \sqrt{3.24 + 21.6}] / 2 \\
 x = [-1.8 \pm 4.98] / 2 \\
 x = [-1.8 + 4.98] / 2 = 1.59 \\
 [\text{PCl}_5] = 3.0 - x = 3 - 1.59 = 1.41 \text{ M} \\
 [\text{PCl}_3] = [\text{Cl}_2] = x = 1.59 \text{ M}
 \end{array}$$

6.7 RELATIONSHIP BETWEEN EQUILIBRIUM CONSTANT K , REACTION QUOTIENT Q AND GIBBS ENERGY G

The value of K_c for a reaction does not depend on the rate of the reaction. However, as you have studied in Unit 5, it is directly related to the thermodynamics of the reaction and in particular, to the change in Gibbs energy, ΔG . If,

- ΔG is negative, then the reaction is spontaneous and proceeds in the forward direction.
- ΔG is positive, then reaction is considered non-spontaneous. Instead, as reverse reaction would have a negative ΔG , the products of the forward reaction shall be converted to the reactants.
- ΔG is 0, reaction has achieved equilibrium; at this point, there is no longer any free energy left to drive the reaction.

A mathematical expression of this thermodynamic view of equilibrium can be described by the following equation:

$$\Delta G = \Delta G^\ominus + RT \ln Q \quad (6.21)$$

where, G^\ominus is standard Gibbs energy.

At equilibrium, when $\Delta G = 0$ and $Q = K_c$, the equation (6.21) becomes,

$$\begin{aligned}
 \Delta G &= \Delta G^\ominus + RT \ln K = 0 \\
 \Delta G^\ominus &= -RT \ln K \\
 \ln K &= -\Delta G^\ominus / RT
 \end{aligned} \quad (6.22)$$

Taking antilog of both sides, we get,

$$K = e^{-\Delta G^\ominus / RT} \quad (6.23)$$

Hence, using the equation (6.23), the reaction spontaneity can be interpreted in terms of the value of ΔG^\ominus .

- If $\Delta G^\ominus < 0$, then $-\Delta G^\ominus / RT$ is positive, and $e^{-\Delta G^\ominus / RT} > 1$, making $K > 1$, which implies a spontaneous reaction or the reaction which proceeds in the forward direction to such an extent that the products are present predominantly.
- If $\Delta G^\ominus > 0$, then $-\Delta G^\ominus / RT$ is negative, and $e^{-\Delta G^\ominus / RT} < 1$, that is, $K < 1$, which implies a non-spontaneous reaction or a reaction which proceeds in the forward direction to such a small degree that only a very minute quantity of product is formed.

Problem 6.10

The value of ΔG^\ominus for the phosphorylation of glucose in glycolysis is 13.8 kJ/mol. Find the value of K_c at 298 K.

Solution

$$\Delta G^\ominus = 13.8 \text{ kJ/mol} = 13.8 \times 10^3 \text{ J/mol}$$

$$\text{Also, } \Delta G^\ominus = -RT \ln K_c$$

$$\text{Hence, } \ln K_c = -13.8 \times 10^3 \text{ J/mol} / (8.314 \text{ J mol}^{-1} \text{K}^{-1} \times 298 \text{ K})$$

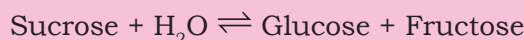
$$\ln K_c = -5.569$$

$$K_c = e^{-5.569}$$

$$K_c = 3.81 \times 10^{-3}$$

Problem 6.11

Hydrolysis of sucrose gives,



Equilibrium constant K_c for the reaction is 2×10^{13} at 300K. Calculate ΔG^\ominus at 300K.

Solution

$$\Delta G^\ominus = -RT \ln K_c$$

$$\Delta G^\ominus = -8.314 \text{ J mol}^{-1} \text{K}^{-1} \times 300 \text{ K} \times \ln(2 \times 10^{13})$$

$$\Delta G^\ominus = -7.64 \times 10^4 \text{ J mol}^{-1}$$

6.8 FACTORS AFFECTING EQUILIBRIA

One of the principal goals of chemical synthesis is to maximise the conversion of the

reactants to products while minimising the expenditure of energy. This implies maximum yield of products at mild temperature and pressure conditions. If it does not happen, then the experimental conditions need to be adjusted. For example, in the Haber process for the synthesis of ammonia from N_2 and H_2 , the choice of experimental conditions is of real economic importance. Annual world production of ammonia is about hundred million tones, primarily for use as fertilisers.

