3.0 INTRODUCTORY REMARKS

Much of the material covered in Chapter 2 will now be repeated in a form applicable to nonideal systems. Here we shall be particularly concerned about the proper characterization of the chemical potential for a nonideal phase. Once this quantity is known all thermodynamic properties of the system can be determined. Particular emphasis will be placed on the fact that many alternative descriptions are possible: Though they may look different, pains will be taken to ensure that the various final mathematical formulations all describe a given system in a unique fashion.

3.1 THERMODYNAMIC TREATMENT OF NONIDEAL GASES

(a) We commence with our study of nonideal gaseous systems. Here, as well as later, two important interrelated principles are invoked: (i) the formulations developed in Chapters 1 and 2 for ideal gases are so convenient that it is worth preserving their form for nonideal systems. (ii) The present analysis must ultimately reduce to the treatment of Chapter 2 in the limit of very low total pressures and elevated temperatures, since it is well established that in these circumstances all gases approach ideal behavior.

Equation (2.4.15) relates the chemical potential \( \mu_1 \) of an
ideal gas to the form $RT \ln P_i$; this suggests that we introduce a functional form $RT \ln f_i$ such that for a nonideal gas $\mu_i$ should vary as $RT \ln f_i$. In the limit of low pressures $f_i$ should approach the partial pressure $P_i$. Here $f_i$ is termed the activity or fugacity of the $i$th component in the gas phase. Since $\mu_i$ is known only to within an arbitrary constant, we can specify uniquely only the difference in chemical potential of a nonideal gas in two states, $1$ and $2$, as characterized by the corresponding fugacities $f_1$ and $f_2$. This difference will be expressed as

$$\mu_i(T,f_2) - \mu_i(T,f_1) = RT \ln f_2 - RT \ln f_1,$$  \hspace{1cm} (3.1.1)

so that the strict analogy to the ideal gas situation (in which $f$ is replaced by $P$) will be preserved. Now let $1$ be any arbitrary fixed reference state for which the gas has the fugacity $f_1^0$, and let $2$ be any other state of the gaseous system for which its fugacity is $f_2$. Then Eq. (3.1.1) becomes

$$\mu_i(T,f_2) = \mu_i(T,f_1^0) + RT \ln \left(\frac{f_2}{f_1^0}\right).$$  \hspace{1cm} (3.1.2)

This equation is self-consistent since it reduces to an identity when $f_1 = f_2^0$. Suppose the standard state is now chosen at such a low total pressure that the gas is sensibly ideal. Then the distinction between pressure and fugacity disappears, as discussed earlier in (ii). We now may set $f_1^0 = P_1^0$, and adopt Eq. (2.4.15), according to which

$$\mu_i(T,P_1^0) = \mu_i^{0P}(T) + RT \ln P_1^0.$$  \hspace{1cm} (3.1.3)

When (3.1.3) is substituted in (3.1.2) with $f_1^0 = P_1^0$ one obtains the canonical form

$$\mu_i(T,f_1) = \mu_i^{0P}(T) + RT \ln f_1.$$  \hspace{1cm} (3.1.4a)

The standard state in Eq. (3.1.4a) is the chemical potential of the gas at unit activity if all interactions could be turned
off so that the gas would be ideal. The fact that such a state cannot be realized in practice need not act as a deterrent: So long as all changes in properties of the actual gas are always referred to this particular state, which is a reference point and can thus be arbitrarily chosen, one will always obtain self-consistent results. To demonstrate these matters explicitly we introduce the activity or fugacity coefficient $\gamma_i$, defined by $\gamma_i = f_i/P_i$, to rewrite (3.1.4a) as

$$\mu_i(T,f_i) = \mu_i^{\text{op}}(T) + RT \ln \gamma_i + RT \ln P_i.$$  \hfill (3.1.4b)

We see now that $\mu_i^{\text{op}}$ is that value of $\mu_i$ when $P_i = 1$ and $\gamma_i = 1$ are both satisfied.

If one wished to refer all quantities to a state which is in fact experimentally accessible, one could obtain a form analogous to (3.1.4a) by setting $f_i = 1$, so that Eq. (3.1.2) reads

$$\mu_i(T,f_i) = \mu_i(T,1) + RT \ln f_i.$$  \hfill (3.1.5)

The distinction between (3.1.5) and (3.1.4) is that $\mu_i(T,1)$ is the value of the chemical potential of the real gas at unit fugacity. On comparing (3.1.4a) and (3.1.5) one notices that consistency requires the fugacity scale for the two cases to be different. For better or for worse, the thermodynamic characterization of real gases is almost invariably based on Eq. (3.1.4).

