Chapter 8:Chemical Reaction Equilibria

8.1 Introduction

Reaction chemistry forms the essence of chemical processes. The very distinctiveness of the chemical industry lies in its quest for transforming less useful substances to those which are useful to modern life. The perception of old art of 'alchemy' bordered on the magical; perhaps in today's world its role in the form of modern chemistry is in no sense any less. Almost everything that is of use to humans is manufactured through the route of chemical synthesis. Such reactive processes need to be characterized in terms of the maximum possible yield of the desired product at any given conditions, starting from the raw materials (i.e., reactants). The theory of chemical reactions indicates that rates of reactions are generally enhanced by increase of temperature. However, experience shows that the maximum quantum of conversion of reactants to products does not increase monotonically. Indeed for a vast majority the maximum conversion reaches a *maximum* with respect to reaction temperature and subsequently diminishes. This is shown schematically in fig. 8.1.
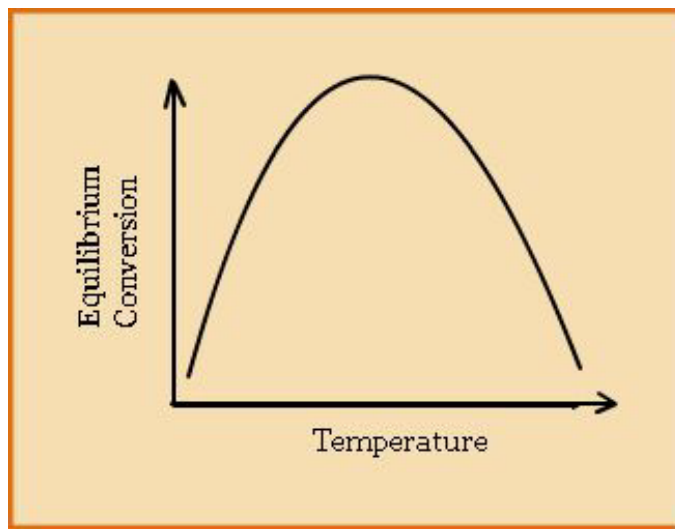

Fig. 8.1 Schematic of Equilibrium Reaction vs. Temperature

The reason behind this phenomenon lies in the molecular processes that occur during a reaction. Consider a typical reaction of the following form occurring in gas phase: $A(g) + B(g) \rightarrow C(g) + D(g)$. The reaction typically begins with the reactants being brought together in a reactor. In the initial phases, molecules of A and B collide and form reactive complexes, which are eventually converted to the products C and D by means of molecular rearrangement. Clearly then the early phase of the reaction process is dominated by the presence and depletion of A and B. However, as the process

continues, the fraction of C and D in the reactor increases, which in turn enhances the likelihood of these molecules colliding with each other and undergoing transformation into A and B. Thus, while initially the *forward* reaction dominates, in time the *backward* reaction becomes increasingly significant, which eventually results in the two rates becoming equal. After this point is reached the concentrations of each species in the reactor becomes fixed and displays no further propensity to change unless propelled by any externally imposed "disturbance"(say, by provision of heat). Under such a condition the reaction is said to be in a state of *equilibrium*. The magnitude of all measurable macroscopic variables (T, P and composition) characterizing the reaction remains constant. Clearly under the equilibrium state the percentage conversion of the reactants to products must be the *maximum* possible at the given temperature and pressure. Or else the reaction would progress further until the state of equilibrium is achieved. The principles of chemical reaction thermodynamics are aimed at the prediction of this equilibrium conversion.

The reason why the equilibrium conversion itself changes with variation of temperature may be appreciated easily. The rates of the forward and backward reactions both depend on temperature; however, an increase in temperature will, in general, have different impacts on the rates of each. Hence the extent of conversion at which they become identical will vary with temperature; this prompts a change in the equilibrium conversion. Reactions for which the conversion is 100% or nearly so are termed *irreversible*, while for those which never attains complete conversion are essentially *reversible* in nature. The fact that a maxima may occur in the conversion behaviour (fig. 8.1) suggests that for such reactions while the forward reaction rates dominate at lower temperatures, while at higher temperatures the backward reaction may be predominant.

The choice of the reaction conditions thus depends on the maximum (or equilibrium) conversion possible. Further, the knowledge of equilibrium conversions is essential to intensification of a process. Finally, it also sets the limit that can *never* be crossed in practice regardless of the process strategies. This forms a primary input to the determination of the economic viability of a manufacturing process. If reaction equilibria considerations suggest that the maximum possible conversion over practical ranges of temperature is lower than that required for commercial feasibility no further effort is useful in its further development. On the other hand if the absolute maximum conversion is high then the question of optimizing the process conditions attain significance. Exploration of the best strategy for conducting the reaction (in terms of temperature, pressure, rate enhancement by use of catalytic aids, etc) then offers a critical challenge.

This chapter develops the general thermodynamic relations necessary for prediction of the equilibrium conversion of reactions. As we shall see, as in the case of phase equilibria, the Gibbs free energy of a reaction constitutes a fundamental property in the estimation of equilibrium conversion. The next section presents method of depicting the conversion by the means of the reaction co-ordinate, which is followed by estimation of the heat effects associated with all reactions. The principles of reaction equilibria are then developed.

8.2 Standard Enthalpy and Gibbs free energy of reaction

From the foregoing discussion it may be apparent that a chemical reaction may be carried out in diverse ways by changing temperature, pressure, and feed composition. Each of the different conditions would involve different conversions and heat effects. Thus there is need to define a "standard" way of carrying out a reaction. If all reactions were carried out in the same standard manner, it becomes possible to compare them with respect to heat effects, and equilibrium conversion under the same conditions. In general all reactions are subject to heat effects, whether small or large. A reaction may either release heat (exothermic) or absorb heat (endothermic). However, it is expected that the heat effect will vary with temperature. Thus, there is a need to develop general relations that allow computation of the heat effect associated with a reaction at any temperature.

Consider a reaction of the following form:

$$|\alpha_1| A_1 + |\alpha_2| A_2 \rightarrow |\alpha_3| A_3 + |\alpha_4| A_4 \qquad\qquad ..(8.1)$$

The reactants (A_1 and A_2) and products (A_3 and A_4) may be gaseous, liquid or solid. The term $|\alpha_i|$ is the stoichiometric coefficient corresponding to the chemical species A_i. For the purpose of development of the reaction equilibria relations it is convenient to designate the stoichiometric numbers of the reactants as *negative*, while those of the products as *positive*. This is to signify that reactants are *depleted* in proportion to their stoichiometric numbers, while the products are formed in proportion to their stoichiometric numbers. Consider, for example, the following gas-phase reaction:

$$CH_4(g) + 2O_2(g) \rightleftarrows CO_2(g) + 2H_2O(g)$$
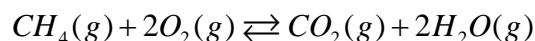
The stoichiometric numbers are written as follows: $\alpha_{CH_4} = -1$; $\alpha_{O_2} = -2$; $\alpha_{CO_2} = 1$; $\alpha_{H_2O} = 2$.