Equilibrium constant, K_c is independent of initial concentrations. But if a system at equilibrium is subjected to a change in the concentration of one or more of the reacting substances, then the system is no longer at equilibrium; and net reaction takes place in some direction until the system returns to equilibrium once again. Similarly, a change in temperature or pressure of the system may also alter the equilibrium. In order to decide what course the reaction adopts and *make a qualitative prediction* about the effect of a change in conditions on equilibrium we use **Le Chatelier's principle**. It states that a **change in any of the factors that determine the equilibrium conditions of a system will cause the system to change in such a manner so as to reduce or to counteract the effect of the change**. This is applicable to all physical and chemical equilibria.

We shall now be discussing factors which can influence the equilibrium.

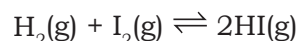
6.8.1 Effect of Concentration Change

In general, when equilibrium is disturbed by the addition/removal of any reactant/products, Le Chatelier's principle predicts that:

- The concentration stress of an *added* reactant/product is relieved by net reaction in the direction that consumes the added substance.
 - The concentration stress of a *removed* reactant/product is relieved by net reaction in the direction that *replenishes* the removed substance.
- or in other words,

“When the concentration of any of the reactants or products in a reaction at equilibrium is changed, the composition of the equilibrium mixture changes so as to minimize the effect of concentration changes”.

Let us take the reaction,



If H_2 is added to the reaction mixture at equilibrium, then the equilibrium of the reaction is disturbed. In order to restore it, the reaction proceeds in a direction wherein H_2 is consumed, i.e., more of H_2 and I_2 react to form HI and finally the equilibrium shifts in right (forward) direction (Fig.6.8). This is in accordance with the Le Chatelier's principle which implies that in case of addition of a reactant/product, a new equilibrium will be set up in which the concentration of the reactant/product should be less than what it was after the addition but more than what it was in the original mixture.

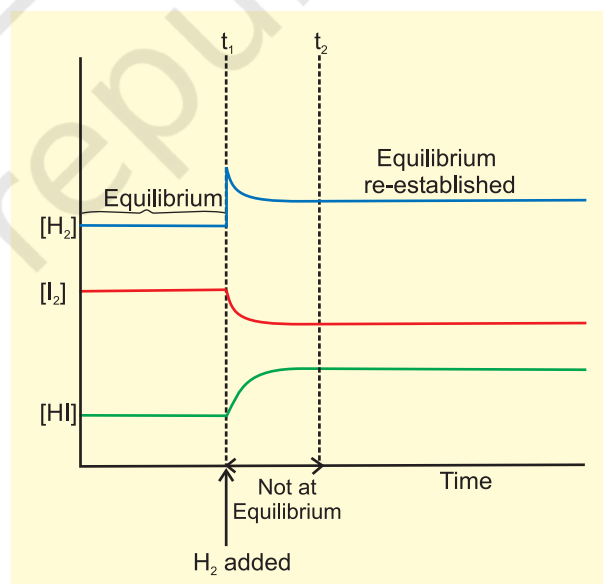


Fig. 6.8 Effect of addition of H_2 on change of concentration for the reactants and products in the reaction, $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$

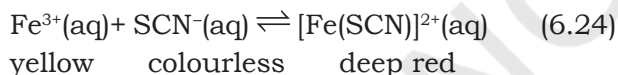
The same point can be explained in terms of the reaction quotient, Q_c ,

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

Addition of hydrogen at equilibrium results in value of Q_c being less than K_c . Thus, in order to attain equilibrium again reaction moves in the forward direction. Similarly, we can say that removal of a product also boosts the forward reaction and increases the concentration of the products and this has great commercial application in cases of reactions, where the product is a gas or a volatile substance. In case of manufacture of ammonia, ammonia is liquified and removed from the reaction mixture so that reaction keeps moving in forward direction. Similarly, in the large scale production of CaO (used as important building material) from CaCO_3 , constant removal of CO_2 from the kiln drives the reaction to completion. It should be remembered that continuous removal of a product maintains Q_c at a value less than K_c and reaction continues to move in the forward direction.

Effect of Concentration – An experiment

This can be demonstrated by the following reaction:



$$K_c = \frac{[\text{Fe}(\text{SCN})^{2+}(\text{aq})]}{[\text{Fe}^{3+}(\text{aq})][\text{SCN}^{-}(\text{aq})]} \quad (6.25)$$

A reddish colour appears on adding two drops of 0.002 M potassium thiocyanate solution to 1 mL of 0.2 M iron(III) nitrate solution due to the formation of $[\text{Fe}(\text{SCN})]^{2+}$. The intensity of the red colour becomes constant on attaining equilibrium. This equilibrium can be shifted in either forward or reverse directions depending on our choice of adding a reactant or a product. The equilibrium can be shifted in the opposite direction by adding reagents that remove Fe^{3+} or SCN^{-} ions. For example, oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$), reacts with Fe^{3+} ions to form the stable complex ion $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$, thus decreasing the concentration of free $\text{Fe}^{3+}(\text{aq})$. In accordance with the Le Chatelier's principle, the concentration stress of removed Fe^{3+} is relieved by dissociation of $[\text{Fe}(\text{SCN})]^{2+}$ to replenish the Fe^{3+} ions. Because the

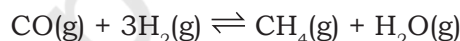
concentration of $[\text{Fe}(\text{SCN})]^{2+}$ decreases, the intensity of red colour decreases.

