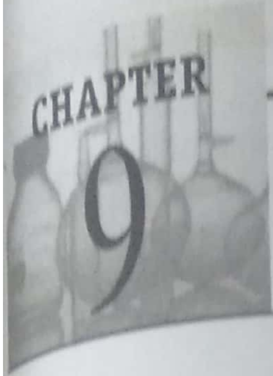

CHAPTER 9

Chemical Reaction Equilibria

The chemical process industries are concerned with the transformation of raw materials into useful products. Such transformation in most cases is achieved by means of chemical reactions. The design and operation of reaction equipment are therefore quite an important field in the chemical engineering profession. To be successful in this profession, the chemical engineer should be versatile with the thermodynamics and kinetics of chemical reactions. Thermodynamics predicts the equilibrium conversion that would be achieved in a chemical reaction and also the effect of operating conditions on it, whereas the kinetics deals with the rate or speed with which the desired conversion is attained in practice. Thermodynamic analysis can also give information about the feasibility of chemical reactions.

The progress and extent of a chemical reaction are affected by changes in the reaction conditions like temperature, pressure, composition of the reactants, etc. For example, in the synthesis of methanol from carbon monoxide and hydrogen, the equilibrium conversion as well as the rate of reaction are affected by changing the pressure, temperature or the relative amounts of carbon monoxide and hydrogen in the reactant stream. The influence of these controllable variables on the thermodynamics of reaction, or to be specific, on the equilibrium conversion, in some situation may be in conflict with the influence of these variables on the kinetics of the reaction. This can be illustrated by considering the effect of temperature on the oxidation of sulphur dioxide to sulphur trioxide. The rate of this reaction increases with temperature and from the point of view of rate alone it is better to operate the reactor at as high a temperature as permissible. However, the equilibrium conversion to sulphur trioxide falls off sharply with increase in temperature. The conversion is above 90% at temperatures near 800 K, but it is only 50% at 950 K. It is clear that both the kinetics (the rate) and thermodynamics (the equilibrium) of the reaction must be considered in the choice of reaction conditions in the commercial process for any chemical reaction. The purpose of the present chapter is to identify the role of thermodynamics in the design and operation of chemical reaction systems.

Equilibrium conversion of a reaction sets a limit and provides a goal by which we measure improvement in the process. It is impossible at a given set of conditions to attain a conversion that is better than the equilibrium value calculated from thermodynamic principles. Even if this conversion is not attainable in practice within a reasonable time, its knowledge is valuable because it represents the best that can be expected from the reaction. It tells us whether or not an experimental investigation of a proposed new process is worthwhile. There is no point in trying improvement in the process by improving the rate by introducing suitable catalysts, if thermodynamics predicts an equilibrium yield, of say, only 20% whereas a 50% yield is necessary for the process to be economically viable. The choice of an appropriate catalyst may give a better reaction rate, but it will not alter the equilibrium yield of the product. The emphasis in this chapter is on determining the conversion at equilibrium and on predicting the effect of controllable variables like temperature and pressure on the conversion.

9.1 REACTION STOICHIOMETRY

The generalised representation of a chemical reaction is given by

$$0 = \sum_i \nu_i A_i \tag{9.1}$$

where A is the chemical symbol for the various species taking part in the reaction and ν is the stoichiometric number. Consider the reaction

$$2A + 3B \rightarrow L + 2M$$

This is a special case of the general form of Eq. (9.1), with $\nu_L = 1$, $\nu_M = 2$, $\nu_A = -2$, and $\nu_B = -3$. In the general form, this reaction may be represented as

$$0 = L + 2M - 2A - 3B$$

The stoichiometric numbers are positive for products, negative for reactants and zero for inert species. The changes in the number of moles of various species taking part in the reaction are in direct proportion to their stoichiometric numbers. Let Δn_i denote the change in the number of moles of component i due to the reaction. For one mole of A disappearing in the reaction $\Delta n_A = -1$, $\Delta n_B = -1.5$, $\Delta n_L = 0.5$ and $\Delta n_M = 1$. We see that

$$\frac{\Delta n_A}{\nu_A} = \frac{\Delta n_B}{\nu_B} = \frac{\Delta n_L}{\nu_L} = \frac{\Delta n_M}{\nu_M}$$

For differential amounts of the species, the above result can be written as

$$\frac{dn_A}{\nu_A} = \frac{dn_B}{\nu_B} = \frac{dn_L}{\nu_L} = \frac{dn_M}{\nu_M}$$

For the thermodynamic analysis of chemical reactions the concept of 'extent of reaction,' also called 'reaction coordinate' is useful. It is denoted by ε. The reaction coordinate measures the progress of a reaction and is defined as the degree to which a reaction has advanced. It has the advantage that the change in the extent of reaction $d\varepsilon$ is the same for each component, whereas the changes in the number of moles are different for different species taking part in the reaction. The extent of reaction and the number of moles taking part in the reaction are related as

$$\frac{dn_i}{\nu_i} = d\varepsilon$$

or

$$dn_i = \nu_i \, d\varepsilon \tag{9.2}$$

For the initial state of the system, that is, before the reaction, the value of ε is zero.

***EXAMPLE* 9.1** Derive the relationship between the mole fraction of the components taking part in the reaction and the extent of the reaction.

Solution Let n_{i0} be the number of moles of the species initially present in the system and n_i the number of moles present after the reaction. Then $n_i = n_{i0} + \Delta n_i$ where Δn_i is the change in the number of moles of i due to the reaction. Integration of Eq. (9.2) yields

$$\Delta n_i = \nu_i \int_0^{\varepsilon} d\varepsilon = \nu_i \, \varepsilon$$

Therefore,

$$n_i = n_{i0} + \nu_i \varepsilon \tag{9.3}$$

The mole fraction of component i in the reaction mixture is y_i.

$$y_i = \frac{n_i}{\Sigma n_i} = \frac{n_{i0} + \nu_i \varepsilon}{\Sigma n_{i0} + \varepsilon \, \Sigma \nu_i} = \frac{n_{i0} + \nu_i \varepsilon}{n_0 + \varepsilon \nu} \tag{9.4}$$

where $n_0 = \Sigma \, n_{i0}$, the total number of moles initially present in the system and $\nu = \Sigma \, \nu_i$, the sum of the stoichiometric numbers.

***EXAMPLE* 9.2** A gas mixture containing 2 moles nitrogen, 7 moles hydrogen and 1 mole ammonia initially, is undergoing the following reaction:

$$N_2 + 3H_2 \rightarrow 2NH_3$$

(a) Derive expressions for the mole fractions of various components in the reaction mixture in terms of the extent of reaction.
(b) Explain how the conversion of limiting reactant is related to the extent of reaction.

Solution (a) Equations (9.3) and (9.4) relate the mole fraction of various constituents in the system to the extent of reaction.

$$n_0 = \Sigma \, n_{i0} = 2 + 7 + 1 = 10$$

$$\nu = \Sigma \, \nu_i = 2 - 1 - 3 = -2$$

$$y_{N_2} = \frac{n_{N_2,0} + \nu_{N_2} \varepsilon}{n_0 + \varepsilon \nu} = \frac{2 - \varepsilon}{10 - 2\varepsilon}$$

$$y_{H_2} = \frac{n_{H_2,0} + \nu_{H_2} \varepsilon}{n_0 + \varepsilon \nu} = \frac{7 - 3\varepsilon}{10 - 2\varepsilon}$$

$$y_{NH_3} = \frac{n_{NH_3,0} + \nu_{NH_3} \varepsilon}{n_0 + \varepsilon \nu} = \frac{1 + 2\varepsilon}{10 - 2\varepsilon}$$

(b) The limiting reactant here is nitrogen. Let the fractional conversion of nitrogen be z. Then

Moles of nitrogen in the reaction mixture is $= n_{N_2,0} - z n_{N_2,0}$

Moles of nitrogen in the mixture in terms of the extent of reaction is $= n_{N_2,0} + \nu_{N_2} \varepsilon$

Comparing the two results, we see that

$$z = -\frac{\nu_{N_2}\,\varepsilon}{n_{N_2,0}}$$

Since the stoichiometric number is negative for a reactant, the conversion given by the above equation will be always positive. The relationship between conversion and the extent of reaction can be written as

$$z = \frac{|\nu_{N_2}|\,\varepsilon}{n_{N_2,0}}$$

In general, conversion can be treated as the fractional extent of reaction and is written as

$$z = \frac{\varepsilon}{n_{i0}/|\nu_i|} \tag{9.5}$$

EXAMPLE 9.3 Derive the relationship between mole fraction of species in multiple reactions and the extent of reactions.

Solution When two or more reactions occur simultaneously, the number of moles of each component changes because of several reactions. Equation (9.2) can be modified as

$$dn_i = \sum_j \nu_{i,j}\, d\varepsilon_j \tag{9.6}$$

Here, $\nu_{i,j}$ is the stoichiometric number for species i in the jth reaction and ε_j is the extent of this reaction. Equation (9.3) is modified to account for the multiple reactions, and the number of moles of i after the reaction is

$$n_i = n_{i0} + \sum_j \nu_{i,j}\,\varepsilon_j \tag{9.7}$$

The total number of moles is obtained by summing the number of moles of individual species.

$$n = \sum_i n_{i0} + \sum_i \sum_j \nu_{i,j}\varepsilon_j = n_0 + \sum_j \left(\sum_i \nu_{i,j}\right)\varepsilon_j$$

Let $\sum_i \nu_{i,j} = \nu_j$, the sum of the stoichiometric numbers in the jth reaction. Then the above equation can be written as

$$n = n_0 + \sum_j \nu_j\varepsilon_j \tag{9.8}$$

The mole fraction of component i in the mixture is

$$y_i = \frac{n_i}{n} = \frac{n_{i0} + \sum_j \nu_{i,j}\varepsilon_j}{n_0 + \sum_j \nu_j\varepsilon_j} \tag{9.9}$$

EXAMPLE 9.4 A gas mixture containing 3 mol CO_2, 5 mol H_2 and 1 mol water is undergoing the following reactions:

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$$

$$CO_2 + H_2 \rightarrow CO + H_2O$$

Develop expressions for the mole fraction of the species in terms of the extent of reaction.

Solution The total moles initially present,

$$n_0 = 3 + 5 + 1 = 9$$

For the first reaction,

$$\nu_1 = -1 - 3 + 1 + 1 = -2$$

For the second reaction,

$$\nu_2 = -1 - 1 + 1 + 1 = 0$$

The mole fractions are calculated using Eq. (9.9)

$$y_{CO_2} = \frac{3 + (-1) \times \varepsilon_1 + (-1) \times \varepsilon_2}{9 + (-2) \times \varepsilon_1 + (0) \times \varepsilon_2} = \frac{3 - \varepsilon_1 - \varepsilon_2}{9 - 2\varepsilon_1}$$

Similarly,

$$y_{H_2} = \frac{5 - 3\varepsilon_1 - \varepsilon_2}{9 - 2\varepsilon_1}, \qquad y_{CH_3OH} = \frac{\varepsilon_1}{9 - 2\varepsilon_1}$$

$$y_{H_2O} = \frac{1 + \varepsilon_1 + \varepsilon_2}{9 - 2\varepsilon_1}, \qquad y_{CO} = \frac{\varepsilon_2}{9 - 2\varepsilon_1}$$

9.2 CRITERIA OF CHEMICAL REACTION EQUILIBRIUM

We have developed the criteria of phase equilibrium in Chapter 8. At constant temperature and pressure, the transfer of materials from one phase to another under equilibrium is found to occur with no change in the free energy. Stated mathematically,

$$dG^t_{T,P} = 0 \tag{9.10}$$

Here $G^t_{T,P}$ is the total Gibbs free energy of the system at constant temperature and pressure. This criterion is quite general and is not restricted to physical transformations. When a chemical reaction occurs at equilibrium there is no change in the Gibbs free energy of the system, provided the change is taking place at constant temperature and pressure.

Consider a closed system in which a chemical reaction represented by the following general equation has been allowed to reach a state of equilibrium at a given temperature and pressure.

$$aA + bB \rightarrow lL + mM \tag{9.11}$$

An infinitesimal change is allowed to occur in the system whereby the number of moles of various species change. The increments in the number of moles are dn_A, dn_B, dn_L and dn_M for components

A, B, L and M respectively. The free energy change for the process occurring at constant temperature and pressure is given by [see Eq. (7.36)]

$$dG^t_{T,P} = \Sigma \mu_i \, dn_i \tag{9.12}$$

where μ_i is the chemical potential of component i. For the reaction under consideration, Eq. (9.12) takes the form

$$dG^t_{T,P} = \mu_L \, dn_L + \mu_M \, dn_M + \mu_A \, dn_A + \mu_B \, dn_B$$

By Eq. (9.2), $dn_i = \nu_i \, d\varepsilon$, so that the above equation becomes

$$\begin{aligned} dG^t_{T,P} &= (\nu_L\mu_L + \nu_M\mu_M + \nu_A\mu_A + \nu_B\mu_B) \, d\varepsilon \\ &= (l\mu_L + m\mu_M - a\mu_A - b\mu_B) \, d\varepsilon \end{aligned} \tag{9.13}$$

where $-a$, $-b$, l and m are the stoichiometric numbers which are positive for products and negative for the reactants and ε is the extent of reaction. In general, for an infinitesimal change in a reacting system, we can write Eq. (9.13) as

$$dG^t_{T,P} = \Sigma \mu_i \nu_i \, d\varepsilon \tag{9.14}$$

Since the process is occurring at equilibrium conditions, Eq. (9.10) should be satisfied so that

$$dG^t_{T,P} = \Sigma \mu_i \nu_i \, d\varepsilon = 0$$

or

$$\Sigma \mu_i \nu_i = 0 \tag{9.15}$$

This is the criterion of equilibrium for chemical reactions. For the present reaction given by Eq. (9.11), this criterion means

$$(l\mu_L + m\mu_M) - (a\mu_A + b\mu_B) = 0 \tag{9.16}$$

The left-hand side of Eq. (9.16) is the free energy change ΔG accompanying the complete reaction under equilibrium conditions. Hence, $\Delta G = 0$ under equilibrium.

The physical significance of the criterion of chemical equilibrium can now be examined. Consider a simple chemical reaction equilibrium: A $\leftrightarrows$ B. Let the extent of the reaction be ε. The change in the number of moles of A = $-\,d\varepsilon$ and the change in the number of moles of B = $d\varepsilon$. The change in free energy at constant temperature and pressure is found out by Eq. (9.14)

$$dG^t = (\mu_B - \mu_A) \, d\varepsilon \tag{9.17}$$

This equation can be written in the following form.

$$\left(\frac{\partial G^t}{\partial \varepsilon}\right)_{T,P} = \mu_B - \mu_A \tag{9.18}$$

Equation (9.18) gives the slope of the curve obtained when the Gibbs free energy is plotted against extent of reaction as in Fig. 9.1.