Finally, to satisfy requirement (ii) we demand that

$$\lim_{P \to 0} \gamma_i = 1, \quad \lim_{P \to 0} f_i = P_i.$$  \hfill (3.1.6)

Here $P$ is the total pressure of all gases combined, including species $i$.

(b) Here as well as later, Eq. (3.1.4a) or (3.1.4b) is purely formal until it is shown either by experimental or by
theoretical methods how $f_1$ is related to $P_1$, i.e., how $\gamma_1$ is to be determined. For this purpose we begin with the reformulation of Eq. (3.1.4a) as

$$d\mu_1 = RT \, d\ln f_1 \quad (T \text{ constant}), \quad (3.1.7)$$

from which, for constant temperature and composition,

$$\left( \frac{\partial \ln f_1}{\partial P} \right)_{T,x_1} = \frac{\bar{V}_i}{RT}. \quad (3.1.8)$$

Note that it is important to specify all operations in terms of the total pressure $P$, since only the total pressure can be readily manipulated experimentally.

Next, introduce a quantity by $b_i = \bar{V}_i - RT/P$ that measures deviations from ideal gas behavior. Then

$$d\ln f_1|_{T,x_1} = \left( \frac{b_i}{RT} + \frac{1}{P} \right) dP - \frac{b_i}{RT} dP + d\ln P, \quad (3.1.9a)$$

or

$$d\ln \left( \frac{f_1}{P} \right)|_{T,x_1} = \frac{b_i}{RT} dP|_{T,x_1}. \quad (3.1.9b)$$

On integration at fixed $T$ and composition from some very low pressure $P_i$ to the pressure $P$ of interest, we obtain

$$\int_{P_i}^{P} d\ln \left( \frac{f_1}{P} \right) = \frac{1}{RT} \int_{P_i}^{P} b_i dP = \ln \left( \frac{f_1}{P} \right) - \ln \left( \frac{f_{1i}}{P_i} \right) \quad (T,x_1 \text{ constant}). \quad (3.1.10)$$

But as $P_i \to 0$, $f_{1i} \to x_i P_i$. Thus, (3.1.10) reduces to

$$\ln \left( \frac{f_1}{P} \right) = \frac{1}{RT} \int_{P_i}^{P} b_i dP + \ln x_i \quad (T,x_i \text{ constant}). \quad (3.1.11)$$

This equation serves to determine $f_1$ once $b_i$ is known in its dependence on $P$. 
(c) Let us specialize to the case of a one-component gas. Here it is simplest to return to (3.1.8):

\[ \ln \left( \frac{f}{f_t} \right) = \frac{1}{RT} \int_{P_t}^{P} \tilde{V} dp \quad (T \text{ constant}). \quad (3.1.12) \]

In this equation \( P_t \) is a very low pressure at which one may set \( P = f \) without appreciable error. An integration by parts yields

\[ \ln \left( \frac{f}{P} \right) = \frac{1}{RT} \left[ P\tilde{V} - P_t\tilde{V}_t - \int_{\tilde{V}_t}^{\tilde{V}} P \, dv \right] \quad (T \text{ constant}), \quad (3.1.13) \]

so that finally

\[ \ln f = \ln P_t + \left( \frac{P\tilde{V}}{RT} - 1 \right) - \frac{1}{RT} \int_{\tilde{V}_t}^{\tilde{V}} P \, dv \quad (T \text{ constant}), \quad (3.1.14) \]

which shows explicitly how \( f \) may be determined analytically or numerically once the equation of state \( P(T,V) \) has been prescribed. In practice one may proceed graphically by using Eq. (3.1.11) with \( f_1 = f \), \( b_1 = b = \tilde{V} - RT/P \), and \( \ln x_1 = 0 \). It is customary to plot \( b/RT \) versus \( P \) and to measure the area under the curve up to the pressure \( P \) of interest. This yields the integral on the right-hand side of Eq. (3.1.11). One should note that at zero pressure \( f/P_t \to 1 \), so that \( \ln (f/P_t) \) vanishes at that point.