Addition of aq. HgCl_2 also decreases red colour because Hg^{2+} reacts with SCN^{-} ions to form stable complex ion $[\text{Hg}(\text{SCN})_4]^{2-}$. Removal of free $\text{SCN}^{-}(\text{aq})$ shifts the equilibrium in equation (6.24) from right to left to replenish SCN^{-} ions. Addition of potassium thiocyanate on the other hand increases the colour intensity of the solution as it shifts the equilibrium to right.

6.8.2 Effect of Pressure Change

A pressure change obtained by changing the volume can affect the yield of products in case of a gaseous reaction where the total number of moles of gaseous reactants and total number of moles of gaseous products are different. In applying Le Chatelier's principle to a heterogeneous equilibrium the effect of pressure changes on solids and liquids can be ignored because the volume (and concentration) of a solution/liquid is nearly independent of pressure.

Consider the reaction,



Here, 4 mol of gaseous reactants ($\text{CO} + 3\text{H}_2$) become 2 mol of gaseous products ($\text{CH}_4 + \text{H}_2\text{O}$). Suppose equilibrium mixture (for above reaction) kept in a cylinder fitted with a piston at constant temperature is compressed to one half of its original volume. Then, total pressure will be doubled (according to $pV = \text{constant}$). The partial pressure and therefore, concentration of reactants and products have changed and the mixture is no longer at equilibrium. The direction in which the reaction goes to re-establish equilibrium can be predicted by applying the Le Chatelier's principle. Since pressure has doubled, the equilibrium now shifts in the forward direction, a direction in which the number of moles of the gas or pressure decreases (we know pressure is proportional to moles of the gas). This can also be understood by using reaction quotient, Q_c . Let $[\text{CO}]$, $[\text{H}_2]$, $[\text{CH}_4]$ and $[\text{H}_2\text{O}]$ be the molar concentrations at equilibrium for methanation reaction. When volume of the reaction mixture is halved, the

partial pressure and the concentration are doubled. We obtain the reaction quotient by replacing each equilibrium concentration by double its value.

$$Q_c = \frac{[\text{CH}_4(\text{g})][\text{H}_2\text{O}(\text{g})]}{[\text{CO}(\text{g})][\text{H}_2(\text{g})]^3}$$

As $Q_c < K_c$, the reaction proceeds in the forward direction.

In reaction $\text{C}(\text{s}) + \text{CO}_2(\text{g}) \rightleftharpoons 2\text{CO}(\text{g})$, when pressure is increased, the reaction goes in the reverse direction because the number of moles of gas increases in the forward direction.

6.8.3 Effect of Inert Gas Addition

If the volume is kept constant and an inert gas such as argon is added which does not take part in the reaction, the equilibrium remains undisturbed. It is because the addition of an inert gas at constant volume does not change the partial pressures or the molar concentrations of the substance involved in the reaction. The reaction quotient changes only if the added gas is a reactant or product involved in the reaction.

6.8.4 Effect of Temperature Change

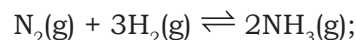
Whenever an equilibrium is disturbed by a change in the concentration, pressure or volume, the composition of the equilibrium mixture changes because the reaction quotient, Q_c no longer equals the equilibrium constant, K_c . However, when a change in temperature occurs, the value of equilibrium constant, K_c is changed.

In general, the temperature dependence of the equilibrium constant depends on the sign of ΔH for the reaction.

- The equilibrium constant for an exothermic reaction (negative ΔH) decreases as the temperature increases.
- The equilibrium constant for an endothermic reaction (positive ΔH) increases as the temperature increases.

Temperature changes affect the equilibrium constant and rates of reactions.

Production of ammonia according to the reaction,



$$\Delta H = -92.38 \text{ kJ mol}^{-1}$$

is an exothermic process. According to Le Chatelier's principle, raising the temperature shifts the equilibrium to left and decreases the equilibrium concentration of ammonia. In other words, low temperature is favourable for high yield of ammonia, but practically very low temperatures slow down the reaction and thus a catalyst is used.

Effect of Temperature – An experiment

Effect of temperature on equilibrium can be demonstrated by taking NO_2 gas (brown in colour) which dimerises into N_2O_4 gas (colourless).