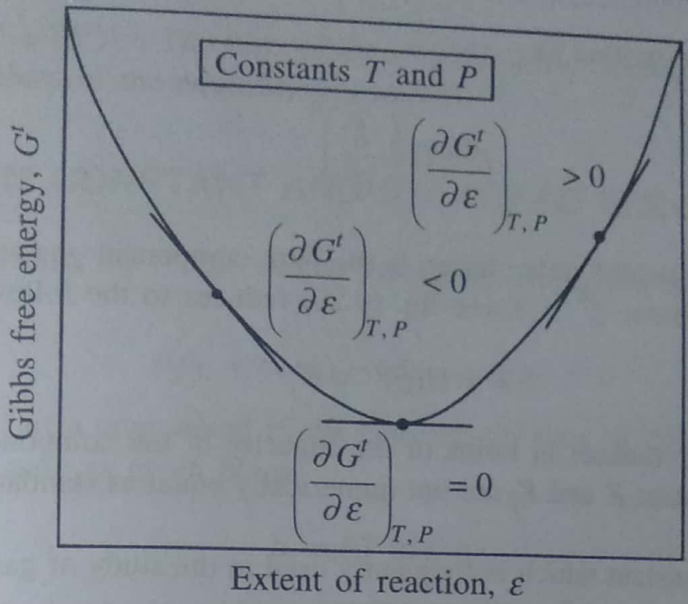

Fig. 9.1 Gibbs free energy of the reaction mixture versus extent of reaction.

The slopes given by Eq. (9.18) are not constant because the chemical potentials are functions of composition, which varies as the extent of reaction changes. Since the reaction proceeds in the direction of decreasing Gibbs free energy G, the forward reaction (A $\rightarrow$ B) takes place if $\mu_A > \mu_B$ and the backward reaction (A $\leftarrow$ B) proceeds if $\mu_A < \mu_B$. When $\mu_A = \mu_B$, the slope of the curve is zero. This occurs at the minimum of the curve and corresponds to the position of chemical equilibrium. The composition of the reaction mixture at the point where the Gibbs free energy is the minimum is the equilibrium composition at the specified temperature and pressure. Thus the criterion of equilibrium, Eq. (9.10), means that differential displacement of chemical reaction can occur at the equilibrium state, but without changing the total Gibbs free energy. If the system is not in chemical equilibrium, the reaction occurring must be irreversible and the total Gibbs free energy must decrease at constant temperature and pressure.

9.3 EQUILIBRIUM CONSTANT

Consider the chemical reaction given by Eq. (9.11)

$$aA + bB \rightarrow lL + mM$$

The equilibrium constant K or K_a for this reaction is defined in terms of the activities of the reactants and the products as

$$K = K_a = \frac{a_L^l \, a_M^m}{a_A^a \, a_B^b} = \Pi a_i^{\nu_i} \tag{9.19}$$

where a_i is the activity of component i in the reaction mixture and ν_i is the stoichiometric number of i. Activities of the species appearing in Eq. (9.19) are raised to the respective stoichiometric numbers. Since the activity is defined as the ratio of the fugacity of the component in the solution to the fugacity in the standard state,

$$a_i = \frac{\bar{f}_i}{f_i^0}$$

Equation (9.19) can also be written as

$$K = \Pi \left(\frac{\bar{f}_i}{f_i^0} \right)^{\nu_i} \tag{9.20}$$

For gaseous systems, the standard state chosen is the pure component gas at a pressure at which the fugacity is unity. Therefore, $f_i^0 = 1$ and Eq. (9.20) reduces to the following form:

$$K = \Pi(\bar{f}_i)^{\nu_i} = K_f \tag{9.21}$$

where K_f is an equilibrium constant in terms of the fugacity of the components. For liquids and solids, the equilibrium constant K and K_f are not numerically equal as standard state fugacities are not unity.

Another equilibrium constant which is frequently used in the study of gaseous reactions is K_p, the equilibrium constant in terms of partial pressures.

$$K_p = \Pi(\bar{p}_i)^{\nu_i} \tag{9.22}$$

Using the relation that fugacity of a component in a gas mixture is equal to the product of fugacity coefficient and the partial pressure, Eq. (9.21) can be written as

$$K = K_f = \Pi(\bar{\phi}_i\, \bar{p}_i)^{\nu_i} = \Pi(\bar{\phi}_i)^{\nu_i}\; \Pi(\bar{p}_i)^{\nu_i} \tag{9.23}$$

Denoting $\Pi(\bar{\phi}_i)^{\nu_i}$ by K_ϕ, we can write Eq. (9.23) as

$$K = K_f = K_\phi K_p \tag{9.24}$$

This relationship is applicable for gaseous systems. If the gas mixture behaves as an ideal gas, then $K_\phi = 1$ and Eq. (9.24) leads to

$$K = K_f = K_p \tag{9.25}$$

The numerical value of the equilibrium constant depends upon the form of the stoichiometric equation. Consider the decomposition of water vapour into hydrogen and oxygen as represented by the following equation:

$$2H_2O \rightarrow 2H_2 + O_2$$

The equilibrium constant K' for this reaction is calculated as

$$K' = \frac{a_{H_2}^2\, a_{O_2}}{a_{H_2O}^2}$$

The same reaction may be represented by the following equation:

$$H_2O \rightarrow H_2 + \frac{1}{2} O_2$$

The equilibrium constant K'' for this reaction is

$$K'' = \frac{a_{H_2} a_{O_2}^{1/2}}{a_{H_2O}}$$

Thus, it is seen that $K'' = (K')^{1/2}$. The form of the stoichiometric equation should be specified along with the numerical values of the equilibrium constant.

9.4 EQUILIBRIUM CONSTANT AND STANDARD FREE ENERGY CHANGE

The criterion of equilibrium, Eq. (9.15), can be written for the general chemical reaction represented by Eq. (9.11) as

$$(l\mu_L + m\mu_M) - (a\mu_A + b\mu_B) = 0 \tag{9.16}$$

The chemical potential of a component in the equilibrium state of the reaction mixture is related to its fugacity in that state as given below

$$\mu_i = RT \ln \bar{f}_i + C \tag{9.26}$$

Suppose that at the same temperature, but at another state, which may be called the standard state, the free energy of component i is μ_i^0. Then,

$$\mu_i^0 = RT \ln f_i^0 + C \tag{9.27}$$

C is a constant that depends only on temperature. Since the temperature in the standard state is the same as that in the equilibrium state, C can be eliminated from Eq. (9.26) using Eq. (9.27) as,

$$\mu_i = \mu_i^0 + RT \ln \frac{\bar{f}_i}{f_i^0} = \mu_i^0 + RT \ln a_i \tag{9.28}$$

where a_i is the activity of species i in the mixture. Express the chemical potential of all the components as in Eq. (9.28) and substitute in Eq. (9.16). The resulting expression is

$$(l\mu_L^0 + m\mu_M^0) - (a\mu_A^0 + b\mu_B^0) + RT \ln \frac{a_L^l a_M^m}{a_A^a a_B^b} = 0 \tag{9.29}$$

Equation (9.29) can be put into the following form:

$$(l\mu_L^0 + m\mu_M^0) - (a\mu_A^0 + b\mu_B^0) = -RT \ln \frac{a_L^l a_M^m}{a_A^a a_B^b} \tag{9.30}$$

That is,

$$\Sigma \mu_i^0 \nu_i = -RT \ln \frac{a_L^l a_M^m}{a_A^a a_B^b}$$

The left-hand side gives the standard free energy change ΔG^0, the free energy change accompanying the reaction when each of the reactants and the products is in its standard state. Using the definition of the equilibrium constant [Eq. (9.19)], the above equation is written as

$$\boxed{\Delta G^0 = -RT \ln K} \tag{9.31}$$

Thus the equilibrium constant is determined by the standard free energy change and the temperature.

The standard free energy change depends on the temperature, the specification of standard state for each component and the number of moles involved in the stoichiometric equation under consideration. The numerical values of the equilibrium constant will be of no significance unless accompanied by the specifications for these three factors. However, it is independent of pressure at equilibrium. The effect of the reaction stoichiometry on the equilibrium constant has already been discussed. The choice of standard state is being dealt with in the following section.

9.4.1 Choice of Standard State

Though the choice of standard state in Eq. (9.31) is arbitrary and is left to our convenience, certain conventions are followed in this choice. The choice of pure component standard state will be convenient in many situations, as this requires only the specification of temperature and pressure for defining the state completely. The temperature in the standard state is the same as that of the reaction. If the standard state chosen for a substance is a solution, the composition must also be specified.

For gases, as has been pointed out earlier, the standard state chosen is the pure component at the temperature of the reaction and at unit fugacity. Fugacity will be unity at 1 bar (or 1 atm) if the gas behaves as an ideal gas at this condition. For ideal gases, therefore, the standard state pressure approaches 1 bar and ΔG^0 can be easily evaluated at this pressure. By this choice, $K = K_f$ and Eq. (9.31) becomes

$$\Delta G^0 = -RT \ln K_f \tag{9.32}$$

The standard state of unit fugacity may not be convenient for reactions involving solids, liquids or solutions. By convention, the standard state chosen for solids and liquids is the pure solid or liquid as the case may be, at a pressure of 1 bar (or 1 atm), the temperature being the same as the temperature of the reaction.

9.4.2 Feasibility of a Reaction

From the values of standard free energy change, we can formulate an approximate criterion for the feasibility of a chemical reaction, which will be useful in preliminary exploratory work. It would be worthwhile to have some idea about whether or not the equilibrium is favourable, before we search for catalysts and other conditions necessary to cause the reaction. If the reaction is not thermodynamically feasible, there is no point in pursuing a long and expensive experimental investigation on improving the rate of reaction.

Any reaction starting with pure reactants uncontaminated with any of the products will have a tendency to proceed to some extent, though this may be infinitesimally small. It is the value of the equilibrium constant, which, in turn, is related to the standard free energy of the reaction that gives the necessary information on the thermodynamic possibility of the reaction. Even the decomposition of water vapour to hydrogen and oxygen will proceed to some extent under atmospheric temperature and pressure. From the value of the standard free energy change, ΔG^0, the equilibrium constant for the reaction

$$H_2O\,(g) \rightarrow H_2 + \frac{1}{2}O_2$$

at 298 K is found to be about 1 × 10^{-40}. This means that the extent of decomposition of water vapour is infinitesimally small at equilibrium and the reaction is not thermodynamically feasible

If ΔG^0 for a reaction is zero, then $K = 1$, the reaction proceeds to a considerable extent before equilibrium is reached. If ΔG^0 is negative, then $K > 1$, the reaction is quite favourable. But the situation becomes less favourable as ΔG^0 increases in the positive direction. It should be borne in mind that many reactions with positive values of ΔG^0 are certainly feasible from the standpoint of industrial operation. For example, the methanol synthesis reaction with $\Delta G^0 = 46{,}200$ kJ/kmol at 600 K is found to be feasible. This reaction is carried out at high pressure to overcome the unfavourable free energy change. In short, there is no well-defined demarcation to separate favourable and unfavourable reactions. The following guide may be useful as an approximate criterion for ascertaining the feasibility of chemical reactions:

$\Delta G^0 < 0$, the reaction is promising.

$0 < \Delta G^0 < 40{,}000$ kJ/kmol, the reaction may or may not be possible and needs further study.

$\Delta G^0 > 40{,}000$ kJ/kmol, the reaction is very unfavourable.

EXAMPLE 9.5 Device a series of hypothetical steps for carrying out the gas-phase reaction

$$a\text{A} + b\text{B} \rightarrow l\text{L} + m\text{M}$$

when the reactants and the products are at their standard state. Show that the free energy changes calculated for these series of steps add up to give the same result as the one provided by Eq. (9.31).

Solution The free energy change accompanying the process in which the reactants at their standard state are converted to products also at their standard state may be calculated via any convenient path.

Let us assume the following computational path for carrying out the reaction, which is represented in Fig. 9.2.

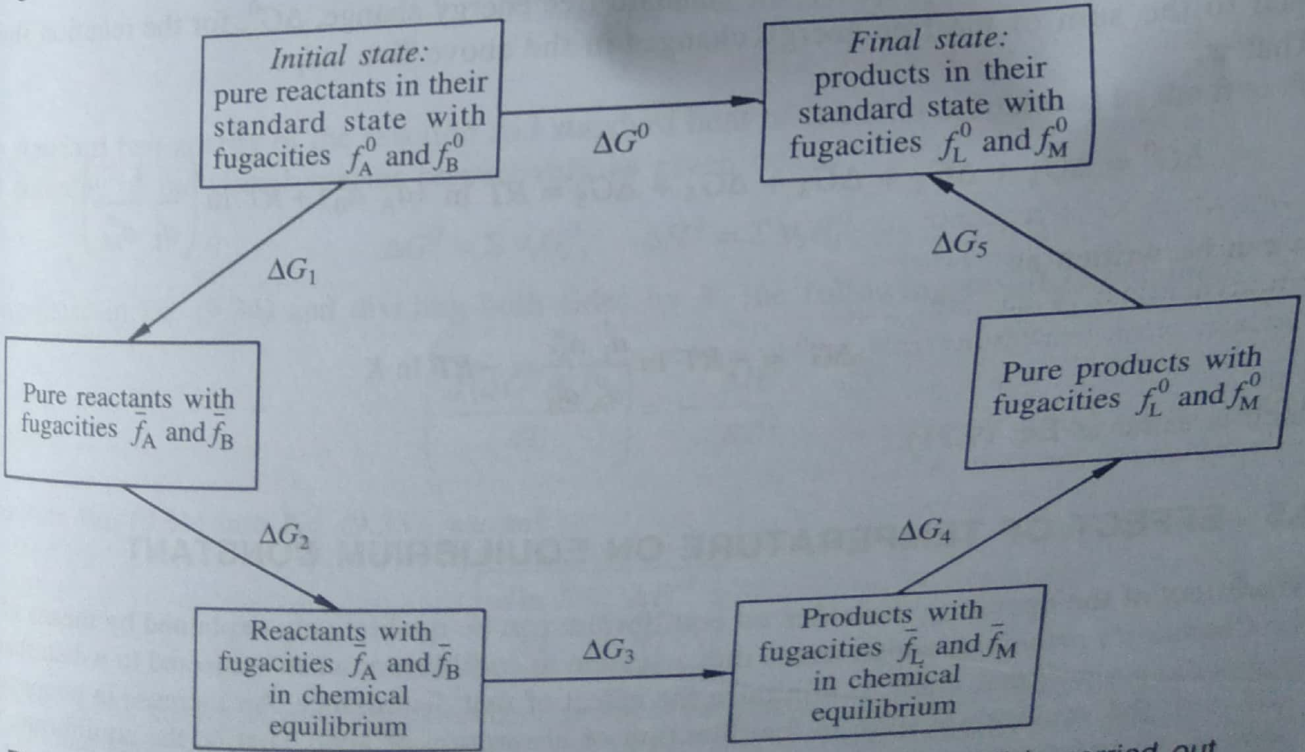

Fig. 9.2 Hypothetical stages through which the reaction in Example 9.5 is carried out.

Step 1: The reactants are initially in their pure form and are at their standard state of unit fugacity and at the temperature of the reaction. Then they are compressed to a fugacity of the reaction mixture at equilibrium. The free energy change for this process is ΔG_1.

$$\Delta G_1 = RT\left(a \ln \frac{\bar{f}_A}{f_A^0} + b \ln \frac{\bar{f}_B}{f_B^0}\right) = RT\,(\ln a_A^a + \ln a_B^b) = RT \ln (a_A^a a_B^b)$$

Step 2: The pure reactants are introduced to the reaction system through membranes permeable only to single species. Since the fugacities of the components before and after this step are the same, the free energy change ΔG_2 for this process is zero. $\Delta G_2 = 0$.