As an alternative one can introduce an appropriate equation of state \( P = P(T,\tilde{V}) \) into Eq. (3.1.14). The lower limit of the integrated form for the last term in Eq. (3.1.14) will then contain \( \tilde{V}_t \), which quantity dominates all others. All terms involving \( \tilde{V}_t^{-1} \) may be neglected, and \( \tilde{V}_t \) in the argument of terms such as \( \ln (1/\tilde{V}_t) \) may be replaced by \( P_t/RT \); the resulting \( - \ln P_t \) term will then cancel against the first term on the right of Eq. (3.1.14). As an alternative approach one should note that at very low pressures the gas is ideal, so that the lower limit for the integral on the right of Eq. (3.1.14) is
specified by \( RT/P_i \). Then the choice of \( P_i \) in the first term dictates the lower limit of the integral. Hence, the final result does not depend on the chosen value of \( P_i \), so long as the latter is in the domain where the actual gas is sensibly ideal in its properties. The reader is invited to test this qualitative discussion by working out Exercise 3.1.1 in detail. One should also note that in Eq. (3.1.14), \( \bar{V}_i = RT/P \), and that \( \bar{V} \) is the molar volume of the gas measured at the temperature \( T \) of interest and at the value \( P \) for which \( f \) is to be determined; \( \bar{V} \) is found by inversion of \( P = P(T,V) \).

EXERCISES

3.1.1 Write out an equation specifying \( \ln f \) for a gas satisfying the van der Waals equation of state \( P = RT/(\bar{V} - b) - a\bar{V}^{-2} \).

3.1.2 (a) Determine the fugacity of a gas which obeys the truncated virial equation, \( P(\bar{V} - B) = RT \). (b) \( P-V-T \) data for helium at 40°F and pressures up to 4000 psi are specified by the empirical relation \( P\bar{V}/RT = 1 + bP, b = 3.55 \times 10^{-5} \text{ psi}^{-1} \). Find \( f \) in atmospheres at \( P = 250 \text{ atm} \) and at 40°F. (c) What is \( \mu \) (actual) - \( \mu \) (ideal)?

3.1.3 Given the following virial equation of state for \( \text{CH}_4(g) \) at 20°C (when \( P \) is in atmospheres and \( \bar{V} \) in liter/mol):
\[
P\bar{V} = 24.055 - 4.8678(10^{-2})P + 8.956(10^{-5})P^2 + 10.486(10^{10})P^4,
\]
find its fugacity at that temperature and at a pressure of 300 atm.

3.1.4 At 800 K the following values are reported for the density of steam:

<table>
<thead>
<tr>
<th>Pressure (atm)</th>
<th>1</th>
<th>10</th>
<th>20</th>
<th>40</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>120</td>
<td>160</td>
<td>200</td>
<td></td>
</tr>
<tr>
<td>240</td>
<td>280</td>
<td>300</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Density (g/cc)</th>
<th>0.00027464</th>
<th>0.0027648</th>
<th>0.0055709</th>
<th>0.011312</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.023344</td>
<td>0.036184</td>
<td>0.049937</td>
<td>0.064724</td>
</tr>
<tr>
<td></td>
<td>0.08070</td>
<td>0.09803</td>
<td>0.1073</td>
<td></td>
</tr>
</tbody>
</table>

What is the fugacity and the activity coefficient of steam at 800 K and 300 atm?

3.1.5 For CO the following results are cited at 0°C:

\[
P(\text{atm}) = 25, 50, 100, 200, 400, 800, 1000
\]

| \( \bar{V}/RT \) | 0.985 | 0.9792 | 0.9741 | 1.0196 | 1.2482 | 1.8057 | 2.0819 |

Determine the fugacity of CO at 100, 400, 1000 atm and at 0°C.

3.1.6 The fugacity of Hg(\( \ell \)) at 100°C and 1.0 at is 0.272 mm Hg; its density as a liquid is 13.35 g cm\(^{-3}\), and its gram-atomic weight is 200.6 g mol\(^{-1}\). Find its fugacity at the same temperature under a pressure of 100.0 atm, assuming Hg(\( \ell \)) to be incompressible.
3.1.7 (a) The partial molar volumes for N\textsubscript{2} have been determined as a function of pressure as follows (0°C):

<table>
<thead>
<tr>
<th>P(atm)</th>
<th>50</th>
<th>100</th>
<th>200</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\bar{V}_{N_2}) (cm\textsuperscript{3}/mole)</td>
<td>447.5</td>
<td>226.7</td>
<td>120.3</td>
</tr>
</tbody>
</table>

Determine the fugacity of N\textsubscript{2} in a N\textsubscript{2}-H\textsubscript{2} mixture at a total pressure of 200 atm when \(x_2 = 0.4\). Compare this result with the ideal gas pressure. (b) Find \(G_{273}\) for the transfer of two moles of N\textsubscript{2}(g) from its pure form at 200 atm and 273 K to the H\textsubscript{2}-N\textsubscript{2} mixture under a total pressure of 200 atm and at 273 K for which \(x_{N_2} = 0.4\). The equation of state for N\textsubscript{2} is \(P\bar{V} = RT - 1.0515 \times 10^{-2}P + 8.626 \times 10^{-5}P^2 - 6.910 \times 10^{-8}P^3 + 1.704 \times 10^{-11}P^4\) (P in atm). (c) Repeat (b), assuming ideal conditions throughout.