The *standard enthalpy of reaction* $\Delta H_{T_0}^o$ at say at any temperature T is defined in the following manner: it is the *change* in enthalpy that occurs when $|\alpha_1|$ moles of A_1 and $|\alpha_2|$ moles of B_2 in their

standard states at temperature T convert *fully* to form $|\alpha_3|$ moles of A_3 and $|\alpha_4|$ moles of A_4 in their respective standard states at the same temperature T. The standard states commonly employed are as follows:

— *Gases*: the pure substance in the ideal gas state at 1 bar

— *Liquids and Solids*: the pure liquid or solid at 1 bar

The conceptual schema of a standard reaction is depicted in fig. 8.1. All reactants *enter* and products *leave* the reactor in *pure* component form at the same temperature T, and at their respective standard states. In the literature, data on the standard enthalpy of reaction is typically reported at a
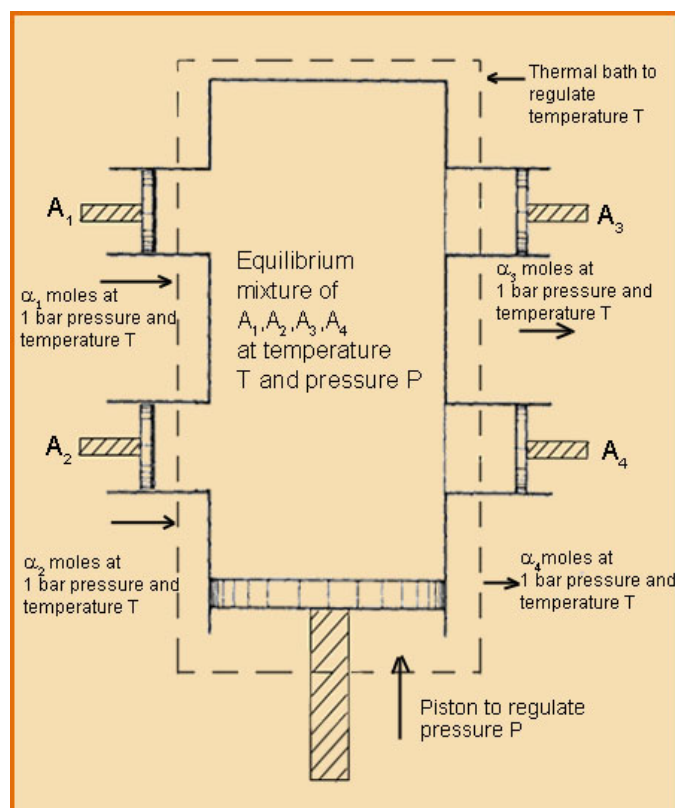

Fig. 8.2 Apparatus in which a gas-phase reaction occurs at equilibrium (van't Hoff equilibrium box)

temperature of 298^0K. Using the sign convention adopted above, the standard enthalpy of reaction at any temperature T may be mathematically expressed as follows:

$$\Delta H_T^0 = \sum_i \alpha_i H_{i,T}^0 \qquad\qquad ..(8.2)$$

Where, $H_{i,T}^0$ is the standard state enthalpy of species 'i' at the temperature T, and the summation is over all the reactants and products. For example, on expansion the eqn. 8.2 takes the following form for the reaction depicted in eqn. 8.1:

$$\Delta H_T^0 = \alpha_3 H_{3,T}^0 + \alpha_4 H_{4,T}^0 - \alpha_1 H_{1,T}^0 - \alpha_2 H_{2,T}^0 \quad ..(8.2)$$

If we further consider that each molecular species 'i' is formed from j elements each, an expression for the standard enthalpy of formation results:

$$\Delta H_{f_i,T}^0 = H_{i,T}^0 - \sum_j \alpha_j H_{j,T}^0 \quad ..(8.3)$$

Where, the summation is over all j constituent elements that make up the ith molecule, $\Delta H_{f_i,T}^0$ is *standard state enthalpy of formation* of the ith molecule at T, and $H_{j,T}^0$ the standard state enthalpy of the jth atomic species. If all $H_{j,T}^0$ are *arbitrarily* set to zero as the basis of calculation then eqn. 8.3 simplifies to:

$$H_{i,T}^0 = \Delta H_{f_i,T}^0 \quad ..(8.4)$$

In such a case eqn. 1 becomes:

$$\Delta H_T^0 = \sum_i \alpha_i \Delta H_{f_i,T}^0 \quad ..(8.5)$$

Values of Standard Enthalpy of formation of select substances are shown in Appendix VIII.

For simplicity in the subsequent equations we drop the subscript T, but implicitly all terms correspond to temperature T. Now writing H_i^0 in a differential form:

$$dH_i^0 = C_{P_i}^0 dT \quad ..(8.6)$$

Where $C_{P_i}^0$ is the specific heat of the ith species corresponding to its standard state. Note that since the standard state pressure for all substances is 1 bar in terms of pressure, for gases $C_{P_i}^0 = C_{P_i}^{ig}$, while for liquids and solids it is the *actual* value of the specific heat at 1 bar $(C_{P_i}^0 = C_{P_i})$. Since the specific heat of liquids and solids are weakly dependent on pressure, it helps write eqn. 8.6 in the general form shown. The following summation may be applied on eqn. 8.6 to give:

$$\sum_i \alpha_i dH_i^0 = \sum_i \alpha_i C_{P_i}^0 dT \quad ..(8.7)$$

Since each ξ_i is constant one may write:

$$\sum_i d(\alpha_i H_i^0) = d\sum_i \alpha_i H_i^0 \qquad ..(8.8)$$

Or: $d\sum_i \alpha_i H_i^0 = \sum_i \alpha_i C_{P_i}^0 dT \qquad ..(8.9)$

Thus: $d\Delta H^0 = \sum_i \alpha_i C_{P_i}^0 dT = \Delta C_P^o dT \qquad ..(8.10)$

Where, $\Delta C_P^o = \sum_i \alpha_i C_{P_i}^o$

Thus on integrating eqn. 8.10, between a datum T_0 and any T, we have:

$$\Delta H_T^o = \Delta H_0^o + \int_{T_0}^T \Delta C_P^o dT \qquad ..(8.11)$$

Note that since the standard state pressure is always at 1 bar, for all species one may write the general form of relation for specific heat capacity:

$$C_{P_i}^o = A_i + B_i T + C_i T^2 + ... \qquad ..(8.12)$$

(The values of and $C_{P_i}^o$ thus are those shown in *Appendix III*).