Step 3: The introduction of the reactants disturbs the state of equilibrium prevailing in the reaction system. To bring the system back to the equilibrium condition the forward reaction occurs at the given temperature and pressure. According to the criterion of equilibrium, this reaction proceeds without any change in the free energy of the system. Therefore, $\Delta G_3 = 0$.

Step 4: The product gases are separated by means of membranes into pure components at the reaction temperature and pressure. As in step 2, the free energy change in this process is zero. That is, $\Delta G_4 = 0$.

Step 5: The pure components with fugacities equal to $f_i = \bar{f}_i$ are expanded to standard state fugacities f_i^0. The free energy change for this step,

$$\Delta G_5 = RT\left(l \ln \frac{f_L^0}{\bar{f}_L} + m \ln \frac{f_M^0}{\bar{f}_M}\right) = RT\left(l \ln \frac{1}{a_L} + m \ln \frac{1}{a_M}\right) = RT \ln\left(\frac{1}{a_L^l\, a_M^m}\right)$$

As the free energy is a state property, the standard free energy change, ΔG^0, for the reaction should be equal to the sum of the free energy changes in the above five steps.

That is,

$$\Delta G^0 = \Delta G_1 + \Delta G_2 + \Delta G_3 + \Delta G_4 + \Delta G_5 = RT \ln\,(a_A^a\, a_B^b) + RT \ln\left(\frac{1}{a_L^l\, a_M^m}\right)$$

This can be written as

$$\Delta G^0 = -RT \ln \frac{a_L^l\, a_M^m}{a_A^a\, a_B^b} = -RT \ln K$$

which is same as Eq. (9.31).

9.5 EFFECT OF TEMPERATURE ON EQUILIBRIUM CONSTANT

The effect of the operating variables on equilibrium can be qualitatively explained by means of the *Le Chatelier's principle*, which states that a system at equilibrium when subjected to a disturbance, responds in a way that tends to minimise the effect of that disturbance. An increase in temperature will shift the equilibrium state in the direction of absorption of heat. That is, the equilibrium will shift in the endothermic direction if the temperature is raised, for then, energy is absorbed as heat. In a similar way, the equilibrium can be expected to shift in the exothermic direction if the temperature is lowered, for then the reduction in temperature is opposed. Thus, an endothermic reaction is favoured by an increase in temperature and an exothermic reaction is favoured by a decrease in temperature. Or stated in another way, increased temperature favours the reactants in exothermic reactions and the products in endothermic reactions.

The effect of temperature on equilibrium constant is quantitatively expressed by *van't Hoff equation*, which is developed below. The relationship of equilibrium constant to the standard free energy of reaction is given by Eq. (9.31). The standard state is identified by specifying a definite pressure (or fugacity), but the temperature is always the same as that of the reaction mixture at equilibrium. ΔG^0 and hence K will vary with this temperature.

For a single species the effect of temperature on its free energy is predicted by Gibbs–Helmholtz equation [Eq. (6.73)].

$$\left(\frac{\partial (G_i/T)}{\partial T}\right)_P = -\frac{H_i}{T^2}$$

For the substance in its standard state, Eq. (6.73) can be written as

$$\left(\frac{d(G_i^0/T)}{dT}\right) = -\frac{H_i^0}{T^2} \tag{9.33}$$

Note that the partial derivative notation is dropped from the above equation, as the standard free energy, by virtue of the definition of the standard state, depends on the equilibrium temperature, but not on the equilibrium pressure. Multiplying the above equation by ν_i and summing over all species present in the system, we get

$$\left(\frac{d\Sigma\, \nu_i G_i^0/T)}{dT}\right) = -\frac{\Sigma\, \nu_i H_i^0}{T^2} \tag{9.34}$$

The standard free energy of the reaction and standard heat of reaction are related to the free energy and enthalpy of individual species respectively as given below.

$$\Delta G^0 = \Sigma\, \nu_i G_i^0, \qquad \Delta H^0 = \Sigma\, \nu_i H_i^0$$

Using these in Eq. (9.34) and dividing both sides by R, the following result is obtained.

$$\left(\frac{d(\Delta G^0/RT)}{dT}\right) = -\frac{\Delta H^0}{RT^2} \tag{9.35}$$

Substitute Eq. (9.31) into Eq. (9.35), we get

$$\boxed{\frac{d\ln K}{dT} = \frac{\Delta H^0}{RT^2}} \tag{9.36}$$

Equation (9.36), known as *van't Hoff equation,* predicts the effect of temperature on the equilibrium constant and hence on the equilibrium yield. ΔH^0 in Eq. (9.36) is the standard heat of reaction. It is apparent that if ΔH^0 is negative, i.e. if the reaction is exothermic, the equilibrium constant decreases as the reaction temperature increases. Alternatively, for an endothermic reaction, the equilibrium constant will increase with increase in temperature.

If ΔH^0, the standard heat of reaction, is constant, Eq. (9.36) on integration yields

$$\ln \frac{K}{K_1} = -\frac{\Delta H^0}{R}\left(\frac{1}{T} - \frac{1}{T_1}\right) \tag{9.37}$$

K and K_1 are the equilibrium constant values at temperatures T and T_1 respectively. Equation (9.37) may be used to evaluate the equilibrium constant with good results over small temperature ranges. The equation is exact if ΔH^0 is independent of temperature. A reasonably accurate method of interpolation or extrapolation of equilibrium constant is provided by plotting ln K versus reciprocal of temperature, which leads to a straight line according to Eq. (9.37).

The variation of the standard heat of reaction with temperature may be taken into account if the molal heat capacities of the various species taking part in the reaction are known as functions of temperature. Suppose that the specific heats at constant pressure are expressed as a power function in T.

$$C_P = \alpha + \beta T + \gamma T^2 \tag{9.38}$$

Then the effect of temperature on the standard heat of reaction may be developed as follows: Since heat of reaction is the enthalpy change between the given initial and final states, it may be evaluated by devising any convenient path between these terminal states for which the enthalpy changes are readily available. Assume that the standard heat at temperature T_1, $\Delta H^0_{T_1}$, is known and it is desired to calculate the standard heat at temperature T.

The actual reaction occurring at temperature T for which the heat of reaction is ΔH^0_T may be treated as occurring along the three paths as depicted in Fig. 9.3.

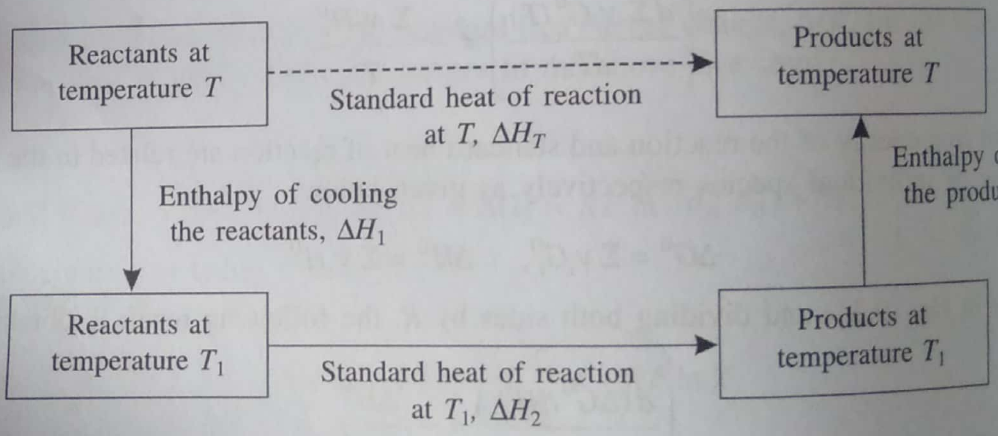

Fig. 9.3 Method of estimating the standard heat of reaction at temperature T given the standard heat of reaction at T_1.

1. The reactants are cooled from temperature T to T_1. The enthalpy change for this step is

$$\Delta H_1 = \sum_{\text{Reactants}} \int_{T}^{T_1} n_i\, C_{P,i}\, dT = \sum_{\text{Reactants}} \int_{T_1}^{T} \nu_i\, C_{P,i}\, dT \tag{9.39}$$

2. The reaction is allowed to occur at temperature T_1. The enthalpy change is

$$\Delta H_2 = \Delta H^0_{T_1} \tag{9.40}$$

3. The temperature of the products is raised from T_1 to T in this step. The enthalpy change is

$$\Delta H_3 = \sum_{\text{Products}} \int_{T_1}^{T} n_i C_{P,i}\, dT = \sum_{\text{Products}} \int_{T_1}^{T} \nu_i C_{P,i}\, dT \tag{9.41}$$

The standard heat of reaction at temperature T, is obtained by adding the preceding three equations.

$$\Delta H_T^0 = \Delta H_1 + \Delta H_2 + \Delta H_3 = \sum_{\text{Reactants}} \int_{T_1}^{T} \nu_i C_{P,i}\, dT + \Delta H_{T_1}^0 + \sum_{\text{Products}} \int_{T_1}^{T} \nu_i C_{P,i}\, dT$$

The above result can be written as

$$\Delta H_T^0 = \Delta H_{T_1}^0 + \int_{T_1}^{T} \left(\sum_i \nu_i C_{P,i} \right) dT \tag{9.42}$$

The summation in the above equation is over all the species taking part in the reaction. Using Eq. (9.38) in Eq. (9.42), we can write it as

$$\Delta H_T^0 = \Delta H_{T_1}^0 + \int_{T_1}^{T} \Delta C_P\, dT \tag{9.43}$$

where

$$\Delta C_P = \Delta\alpha + \Delta\beta T + \Delta\gamma T^2 \tag{9.44}$$

and

$$\Delta\alpha = \sum \nu_i \alpha_i, \quad \Delta\beta = \sum \nu_i \beta_i, \quad \Delta\gamma = \sum \nu_i \gamma_i \tag{9.45}$$

Equation (9.43) may be expanded to yield the following result.

$$\Delta H_T^0 = \Delta H_{T_1}^0 + \Delta\alpha (T - T_1) + \frac{1}{2}\Delta\beta (T^2 - T_1^2) + \frac{1}{3}\Delta\gamma (T^3 - T_1^3)$$

The constants appearing in the above equation can be grouped together to a single constant $\Delta H'$, so that we have

$$\Delta H_T^0 = \Delta H' + \Delta\alpha T + \frac{\Delta\beta}{2} T^2 + \frac{\Delta\gamma}{3} T^3 \tag{9.46}$$

The constant $\Delta H'$ in the above equation can be evaluated if the heat of reaction at a single temperature is known. Equation (9.46) can then be used for the evaluation of the heat of reaction at any temperature T.

Substitute Eq. (9.46) into Eq. (9.36) and integrate the resulting expression. The result is

$$\ln K = -\frac{\Delta H'}{RT} + \frac{\Delta\alpha}{R} \ln T + \frac{\Delta\beta}{2R} T + \frac{\Delta\gamma}{6R} T^2 + A \tag{9.47}$$

A in Eq. (9.47) is a constant of integration, which may be evaluated from the knowledge of the equilibrium constant at one temperature. Equation (9.31) relates the equilibrium constant to the standard free energy change. Using this relationship, we get

$$\Delta G^0 = \Delta H' - \Delta\alpha T \ln T - \frac{\Delta\beta}{2} T^2 - \frac{\Delta\gamma}{6} T^3 - ART \tag{9.48}$$

9.5.1 Evaluation of Equilibrium Constants

Equation (9.47) can be used for the evaluation of the equilibrium constant, provided, we know the dependence of heat capacities on temperature and we also have enough information for the evaluation of the constants $\Delta H'$ and A. Assuming that the heat capacity data are available, the general methods used for the evaluation of the constants $\Delta H'$ and A are listed below.

Method 1. K may be calculated from the experimentally measured composition of the equilibrium mixture using Eq. (9.19). If K values are thus known at two different temperatures, they may be substituted into Eq. (9.47). The resulting two equations are solved for the constants $\Delta H'$ and A.

Method 2. Standard heat of reaction at one temperature and one value for the equilibrium constant that is determined by direct experimental measurements are available. The former is used in Eq. (9.46) for the evaluation of the constant $\Delta H'$ and the latter in Eq. (9.47) for evaluating the constant A.

Method 3. This method involves no direct experimental measurements for the equilibrium constant and therefore this is the most convenient and most widely used method. The method makes use of thermal data only, usually in the form of standard heat of reaction ΔH^0, and a standard free energy change of reaction ΔG^0. Then the constants $\Delta H'$ and A are evaluated using Eq. (9.46) and Eq. (9.48) respectively.

ΔH^0 for a reaction may be evaluated from the standard heat of formation, ΔH_f^0, that are tabulated for most of the compounds. The standard free energy of a reaction can be estimated from the values of standard free energy of formation, ΔG_f^0 of the various species participating in the reaction and their respective stoichiometric numbers as

$$\Delta G^0 = \Sigma\, \nu_i\, \Delta G_{i,f}^0 \tag{9.49}$$

Noting that the stoichiometric numbers are positive for products and negative for the reactants, the above may well be written as

$$\Delta G^0 = \sum_{\text{Products}} |\nu_i|\, \Delta G_{i,f}^0 - \sum_{\text{Reactants}} |\nu_i|\, \Delta G_{i,f}^0 \tag{9.50}$$

That is, the standard free energy of a reaction is the algebraic sum of the free energies of formation of the products minus the algebraic sum of the free energies of formation of the reactants. When an element enters into a reaction, its standard free energy of formation may be taken to be zero.

9.5.2 Giauque Functions

Data for calculation of standard free energy of reactions are sometimes tabulated as *Giauque functions*. These are Gibbs free energy functions that vary very slowly with temperature. Two such functions are in general use—the first is referred to 0 K and the second referred to 298 K. These are written as

$$\phi_0 = \frac{G_T^0 - H_0^0}{T}, \qquad \phi_{298} = \frac{G_T^0 - H_{298}^0}{T} \tag{9.51}$$

where G_T^0, H_T^0, H_{298}^0 are respectively the free energy in the standard state at temperature T, the enthalpy in the standard state at T and the enthalpy in the standard state at 298 K. Because only standard state properties are involved, these functions depend only on temperature. This temperature dependence is found to be very weak which makes these functions suitable for tabular interpolation. Using the definition of free energy, we can show that

$$\begin{aligned} \phi_0 &= \frac{H_T^0 - H_0^0}{T} - S_T^0 \\ \phi_T &= \frac{H_T^0 - H_{298}^0}{T} - S_T^0 \end{aligned} \tag{9.52}$$

From Eq. (9.51) we see that

$$\begin{aligned} \phi_{298} + \frac{H_{298}^0}{T} &= \phi_0 + \frac{H_0^0}{T} \\ \phi_{298} &= \phi_0 - \left(\frac{H_{298}^0 - H_0^0}{T} \right) \end{aligned} \tag{9.53}$$

The difference in enthalpy values, the terms in brackets in Eq. (9.53), needed for applying Eq. (9.53) also are listed in tables along with ϕ_0. The standard free energy change of a reaction may be calculated from the Gibbs free energy functions. Equation (9.51) can be rearranged as

$$\frac{G_T^0}{T} = \phi_0 + \frac{H_0^0}{T} \tag{9.54}$$

$$\frac{G_T^0}{T} = \phi_{298} + \frac{H_{298}^0}{T} \tag{9.55}$$

The Gibbs free energy at the standard state for each of the species taking part in the reaction as given by Eq. (9.54) or Eq. (9.55) multiplied by the respective stoichiometric numbers add together to give the standard free energy of the reaction.

$$\frac{\Delta G_T^0}{T} = \frac{\Sigma \nu_i G_{T,i}^0}{T} = \Sigma \nu_i \phi_{0,i} + \frac{\Sigma \nu_i H_{0,i}^0}{T} = \Sigma \nu_i \phi_{298,i} + \frac{\Sigma \nu_i \Delta H_{298,i}^0}{T}$$

Noting that the enthalpy of a substance in its standard state, H_i^0, is equal to the standard enthalpy $\Delta H_{f,i}^0$, we get the following useful results:

$$\frac{\Delta G_T^0}{T} = \Sigma \nu_i \phi_{0,i} + \frac{\Sigma \nu_i \Delta H_{f,0,i}^0}{T} \tag{9.56}$$

$$\frac{\Delta G_T^0}{T} = \Sigma \nu_i \phi_{298,\,i} + \frac{\Sigma \nu_i \Delta H_{f,\,298,\,i}^0}{T} \tag{9.57}$$

Note that the enthalpy of a compound in the standard state, H_i^0, is the same as its standard enthalpy of formation, $\Delta H_{f,i}^0$. The standard free energy of a reaction determined using Eqs. (9.56) or (9.57) may be used in Eq. (9.31) to calculate the equilibrium constant.

