At equilibrium:

(0.48 – x)bar   2x bar

$$K_p = \frac{p_{CO}^2}{p_{CO_2}}$$

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

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

$4x^2 = 1.44 - x$

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

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

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

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

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

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

$x = 2.66/8 = 0.33$

The equilibrium partial pressures are,

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

$p_{CO_2} = 0.48 - x = 0.48 - 0.33 = 0.15$ bar

7.6 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.

7.6.1 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) $H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$ at 300K has $K_c = 4.0 \times 10^{31}$.

(c) $H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$ 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) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$, 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 generarlisations are illustrated in Fig. 7.6

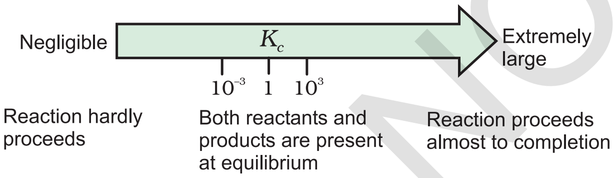

Fig.7.6 *Dependence of extent of reaction on* K_c

7.6.2 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** $\boldsymbol{Q}$. 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:

$$a\,A + b\,B \rightleftharpoons c\,C + d\,D \qquad (7.19)$$

$$Q_c = [C]^c[D]^d / [A]^a[B]^b \qquad (7.20)$$

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,

$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$; $K_c = 57.0$ at 700 K.

Suppose we have molar concentrations $[H_2]_t = 0.10M$, $[I_2]_t = 0.20$ M and $[HI]_t = 0.40$ 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,

$$Q_c = [HI]_t^2 \,/\, [H_2]_t\,[I_2]_t = (0.40)^2 / (0.10)\times(0.20) = 8.0$$

Now, in this case, Q_c (8.0) does not equal K_c (57.0), so the mixture of $H_2(g)$, $I_2(g)$ and HI(g) is not at equilibrium; that is, more $H_2(g)$ and $I_2(g)$ will react to form more HI(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. 7.7) :

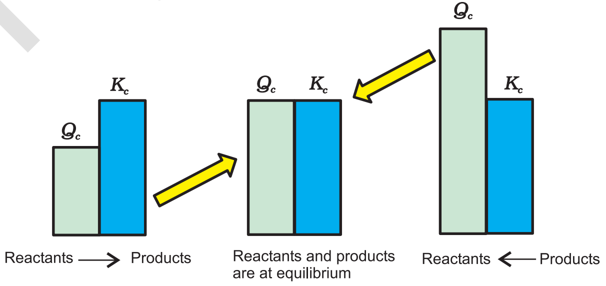

Fig. 7.7 *Predicting the direction of the reaction*

- 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 7.7

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

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

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

7.6.3 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:

(a) the initial concentration,
(b) the change in concentration on going to equilibrium, and
(c) 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 7.8

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

$N_2O_4 (g) \rightleftharpoons 2NO_2 (g)$

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 of the gas (n) = 13.8g/92 g = 0.15

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

Temperature $(T) = 400$ K

$pV = nRT$

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

$p = 4.98$ bar

	N_2O_4	$\rightleftharpoons$	$2NO_2$
Initial pressure:	4.98 bar		0
At equilibrium:	(4.98 – x) bar		2x bar

Hence,

p_{total} at equilibrium $= p_{N_2O_4} + p_{NO_2}$

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

$9.15 = 4.98 + x$

$x = 9.15 - 4.98 = 4.17$ bar

Partial pressures at equilibrium are,

$p_{N_2O_4} = 4.98 - 4.17 = 0.81$bar

$p_{NO_2} = 2x = 2 \times 4.17 = 8.34$ bar

$K_p = \left(p_{NO_2}\right)^2 / p_{N_2O_4}$

$= (8.34)^2/0.81 = 85.87$

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

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

$K_c = 2.586 = 2.6$

Problem 7.9

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

	PCl_5	$\rightleftharpoons$	PCl_3 +	Cl_2
Initial concentration:	3.0		0	0

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

(3-x) x x

$K_c = [PCl_3][Cl_2]/[PCl_5]$

$1.8 = x^2/ (3 – x)$

$x^2 + 1.8x – 5.4 = 0$

$x = [–1.8 \pm \sqrt{(1.8)^2 – 4(–5.4)}]/2$

$x = [–1.8 \pm \sqrt{3.24 + 21.6}]/2$

$x = [–1.8 \pm 4.98]/2$

$x = [–1.8 + 4.98]/2 = 1.59$

$[PCl_5] = 3.0 – x = 3 –1.59 = 1.41$ M

$[PCl_3] = [Cl_2] = x = 1.59$ M

7.7 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 6, 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:

$$\Delta G = \Delta G^\ominus + RT \ln Q \qquad (7.21)$$

where, $G^\ominus$ is standard Gibbs energy.

At equilibrium, when $\Delta G = 0$ and $Q = K_c$, the equation (7.21) becomes,

$$\Delta G = \Delta G^\ominus + RT \ln K = 0$$

$$\Delta G^\ominus = – RT \ln K \qquad (7.22)$$

$$\ln K = –\Delta G^\ominus / RT$$

Taking antilog of both sides, we get,

$$K = e^{-\Delta G^\ominus / RT} \qquad (7.23)$$

Hence, using the equation (7.23), the reaction spontaneity can be interpreted in terms of the value of $\Delta G^\ominus$.

