At equilibrium:

$\qquad$ (0.48 – x)bar $\qquad$ 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

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

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

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

$\quad = (-3 + 5.66)/8$ (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.
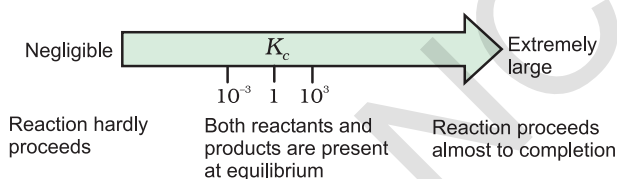
These generarlisations are illustrated in Fig. 7.6

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 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:

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

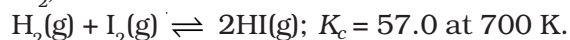$Q_c = [C]^c[D]^d / [A]^a[B]^b$ (7.20)

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) :

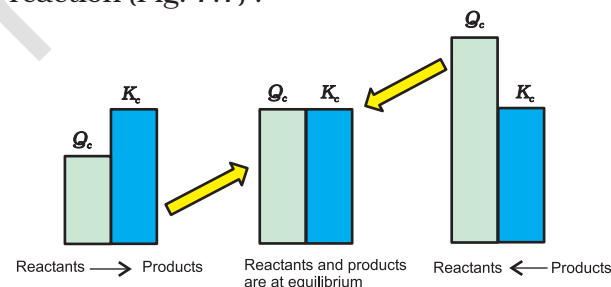**Fig. 7.7** *Predicting the direction of the reaction*

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

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

Temperature (T) = 400 K

$pV = nRT$

$p \times 1L = 0.15$ mol $\times 0.083$ bar L mol^{-1}K^{-1}
$\times 400$ 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:
$$(3-x) \qquad x \qquad x$$
$K_c = [PCl_3][Cl_2]/[PCl_5]$
$1.8 = x^2/ (3 - x)$
$x^2 + 1.8x - 5.4 = 0$
$x = [-1.8 \pm \sqrt{(1.8)^2 - 4(-5.4)}]/2$
$x = [-1.8 \pm \sqrt{3.24 + 21.6}]/2$
$x = [-1.8 \pm 4.98]/2$
$x = [-1.8 + 4.98]/2 = 1.59$
$[PCl_5] = 3.0 - x = 3 -1.59 = 1.41$ 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 $= 13.8 \times 10^3$ J/mol

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

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

$\ln K_c = - 5.569$

$K_c = e^{-5.569}$

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

Problem 7.11

Hydrolysis of sucrose gives,

Sucrose + $H_2O \rightleftharpoons$ Glucose + Fructose
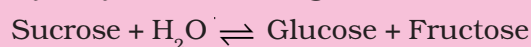
Equilibrium constant K_c for the reaction is 2×10^{13} at 300K. Calculate $\Delta G^\ominus$ at 300K.

Solution

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

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

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

7.8 FACTORS AFFECTING EQUILIBRIA

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