EXAMPLE 9.6 Calculate the equilibrium constant at 298 K of the reaction

$$N_2O_4\,(g) \rightarrow 2NO_2\,(g)$$

given that the standard free energies of formation at 298 K are 97,540 J/mol for N_2O_4 and 51,310 J/mol for NO_2.

Solution Using Eq. (9.50) for the dissociation of N_2O_4,

$$\Delta G^0 = 2 \times 51{,}310 - 97{,}540 = 5080 \text{ J/mol}$$

From Eq. (9.31),

$$\Delta G^0 = -RT \ln K$$

which gives

$$\ln K = -\frac{\Delta G^0}{RT} = -\frac{5080}{8.314 \times 298} = -2.0504$$

Therefore, $K = 0.1287$.

EXAMPLE 9.7 The standard heat of formation and standard free energy of formation of ammonia at 298 K are –46,100 J/mol and –16,500 J/mol respectively. Calculate the equilibrium constant for the reaction

$$N_2\,(g) + 3H_2\,(g) \rightarrow 2NH_3\,(g)$$

at 500 K assuming that the standard heat of reaction is constant in the temperature range 298 to 500 K.

Solution The standard free energy of reaction is estimated from Eq. (9.50).

$$\Delta G^0 = \sum_{\text{Products}} |\nu_i|\,\Delta G_{i,f}^0 - \sum_{\text{Reactants}} |\nu_i|\,\Delta G_{i,f}^0$$

The second summation yields zero as the free energy of formation of the elements are zero.

$$\Delta G^0 = \sum_{\text{Products}} |\nu_i|\,\Delta G_{i,f}^0 = 2 \times -16{,}500 = -33{,}000 \text{ J/mol}$$

Using Eq. (9.31),

$$\ln K = -\frac{\Delta G^0}{RT} = \frac{33{,}000}{8.314 \times 298} = 13.3195$$

Therefore,

$$K \text{ at } 298 \text{ K} = 6.0895 \times 10^5$$

The standard heat of reaction at 298 K = 2 × – 46,100 = – 92,200 J/mol. This is assumed constant within the temperature range involved. Now use Eq. (9.37) to evaluate the equilibrium constant.

$$\ln \frac{K}{K_1} = -\frac{\Delta H^0}{R}\left(\frac{1}{T} - \frac{1}{T_1}\right)$$

$$\ln \frac{K}{6.0895 \times 10^5} = \frac{92{,}200}{8.314}\left(\frac{1}{500} - \frac{1}{298}\right) = -15.0344$$

Therefore, the equilibrium constant at 500 K, $K = 0.18$

***EXAMPLE* 9.8** *n*-Butane is isomerised to *i*-butane by the action of catalyst at moderate temperatures. It is found that the equilibrium is attained at the following compositions.

Temperature, K	Mol %, *n*-butane
317	31.00
391	43.00

Assuming that activities are equal to the mole fractions, calculate the standard free energy of the reaction at 317 K and 391 K and average value of heat of reaction over this temperature range.

Solution Since activities are equal to mole fractions, $K = y_{ib}/y_{nb}$, where y_{ib} is the mole fraction of *i*-butane and y_{nb} the mole fraction of *n*-butane in the equilibrium mixture. Therefore,

$$\text{At 317 K,} \qquad K = \frac{0.69}{0.31} = 2.2258$$

$$\text{At 391 K,} \qquad K = \frac{0.57}{0.43} = 1.3255$$

Equation (9.31) gives

$$\Delta G^0 = -RT \ln K$$

$$\Delta G^0_{317} = -8.314 \times 317 \ln 2.2258 = -2108.74 \text{ J/mol}$$

$$\Delta G^0_{391} = -8.314 \times 391 \ln 1.3255 = -916.03 \text{ J/mol}$$

Assuming that the heat of reaction is independent of temperature we can use Eq. (9.37) for calculating it.

$$\ln \frac{K_2}{K_1} = -\frac{\Delta H^0}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln \frac{2.2258}{1.3255} = -\frac{\Delta H^0}{8.314}\left(\frac{1}{317} - \frac{1}{391}\right)$$

Therefore, $\Delta H^0 = -7218.02$ J/mol.

EXAMPLE 9.9 Estimate the standard free energy change and equilibrium constant at 700 K for the reaction

$$N_2\,(g) + 3H_2\,(g) \rightarrow 2NH_3\,(g)$$

given that the standard heat of formation and standard free energy of formation of ammonia at 298 K to be – 46,100 J/mol and –16,500 J/mol respectively. The specific heat (J/mol K) data are given below as function of temperature (K):

$$C_P = 27.27 + 4.93 \times 10^{-3}T \quad \text{for } N_2$$

$$C_P = 27.01 + 3.51 \times 10^{-3}T \quad \text{for } H_2$$

$$C_P = 29.75 + 25.11 \times 10^{-3}T \quad \text{for } NH_3$$

Solution The standard heat of reaction and standard free energy of reaction at 298 K were estimated in Example 9.7.

$$\Delta H^0 = -92{,}200 \text{ J/mol}; \ \Delta G^0 = -33{,}000 \text{ J/mol}$$

Also,

$$\Delta\alpha = 2 \times 29.75 - 27.27 - 3 \times 27.01 = -48.8$$

$$\Delta\beta = (2 \times 25.11 - 4.93 - 3 \times 3.51) \times 10^{-3} = 34.76 \times 10^{-3}$$

Equation (9.46) gives

$$-92{,}200 = \Delta H' - 48.8T + 17.38 \times 10^{-3}T^2$$

$$= \Delta H' - 48.8 \times 298 + 17.38 \times 10^{-3} \times (298)^2$$

$$= \Delta H' - 1.3 \times 10^4$$

Therefore, $\Delta H' = -7.9201 \times 10^4$. Equation (9.48) gives

$$-33{,}000 = \Delta H' - \Delta\alpha T \ln T - \frac{\Delta\beta}{2}T^2 - ART$$

$$= -7.9201 \times 10^4 + 48.8 \times 298 \times \ln 298 - 17.38 \times 10^{-3} \times 298^2 - A \times 8.314 \times 298$$

$$= 2105 - 2477.57\,A$$

Therefore, $A = 14.169$. Substitute $\Delta H'$ and A into Eq. (9.47) and Eq. (9.48), we get

$$\ln K = \frac{79{,}201}{RT} - \frac{48.8}{R}\ln T + \frac{17.38 \times 10^{-3}}{R}T + 14.169 \tag{9.58}$$

$$\Delta G^0 = -79{,}201 + 48.8\,T \ln T - 17.38 \times 10^{-3}T^2 - 14.169RT \tag{9.59}$$

Put $T = 700$ K in the above equations. Equation (9.58) gives $K = 1 \times 10^{-4}$; Eq. (9.59) gives $\Delta G^0 = 53{,}607$ J/mol.

EXAMPLE 9.10 Evaluate the equilibrium constant at 600 K for the reaction

$$CO\,(g) + 2H_2\,(g) \rightarrow CH_3OH\,(g)$$

given that the Gibbs free energy function

$$\phi_{298} = \frac{G_T^0 - H_{298}^0}{T}$$

for CO, H_2 and methanol at 600 K are respectively −203.81, −136.39 and −249.83 J/mol K. The heats of formation at 298 K of CO (g) and CH_3OH (g) at 298 K are −110,500 J/mol and −200,700 J/mol.

Solution The standard free energy of formation at 600 K is evaluated by means of Eq. (9.57).

$$\frac{\Delta G_T^0}{T} = \Sigma \nu_i \phi_{298,\,i} + \frac{\Sigma \nu_i \Delta H_{f,\,298,\,i}^0}{T}$$

$$\frac{\Delta G_{600}^0}{600} = 1(-249.83) - 1(-203.81) - 2(-136.39) + \frac{1}{600}\,[1(-200{,}700) - 1(-110{,}500)]$$

$$= 76.4267$$

From Eq. (9.31),

$$-R \ln K = \frac{\Delta G^0}{T}$$

$$\ln K = -\frac{76.4267}{8.314} = -9.1925$$

$$K = 1.018 \times 10^{-4}$$

EXAMPLE **9.11** Calculate the equilibrium constant for the reaction

$$N_2\,(g) + 3H_2\,(g) \rightarrow 2NH_3\,(g)$$

at 500 K, given that the free energy function

$$\phi_0 = \frac{G_T^0 - H_0^0}{T}$$

at 500 K for nitrogen, hydrogen and ammonia are respectively −177.5, −116.9 and −176.9 J/mol K. The function $(H_{298}^0 - H_0^0)$ for nitrogen, hydrogen and ammonia are respectively 8669, 8468 and 9920 J/mol. The free energy of formation of ammonia at 298 K is −46,100 J/mol.

Solution Equation (9.53) gives

$$\Sigma \nu_i \phi_{298,\,i} = \Sigma \nu_i\, \phi_{0,\,i} - \Sigma\, \nu_i \left(\frac{H_{298,\,i}^0 - H_{0,\,i}^0}{T} \right)$$

$$= 2(-176.9) - 1(-177.5) - 3(-116.9) - (2 \times 9920 - 1 \times 8669 - 3 \times 8468)/500$$

$$= 174.4 + 28.466 = 202.87 \text{ J/mol K}$$

Equation (9.57) can be used to evaluate ΔG^0_{500}.

$$\frac{\Delta G^0_T}{T} = \Sigma \nu_i \phi_{298,\,i} + \frac{\Sigma \nu_i \Delta H^0_{f,\,298,\,i}}{T}$$

$$= 202.87 + 2(-46{,}100)/500 = 18.47 \text{ J/mol K}$$

Therefore,

$$\ln K = -\frac{18.47}{R} = -2.2215$$

$$K = 0.1084$$

9.6 EFFECT OF PRESSURE ON EQUILIBRIUM

9.6.1 Effect of Pressure on Equilibrium Constant

We have shown that the equilibrium constant K is related to the standard free energy change by the equation, $\Delta G^0 = -RT \ln K$, where K is defined by Eq. (9.19) as

$$K = \frac{a_{\rm L}^l\, a_{\rm M}^m}{a_{\rm A}^a\, a_{\rm B}^b} = \Pi a_i^{\nu_i}$$

The equilibrium constant defined above is independent of the pressure. By Eq. (9.31), the equilibrium constant is known if the standard free energy of the reaction and the reaction temperature are known. The standard free energy of a reaction is determined by the free energies of the substances in their standard states. The standard states are defined by specifying a pressure and are in no way affected by the reaction pressure. That is, the standard free energy of a reaction, and hence, the equilibrium constant are not affected by changes in the equilibrium pressure.

9.6.2 Effect of Pressure on Equilibrium Composition

Though the equilibrium constant is unaffected by pressure, it does affect the equilibrium composition in gas-phase reactions. This effect is explained qualitatively by Le Chatelier's principle. Consider for example, the equilibrium in the gas-phase reaction A → 2B. When pressure is applied to this system, it responds in such a way as to minimise the effect of the increase in pressure. This is achieved by decreasing the number of moles in the system, which in turn is achieved by the reaction A ← 2B. Thus, increase in pressure decreases the number of B molecules and increases the number of A molecules. By the same reasoning we can deduce that in the case of the reaction $N_2 + 3H_2 \rightarrow 2NH_3$ formation of ammonia will be favoured by an increase in pressure as there is a reduction in the number of moles due to this reaction. It should be remembered that when the composition of the system changes in this manner in response to increase or decrease in pressure, it does so without changing the equilibrium constant.

Except at very high pressures, properties of solids, liquids or solutions are not affected appreciably by pressure. Therefore, the equilibrium concentrations in reactions involving solids, liquids or solutions are not affected significantly by changes in pressure.

To predict the effect of pressure quantitatively, the relationship between equilibrium constant and equilibrium composition must be established. Equation (9.19) defines the equilibrium constant as a function of activities of the species in the reacting system. The activities of the components are affected by changes in pressure, temperature and composition. As K is independent of pressure, and activities are not, it requires that the activities of the components change with pressure in such a way that the complex function of activities, which we have defined as equilibrium constant, remains unaltered. The equilibrium constant written in terms of activities, K, and the equilibrium constant K_f, which is written in terms of the fugacities of the components were shown to be equal for gaseous systems employing ideal-gas standard state through Eq. (9.21).

$$K = \Pi(\bar{f}_i)^{\nu_i} = K_f$$

Fugacities can be written as product of fugacity coefficient and partial pressure of the component in the mixture.

$$\bar{f}_i = \phi_i \, (y_i \, P) \tag{9.60}$$

Rewrite Eq. (9.21) using Eq. (9.60).

$$K = K_f = \Pi \, (\phi_i \, y_i \, P)^{\nu_i}$$

The above equation can be put into the following forms:

$$K = (\Pi \phi_i^{\nu_i}) \, (\Pi \, y_i^{\nu_i}) \, P^{\nu} \tag{9.61}$$

In the above equation, $\nu = \sum \nu_i = l + m - a - b$, for the general reaction given by Eq. (9.11) and P is the reaction pressure.

Let $K_\phi = \Pi \phi_i^{\nu_i}$ and $K_y = \Pi \, y_i^{\nu_i}$. Then Eq. (9.61) gets modified as

$$K = K_\phi K_y P^{\nu} \tag{9.62}$$

K_y in Eq. (9.62) may be treated as an equilibrium constant in terms of composition. Equation (9.62) provides the necessary expression relating the equilibrium constant and the equilibrium composition. If the reaction mixture behaves as an ideal gas, K_ϕ is unity and Eq. (9.62) reduces to

$$K = K_y P^{\nu} \tag{9.63}$$

Since, K is independent of pressure, the variation in the P^{ν} term in the above equations must be balanced by a corresponding change in the value for K_y. The change in K_y means the change in the equilibrium compositions. If there is a decrease in the number of moles during the reaction as in the case of ammonia synthesis reaction, ν will be negative. An increase in pressure in this case will decrease P^{ν} and as a result, K_y and the equilibrium yield would increase. On the other hand, if the reaction results in an increase in the number of moles, ν will be positive and the equilibrium yield would decrease with increase in pressure.