- 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 7.10

The value of $\Delta G^\ominus$ 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 kJ/mol = 13.8 × 10^3J/mol

Also, $\Delta G^\ominus = – RT \ln K_c$

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

$\ln K_c = – 5.569$

$K_c = e^{-5.569}$

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

Problem 7.11

Hydrolysis of sucrose gives,

Sucrose + $H_2O \rightleftharpoons$ Glucose + Fructose

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

Solution

$\Delta G^\ominus = – RT \ln K_c$

$\Delta G^\ominus = – 8.314 \text{J mol}^{-1}\text{K}^{-1} \times 300\text{K} \times \ln(2\times10^{13})$

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

7.8 FACTORS AFFECTING EQUILIBRIA

One of the principal goals of chemical synthesis is to maximise the conversion of the reactants to products while minimizing 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 fertilizers.

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.

7.8.1 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,

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

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.7.8). 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.

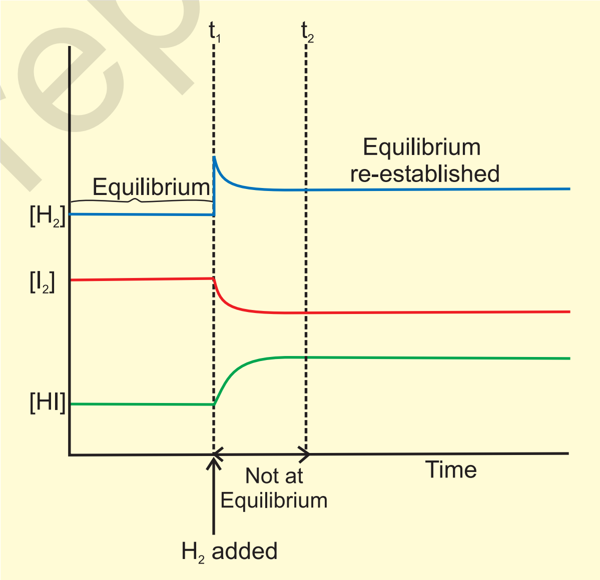

Fig. 7.8 *Effect of addition of H_2 on change of concentration for the reactants and products in the reaction, $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$*

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

$$Q_c = [HI]^2 / [H_2][I_2]$$

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:

$$Fe^{3+}(aq) + SCN^{-}(aq) \rightleftharpoons [Fe(SCN)]^{2+}(aq) \qquad (7.24)$$

yellow colourless deep red

$$K_c = \frac{\left[Fe(SCN)^{2+}(aq)\right]}{\left[Fe^{3+}(aq)\right]\left[SCN^{-}(aq)\right]} \qquad (7.25)$$

A reddish colour appears on adding two drops of 0.002 M potassium thiocynate solution to 1 mL of 0.2 M iron(III) nitrate solution due to the formation of $[Fe(SCN)]^{2+}$. 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 ($H_2C_2O_4$), reacts with Fe^{3+} ions to form the stable complex ion $[Fe(C_2O_4)_3]^{3-}$, thus decreasing the concentration of free Fe^{3+}(aq). In accordance with the Le Chatelier's principle, the concentration stress of removed Fe^{3+} is relieved by dissociation of $[Fe(SCN)]^{2+}$ to replenish the Fe^{3+} ions. Because the concentration of $[Fe(SCN)]^{2+}$ 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 $[Hg(SCN)_4]^{2-}$. Removal of free SCN^- (aq) shifts the equilibrium in equation (7.24) 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 shift the equilibrium to right.

7.8.2 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,

$$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$$

Here, 4 mol of gaseous reactants ($CO + 3H_2$) become 2 mol of gaseous products ($CH_4 + H_2O$). 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 = 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 [CO], $[H_2]$, $[CH_4]$ and $[H_2O]$ 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.

$$Q_c = \frac{[CH_4(g)][H_2O(g)]}{[CO(g)][H_2(g)]^3}$$

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

In reaction $C(s) + CO_2(g) \rightleftharpoons 2CO(g)$, when pressure is increased, the reaction goes in the reverse direction because the number of moles of gas increases in the forward direction.

7.8.3 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.

7.8.4 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,

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) ;$$
$$\Delta H = -92.38 \text{ kJ mol}^{-1}$$

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).

$$2NO_2(g) \rightleftharpoons N_2O_4(g); \Delta H = -57.2 \text{ kJ mol}^{-1}$$

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. 7.9). 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

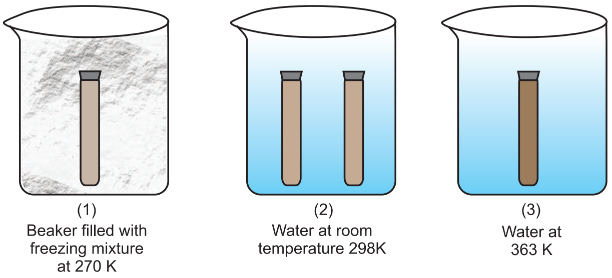

Fig. 7.9 *Effect of temperature on equilibrium for the reaction,* $2NO_2(g) \rightleftharpoons N_2O_4(g)$