Eqn. 8.12 may be substituted in eqn. 8.11 which leads to:

$$\Delta H_T^o = \Delta H_0^o + \int_{T_0}^T \left[(\Delta A) + (\Delta B)T + (\Delta C)T^2 + ... \right] dT \qquad ..(8.13)$$

Where: $\Delta A = \sum_i \alpha_i A_i$; $\Delta B = \sum_i \alpha_i B_i$; $\Delta C = \sum_i \alpha_i C_t$; $\Delta D = \sum_i \alpha_i D_t$; and so on.

The standard enthalpy of reaction is most often reported at 298^0K. Using this value as the datum, the value of the standard heat of reaction at any other temperature can be evaluated using eqn. 8.13. As evident from eqn. 8.5 the enthalpy of a reaction may be recovered from the enthalpy of formation of the individual species for a reaction. Values of standard enthalpy of formation for a select list of compounds are tabulated in Appendix VIII.

In continuance of the foregoing considerations one may also define a standard Gibbs free energy change of a reaction. As we will see in the later sections, this property is essential to computing the equilibrium constant for a reaction at any temperature. As with enthalpy of reaction (eqn. 8.2) the standard Gibbs free energy change at any temperature is given by the function:

$$\Delta G_T^0 = \sum_i \alpha_i G_{i,T}^0 \qquad ..(8.14)$$

Thus, ΔG_T^0 is the difference between the Gibbs energies of the products and reactants when each is in its standard state as a pure substance at the system temperature and at a fixed pressure. Thus, just as the standard enthalpy of reaction is dependent *only* on temperature (the standard state pressure being fixed by definition), so is the Gibbs free energy change of a reaction. It follows that when the temperature is fixed ΔG_T^0 is *independent* of the reaction pressure or composition. Indeed extending the argument, one can define any standard property change of reaction by the same expression; all being functions of temperature alone:

$$\Delta M_T^0 = \sum_i \alpha_i M_{i,T}^0 \qquad ..(8.15)$$

Where: $M \equiv U, H, S, A, G.$

In the context of chemical reaction equlibria the relations between the standard enthalpy of reaction and the standard Gibbs energy change of reaction is of particular significance. Using the form described by eqn. 5.31, since any standard property change of a reaction is only temperature dependent, one may write:

$$H_{i,T}^o = -RT^2 \frac{d\left(G_{i,T}^o / RT\right)}{dT} \qquad ..(8.16)$$

Multiplying of both sides of this equation by α_i and summing over all species one obtains:

$$\sum \alpha_i H_{i,T}^o = -\text{RT}^2 \frac{d\left(\sum \alpha_i G_{i,T}^o / RT\right)}{dT}$$

This may be written as: $\Delta H_T^0 = -RT^2 \dfrac{d\left(\Delta G_T^0 / RT\right)}{dT} \qquad ..(8.17)$

Or: $\dfrac{d\left(\Delta G_T^0 / RT\right)}{dT} = -\dfrac{\Delta H_T^0}{RT^2} \qquad ..(8.18)$

Now substituting eqn. 8.13 in 8.18:

$$\frac{d\left(\Delta G_T^0 / RT\right)}{dT} = -\frac{1}{RT^2}\left[\Delta H_0^o + \left\{(\Delta A) + (\Delta B)T + (\Delta C)T^2 + ...\right\}dT\right]$$

If we know the standard Gibbs free energy change $\Delta G_{T_0}^0$ at a particular temperature T_0 (typically, values are reported at 298^0K) the above equation may be integrated as follows:

$$\frac{\Delta G_T^0}{RT} = \frac{\Delta G_{T_0}^0}{RT_0} - \int_{T_0}^{T}\left\langle\frac{1}{RT^2}\left[\Delta H_0^o + \left\{(\Delta A) + (\Delta B)T + (\Delta C)T^2 + ...\right\}dT\right]\right\rangle dT \qquad ..(8.19)$$

Or finally:

$$\frac{\Delta G_T^0}{T} = \frac{\Delta G_{T_0}^0}{T_0} - \int_{T_0}^{T} \left\langle \frac{1}{T^2} \left[\Delta H_0^o + \left\{ (\Delta A) + (\Delta B)T + (\Delta C)T^2 + ... \right\} dT \right] \right\rangle dT \qquad ..(8.20)$$

Example 8.1

Consider the reaction: $C_2H_4(g) + H_2O(g) \rightarrow C_2H_5OH(g)$. If an equimolar mixture of ethylene and water vapor is fed to a reactor which is maintained at 500 K and 40 bar determine the Gibbs free energy of the reaction, assuming that the reaction mixture behaves like an ideal gas. Assume the following ideal gas specific heat data: $C_p^{ig} = a + bT + cT^2 + dT^3 + eT^{-2}$ (J/mol); T(K).

Species	a	bx10^3	cx10^6	dx10^9	ex10^{-5}
C_2H_4	20.691	205.346	– 99.793	18.825	-
H_2O	4.196	154.565	– 81.076	16.813	-
C_2H_5OH	28.850	12.055	-	-	1.006

(Click for Solution)

8.3 The Reaction Coordinate

Consider again the general chemical reaction depicted in eqn. 8.1:

$$|\alpha_1|A_1 + |\alpha_2|A_2 = |\alpha_3|A_3 + |\alpha_4|A_4$$
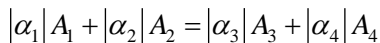
During the progress of the reaction, at each point the extent of depletion of the reactants, and the enhancement in the amount of product is exactly in proportion to their respective stoichiometric coefficients. Thus for any change dn_i in the number of moles of the ith species for a differential progress of the reaction one may write:

$$\frac{dn_1}{\alpha_1} = \frac{dn_2}{\alpha_2} = ... = \frac{dn_3}{\alpha_3} = \frac{dn_4}{\alpha_4} \qquad ..(8.21)$$

Since all terms are equal, they can all be set equal to a single quantity $d\xi$, defined to represent *the extent of reaction* as follows:

$$\frac{dn_1}{\alpha_1} = \frac{dn_2}{\alpha_2} = ... = \frac{dn_3}{\alpha_3} = \frac{dn_4}{\alpha_4} = d\xi \qquad ..(8.22)$$

The general relation between a differential change dn_i in the number of moles of a reacting species and $d\xi$ is therefore: $dn_i = \alpha_i d\xi$ (i = 1,2, ...N) $\qquad ..(8.23)$

This new variable ξ, called the *reaction coordinate*, describe the extent of conversion of reactants to products for a reaction. Thus, it follows that the value of ξ is zero at the start of the reaction. On the other hand when $\xi = 1$, it follows that the reaction has progressed to an extent at which point each reactant has depleted by an amount equal to its stoichiometric number of moles while each product has formed also in an amount equal to its stoichiometric number of moles. For dimensional consistency one designates such a degree of reaction as corresponding to $\Delta\xi = 1$ mole.