The above observations are in agreement with the Le Chatelier's principle. In addition, Eq. (9.62) can be used to explain the effect of pressure on reactions where ν is zero, which cannot be explained by Le Chatelier's principle. One would expect pressure to have no effect on reaction such as the water-gas shift reaction

$$CO\,(g) + H_2O\,(g) \rightarrow CO_2\,(g) + H_2\,(g)$$

because there is no change in the number of moles during the reaction. The effect of pressure on the equilibrium composition in this case can be explained by the effect of pressure on K_ϕ. K_ϕ measures the deviation from ideal-gas behaviour, and its value may change with change in pressure. If K_ϕ decreases in any reaction, then K_y and the equilibrium yield would increase even when ν is zero. The effect of pressure on K_ϕ can be calculated from fugacity coefficients. It is seen that when the compressibility of the products is greater than the compressibility of the reactants, K_ϕ decreases with pressure, thereby increasing the conversion.

EXAMPLE 9.12 Industrial grade methanol can be produced according to the reaction

$$CO(g) + 2H_2(g) \Leftrightarrow CH_3OH(g)$$

For this reaction, $\Delta G^0_{400} = -1.3484$ kJ. If an equimolar mixture of CO and H_2 is fed to a reactor maintained at 400 K and 10 bar, determine the fraction of CO that is converted into CH_3OH at equilibrium. Assume that the reaction mixture behaves like an ideal gas.

Solution Basis: 1 mol CO and 1 mol hydrogen in the reaction mixture.

Let ε be the extent of reaction. The mole fractions of the components under equilibrium are:

$$y_{CO}\text{: } 0.5,\ y_{H_2}\text{: } (1 - 2\varepsilon)/2(1 - \varepsilon),\ y_{CH_3OH}\text{: } \varepsilon/2(1 - \varepsilon)$$

$$K_y = \frac{y_{CH_3OH}}{y_{CO}y^2_{H_2}} = \frac{4\varepsilon(1 - \varepsilon)}{(1 - 2\varepsilon)^2}$$

By Eq. (9.63), $K = K_yP^\nu$.

Here, $\nu = -2$. Thus, $K = K_yP^{-2}$. Also,

$$K = \exp\left[-\frac{\Delta G^0}{RT}\right] = \exp\left(\frac{1348.4}{8.314 \times 400}\right) = 1.5$$

so that now we have

$$K_y = \frac{4\varepsilon(1-\varepsilon)}{(1-2\varepsilon)^2} = 1.5 \times P^2 = 1.5 \times 10^2 = 150$$

Solving this, we get $\varepsilon = 0.4593$ and 0.5407. The extent of reaction cannot be greater than 0.5.

Therefore, $\varepsilon = 0.4593$. The fraction of CO converted is $z = \dfrac{|\nu_i|\varepsilon}{n_{i,0}} = 0.4593$.

EXAMPLE 9.13 A compound M polymerises in the gas phase at low pressure to M_n, where $n > 1$.

(a) Show that the mole fraction of the polymer at equilibrium increases with increase in pressure at constant temperature

(b) The mole fraction of the polymer in the equilibrium mixture at 300 K is 0.15 at 1 bar and 0.367 at 2 bar. Find the value of n.

Solution (a) The reaction is $nM \rightarrow M_n$. There is a decrease in the number of moles during the forward reaction. The increase in pressure therefore favours the polymerisation reaction and as a result, the mole fraction of the polymer at equilibrium increases with pressure.

(b) From Eq. (9.62), $K_y = (K/K_\phi)P^{-\nu}$. Assuming ideal gas behaviour, $K_y = KP^{-\nu}$. Here, $\nu = 1 - n$ and at 1 bar,

$$K_y = \text{mole fraction of } M_n/(\text{mole fraction of } M)^n = 0.15/0.85^n$$

$$K_y \text{ at 2 bar} = 0.367/0.633^n$$

Therefore,

$$0.15/0.85^n = KP^{n-1} = K$$

$$0.367/0.633^n = KP^{n-1} = K \times 2^{n-1}$$

Dividing the second equation by the first,

$$2^{n-1} = \frac{0.367}{0.15} \times \left(\frac{0.85}{0.633}\right)^n = 2.4467 \times 1.3428^n$$

On solving, we get $n = 4$.

EXAMPLE 9.14 In the synthesis of ammonia, stoichiometric amounts of nitrogen and hydrogen are sent to a reactor where the following reaction occurs

$$N_2 + 3H_2 \rightarrow 2NH_3$$

The equilibrium constant for the reaction at 675 K may be taken equal to 2×10^{-4}.

(a) Determine the per cent conversion of nitrogen to ammonia at 675 K and 20 bar.

(b) What would be the conversion at 675 K and 200 bar?

Solution Basis: 1 mol nitrogen and 3 mol hydrogen are in the reactant mixture. Let ε be the extent of reaction. Then the number of moles of various species at equilibrium are calculated using Eq. (9.3) as $n_i = n_{i0} + \nu_i\varepsilon$. Thus the moles of nitrogen, hydrogen and ammonia at equilibrium are, respectively, $1 - \varepsilon$, $3 - 3\varepsilon$ and 2ε. Total moles at equilibrium is $= 4 - 2\varepsilon$. The mole fractions of nitrogen, hydrogen and ammonia are, respectively,

$$\frac{1-\varepsilon}{4-2\varepsilon}, \quad \frac{3(1-\varepsilon)}{4-2\varepsilon}, \quad \frac{2\varepsilon}{4-2\varepsilon}$$

The sum of stoichiometric numbers, $\nu = 2 - 1 - 3 = -2$. Equation (9.62) gives

$$K_y = (K/K_\phi)P^{-\nu} = KP^2$$

In arriving at this result ideal behaviour is assumed, so that $K_\phi = 1$.

Thus we have the necessary relation connecting the equilibrium composition and pressure.

$$\frac{[2\varepsilon/(4-2\varepsilon)]^2}{[(1-\varepsilon)/(4-2\varepsilon)]\,[3(1-\varepsilon)/(4-2\varepsilon)]^3} = 2 \times 10^{-4}\, P^2$$

That is,

$$\frac{4\varepsilon^2(4-2\varepsilon)^2}{27(1-\varepsilon)^4} = 2 \times 10^{-4}\, P^2$$

$$\frac{\varepsilon(4-2\varepsilon)}{(1-\varepsilon)^2} = 3.6742 \times 10^{-2}\, P \tag{9.64}$$

(a) When $P = 20$ bar,

$$\frac{\varepsilon(4-2\varepsilon)}{(1-\varepsilon)^2} = 0.73485$$

$$2.73485\varepsilon^2 - 5.4697\varepsilon + 0.73485 = 0$$

Solving this, $\varepsilon = 0.1448$. Fractional conversion of nitrogen,

$$z = \frac{|\nu_i|\,\varepsilon}{n_{i0}} = \varepsilon = 0.1448$$

That is, conversion of nitrogen = 14.48%.

(b) When $P = 200$ bar,

$$\frac{\varepsilon(4-2\varepsilon)}{(1-\varepsilon)^2} = 7.3485$$

$$9.3485\varepsilon^2 - 18.697\varepsilon + 7.3485 = 0$$

Therefore, $\varepsilon = 0.5375$. So, conversion of nitrogen = 53.75%.

We see that the increase in pressure favours the formation of ammonia as this reaction is accompanied by a decrease in the number of moles.

9.7 OTHER FACTORS AFFECTING EQUILIBRIUM CONVERSION

The reaction conditions that influence the extent of reaction under equilibrium are the temperature, pressure, presence of inert materials, presence of excess of reactants and presence of the products of the reaction in the initial mixture. The effects of temperature and pressure on the equilibrium composition have already been discussed in the previous sections. Here, we discuss the effects of other factors.

Rearrange Eq. (9.62) to the following form.

$$K_y = \frac{K}{K_\phi} P^{-\nu} \tag{9.65}$$

K_y in Eq. (9.65) may be written as

$$K_y = \Pi\left(\frac{n_i}{N}\right)^{\nu_i} \tag{9.66}$$

where i is any species taking part in the reaction and n_i is the number of moles of i. N represents the total number of moles in the reaction mixture, and if any inert material is present in the system, N includes n_I moles of inert material also.

$$N = \Sigma n_i + n_I$$

Combining Eqs. (9.65) and (9.66) we obtain

$$\Pi\left(\frac{n_i}{N}\right)^{\nu_i} = N^{-\nu}\,\Pi n_i^{\nu_i} = \frac{K}{K_\phi} P^{-\nu}$$

or

$$\Pi n_i^{\nu_i} = \frac{K}{K_\phi}\left(\frac{N}{P}\right)^{\nu} \tag{9.67}$$

Any changes in the reaction conditions that results in an increase in the right-hand side of Eq. (9.67) leads to an improved conversion.

9.7.1 Presence of Inert Materials

Diluting the reaction mixture with an inert material will increase N in Eq. (9.67). This will result in an increased conversion, if ν is positive. That is, if the reaction proceeds with an increase in the number of moles, presence of inerts in the system will increase the equilibrium yield. The effect, as we see, is just the opposite to the effect of increased pressure in such reactions. The presence of inerts will decrease conversion if the reaction is accompanied by a decrease in the number of moles; and the inerts present in the system will have no influence on the degree of completion if ν is zero, that is, if there is no change in the number of moles during a reaction.

EXAMPLE **9.15** A mixture of 1 mol CO, and 1 mol water vapour is undergoing the water-gas shift reaction at a temperature of 1100 K and a pressure of 1 bar.

$$CO\,(g) + H_2O\,(g) \rightarrow CO_2\,(g) + H_2\,(g)$$

The equilibrium constant for the reaction is $K = 1$. Assume that the gas mixture behaves as ideal gas. Calculate

(a) The fractional dissociation of steam

(b) The fractional dissociation of steam if the reactant stream is diluted with 2 mol nitrogen.

Solution The mole fractions of the species at equilibrium are related to the equilibrium constant which is given by

$$K_y = \frac{K}{K_\phi} P^{-\nu} \tag{9.65}$$

where ν is the sum of stoichiometric numbers. Here, $\nu = 1 + 1 - 1 - 1 = 0$. As the gas mixture behaves as an ideal gas, $K_\phi = 1$. Equation (9.65) gives $K_y = K = 1$. K_y is related to the mole fractions of various components as $K_y = \Pi\, y_i^{\nu_i}$. Equation (9.4) gives the relationship between mole fractions and extent of reaction at equilibrium as

$$y_i = \frac{n_{i0} + \nu_i \varepsilon}{n_0 + \varepsilon \nu}$$

(a) The mole fractions of the constituents in the equilibrium mixture are expressed in terms of the extent of reaction as given in the table below:

Component	ν_i	n_{i0}, mol	y_i
CO	−1	1	$(1-\varepsilon)/2$
H_2O	−1	1	$(1-\varepsilon)/2$
CO_2	+1	0	$\varepsilon/2$
H_2	+1	0	$\varepsilon/2$
n_0		2	

$$K_y = 1 = \frac{y_{CO_2}\, y_{H_2}}{y_{CO}\, y_{H_2O}} = \frac{(\varepsilon/2)(\varepsilon/2)}{[(1-\varepsilon)/2][(1-\varepsilon)/2]} = \frac{\varepsilon^2}{(1-\varepsilon)^2}$$

Solving the above, $\varepsilon = 0.5$.
Conversion of steam z is obtained from Eq. (9.5)

$$z = \frac{|\nu_i|\, \varepsilon}{n_{i0}} = 0.5$$

This means that 50% of steam is converted in the reaction.

(b)

Component	ν_i	n_{i0}, mol	y_i
CO	−1	1	$(1-\varepsilon)/4$
H_2O	−1	1	$(1-\varepsilon)/4$
CO_2	+1	0	$\varepsilon/4$
H_2	+1	0	$\varepsilon/4$
N_2		2	
n_0		4	

$$K_y = 1 = \frac{y_{CO_2}\, y_{H_2}}{y_{CO}\, y_{H_2O}} = \frac{(\varepsilon/4)(\varepsilon/4)}{[(1-\varepsilon)/4][(1-\varepsilon)/4]} = \frac{\varepsilon^2}{(1-\varepsilon)^2}$$

$\varepsilon = 0.5$. The conversion of water vapour is 50%.

The conversion remains the same as that resulted when the reactant stream contained only the stoichiometric quantities of CO and H_2O vapour. This is because $\nu = 0$ or the reaction produces no change in the number of moles.

EXAMPLE 9.16 Ammonia synthesis reaction is represented by

$$N_2 + 3H_2 \rightarrow 2NH_3$$

The reactant stream consists of 1 mol N_2, 3 mol H_2 and 2 mol argon. The temperature and pressure of the reaction are 675 K and 20 bar. The equilibrium constant for the reaction is 2×10^{-4}. Determine how the conversion of nitrogen is affected by the presence of argon.

Solution The total number of moles of the initial mixture, $n_0 = 1 + 3 + 2 = 6$.

$$\nu = \sum \nu_i = -1 - 3 + 2 = -2$$

$$y_i = \frac{n_{i0} + \nu_i \varepsilon}{n_0 + \varepsilon \nu} = \frac{n_{i0} + \nu_i \varepsilon}{6 - 2\varepsilon}$$

Component	ν_i	n_{i0}, mol	y_i
N_2	−1	1	$(1 - \varepsilon)/(6 - 2\varepsilon)$
H_2	−3	3	$3(1 - \varepsilon)/(6 - 2\varepsilon)$
NH_3	+2	0	$2\varepsilon/(6 - 2\varepsilon)$
A		2	
n_0		6	

$$K_y = \frac{K}{K_\phi} P^{-\nu} = KP^2$$

$$\frac{[2\varepsilon/(6 - 2\varepsilon)]^2}{[(1 - \varepsilon)/(6 - 2\varepsilon)]\,[3(1 - \varepsilon)/(6 - 2\varepsilon)]^3} = 2 \times 10^{-4} \times 20^2$$

$$\frac{[\varepsilon/(3 - \varepsilon)]^2}{[(1 - \varepsilon)/(3 - \varepsilon)]\,[(1 - \varepsilon)/(3 - \varepsilon)]^3} = 2 \times 10^{-4} \times 20^2 \times \frac{1}{2} \times \left(\frac{3}{2}\right)^3 = 0.1350$$

$$\frac{\varepsilon(3 - \varepsilon)}{(1 - \varepsilon)^2} = 0.3674$$

Solving we get, $\varepsilon = 0.1022$. Thus, it is seen that the conversion of nitrogen decreases to 10.22% in the presence of argon, from a value of 14.48% (Example 9.14) achieved in the absence of argon.

EXAMPLE 9.17 The reaction $N_2 + O_2 \Leftrightarrow 2NO$ takes place in the gas phase at 2975 K and 2025 kPa. The reaction mixture initially comprises 15 mol percent oxygen, 77 mol percent nitrogen and the rest inerts. The standard Gibbs free energy change for the reaction is 113.83 kJ/mol at this temperature. Assuming ideal gas behaviour, calculate the partial pressures of all species at equilibrium. How is the conversion of oxygen affected when the initial mixture were free of inerts?