NO_2 gas prepared by addition of Cu turnings to conc. HNO_3 is collected in two 5 mL test tubes (ensuring same intensity of colour of gas in each tube) and stopper sealed with araldite. Three 250 mL beakers 1, 2 and 3 containing freezing mixture, water at room temperature and hot water (363K), respectively, are taken (Fig. 6.9). Both the test tubes are placed in beaker 2 for 8-10 minutes. After this one is placed in beaker 1 and the other in beaker 3. The effect of temperature on direction of reaction is depicted very well in this experiment. At low temperatures in beaker 1, the forward reaction of formation of N_2O_4 is preferred, as reaction is exothermic, and thus, intensity of brown colour due to NO_2 decreases. While in beaker 3, high temperature favours the reverse reaction of

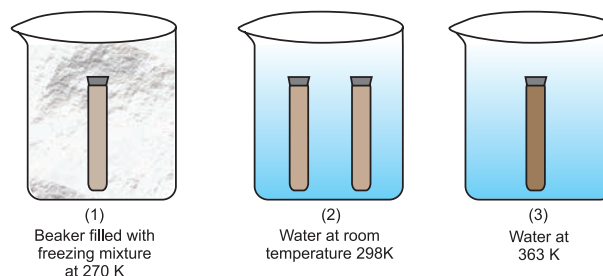
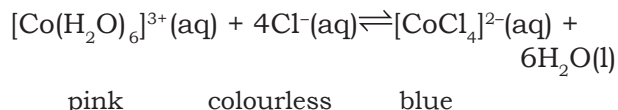


Fig. 6.9 Effect of temperature on equilibrium for the reaction, $2\text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g})$

formation of NO_2 and thus, the brown colour intensifies.

Effect of temperature can also be seen in an endothermic reaction,



At room temperature, the equilibrium mixture is blue due to $[\text{CoCl}_4]^{2-}$. When cooled in a freezing mixture, the colour of the mixture turns pink due to $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$.

6.8.5 Effect of a Catalyst

A catalyst increases the rate of the chemical reaction by making available a new low energy pathway for the conversion of reactants to products. It increases the rate of forward and reverse reactions that pass through the same transition state and does not affect equilibrium. Catalyst lowers the activation energy for the forward and reverse reactions by exactly the same amount. Catalyst does not affect the equilibrium composition of a reaction mixture. It does not appear in the balanced chemical equation or in the equilibrium constant expression.

Let us consider the formation of NH_3 from dinitrogen and dihydrogen which is highly exothermic reaction and proceeds with decrease in total number of moles formed as compared to the reactants. Equilibrium constant decreases with increase in temperature. At low temperature rate decreases and it takes long time to reach at equilibrium, whereas high temperatures give satisfactory rates but poor yields.

German chemist, Fritz Haber discovered that a catalyst consisting of iron catalyse the reaction to occur at a satisfactory rate at temperatures, where the equilibrium concentration of NH_3 is reasonably favourable. Since the number of moles formed in the reaction is less than those of reactants, the yield of NH_3 can be improved by increasing the pressure.

Optimum conditions of temperature and pressure for the synthesis of NH_3 using catalyst are around 500°C and 200 atm.

Similarly, in manufacture of sulphuric acid by *contact process*,

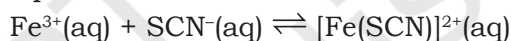


though the value of K is suggestive of reaction going to completion, but practically the oxidation of SO_2 to SO_3 is very slow. Thus, platinum or divanadium penta-oxide (V_2O_5) is used as catalyst to increase the rate of the reaction.

Note: If a reaction has an exceedingly small K , a catalyst would be of little help.

6.9 IONIC EQUILIBRIUM IN SOLUTION

Under the effect of change of concentration on the direction of equilibrium, you have incidentally come across with the following equilibrium which involves ions:



There are numerous equilibria that involve ions only. In the following sections we will study the equilibria involving ions. It is well known that the aqueous solution of sugar does not conduct electricity. However, when common salt (sodium chloride) is added to water it conducts electricity. Also, the conductance of electricity increases with an increase in concentration of common salt. Michael Faraday classified the substances into two categories based on their ability to conduct electricity. One category of substances conduct electricity in their aqueous solutions and are called *electrolytes* while the other do not and are thus, referred to as *non-electrolytes*. Faraday further classified electrolytes into *strong* and *weak* electrolytes. Strong electrolytes on dissolution in water are ionized almost completely, while the weak electrolytes are only partially dissociated. For example, an aqueous solution of sodium chloride is comprised entirely of sodium ions and chloride ions, while that of acetic acid mainly contains unionized acetic acid molecules and only some acetate ions and hydronium ions. This is because there is almost 100% ionization in case of sodium chloride as compared to less than 5% ionization of acetic acid which is a weak electrolyte. It should be noted