Now, considering that at the point where the reaction has proceeded to an arbitrary extent characterized by ξ (such that $\xi > 0$), the number of moles of ith species is n_i we obtain the following relation:

$\int_{n_{i0}}^{n_i} dn_i = \alpha_i \int_0^{\xi} d\eta$; where, η is a dummy variable and $n_{i0} =$ initial number of moles of 'i'. Thus:

$$n_i = n_{i_o} + \alpha_i \xi \;;(i = 1,2,...,N) \tag{8.24}$$

Thus the *total* number of moles of all species corresponding to ξ extent of reaction:

$$n = \sum n_i = \sum n_{i_o} + \xi \sum \alpha_i \tag{8.25}$$

Or: $n = n_0 + \alpha\xi \tag{8.26}$

Where:

$$n_0 = \sum n_{i_o} \tag{8.27}$$

$$\alpha = \sum \alpha_i \tag{8.28}$$

Thus, $y_i = \dfrac{n_i}{n} = \dfrac{n_{i_{io}} + \alpha_i \xi}{n_o + \alpha\xi} \tag{8.29}$

Example 8.2

Consider the following reaction: A(g) + B(g) = C(g) + 3D(g).

Intially the following number of moles are introduced in the reactor. Obtain the mole fraction expressions in terms of reaction coordinate.

$n_{0,A} = 2$ mol, $n_{0,B} = 1$ mol, $n_{0,C} = 1$ mol $n_{0,D} = 4$ mol

(Click for Solution)

The foregoing approach may be easily extended to develop the corresponding relations for a set of multiple, independent reactions which may occur in a thermodynamic system. In such a case each reaction is assigned an autonomous reaction co-ordinate ξ_j (to represent the jth reaction). Further the stoichiometric coefficient of the ith species as it appears in the jth reaction is designated by $\alpha_{i,j}$. Since a species may participate in more than a single reaction, the change in the total number of moles of the species at any point of time would be the sum of the change due each independent reaction; thus, in general:

$$dn_i = \sum_j \alpha_{i,j} d\xi_j \qquad (i = 1,2,...N) \qquad\qquad\qquad ..(8.30)$$

On integrating the above equation starting from the initial number of moles n_{i_o} to n_i corresponding to the reaction coordinate ξ_j of each reaction:

$$\int_{n_{i0}}^{n_i} dn_i = \int_0^{\xi_i} \sum_j \alpha_{i,j} d\xi_j \ (i = 1,2,...,N) \qquad\qquad\qquad ..(8.31)$$

Or: $n_i = n_{i_o} + \sum_j \alpha_{i,j} \xi_j$ $\qquad\qquad\qquad ..(8.32)$

Summing over all species gives:

$$\sum_i n_i = \sum_i n_{i_o} + \sum_i \sum_j \alpha_{i,j} d\xi_j \qquad\qquad\qquad ..(8.33)$$

Now: $\sum_i n_i = n$ and, $\sum_i n_{i_o} = n_0$ $\qquad\qquad\qquad ..(8.34)$

We may interchange the order of the summation on the right side of eqn. (8.33); thus:

$$\sum_i \sum_j \alpha_{i,j} d\xi_j = \sum_j \sum_i \alpha_{i,j} d\xi_j \qquad\qquad\qquad ..(8.35)$$

Thus, using eqns. 8.34 and 8.35, eqn. 8.33 may be written as:

$$n = n_0 + \sum_j \left(\sum_i \alpha_{i,j} \right) \xi_j \qquad\qquad\qquad ..(8.36)$$

In the same manner as eqn. 8.28, one may write:

$$\alpha_j = \sum_i \alpha_{i,j} \qquad\qquad\qquad ..(8.37)$$

Thus eqn. 8.33 becomes: $n = n_0 + \sum_j \alpha_j \xi_j$ $\qquad\qquad\qquad ..(8.38)$

Using eqns. 8.32 and 8.38 one finally obtains:

$$y_i = \frac{n_{i_o} + \sum_j \alpha_{i,j}\xi_j}{n_o + \sum_j \alpha_j \xi_j} \qquad (i = 1,2,....,N) \qquad ..(8.39)$$

<u>**Example 8.3**</u>

Consider the following simultaneous reactions. Express the reaction mixture composition as function of the reaction co-ordinates. All reactants and products are gaseous.

A + B = C + 3D   ..(1)

A + 2B = E + 4D   ..(2)

Initial number of moles: $n_{0,A} = 2$ mol; $n_{0,B} = 3$ mol

(Click for Solution)

8.4 Criteria for Chemical Reaction Equilibrium

The general criterion for thermodynamic equilibrium was derived in section 6.3 as:

$$(dG^t)_{T,P} \leq 0 \qquad\qquad ..(6.36b)$$

As already explained, the above equation implies that if a closed system undergoes a process of change while being under thermal and mechanical equilibrium, for all incremental changes associated with the compositions of each species, the total Gibbs free energy of the system would decrease. At complete equilibrium the equality sign holds; or, in other words, the Gibbs free energy of the system corresponds to the minimum value possible under the constraints of constant (and uniform) temperature and pressure. Since the criterion makes no assumptions as to the nature of the system in terms of the number of species or phases, or if reactions take place between the species, it may also be applied to determine a specific criterion for a reactive system under equilibrium.

As has been explained in the opening a paragraph of this chapter, at the initial state of a reaction, when the reactants are brought together a state of non-equilibrium ensues as reactants begin undergoing progressive transformation to products. However, a state of equilibrium must finally attain when the rates of forward and backward reactions equalize. Under such a condition, no further change in the composition of the residual reactants or products formed occurs. However, if we consider this particular state, we may conclude that while in a macroscopic sense the system is in a state of *static* equilibrium, in the microscopic sense there is dynamic equilibrium as reactants convert to products and vice versa. Thus the system is subject to minute fluctuations of concentrations of each species.

However, by the necessity of maintenance of the dynamic equilibrium the system always returns to the state of stable thermodynamic equilibrium. In a macroscopic sense then the system remains under the under equilibrium state described by eqn. 6.36b. It follows that in a reactive system at the state of chemical equilibrium the Gibbs free energy is minimum subject to the conditions of thermal and mechanical equilibrium.