Solution Basis: 15 mol oxygen, 77 mol nitrogen and 8 mol inert in the reaction mixture. Let ε be the extent of reaction. The mole fractions of the components under equilibrium are:

Oxygen: $(15 - \varepsilon)/100$, Nitrogen: $(77 - \varepsilon)/100$, NO: $2\varepsilon/100$

$$K_y = \frac{(2\varepsilon)^2}{(15 - \varepsilon)\,(77 - \varepsilon)}$$

$K = K_y P^\nu$. Here, $\nu = 0$. Thus, $K = K_y$. Also,

$$K = \exp\left[-\frac{\Delta G^0}{RT}\right] = \exp\left(-\frac{113.83 \times 1000}{8.314 \times 2975}\right) = 0.01$$

so that now we have

$$K_y = 0.01 = \frac{(2\varepsilon)^2}{(15-\varepsilon)(77-\varepsilon)}$$

or $\varepsilon = 1.59$

Mole fractions are:

$$\text{Oxygen: } \frac{15 - 1.59}{100} = 0.1341$$

$$\text{Nitrogen: } \frac{77 - 1.59}{100} = 0.7541$$

$$\text{NO: } \frac{2 \times 1.59}{100} = 0.0318$$

$$\text{Inerts: } \frac{8}{100} = 0.08$$

Partial pressures are obtained by multiplying the mole fractions by the total pressure. The values are given below:

O_2: 271.6 kPa, N_2: 1527.1 kPa, NO: 64.4 kPa, Inerts: 162 kPa

If the initial mixture were free of inerts, the mole fractions of the components under equilibrium will be Oxygen: $(15 - \varepsilon)/92$, Nitrogen: $(77 - \varepsilon)/92$, NO: $2\varepsilon/92$ and the equilibrium constant will be given by the same expression as before:

$$K_y = \frac{(2\varepsilon)^2}{(15 - \varepsilon)(77 - \varepsilon)}$$

which means that $\varepsilon = 1.59$ or the conversion of oxygen is $z = \dfrac{|\nu_i|\varepsilon}{n_{i0}} = \dfrac{1.59}{15} \times 100 = 10.6\%$, which is the same as the conversion obtained in the presence of inerts. Inerts will not influence the conversion in those reactions in which $\nu = 0$.

9.7.2 Presence of Excess of Reactants

When the reactants are not present in stoichiometric proportions, increasing the number of moles of the excess reactant will result in increase in the number of moles of the products and improved conversion of the limiting reactant at equilibrium. This is evident from the left-hand side of

Eq. (9.67), the value of which increases when the number of moles of the excess reactant is increased. Therefore, it is desirable to supply all the reactants except the limiting reactant in excess of the stoichiometric requirement, in order to increase the conversion with respect to the limiting reactant.

EXAMPLE 9.18 One mole steam undergoes the water-gas shift reaction at a temperature of 1100 K and a pressure of 1 bar.

$$CO\,(g) + H_2O\,(g) \rightarrow CO_2\,(g) + H_2\,(g)$$

The equilibrium constant for the reaction is $K = 1$. Assuming ideal gas behaviour, calculate the fractional dissociation of steam in the following cases and discuss the effect of the presence of excess reactant on the extent of reaction.

(a) CO supplied is 100% in excess of the stoichiometric requirement.
(b) CO supplied is only 50% of the theoretical requirement.

Solution Basis: 1 mol water vapour present in the reactant stream.

(a)

Component	ν_i	n_{i0}, mol	y_i
CO	-1	2	$(2-\varepsilon)/3$
H_2O	-1	1	$(1-\varepsilon)/3$
CO_2	$+1$	0	$\varepsilon/3$
H_2	$+1$	0	$\varepsilon/3$
n_0		3	

Therefore,

$$\frac{\varepsilon^2}{(1-\varepsilon)(2-\varepsilon)} = 1$$

Therefore, $\varepsilon = 0.667$ and $z = 0.667/1 = 0.667$. That is, conversion of steam is 66.7%.

(b)

Component	ν_i	n_{i0}, mol	y_i
CO	-1	0.5	$(0.5-\varepsilon)/1.5$
H_2O	-1	1	$(1-\varepsilon)/1.5$
CO_2	$+1$	0	$\varepsilon/1.5$
H_2	$+1$	0	$\varepsilon/1.5$
n_0		1.5	

Therefore,

$$\frac{\varepsilon^2}{(0.5-\varepsilon)(1-\varepsilon)} = 1$$

Therefore, $\varepsilon = 0.333$; $z = 0.333$. So only 33.3% of steam get converted.

We see that the equilibrium conversion of water vapour was 50% when the reactants were in stoichiometric proportions, it increases to 66.7% when CO was present 100% in excess and falls to 33.3% when CO becomes the limiting reactant.

EXAMPLE 9.19 Ethanol is produced by the vapour phase hydration of ethylene according to the reaction:

$$C_2H_4(g) + H_2O(g) \Leftrightarrow C_2H_5OH(g)$$

The reactor operates at 400 K and 2 bar and the feed is a gas mixture of ethylene and steam in the ratio 1:3. The equilibrium constant is 0.25. Estimate the composition (mol %) of the equilibrium mixture. Assume ideal gas behaviour. How is the conversion of ethylene affected when the initial reactant stream contains stoichiometric quantities of the reactants?

Solution Basis: 1 mole of ethylene and 3 moles of N_2 in the reactant stream. $K = K_y P^{\nu}$. Here, $\nu = -1$. Therefore, $0.25 = K_y 2^{-1}$.

Hence,

$$K_y = 2\ K = 0.5$$

Let ε be the extent of reaction. Then the mole fraction in the equilibrium mixture are: Ethylene: $(1 - \varepsilon)/(4 - \varepsilon)$, Steam: $(3 - \varepsilon)/(4 - \varepsilon)$, Ethanol: $\varepsilon/(4 - \varepsilon)$
Using these values, we get

$$K_y = 0.5 = \frac{\varepsilon(4 - \varepsilon)}{(1 - \varepsilon)(3 - \varepsilon)}$$

This gives $\varepsilon = 0.268$. The mol fractions in the equilibrium mixture are:

$$\text{Ethylene:}\quad \frac{1-\varepsilon}{4-\varepsilon} = \frac{0.732}{3.732} = 0.196$$

$$\text{Steam:}\quad \frac{3-\varepsilon}{4-\varepsilon} = \frac{2.732}{3.732} = 0.732$$

$$\text{Ethanol:}\quad \frac{\varepsilon}{4-\varepsilon} = \frac{0.268}{3.732} = 0.072$$

Equilibrium mixture contains 19.6% ethylene, 73.2% steam and 7.2% ethanol.

Let the initial mixture contain 1 mol ethylene and 1 mol steam and let ε be the extent of eaction. Then the mole fraction in the equilibrium mixture are:

Ethylene: $(1 - \varepsilon)/(2 - \varepsilon)$, Steam: $(1 - \varepsilon)/(2 - \varepsilon)$, Ethanol: $\varepsilon/(2 - \varepsilon)$

Using these values, we get

$$K_y = 0.5 = \frac{\varepsilon(2-\varepsilon)}{(1-\varepsilon)^2}$$

Solving this, we get $\varepsilon = 0.183$. That is, conversion of ethylene is 18.3%. The conversion was 8% in the first case when excess of water vapour was present in the reactant stream.

9.7.3 Presence of Products

If the initial reaction mixture contained any of the products of the reaction, then the number of moles of that product formed by the reaction so as to establish equilibrium will decrease as indicated by Eq. (9.67). Therefore, the addition of the products to the original reactant stream decreases the equilibrium conversion.

EXAMPLE 9.20 A gas mixture which contained 1 mol CO, 1 mol water vapour and 1 mol CO_2 is undergoing the following reaction at a temperature of 1100 K and a pressure of 1 bar.

$$CO\,(g) + H_2O\,(g) \rightarrow CO_2\,(g) + H_2\,(g)$$

The equilibrium constant for the reaction is $K = 1$. Assume that the gas mixture behaves as ideal gas. Calculate the fractional dissociation of steam and discuss the effect of the presence of the products on the equilibrium conversion.

Solution The mole fractions of the different species in the equilibrium mixture is expressed in terms of the extent of reaction as below:

Component	ν_i	$n_{i\,0}$, mol	y_i
CO	–1	1	$(1 - \varepsilon)/3$
H_2O	–1	1	$(1 - \varepsilon)/3$
CO_2	+1	1	$(1 + \varepsilon)/3$
H_2	+1	0	$\varepsilon/3$
	n_0	3	

$$K_y = 1 = \frac{y_{CO_2}\, y_{H_2}}{y_{CO}\, y_{H_2O}} = \frac{[(1+\varepsilon)/3]\,\varepsilon/3}{[(1-\varepsilon)/3]\,[(1-\varepsilon)/3]} = \frac{\varepsilon(1+\varepsilon)}{(1-\varepsilon)^2}$$

Solving the above equation, we get $\varepsilon = 0.333$, which means that the conversion of water vapour gets reduced to 33.3% due to the presence of CO_2, the product of the reaction in the reactant stream.

EXAMPLE 9.21 A gas mixture containing 25% CO, 55% H_2 and 20% inert gas is to be used for methanol synthesis. The gases issue from the catalyst chamber in chemical equilibrium with respect to the reaction

$$CO\,(g) + 2H_2\,(g) \rightarrow CH_3OH\,(g)$$

at a pressure of 300 bar and temperature of 625 K. Assume that the equilibrium mixture forms an ideal solution and K_f and K_ϕ are 4.9×10^{-5} and 0.35 respectively. What is the per cent conversion of CO?

Solution Basis: 100 moles of initial gas mixture.
Let ε be the extent of reaction at equilibrium. $n_0 = 100$.

$$\nu = -1 - 2 + 1 = -2$$

The mole fractions in the equilibrium mixture are calculated using Eq. (9.4)

$$y_i = \frac{n_{i0} + \nu_i \varepsilon}{n_0 + \varepsilon \nu} = \frac{n_{i0} + \nu_i \varepsilon}{100 - 2\varepsilon}$$

Component	ν_i	n_{i0}, mol	y_i
CO	–1	25	$(25 - \varepsilon)/(100 - 2\varepsilon)$
H_2	–2	55	$(55 - 2\varepsilon)/(100 - 2\varepsilon)$
Inert gas	–	20	–
CH_3OH	+1	0	$\varepsilon/(100 - 2\varepsilon)$
n_0		100	

For gases, $K = K_f$. Therefore,

$$K_y = \frac{K_f}{K_\phi} P^{-\nu}$$

$$\frac{\varepsilon/(100 - 2\varepsilon)}{[(25 - \varepsilon)/(100 - 2\varepsilon)]\,[(55 - 2\varepsilon)/(100 - 2\varepsilon)]^2} = \frac{4.9 \times 10^{-5}}{0.35} \times 300^2$$

$$\frac{\varepsilon(100 - 2\varepsilon)^2}{(25 - \varepsilon)\,(55 - 2\varepsilon)^2} = 12.6$$

Solving this we get $\varepsilon = 15.25$; fractional conversion of CO,

$$z = \frac{|\nu_i|\,\varepsilon}{n_{i0}} = 15.25/25 = 0.61$$

Therefore, 61% of CO gets converted.

***EXAMPLE* 9.22** A gas mixture consisting of 60% H_2, 20% N_2 and the rest inert gas is passed over a suitable catalyst for the production of ammonia.

$$\frac{1}{2} N_2 + \frac{3}{2} H_2 \rightarrow NH_3$$

The equilibrium constant $K_p = 1.25 \times 10^{-2}$. The pressure is maintained at 50 bar. Assume ideal gas behaviour for the gas mixture. Determine the composition of the gases leaving the reactor.

Solution Basis: 100 moles of the reactant gases.

$$\nu = -\frac{1}{2} - \frac{3}{2} + 1 = -1$$

Component	ν_i	n_{i0}, mol	y_i
N_2	$-1/2$	20	$[20 - (\varepsilon/2)]/(100 - \varepsilon)$
H_2	$-3/2$	60	$[60 - (3\varepsilon/2)]/(100 - \varepsilon)$
NH_3	$+1$	0	$\varepsilon/(100 - \varepsilon)$
Inert gas	–	20	–
n_0		100	

Since,

$$K_y = K_P P^{-\nu}$$

Then,

$$\frac{\varepsilon/(100 - \varepsilon)}{[\{20 - (\varepsilon/2)\}/(100 - \varepsilon)]^{1/2}\,[\{60 - (3\varepsilon/2)\}/(100 - \varepsilon)]^{3/2}} = (1.25 \times 10^{-2})\,50 = 0.625$$

$$\frac{\varepsilon(100 - \varepsilon)}{[20 - (\varepsilon/2)]^{1/2}\,[60 - (3\varepsilon/2)]^{3/2}} = 0.625$$

Solving this, we get $\varepsilon = 8.71$. Mole fraction of nitrogen is obtained as

$$[20 - (\varepsilon/2)]/(100 - \varepsilon) = 0.1714$$

and mole fraction of hydrogen is

$$[60 - (3\varepsilon/2)]/(100 - \varepsilon) = 0.5141$$

Mole fraction of ammonia:

$$\varepsilon/(100 - \varepsilon) = 0.0954$$

Mole fraction of inert gas:

$$1 - 0.1714 - 0.5141 - 0.0954 = 0.2191$$

Analysis of exit gases from the reactor:

$N_2 = 17.14\%$, $H_2 = 51.41\%$, $NH_3 = 9.54\%$ and inert gas $= 21.91\%$

9.8 LIQUID-PHASE REACTIONS

The equilibrium constant as defined by Eq. (9.19) is applicable for all chemical reactions.

$$K = \Pi a_i^{\nu_i}$$

For liquid-phase reactions, the evaluation of equilibrium constant using this equation requires a relationship between activity and composition. Since, activity is the ratio of the fugacity to the fugacity in the standard state, such a relationship can be established once the standard state is specified. The standard state for liquid-phase reactions may be the pure liquid at 1 bar and the reaction temperature. The fugacity in this state is not much different from the fugacity of pure liquid at the pressure and temperature of the reaction f_i. This is because, pressure has very negligible effect on the properties of liquids. With this choice, the equilibrium constant becomes

$$K = \Pi\left(\frac{\bar{f}_i}{f_i^0}\right)^{\nu_i} = \Pi\left(\frac{\bar{f}_i}{f_i}\right)^{\nu_i} \tag{9.68}$$

The fugacity of a component in the solution is related to the fugacity in the pure state by $\bar{f}_i = \gamma_i x_i f_i$, where γ_i is the activity coefficient in the solution. Using this in Eq. (9.68), we get

$$K = \Pi\gamma_i^{\nu_i} x_i^{\nu_i} = K_\gamma K_x \tag{9.69}$$

K_γ is an equilibrium constant in terms of activity coefficients. Accurate values of activity coefficients are rarely available and in practical calculations we set $K_\gamma = 1$. This is equivalent to assuming that the solution is ideal and $a_i = x_i$. The components present in large proportions obey Lewis–Randall rule and for them the activity and the mole fraction in the solution are the same. Even if Lewis–Randall rule is not applicable, the assumption that $K_\gamma = 1$ is not a very serious limitation as the function denoted by K_γ may become nearly unity even if the individual activity coefficients are not. Thus

$$K = K_x = \Pi x_i^{\nu_i} \tag{9.70}$$

For components present in low concentration, the standard state of the solute is usually the fictitious or hypothetical state which would exist if the solute obeyed Henry's law over a concentration range extending up to a molality of unity. This hypothetical state is illustrated in Fig. 9.4.