3.2 TEMPERATURE AND PRESSURE DEPENDENCE OF ACTIVITY COEFFICIENTS FOR A GAS

Equation (3.1.14) provides information on the fugacity that corresponds to a given pressure \(P\) and temperature \(T\). It is of interest to determine how \(\gamma\) changes as \(T\) and \(P\) are altered. For this purpose we rewrite Eq. (3.1.4b) for a one-component system as

\[
\ln \gamma = \frac{[\mu(T,P) - \mu^\circ(T)]}{RT} - \ln P, \quad (3.2.1)
\]

from which

\[
(\partial \ln \gamma / \partial T)_P = - \frac{\bar{H}(T,P) - \bar{H}^\circ(T)}{RT^2} = (\partial \ln f / \partial T)_P. \quad (3.2.2)
\]

The right-hand side was obtained by recognizing that since \(P\) is fixed, \(f\) and \(\gamma = f/P\) vary with \(T\) in the same manner.

One minor problem with the preceding formulation is that it involves the hypothetical enthalpy of an ideal gas at 1 atm, which state is not experimentally attainable. [Note again that \(\bar{H}^\circ\) was obtained from the term \(\mu^\circ\) that occurs in the relation \(\mu = \mu^\circ + RT \ln P + RT \ln \gamma\). Thus, \(\mu^\circ\) is the chemical potential when \(\gamma = 1\) and \(P = 1\) atm.] This problem may be circumvented by noting that at very low pressures \(P_i\), where \(\gamma = 1\), \(\mu(T,P_i) = \mu^\circ(T) + RT \ln P_i\).
Then

\[ \mu(T, f) - \mu(T, P_t) = RT \ln P - RT \ln P_i + RT \ln \gamma \quad (3.2.3) \]

and

\[ (\partial \ln \gamma / \partial T)_{P, P_t} = - \frac{\bar{H}(T, P) - \bar{H}(T, P_i)}{RT^2} = (\partial \ln f / \partial T)_{P, P_t}. \quad (3.2.4) \]

In the above, both \( P \) and \( P_t \) must remain fixed. Correspondingly, the central term relates to the enthalpy of the actual gas at the pressure \( P \) of interest and at the low pressure \( P_t \). Methods for evaluating \( \bar{H}(T, P) - \bar{H}(T, P_t) \) were developed in Section 1.20; alternatively, the desired information can be found from the equation of state, Eq. (1.18.13b).

One can return to Eq. (3.2.1) to determine

\[ (\partial \ln f / \partial P)_T = (1/RT)(\partial \mu / \partial P)_T - 1/P = \tilde{V}/RT - 1/P. \quad (3.2.5) \]

On the other hand, the definition of \( \gamma = f/P \) leads to the result

\[ (\partial \ln \gamma / \partial P)_T = (\partial \ln f / \partial P)_T - 1/P. \quad (3.2.6) \]

Hence,

\[ (\partial \ln f / \partial P)_T = \tilde{V}(T, P)/RT. \quad (3.2.7) \]

Clearly the equation of state \( \tilde{V}(T, P) \) will have to be specified in order to show explicitly how \( f \) varies with \( P \). Equation (3.2.7) is another version of (3.1.8).

**EXERCISES**

3.2.1 Carefully examine the derivation starting with Eq. (3.2.7) and show how it would have to be altered if Eq. (3.2.4) were adopted in place of Eq. (3.2.5) as a relation specifying \( f_i \).
3.2.2 The equation of state for a nonideal gas proposed by Berthelot (1907) reads

\[ P\tilde{V} = RT + \frac{9R}{128} \frac{PT_c}{P_c} \left( 1 - \frac{6T_c^2}{T^2} \right). \]

(a) Determine the fugacity of a Berthelot gas as a function of pressure. Show that approximately \( f \approx P + \left( \frac{9T_cP^2}{128 TP_c} \right)(1 - 6T_c^2/T^2). \)  
(b) Determine the enthalpy, entropy, and Gibbs free energy of the gas.  
(c) Determine \( \tilde{H}(T,P) \) and \( \tilde{H}(T,P_f) \).