The above considerations hold regardless of the number of reactants or the reactions occurring in the system. Since the reaction co-ordinate is the single parameter that relates the compositions of all the species, the variation of the total Gibbs free energy of the system as a function of the reaction co-ordinate may be shown schematically as in fig. 8.3; here ξ_e is the value of the reaction co-ordinate at equilibrium.
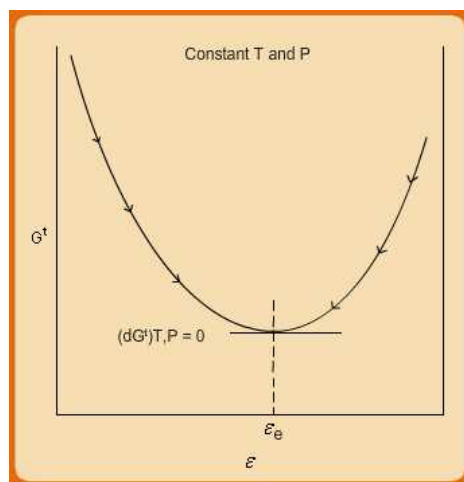

Fig. 8.3 Variation of system Gibbs free energy with equilibrium conversion

8.5 The Equilibrium Constant of Reactions

Since chemical composition of a reactive system undergoes change during a reaction, one may use the eqn. 6.41 for total differential of the Gibbs free energy change (for a single phase system):

$$d(nG) = (nV)dP - (nS)dT + \sum \mu_i dn_i \qquad ..(6.41)$$

For simplicity considering a single reaction occurring in a closed system one can rewrite the last equation using eqn. 8.3:

$$d(nG) = (nV)dP - (nS)dT + \sum \mu_i \alpha_i d\xi \qquad ..(8.40)$$

It follows that: $\sum \alpha_i \mu_i = \left[\dfrac{\partial(nG)}{\partial \xi} \right]_{T,P}$ \qquad ..(8.41)

On further applying the general condition of thermodynamic equilibrium given by eqn. 6.36b it follows that:

$$\left[\frac{\partial(nG)}{\partial\xi}\right]_{T,P} \equiv \left[\frac{\partial G^t}{\partial\xi}\right]_{T,P} = 0 \qquad \text{..(8.42)}$$

Hence by eqn. 8.41 and 8.42:

$$\sum\alpha_i\mu_i = 0 \qquad \text{..(8.43)}$$

Since the reactive system is usually a mixture one may use the eqn. 6.123:

$$d\mu_i = d\bar{G}_i = RTd\ln\hat{f}_i \text{; at constant T} \qquad \text{..(6.123)}$$

Integration of this equation at constant T from the standard state of species i to the reaction pressure:

$$\mu_{i,T} = G_{i,T}^o + RT\,ln\,\frac{\hat{f}_i}{f_i^o} \qquad \text{..(8.44)}$$

The ratio $\hat{f}_i/f_i^o$ is called the activity $\hat{a}_i$ of species i in the reaction mixture, i.e.:

$$\hat{a}_i = \frac{\hat{f}_i}{f_i^o} \qquad \text{..(8.45)}$$

Thus, the preceding equation becomes: $\mu_{i,T} = G_{i,T}^0 + RT\ln\hat{a}_i$ ..(8.46)

Using eqns. 8.46 and 8.44 in eqn. 8.43 to eliminate μ_i gives:

$$\sum\alpha_i(G_{i,T}^o + RT\,ln\,\hat{a}_i) = 0 \qquad \text{..(8.47)}$$

On further re-organization we have:

$$\sum v_i G_{i,T}^o + RT\sum\ln\left(\hat{a}_i\right)^{\alpha_i} = 0$$

$$\ln\left[\prod(\hat{a}_i)^{\alpha_i}\right] = -\frac{\sum\alpha_i G_{i,T}^o}{RT} \qquad \text{..(8.48)}$$

Where, $\prod$ signifies the product over all species i. Alternately:

$$\prod(\hat{a}_i)^{\alpha_i} = exp\left(-\frac{\sum\alpha_i G_{i,T}^o}{RT}\right) \qquad \text{..(8.49)}$$

$$\prod(\hat{a}_i)^{\alpha_i} = \prod\left(\hat{f}_i / f_i^0\right)^{\alpha_i} = K_T \qquad \text{..(8.50)}$$

On comparing eqns. 8.49 and 8.50 it follows: $K_T = exp\left(-\frac{\sum\alpha_i G_{i,T}^o}{RT}\right)$ ..(8.51)

The parameter K_T is defined as the equilibrium constant for the reaction at a given temperature. Since the standard Gibbs free energy of pure species, $G_{i,T}^o$, depends only on temperature, the equilibrium constant K_T is also a function of temperature alone. On the other hand, by eqn. 8.50 K_T is a function of $\hat{f}_i$, which is in turn a function of composition, temperature and pressure. Thus, it follows that since temperature fixes the equilibrium constant, any variation in the pressure of the reaction must lead to a change of equilibrium composition subject to the constraint of K_T remaining constant. Equation (8.51) may also be written as:

$$-RT \ln K_T = \sum \alpha_i G_{i,T}^o = \Delta G_T^0 \qquad ..(8.52)$$

$$\ln K_T = -\frac{\Delta G_T^0}{RT} \qquad ..(8.53)$$

Taking a differential of eqn. 8.53:

$$\frac{d \ln K_T}{dT} = -\frac{d\left(\Delta G_T^0 / RT\right)}{dT} \qquad ..(8.53)$$

Now using eqn. 8.18:

$$\frac{d \ln K_T}{dT} = \frac{\Delta H_T^0}{RT^2} \qquad ..(8.54)$$

On further use of eqn. 8.13:

$$\frac{d \ln K_T}{dT} = \frac{\Delta H_0^o + \int_{T_0}^{T}\left[(\Delta A) + (\Delta B)T + (\Delta C)T^2 + ...\right]}{RT^2}$$

Lastly, upon integration one obtains the following expression:

$$\ln K_T = \ln K_{T_0} - \frac{\Delta H_0^o + \int_{T_0}^{T}\left[(\Delta A) + (\Delta B)T + (\Delta C)T^2 + ...\right]dT}{RT^2} \qquad ..(8.55)$$

Where, K_{T_0} is the reaction equilibrium constant at a temperature T_0.

If ΔH_T^0, is assumed independent of T (i.e. ΔH_{avg}^0, over a given range of temperature $(T_2 - T_1)$, a simpler relationship follows from eqn. 8.54:

$$\ln \frac{K_{T2}}{K_{T1}} = -\frac{\Delta H_{avg}^0}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \qquad ..(8.55)$$

The above equation suggests that a plot of $\ln K_T$ vs. $1/T$ is expected to approximate a straight line. It also makes possible the estimation of the equilibrium constant at a temperature given its values at

another temperature. However, eqn. 8.55 provides a more rigorous expression of the equilibrium constant as a function of temperature.

Equation 8.54 gives an important clue to the variation of the equilibrium constant depending on the heat effect of the reaction. Thus, if the reaction is exothermic, i.e., $\Delta H_T^0 < 0,$ the equilibrium constant decreases with increasing temperature. On the other hand, if the reaction is endothermic, i.e., $\Delta H_T^0 > 0,$ equilibrium constant increases with increasing temperature. As we shall see in the following section, the equilibrium conversion also follows the same pattern.

Example 8.4

Consider again the reaction: $C_2H_4(g)$ + $H_2O(g) \rightarrow C_2H_5OH(g)$. If an equimolar mixture of ethylene and water vapor is fed to a reactor which is maintained at 500 K and 40 bar determine the equilibrium constant, assuming that the reaction mixture behaves like an ideal gas. Assume the following ideal gas specific heat data: C_p^{ig} = a + bT + cT² + dT³ + eT⁻² (J/mol); T(K).