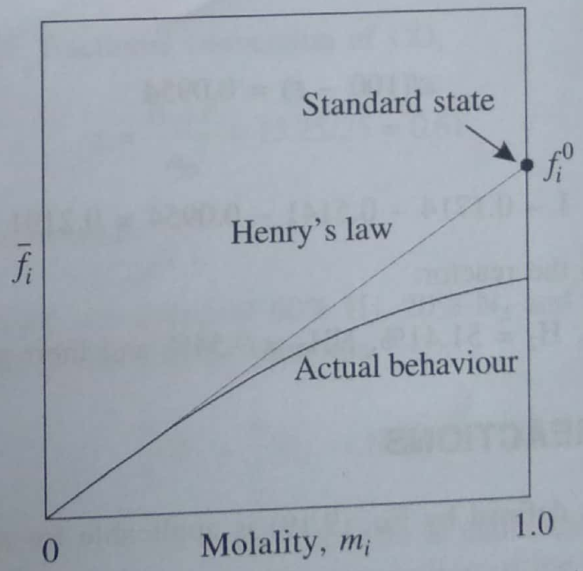

Fig. 9.4 Standard state based on Henry's law.

The fugacity and molality (mol/kg solvent) are related as

$$\bar{f}_i = K_i m_i \tag{9.71}$$

where K_i is the Henry's law constant and m_i is the molality. Using the hypothetical standard state, it can be shown that the standard state fugacity is equal to the Henry's law constant and the activity and the molality are equal. That is

$$a_i = m_i \tag{9.72}$$

With this choice for the standard state, a very simple relationship exists between the activity and the concentration for cases where Henry's law is applicable.

9.9 HETEROGENEOUS REACTION EQUILIBRIA

In the study of heterogeneous reaction equilibria presented in this section, we are concerned with a gas phase that is in equilibrium with a liquid or a solid phase. When the heterogeneous system is in equilibrium we would have to consider the equilibrium with respect to chemical reactions in the gas phase as well as the phase equilibria between the components in the gas phase and the liquid or the solid phase as the case may be.

9.9.1 Reactions in Solutions

Consider the reaction between a gas A and liquid B to produce a solution C.

$$\text{A (g)} + \text{B (l)} \rightarrow \text{C (aq)}$$

The equilibrium in this reaction can be studied in different ways:

1. The reaction may be assumed to take place entirely within the gas phase and the equilibrium constant for the reaction is evaluated using the standard state for gases, i.e. the ideal gas standard state at a pressure of 1 bar and the reaction temperature. The resulting equations are coupled with equations for material transfer between phases to maintain equilibrium.
2. The reaction is assumed to occur in the liquid phase with simultaneous transfer of material between phases to maintain equilibrium. The calculations of reaction equilibria are based on the liquid standard state.
3. The third method involves the use of mixed standard states. Thus, the standard state for A is the pure ideal gas at 1 bar, that for B is pure liquid at 1 bar, and for C it is the solute in an ideal 1-molal aqueous solution. The equilibrium constant in this case may be evaluated as

$$K = \frac{a_C}{a_A a_B} = \frac{m_C}{(\bar{f}_A)(\gamma_B x_B)} \tag{9.73}$$

All the above methods give the same results for equilibrium compositions, but the values for equilibrium constant depend on the choice of the standard state.

9.9.2 Equilibria involving Pure Solids and Liquids

When a pure liquid or a pure solid is involved in a heterogeneous reaction with gases, its activity may be taken as unity provided the pressure of the system is not much different from the standard state. Activity as we know, is defined as the ratio of the fugacity to the fugacity in the standard state. The fugacity in the standard state is almost equal to that in the equilibrium state, as these two states differ only in their pressures and not in their temperatures. Pressure, unless extremely high, has only a negligible effect on the properties of liquids and solids. Where the standard state for solids and liquids is taken at 1 bar or at low equilibrium vapour pressures, the activities of pure solids and pure liquids may be taken as unity at moderate pressures. Therefore, the composition of the gaseous phase at equilibrium is not affected by the presence of the solid or liquid.

9.9.3 Pressures of Decomposition

Many solid compounds decompose to give another solid and a gas, as in the calcination of calcium carbonate to CO_2 and lime.

$$CaCO_3\,(s) \rightarrow CaO\,(s) + CO_2\,(g)$$

The equilibrium constant for this reaction is

$$K = \frac{a_{CO_2}\, a_{CaO}}{a_{CaCO_3}} \tag{9.74}$$

The activities of the solid components present at equilibrium are close to unity provided the pressure is moderate and both solids are present at equilibrium. Since the standard state for gases is the ideal-gas state at 1 bar, the standard state fugacity is equal to unity and therefore, the activity of CO_2 in the equilibrium mixture is equal to its fugacity, $\bar{f}_{CO_2}$. But fugacity of a component is equal to its partial pressure at low pressures and, therefore, Eq. (9.74) reduces to

$$K = \bar{p}_{CO_2} \tag{9.75}$$

This is the equilibrium partial pressure exerted by CO_2 and its value depends only on temperature. If the partial pressure is lowered below this equilibrium value, $CaCO_3$ will decompose and will eventually disappear. On the other hand, if the pressure on the system is kept above the equilibrium partial pressure, CaO will combine with CO_2 resulting in the formation of $CaCO_3$.

For a general solid decomposition reaction represented by

$$a\mathrm{A}\,(s) \rightarrow l\mathrm{L}\,(s) + m\mathrm{M}\,(g)$$

the above treatment can be generalised as

$$K = a_{\mathrm{M}}^{m} = \bar{p}_{\mathrm{M}}^{m} = \exp\left(\frac{-\Delta G^0}{RT}\right) \tag{9.76}$$

$$\ln \bar{p}_{\mathrm{M}} = \frac{-\Delta G^0}{mRT} = -\frac{1}{mRT}\,(\Delta H^0 - T\Delta S^0) \tag{9.77}$$

In the above equation, m is the stoichiometric coefficient; ΔH^0 and ΔS^0 are the standard heat of reaction and standard entropy of reaction respectively.

EXAMPLE 9.23 Ethylene gas reacts with water forming aqueous solution of ethanol.

$$C_2H_4\,(g) + H_2O\,(l) \rightarrow C_2H_5OH\,(aq)$$

Equilibrium measurements at 530 K and 85 bar showed that the aqueous phase contained 1.5% (mole) ethanol and 95.0% (mole) water. The vapour phase analysed 48% ethylene. The fugacity coefficient for ethylene is estimated to be 0.9. Evaluate the equilibrium constant.

Solution Equation (9.73) may be used for evaluating K.

$$K = \frac{a_C}{a_A a_B} = \frac{m_{C_2H_5OH}}{(\bar{f}_{C_2H_4})(\gamma_{H_2O} x_{H_2O})}$$

The standard state for aqueous solution is 1 molal solution; for water, it is pure liquid water at 1 bar; and for gaseous ethylene, it is the pure ethylene at 1 bar.

The molality of aqueous solution = moles ethanol/kg water

$$= 1.5/(95.0 \times 18 \times 10^{-3}) = 0.8772 \text{ mol/kg water}$$

Fugacity of ethylene is denoted by $\bar{f}_{C_2H_4}$, and it is estimated as

$$\bar{f}_{C_2H_4} = \phi_{C_2H_4} \bar{p}_{C_2H_4} = \phi_{C_2H_4} y_{C_2H_4} P = 0.9 \times 0.48 \times 85 = 36.72 \text{ bar}$$

The mole fraction of water is close to 1 so that Raoult's law is applicable. Therefore, the activity coefficient of water may be taken to be unity.

$$K = \frac{0.8772}{36.72 \times 0.95} = 2.5146 \times 10^{-2} \text{ (mol } C_2H_4\text{)/(kg water bar)}$$

EXAMPLE 9.24 Calculate the decomposition pressure of limestone at 1000 K.

$$CaCO_3 (s) \rightarrow CaO (s) + CO_2 (g)$$

The standard free energy of this reaction as function of temperature is

$$\Delta G^0 = 1.8856 \times 10^5 - 243.42T + 11.8478T \ln T - 3.1045 \times 10^{-3}T^2 + 1.7271 \times 10^{-6} T^3 - 4.1784 \times 10^5/T$$

Also calculate the decomposition temperature at 1 bar.

Solution From Eq. (9.75), the decomposition pressure is $\bar{p}_{CO_2} = K$, where K can be calculated by

$$K = \exp\left(-\frac{\Delta G^0}{RT}\right)$$

At 1000 K,

$$\Delta G^0 = 1.8856 \times 10^5 - 243420 + 81842 - 3105 + 1727 - 418 = 25186 \text{ J}$$

Therefore,

$$K = \exp\left(-\frac{25186}{8.314 \times 1000}\right) = 0.048 = \bar{p}$$

Decomposition pressure at 1000 K = 0.048 bar.

The decomposition temperature at 1 bar can now be determined. $\bar{p}_{CO_2} = K = 1$, so that

$$\Delta G^0 = 0 = 1.8856 \times 10^5 - 243.42T + 11.8478T \ln T - 3.1045 \times 10^{-3}T^2 + 1.7271 \times 10^{-6}T^3 - 4.1784 \times 10^5/T$$

The above equation is solved for T, the temperature at decomposition, 1180 K.

EXAMPLE 9.25 Solid calcium oxalate dissociates at high temperatures into solid calcium carbonate and carbon monoxide:

$$CaC_2O_4(s) \Leftrightarrow CaCO_3(s) + CO(g)$$

The equilibrium pressure of CO between 670 and 700 K is given by

$$\ln P = 14.4 - \frac{9600}{T}$$

where P is in bar and T is in K. Assuming ideal behaviour, calculate ΔG^0, ΔH^0 and ΔS^0 at 675 K.

Solution By Eq. (9.75), $K = \bar{p}_{CO}$

Therefore,

$$\ln K = 14.4 - \frac{9600}{675} = 0.1777 \quad \text{or} \quad K = 1.1946$$

By Eq. (9.31),

$$\Delta G^0 = -RT \ln K = -8.314 \times 675 \times \ln 1.1946 = -997.68 \text{ kJ}$$

By Eq. (9.36),

$$\frac{\Delta H^0}{RT^2} = \frac{d \ln K}{dT} = \frac{d \ln P}{dT} = \frac{9600}{T^2}$$

Therefore, $\Delta H^0 = 9600\,R = 79814.4$ kJ

Thus,

$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$

$$\Delta S^0 = \frac{\Delta H^0 - \Delta G^0}{T} = 119.72 \text{ kJ/K}$$

EXAMPLE 9.26 Iron oxide is reduced to iron by passing over it a mixture of 20% CO and 80% N_2 at 1200 K and 1 bar.

$$FeO(s) + CO(g) \rightarrow Fe(s) + CO_2(g)$$

The equilibrium constant for this reaction is 0.403. Assuming that equilibrium is attained, calculate the weight of metallic iron produced per 100 m^3 of gas admitted at 1200 K and 1 atm. Gas mixture may be assumed to behave as ideal gas.

Solution Basis: 100 mol of gas entering.

The activities of solid components can be taken to be unity.

$$K = \frac{a_{Fe}\, a_{CO_2}}{a_{FeO}\, a_{CO}} = \frac{a_{CO_2}}{a_{CO}}$$

If the gases are assumed to be ideal, then

$$a_i = \bar{p}_i = y_i P$$

and the given equation for equilibrium constant gives

$$y_{CO_2}/y_{CO} = 0.403$$

Let ε be the extent of reaction. Since the initial mixture consists of 20 mol CO and 80 mol N_2, the mole fractions of CO and CO_2 at equilibrium are $(20 - \varepsilon)/100$ and $\varepsilon/100$, respectively. Therefore,

$$\frac{\varepsilon}{20 - \varepsilon} = 0.403$$

Solving this, $\varepsilon = 5.745$. The equilibrium mixture contains 5.745 mol CO_2. Moles of iron produced = 5.745 per 100 mol of initial gas mixture. Also, 100 mol gas mixture at 1200 K and 1 bar is equivalent to

$$100 \times 22.4 \times 10^{-3} \times (1200/273) = 9.846 \text{ m}^3$$

Iron produced per 100 m^3 of gas = $(5.745 \times 55.8 \times 100)/9.846 = 3256$ g = 3.256 kg

9.10 SIMULTANEOUS REACTIONS

With a given set of reactants many reactions may be possible. When we consider the equilibrium yield of methanol in the reaction

$$CO + 2H_2 \rightarrow CH_3OH \tag{9.78}$$

by the methods already discussed, we are in fact ignoring the presence of intermediate product, formaldehyde in the reaction mixture. The above reaction proceeds in two steps in series as:

$$CO + H_2 \rightarrow HCHO \tag{9.79}$$

$$HCHO + H_2 \rightarrow CH_3OH \tag{9.80}$$

For the thermodynamic analysis of a reaction that proceeds in two or more steps, the presence of intermediate products can sometimes be ignored on the assumption that they are very unstable and their concentrations at equilibrium are negligible in comparison with that of the main product. The above assumption is implicit in treating the equilibrium mixture in the methanol synthesis as consisting of only CO, H_2 and CH_3OH. In this case, this assumption is a valid one as formaldehyde is very unstable, but in many other situations, the presence of intermediate products in the reaction mixture at equilibrium also should be taken into account as explained below:

The free energy change for a reaction is equal to the sum of the free energy changes in the individual step reactions. Thus,

$$\Delta G^0 = \Delta G_1^0 + \Delta G_2^0$$

where ΔG_1^0 and ΔG_2^0 are the free energy changes in the two step reactions that occur and ΔG^0 is the standard free energy change in the overall reaction. Since $\Delta G^0 = -RT \ln K$, the above equation gives

$$K = K_1 K_2$$

K_1 and K_2 are the equilibrium constants for the individual steps and K is the equilibrium constant for the combined reaction. For a given value of K, an infinite number of combinations of K_1 and K_2 are possible such that $K = K_1K_2$. For example, let us take $K = 10^{-4}$ and consider the cases where (a) $10^{-4} = 10^{-10} \times 10^6$, (b) $10^{-4} = 10^{-2} \times 10^{-2}$, and (c) $10^{-4} = 10^6 \times 10^{-10}$. For case (a), the concentration of intermediate products at equilibrium would be negligible and correct result would be obtained by considering only the overall reaction. For case (b), there would be considerable amounts of intermediates at equilibrium and their presence cannot be ignored. For case (c), the equilibrium mixture would be mostly intermediates. The use of an overall equilibrium constant for the calculation of equilibrium compositions is limited to cases where the intermediate products are not present in significant quantities.