Species	a	bx10³	cx10⁶	dx10⁹	ex10⁻⁵
C₂H₄	20.691	205.346	– 99.793	18.825	-
H₂O	4.196	154.565	– 81.076	16.813	-
C₂H₅OH	28.850	12.055	-	-	1.006

(Click for solution)

8.6 Reactions involving gaseous species

We now consider eqn. 8.50 that represents a relation that connects equilibrium composition with the equilibrium constant for a reaction. The activities $\hat{a}_i$ in eqn. 8.50 contains the standard state fugacity of each species which – as described in section 8.1 – is chosen as that of pure species at 1 bar pressure. The assumption of such a standard state is necessarily arbitrary, and any other standard state may be chosen. But the specific assumption of 1 bar pressure is convenient from the point of calculations. Obviously the value of the state Gibbs free energy G_i^o of the species needs to correspond to that at the

standard state fugacity. In the development that follows we first consider the case of reactions where all the species are gaseous; the case of liquids and solids as reactants are considered following that.

For a gas the standard state is the *ideal-gas state* of pure i at a pressure of 1 bar. Since a gaseous species at such a pressure is considered to be in an ideal gas state its fugacity is equal to its pressure; hence at the standard state assumed at the present, $f_i^o = 1$ bar for each species of a gas-phase reaction. Thus, the activity and hence eqn. 8.50 may be re-written as follows:

$$\hat{a}_i = \hat{f}_i / f_i^o = \hat{f}_i \qquad \qquad ..(8.56)$$

$$K = \prod \left(\hat{f}_i \right)^{\alpha_i} \qquad \qquad ..(8.57)$$

For the use of eqn. 8.57, the fugacity $\hat{f}_i$ must be specified in bar [or (atm)] because each $\hat{f}_i$ is implicitly divided by f_i^o 1 bar [or 1(atm)]. It follows that the equilibrium constant K_T is dimensionless. This is true also for the case of liquid and/or solid reactive species, though, as is shown later, the standard state fugacity is not necessarily 1 bar, since for condensed phases the fugacity and pressure need not be identical at low pressures.

By eqn. 6.129, for gaseous species, $\hat{f}_i = \hat{\phi}_i y_i P$. Thus eqn. 8.57 may be rewritten as:

$$K_T = \prod \left(\hat{\phi}_i y_i P \right)^{\alpha_i} \qquad \qquad ..(8.58)$$

On further expanding the above equation:

$$K_T = \left\{ \prod \left(\hat{\phi}_i \right)^{\alpha_i} \right\} \left\{ \prod (y_i)^{\alpha_i} \right\} \left\{ \prod (P)^{\alpha_i} \right\} \qquad \qquad ..(8.59)$$

Or:

$$K_T = K_\phi K_y P^\alpha \qquad \qquad ..(8.60)$$

Where:

$$K_\phi = \left\{ \prod \left(\hat{\phi}_i \right)^{\alpha_i} \right\} \qquad \qquad ..(8.61)$$

$$K_y = \left\{ \prod (y_i)^{\alpha_i} \right\} \qquad \qquad ..(8.62)$$

$$\left\{ \prod (P)^{\alpha_i} \right\} = P^{\sum_i \alpha_i} = P^\alpha \qquad \qquad ..(8.63)$$

An alternate from of eqn. 8.60 is:

$$K_\phi K_y = K_T P^{-\alpha} \qquad \qquad ..(8.64)$$

Both the terms K_ϕ and K_y contain the mole fraction y_i of each species. As given by eqn. 8.29 or 8.39, all the mole fractions may be expressed as a function of the reaction co-ordinate ξ of the reaction(s). Hence, for a reaction under equilibrium at a given temperature and pressure the only unknown in eqn. 8.64 is the equilibrium reaction co-ordinate ξ_e. An appropriate model for the fugacity coefficient (based on an EOS: virial, cubic, etc.) may be assumed depending on the pressure, and eqn. 8.64 may then solved using suitable algorithms to yield the equilibrium mole fractions of each species. A relatively simple equation ensues in the event the reaction gas mixture is assumed to be ideal; whence $\hat{\phi}_i = 1.$ Thus, eqn. 8.64 simplifies to:

$$K_y = K_T P^{-\alpha} \qquad\qquad\qquad ..(8.65)$$

Or:

$$\Pi(y_i)^{\alpha_i} = P^{-\alpha} K \qquad\qquad\qquad ..(8.66)$$

Yet another simplified version of eqn. 8.64 results on assuming *ideal solution* behavior for which (by eqn.7.84): $\hat{\phi}_i = \phi_i.$ Thus:

$$K_\phi = \left\{ \Pi(\phi_i)^{\alpha_i} \right\} \qquad\qquad\qquad ..(8.67)$$

This simplification renders the parameter K_ϕ independent of composition. Once again a suitable model for fugacity coefficient (using an EOS) may be used for computing each ϕ_i and eqn. 8.64 solved for the equilibrium conversion.

Example 8.5

Consider the reaction: $C_2H_4(g) + H_2O(g) \rightarrow C_2H_5OH(g)$. If an equimolar mixture of ethylene and water vapor is fed to a reactor which is maintained at 500 K and 40 bar determine the degree of conversion, assuming that the reaction mixture behaves like an ideal gas. Assume the following ideal gas specific heat data: $C_p^{ig} = a + bT + cT^2 + dT^3 + eT^{-2}$ (J/mol); T(K).

| Species	a	bx10³	cx10⁶	dx10⁹	ex10⁻⁵
C_2H_4	20.691	205.346	– 99.793	18.825	-
H_2O	4.196	154.565	– 81.076	16.813	-
C_2H_5OH	28.850	12.055	-	-	1.006

8.7 Reaction equilibria for simultaneous reactions

While we have so far presented reaction equlibria for single reactions, the more common situation that obtains in industrial practice is that of multiple, simultaneous reactions. Usually this occurs due to the presence of 'side' reactions that take place in addition to the main, desired reaction. This leads to the formation of unwanted side products, necessitating additional investments in the form of purification processes to achieve the required purity of the product(s). An example of such simultaneously occurring reaction is:

$$CH_4(g) + 2O_2(g) \rightleftharpoons CO_2(g) + 2H_2O(g)$$

$$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$$
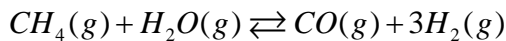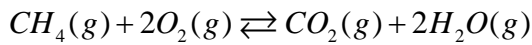
Clearly the challenge in such cases is to determine the reaction conditions (of temperature, pressure and feed composition) that maximize the conversion of the reactants to the desired product(s). Essentially there are two methods to solve for the reaction equilibria in such systems.