In addition to the formation of intermediate products, which subsequently reacts to form the final desired products, many side reactions may also occur within the system. For example, starting with the pairs CO and H_2 some of the possible reactions are:

$$CO + H_2 \rightarrow HCHO$$

$$CO + 2H_2 \rightarrow CH_3OH$$

$$CO + 3H_2 \rightarrow CH_4 + H_2O$$

$$2CO + 5H_2 \rightarrow C_2H_6 + 2H_2O$$

$$3CO + 6H_2 \rightarrow C_3H_7OH + 2H_2O$$

In dealing with methanol synthesis, it was assumed that the side reactions proceeded at a negligible rate in comparison with the steps involved in the synthesis reaction. Theoretically, when the equilibrium yield of a particular component is to be determined, we should consider simultaneous equilibria in all possible reactions between the substances involved. However, for practical calculations, it is possible to reduce the number of reactions that are to be considered.

In the general case when all intermediates and final products must be considered, it is necessary that the equilibrium equations of all reactions must be satisfied by the compositions of the system at equilibrium. Determination of the equilibrium compositions involves simultaneous solution of r equilibrium equations where r is the number of independent reactions that can be written. After determining the number of independent reactions as explained later, the equilibrium constant is evaluated for each reaction by

$$K_j = \Pi a_i^{\nu_{i,j}} \tag{9.81}$$

The mole fractions can be related to the extent of reaction for each reaction and the resulting equations are solved simultaneously.

$$K_j = P^{\nu_j} \Pi y_i^{\nu_{i,j}} \tag{9.82}$$

Here the suffix j is used to represent the jth reaction under consideration. The above equation is written for all r independent reactions. Assuming the equilibrium mixture to behave as ideal gases, these lead to r equations relating the composition to the pressure and the equilibrium constant.

$$K_{y,j} = K_j P^{-\nu_j} \tag{9.83}$$

The method can be illustrated by considering the following simultaneous reactions:

$$aA + b_1B \rightarrow lL + m_1M \tag{9.84}$$

$$lL + b_2B \rightarrow m_2M + nN \tag{9.85}$$

Let the equilibrium constants be K_1 and K_2 for the reactions indicated by Eqs. (9.84) and (9.85) respectively and let the corresponding extent of reaction be ε_1 for reaction (9.84) and ε_2 for reaction (9.85). The initial reactant mixture is assumed to consist of 1 mol A and x mol B. The mole fractions in simultaneous reactions can be calculated using Eq. (9.9).

$$y_i = \frac{n_i}{n} = \frac{n_{i0} + \sum_j \nu_{i,j}\varepsilon_j}{n_0 + \sum_j \nu_j \varepsilon_j}$$

The mole fractions of various components are

$$y_A = (1 - a\varepsilon_1)/[1 + x + (l + m_1 - a - b_1)\varepsilon_1 + (m_2 + n - l - b_2)\varepsilon_2]$$

$$y_B = (x - b_1\varepsilon_1 - b_2\varepsilon_2)/[1 + x + (l + m_1 - a - b_1)\varepsilon_1 + (m_2 + n - l - b_2)\varepsilon_2]$$

$$y_L = l(\varepsilon_1 - \varepsilon_2)/[1 + x + (l + m_1 - a - b_1)\varepsilon_1 + (m_2 + n - l - b_2)\varepsilon_2]$$

$$y_M = (m_1\varepsilon_1 + m_2\varepsilon_2)/[1 + x + (l + m_1 - a - b_1)\varepsilon_1 + (m_2 + n - l - b_2)\varepsilon_2]$$

$$y_N = n\varepsilon_2/[1 + x + (l + m_1 - a - b_1)\varepsilon_1 + (m_2 + n - l - b_2)\varepsilon_2]$$

These are substituted into the following equilibrium relations.

$$\frac{y_L^l \, y_M^{m_1}}{y_A^a \, y_B^{b_1}} = K_1 P^{-(l + m_1 - a - b_1)} \tag{9.86}$$

$$\frac{y_M^{m_2} \, y_N^n}{y_L^l \, y_B^{b_2}} = K_2 P^{-(m_2 + n - l - b_2)} \tag{9.87}$$

These two equations are solved simultaneously to obtain the variables ε_1 and ε_2. Equation (9.9) can now be utilised to evaluate the equilibrium compositions.

EXAMPLE 9.27 Five moles of steam reacts with one mole methane according to the following reaction at 850 K and 1 bar.

$$CH_4 + H_2O \rightarrow CO + 3H_2; \qquad K_1 = 0.574 \tag{9.88}$$

$$CO + H_2O \rightarrow CO_2 + H_2; \qquad K_2 = 2.21 \tag{9.89}$$

Calculate the composition at equilibrium assuming ideal gas behaviour.

Solution Number of moles of a component at equilibrium = $n_i = n_{i0} + \sum_j \nu_{i,j}\,\varepsilon_j$

Let ε_1 and ε_2 be the extent of reactions for reaction (9.88) and (9.89) respectively. Thus at equilibrium the number of moles are,

$$CH_4: 1 - \varepsilon_1, \quad H_2O: 5 - \varepsilon_1 - \varepsilon_2, \quad CO: \varepsilon_1 - \varepsilon_2, \quad H_2: 3\varepsilon_1 + \varepsilon_2, \quad CO_2: \varepsilon_2$$

Total number of moles at equilibrium = $6 + 2\varepsilon_1$. The mole fractions of various components in the equilibrium mixture are:

$$CH_4: (1 - \varepsilon_1)/(6 + 2\varepsilon_1), \quad H_2O: (5 - \varepsilon_1 - \varepsilon_2)/(6 + 2\varepsilon_1)$$

$$CO: (\varepsilon_1 - \varepsilon_2)/(6 + 2\varepsilon_1), \quad H_2: (3\varepsilon_1 + \varepsilon_2)/(6 + 2\varepsilon_1), \quad CO_2: \varepsilon_2/(6 + 2\varepsilon_1)$$

$$K_{y,1} = \frac{y_{CO}\, y_{H_2}^3}{y_{CH_4}\, y_{H_2O}} = \frac{(\varepsilon_1 - \varepsilon_2)(3\varepsilon_1 + \varepsilon_2)^3}{(1 - \varepsilon_1)(5 - \varepsilon_1 - \varepsilon_2)(6 + 2\varepsilon_1)^2}$$

$$K_{y,2} = \frac{y_{CO_2}\, y_{H_2}}{y_{CO}\, y_{H_2O}} = \frac{\varepsilon_2(3\varepsilon_1 + \varepsilon_2)}{(\varepsilon_1 - \varepsilon_2)(5 - \varepsilon_1 - \varepsilon_2)}$$

$$\nu_1 = 1 + 3 - 1 - 1 = 2; \qquad \nu_2 = 1 + 1 - 1 - 1 = 0$$

Substitute these into the following relationships.

$$K_{y,1} = K_1 P^{-\nu_1}, \quad K_{y,2} = K_2 P^{-\nu_2}$$

Note that $K_1 = 0.574$, $K_2 = 2.21$ and $P = 1$ bar. The resulting equations are solved for ε_1 and ε_2. Assume a value for ε_1 and calculate ε_2 by each equation. These two ε_2 values are plotted against ε_1. This is repeated for various assumed ε_1 values. The intersection of the two curves gives the solution. $\varepsilon_1 = 0.9124$; and $\varepsilon_2 = 0.623$. The mole fractions are evaluated by supplying the values of ε_1 and ε_2. The results are:

CH_4: 0.0112, H_2O: 0.4415, CO: 0.0357, H_2: 0.4307 and CO_2: 0.0804

9.11 PHASE RULE FOR REACTING SYSTEMS

We have used the criteria of phase equilibrium to develop the phase rule for non-reacting systems in Chapter 8.

$$F = C - \pi + 2$$

The criterion of phase equilibrium is valid even when chemical reactions occur within the system. However, the phase rule needs modification for it to be applicable for reacting systems. This is because for each independent reaction occurring, an additional constraint is imposed on the system through Eq. (9.15) or (9.31). Thus, the number of degrees of freedom will be reduced by one for each independent chemical reaction. If r independent reactions occur in the system, then the phase rule becomes

$$F = C - \pi - r + 2 \tag{9.90}$$

For example, consider a system containing five components distributed between two phases. If the number of independent chemical reactions occurring is one, then the number of degrees of freedom will be 5 – 2 – 1 + 2 = 4. Assuming that the reaction occurring is a gas-phase isomerisation reaction involving two of the components (say, A and B), we can write the equilibrium relationship as

$$K = \frac{y_A}{y_B}$$

This in fact is a relationship between T, y_A and y_B. Only two of these three variables are therefore independent. As the degree of freedom is 4 it means that in addition to these three variables, two more variables are to be specified to define the intensive state of the system uniquely.

O.A. Hougen, et al., define the number of independent reactions that must be considered as the *least number that includes every reactant and product present to an appreciable extent in all phases of the equilibrium system, and accounts for the formation of each product from the original reactants.* It can be determined as follows:

1. For each chemical compound present in the system, equation for its formation reaction from its elements is written.
2. The elements that are not present in the system are eliminated by properly combining the equations written in step 1.

The number of equations, r, that results from the above procedure is equal to the number of independent chemical reactions occurring.

EXAMPLE 9.28 Determine the number of degrees of freedom in a gaseous system consisting of CO, CO_2, H_2, H_2O and CH_4 in chemical equilibrium.

Solution The number of independent chemical reactions occurring in the system is first determined. The formation reactions for each of the compounds are written:

$$C + \frac{1}{2}O_2 \rightarrow CO \tag{9.91}$$

$$C + O_2 \rightarrow CO_2 \tag{9.92}$$

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O \tag{9.93}$$

$$C + 2H_2 \rightarrow CH_4 \tag{9.94}$$

The elements C and O_2 are not present in the system. C is eliminated first, from Eqs. (9.91), (9.92) and (9.94). Combining Eq. (9.91) with Eq. (9.92) we get

$$CO_2 \rightarrow CO + \frac{1}{2}O_2 \tag{9.95}$$

Combining Eq. (9.91) with Eq. (9.94) gives

$$CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2 \tag{9.96}$$

Equations (9.95), (9.96) and (9.93) form the new set from which O_2 is to be eliminated. Combining Eq. (9.93) with Eq. (9.95) gives

$$CO_2 + H_2 \rightarrow CO + H_2O \tag{9.97}$$

Equation (9.93) is combined with Eq. (9.96) to give

$$3H_2 + CO \rightarrow CH_4 + H_2O \tag{9.98}$$

The equations that remain after this elimination process are Eqs. (9.97) and (9.98) which represent the independent chemical reactions occurring in the system. Therefore, $r = 2$. Equation (9.90) gives the degrees of freedom as $F = C - \pi - r + 2$. Here $C = 5$; $\pi = 1$ and therefore, $F = 4$.

SUMMARY

Thermodynamics of chemical reactions is mainly concerned with the prediction of the equilibrium conversion attainable in a chemical reaction and the effect of operating conditions on the degree of completion of the reaction. The criterion of chemical equilibrium requires that for a chemical reaction occurring at equilibrium, there should be no change in the Gibbs free energy of the system at constant temperature and pressure. If the system is not in chemical equilibrium, the reaction occurring must be irreversible and the total Gibbs free energy must decrease at constant temperature and pressure (Section 9.2).

The equilibrium constant K for a reaction was defined in terms of the activities of the reactants and the products as

$$K = \Pi a_i^{\nu_i}$$

where a_i is the activity of component i in the reaction mixture and ν_i is the stoichiometric number of i (Section 9.3). The equilibrium constant was related to the standard free energy change by Eq. (9.31). Thus the numerical value of the equilibrium constant depends upon the temperature, the form of the stoichiometric equation and the definition of the standard state for each component. However, it is independent of the pressure at equilibrium (Section 9.4). Equation (9.31) also provided an approximate criterion for feasibility of reactions. If ΔG^0 for a reaction is zero, then $K = 1$, the reaction proceeds to a considerable extent before equilibrium is reached. If ΔG^0 is negative, then $K > 1$, the reaction is quite favourable.

The effect of temperature on the equilibrium constant was quantitatively expressed by van't Hoff equation [Eq. (9.36)]. For an exothermic reaction, the equilibrium constant decreases as the reaction temperature increases and for an endothermic reaction, the equilibrium constant will increase with increase in temperature (Section 9.5). Three methods for the evaluation of equilibrium constant were discussed; the one which made use of thermal data in the form of standard heat of reaction ΔH^0, and a standard free energy change of reaction ΔG^0 at a given temperature was found to be the most convenient and widely used. The usefulness of the Giauque functions for tabulation of standard free energy of reactions and calculation of the equilibrium constant was also established.

The equilibrium constant is independent of pressure whereas the composition at equilibrium varies with pressure as evident from Eq. (9.62). If there is a decrease in the number of moles during the reaction, the equilibrium yield would increase with increase in the pressure, whereas if the reaction results in an increase in the number of moles, the equilibrium yield would decrease with increase in pressure. It was also shown that the effect of the presence of inert gas in the reactant stream on the equilibrium conversion was just the opposite of the effect of pressure (Section 9.7).

For liquid-phase reactions, the equilibrium constant may be written as $K = K_\gamma K_x$. K_γ is an equilibrium constant in terms of activity coefficients, which may be assumed, equal to unity. For components present in low concentration, the activity and the molality are equal (Section 9.8). Under heterogeneous equilibrium (Section 9.9), a brief discussion on the reaction between a gas and liquid resulting in the formation of a solution and reaction equilibria in which a solid or liquid reacted with a gas, were provided. Also, it was seen that for reactions in which solid compounds decomposed to give another solid and a gas, the equilibrium constant was equal to the partial pressure of the gas. If the partial pressure was lowered below this equilibrium value the solid would decompose and if the pressure on the system was maintained above this value, the formation of solid was favoured. For simultaneous reactions in which all intermediate and final products in the equilibrium mixture were to be considered for determining the composition, equilibrium equations were written for all the independent reactions and these were solved simultaneously (Section 9.10).

REVIEW QUESTIONS

1. What do you mean by the 'extent of reaction'? How is it related to the mole fraction of the species in the reaction mixture?
2. What is the criterion of chemical reaction equilibria?
3. Define equilibrium constant K of a chemical reaction. How is it related to K_f and K_P?
4. Does the numerical value of the equilibrium constant depend on the form of the stoichiometric equation?
5. How is the equilibrium constant K related to the standard free energy change? Does K vary with pressure?
6. What is the effect of temperature on the equilibrium constant? Using van't Hoff equation predict the effect of increasing the temperature on endothermic and exothermic reactions.
7. How would you predict the feasibility of a reaction from the value of the standard free energy change?
8. How would the equilibrium yield in a gaseous chemical reaction be affected by increasing the pressure, if there is a decrease in the number of moles during the reaction? How would you explain the effect of pressure on reactions such as the water–gas shift reaction, where there is no change in the number of moles?
9. How would the equilibrium yield of ammonia be affected if argon is present in the synthesis gas fed to the ammonia converter?
10. Explain how the equilibrium constant for liquid-phase reactions is evaluated.
11. Show that the equilibrium constant in the decomposition of calcium carbonate into CO_2 and lime is equal to the partial pressure of carbon dioxide. Explain how would you estimate the decomposition pressure? What would happen if the CO_2 pressure is reduced below this value?
12. A reaction proceeds in two steps. The equilibrium constants for the individual steps are K_1 and K_2. What would be the equilibrium constant for the overall reaction?
13. What do you mean by the number of independent reactions in a chemically reacting system? How would you determine it?
14. What is phase rule as applicable to a reacting system?