Method 1: Use of reaction-co-ordinates for each reaction

This is an extension of the method already presented in the last section for single reactions. Consider, for generality, a system containing i chemical species, participating in j *independent* parallel reactions, each defined by a reaction equilibrium constant K_j and a reaction co-ordinate ξ_j. One can then write a set of j equations of the type 8.64 as follows:

$$(K_\phi)_j (K_y)_j = K_{T,j} P^{-\alpha_j} \qquad \qquad ..(8.68)$$

Where, α_j and y_i are given by eqns. 8.37 and 8.39 respectively (as follows):

$$\alpha_j = \sum_i \alpha_{i,j} \qquad \qquad ..(8.37)$$

And, $\quad y_i = \dfrac{n_{i_o} + \sum\limits_j \alpha_{i,j} \xi_j}{n_o + \sum\limits_j \alpha_j \xi_j} \qquad (i = 1,2,....,N) \qquad \qquad ..(8.39)$

Therefore there are j unknown reaction co-ordinates which may be obtained by solving simultaneously j equations of the type 8.68.

Example 8. 6

The following two independent reactions occur in the steam cracking of methane at 1000 K and 1 bar:

$CH_4(g) + H_2O(g) \rightarrow CO(g) + 3H_2(g)$; and $CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g)$. Assuming ideal gas behaviour determine the equilibrium composition of the gas leaving the reactor if an equimolar mixture of CH_4 and H_2O is fed to the reactor, and that at 1000K, the equilibrium constants for the two reactions are 30 and 1.5 respectively.

(Click for solution)

Method 2: Use of Lagrangian Undetermined Multipliers

This method utilizes the well-known Lagrangian method of undetermined multipliers typically employed for optimizing an objective function subject to a set of constraints. As outlined in section 8.3 at the point of equilibrium in a reactive system, the total Gibbs free energy of the system is a minimum. Further, during the reaction process while the total number of moles may not be conserved, the total mass of each atomic species remains constant. Thus, in mathematical terms, the multi-reaction equilibria problem amounts to minimizing the total Gibbs free energy of the system subject to the constraint of conservation of total atomic masses in the system. The great advantage that this approach offers over the previous method is that one does not need to explicitly determine the set of independent chemical reactions that may be occurring in the system.

We formulate below the set of equations that need to be solved to obtain the composition of the system at equilibrium. Let there be N chemical (reactive) species and p (corresponding) elements in a system; further, n_i= initial no of moles of species i; β_{ik} = number of atoms of kth element in the ith chemical species; β_k= total number of atomic masses of kth element as available in the initial feed composition.

$$\sum_i n_i \beta_{ik} = \beta_k; \; \left(k \; = \; 1,2..., \; p \right) \quad\quad\quad ..(8.69)$$

$$\text{Or:} \sum_i n_i \beta_{ik} - \beta_k = 0; \; \left(k \; = \; 1,2..., \; p \right) \quad\quad\quad ..(8.70)$$

Use of p number of Lagrangian multipliers (one for each element present in the system) give:

$$\lambda_k \left(\sum_i n_i \beta_{ik} - \beta_k \right) = 0; \quad (k = 1, 2..., p) \qquad ..(8.71)$$

These equations are summed over p, giving:

$$\sum_p \lambda_k \left(\sum_i n_i \beta_{ik} - \beta_k \right) = 0 \qquad ..(8.72)$$

Let G^t be the total Gibbs free energy of the system. Thus, incorporating p equations of the type 8.72 one can write the total Lagrangian L for the system as follows:

$$L = G^t + \sum_p \lambda_k \left(\sum_i n_i \beta_{ik} - \beta_k \right) \qquad ..(8.73)$$

It may be noted that in eqn. 8.73, L always equals G^t as the second term on the RHS is identically zero. Therefore, *minimum* values of both L and G_t occur when the partial derivatives of L with respect to all the n_i and λ_k are zero.

Thus:
$$\left(\frac{\partial F}{\partial n_i} \right)_{T,P,n_{j \neq i}} = \left(\frac{\partial G^t}{\partial n_i} \right)_{T,P,n_{j \neq i}} + \sum_k \lambda_k \beta_{ik} = 0; \quad (i = 1, 2, ..., N) \qquad ..(8.74)$$

However, the first term on the RHS is the chemical potential of each reactive species in the system; thus eqn. 8.74 may be written as:

$$\mu_i + \sum_k \lambda_k \beta_{ik} = 0; \quad (i = 1, 2, ..., N) \qquad ..(8.75)$$

But by eqn. 8.44:

$$\mu_{i,T} = G^o_{i,T} + RTln\left(\hat{f}_i / f_i^o \right) \qquad ..(8.44)$$

Once again, we consider, for illustration, the case of gaseous reactions for which the standard state pressure for each species is 1 bar, whence, $f_i^0 = 1bar$.

$$\mu_{i,T} = G^o_{i,T} + RTln\left(\hat{f}_i \right) \qquad ..(8.76)$$

$$\mu_{i,T} = \Delta G^o_{f_i,T} + RT \ln\left(y_i \hat{\phi}_i P \right) \qquad ..(8.77)$$

In the above equation $G^o_{i,T}$ may be equated to $\Delta G^o_{f_i,T}$, the latter being the standard Gibbs free energy of formation of the 'i' species (at temperature T). In arriving at this relation, the standard Gibbs free energy of formation of the elements comprising the ith species are arbitrarily set to zero (for convenience of calculations). Thus combining eqns. 8.75 and 8.77 one obtains:

$$\Delta G^o_{f_i,T} + RT \ln\left(y_i \hat{\phi}_i P\right) + \sum_k \lambda_k \beta_{ik} = 0; \quad (i = 1, 2, \ldots, N);$$ ..(8.78)

In eqn. 8.78, the reaction pressure P needs to be specified in bar (as $f_i^0 = 1bar$). Also, if the ith species is an element, the corresponding $\Delta G^0_{f_i,T} = 0$

Further taking the *partial* derivative of the Lagrangian L (of eqn. 8.73) $\left(\partial L / \partial \lambda_k\right)_{n_i, \lambda_{n \neq k}}$ with respect to each of the p undetermined multipliers, an additional set of p equations of type 8.70 obtains. Thus there are a total of $(N + p)$ equations which may be solved simultaneously to obtain the complete set of equilibrium mole fractions of N species.

Example 8.7

The gas n-pentane (1) is known to isomerise into neo-pentane (2) and iso-pentane (3) according to the following reaction scheme: $P_1 \rightleftharpoons P_2; P_2 \rightleftharpoons P_3; P_3 \rightleftharpoons P_1$. 3 moles of pure n-pentane is fed into a reactor at 400^oK and 0.5 atm. Compute the number of moles of each species present at equilibrium.

Species	ΔG^0_f at 400^oK (Cal/mol)
P_1	9600
P_2	8900
P_3	8200

8.8 Reactions involving Liquids and Solids

In many instances of industrially important reactions, the reactants are not only gaseous but are also liquids and / or solids. Such reactions are usually *heterogeneous* in nature as reactants may exist in separate phases. Some examples include:

- Removal of CO_2 from synthesis gas by aqueous solution of potassium carbonate
- Removal of H_2S by ethanolamine or sodium hydroxide
- Air oxidation of aldehydes to acids
- Oxidation of cyclohexane to adipic acid
- Chlorination of benzene

- Decomposition of $CaCO_3$ to CaO and CO_2

In all such instances some species need to dissolve and then diffuse into another phase during the process of reaction. Such reactions therefore require not only reaction equilibria considerations, but that of phase equilibria as well. For simplicity, however we consider here only reaction equilibria of instances where liquid or solid reactive species are involved. The thermodynamic treatment presented below may easily be extended to describe any heterogeneous reaction. The basic relation for the equilibrium constant remains the starting point. By eqn. 8.50 we have:

$$K_T = \prod (\hat{a}_i)^{\alpha_i}$$

..(8.50)

On expanding (by eqn. 6.171):

$$\hat{a}_i = \hat{f}_i(T, P, x_i) / f_i^0$$

..(8.79)

As already mentioned in section 8.1 above, for solids and liquids the usual standard state is the *pure solid or liquid at 1 bar [or 1(atm)] and at the temperature (T) of the system*. However, unlike in the case of gaseous species, the value of f_i^o for such a state cannot be 1 bar (or 1 atm), and eqn.(8.50) cannot be reduced to the form simple form of eqn. 8.57.

Liquid-phase reactants

On rewriting eqn. 8.79:

$$\hat{f}_i(T, P, x_i) = x_i \gamma_i f_i$$

Thus:

$$\hat{a}_i = x_i \gamma_i f_i(T, P) / f_i^0(T, 1bar)$$

..(8.80)

By eqn. 6.115:

$$RTd\ln f_i = V_i dP$$

Thus on integrating:

$$\int_{f_i^0(T, 1bar)}^{f_i(T, P)} d\ln f_i = \int_1^P \frac{V_i}{RT} dP$$

..(8.81)

As we have already seen in section 6.10, the liquid phase properties, such as molar volume, are weakly dependent on pressure; hence their variation with respect to pressure may be, for most practical situations, considered negligible. Thus, if one considers that in the last equation the molar volume V_i is constant over the range $1 - P$ bar, one obtains:

$$\ln\left[\frac{f_i}{f_i^0}\right] = \frac{V_i(P-1)}{RT}$$ ..(8.82)

$$\therefore f_i / f_i^o = \exp\left\{\frac{V_i(P-1)}{RT}\right\}$$ ..(8.83)

Thus, using eqn. 8.53 in 8.50:

$$K_T = \Pi(\hat{a}_i)^{\alpha_i} = \left[\pi(x_i\gamma_i)^{\alpha_i}\right]\left[\Pi(f_i/f_i^o)^{\alpha_i}\right]$$ ..(8.84)

Or: $\Pi(f_i/f_i^o)^{\alpha_i} = \exp\left[\left(\frac{P-1}{RT}\right)\sum\alpha_i V_i\right]$

Thus:

$$K_T = \left[\Pi(x_i\gamma_i)^{\alpha_i}\right]\exp\left[\frac{(P-1)\sum\alpha_i V_i}{RT}\right]$$ ..(8.85)

Except for very high pressure the exponential term on the right side of the above equation: $(P-1)\sum\alpha_i V_i << RT$.

Thus one may approximate:

$$\exp\left[\frac{(P-1)\sum\alpha_i V_i}{RT}\right] \approx 1.0$$

Whence:

$$K_T \simeq \Pi(x_i\gamma_i)^{\alpha_i}$$ ..(8.86)

To use the above equation for prediction of the equilibrium composition one needs to employ a suitable activity coefficient model. The activity coefficient models described in section 6.18 are based on physical interactions between molecules. Hence, their use is not expected to be adequately representative of a situation where molecules are subject to specific chemical forces and are chemically transformed due to formation of intermediate reactive complexes. While it is possible to write models for physical interactions it is generally not feasible to establish quantitative relations that describe the microscopic-level interactions between reactive molecular species. Discussions on approaches to solve such problems may be found elsewhere (J.M. Prausnitz, R.N. Lichtenthaler and E.G. Azevedo, *Molecular Thermodynamics of Fluid-Phase Equilibria,* 3rd ed., Prentice Hall, 1998). Nevertheless, for

the purpose of illustrating an approximate solution, one may simplify eqn. 8.86 by assuming ideal solution behavior, wherein $\gamma_i = 1.0$. Hence:

$$K = \prod (x_i)^{\alpha_i}$$ ..(8.87)

However, since reactive solutions can never be ideal, one way to overcome the difficulty is by defining a reaction equilibrium constant based on molar concentration (say in moles/m³), rather than in terms of mole fractions. Thus:

$$K_c = \prod (C_i)^{\alpha_i}$$ ..(8.88)

Where, C_i = molar concentration of each species.

It is generally difficult to predict the equilibrium constant K_C, and one needs to use experimentally determine values of such constants in order to predict equilibrium compositions.

Example 8.8

Consider the liquid phase reaction: A(l) + B(l) → C(l) + D(l). At 50°C, the equilibrium constant is 0.09. Initial number of moles, $n_{A,0}$ = 1 mole; $n_{B,0}$ = 1 mol Find the equilibrium conversion. Assume ideal solution behaviour.

(Click for solution)

Solid-phase reactants

Consider a solid reactive species now, for which one again starts from eqn. 8.80:

$$\hat{a}_i = \hat{f}_i (T, P, x_i) / f_i^0$$ ..(8.80)

Thus as for a liquid reactant one has

$$\hat{a}_i = (x_i \gamma_i)(f_i / f_i^0) = \hat{a}_i = (x_i \gamma_i) \exp \left[\frac{(P-1)V_i}{RT} \right]$$

As it is for liquid species, V_i for solids is also small and remains practically constant with pressure, thus:

$$\exp \left[\frac{(P-1)\sum \alpha_i V_i}{RT} \right] \approx 1.0$$

In addition, the solid species is typically 'pure' as any dissolved gas or liquid (for a multi-phase reaction) is negligible in amount.

Thus $x_i \sim 1.0, \rightarrow \gamma_i = 1$.

Therefore, for solids $\hat{a}_i = (x_i \gamma_i) \exp\left[\dfrac{(P-1)V_i}{RT}\right] \approx 1.0$ ..(8.89)

Example 8.9

Consider the following reaction: A(s) + B(g) → C(s) + D(g). Determine the equilibrium fraction of B which reacts at 500°C if equal number of moles of A and B are introduced into the reactor initially. The equilibrium constant for the reaction at 500°C is 2.0.

Assignment- Chapter 8