3.2.3 Calculate \( G - G^0, S - S^0, H - H^0, \tilde{C}_p - \tilde{C}_p^0 \) for the process of compressing 1 mol of CO\(_2\) from 1 to 100 atm at 500 K, based on use of (a) the ideal gas law, (b) the truncated virial equation of state \( P\tilde{V} = RT + BP, B = 42.7 \text{ cm}^3/\text{mol}, \) and (c) the Berthelot equation of state with \( P_c = 73.0 \text{ atm, } T_c = 304.2 \text{ K}. \) Compare the results.

3.2.4 Derive an expression which specifies \( (\partial \ln f/\partial T)_P \) in terms of the Joule-Thomson coefficient. [Hint: write out \( H(T,P) - H(T,P_f) \) as \( \int_{P_f}^{P} (\partial H/\partial P)_T dP \).]

3.3 THERMODYNAMIC TREATMENT OF REAL SOLUTIONS

In the specification of the chemical potential for real solutions one begins with the canonical formulation for ideal solutions introduced in Section 2.5,

\[ \mu_1 = \mu_1^* + RT \ln y_1, \quad (3.3.1) \]

where \( y_1 = x_i, c_i, \) or \( m_i. \) Standard operating procedures call for the preservation of this formulation for nonideal solutions also. This is done by introducing activities \( a_i \) such that for actual solutions an equation of the general canonical form

\[ \mu_1 = \mu_1^{**} + RT \ln a_1 \quad (3.3.2) \]

is applicable, in which the choice of \( a_i \) and \( \mu_1^{**} \) depends on what one chooses as concentration units and standard or reference states. Reasons for using Eq. (3.3.2) are sought in Exercise 3.3.1. The specification of \( a_i \) and \( \mu_1^{**} \) requires a rather tedious analysis which will be discussed in detail in Sections 3.4–3.6.
A very important feature of nonideal solutions is their departure from Raoult's Law; in later sections we shall repeatedly examine and make use of the information provided here. **Positive and negative departures from Raoult's Law** for a binary solution are schematically illustrated in Fig. 3.3.1. Attention is directed to the following facts: (a) If one component exhibits a positive (negative) departure from Raoult's Law, the other must do likewise; a proof for this statement is to be furnished in Exercise 3.3.2. (b) As the mole fraction $x_i$ of component $i$ ($i = 1,2$) approaches unity (i.e., as the solution becomes very dilute by virtue of a large excess of component $i$ as solvent), the partial pressure $P_i$ of

![Diagram](image)

**FIGURE 3.3.1** Diagrams showing positive (a) and negative (b) deviations from Raoult's Law. Dashed lines represent $P_i = x_i P_i^*$ ($i = A, B$), ideal behavior. Dotted lines represent Henry's Law.
the solvent closely approaches the value predicted by Raoult's Law: \( \lim_{x_i \to 1} P_i = x_i P_i^* \), where \( P_i^* \) is the partial pressure of pure i. (c) As the mole fraction of component i approaches zero (i.e., when component i is present at infinite dilution) the vapor pressure of the solute does not approach Raoult's Law, but is linearly related to the mole fraction according to the expression \( \lim_{x_i \to 0} P_i = K x_i \). This relationship is known as Henry's Law, and K is known as the Henry's Law constant. (See also Section 2.12.) (d) For ideal solutions Raoult's and Henry's Laws are identical.

We shall now proceed with the methodology for determining \( a_i \), and we return later to the question of determining the extent of the departure of real solutions from Raoult's Law.

EXERCISES

3.3.1 List reasons why the choice of Eq. (3.3.2) is of great convenience in describing physical properties of nonideal solutions.

3.3.2 On the basis of the Duhem-Margules equation, prove that if one component of a binary mixture exhibits positive (negative) deviations from Raoult's Law, the second must do likewise. (See S. Glasstone, "Thermodynamics for Chemists", D. Van Nostrand, New York, 1947, Chapter 14.)

3.3.3 By using Raoult's Law for component 1 and the Gibbs-Duhem relation, show that component 2 must satisfy Henry's Law over the composition range \( x_2 = 1 - x_1 \) for which Raoult's Law applies for component 1. (See S. Glasstone, "Thermodynamics for Chemists", D. Van Nostrand, New York, 1947, Chapter 14.)

3.4 CHARACTERIZATION OF NONIDEAL SOLUTIONS. PRELIMINARIES

(a) The cardinal principle introduced at the outset is the following: Let \( q \) represent any composition variable which specifies the makeup of a uniform solution. In what follows we let \( q \) stand for mole fraction \( x \), molarity \( c \), or molality \( m \): Then the chemical potential of species i in the homogeneous mixture shall be given by the expression
\[ \mu_i(T,P,q_i) - \mu_i(T,P,q_i^\dagger) + RT \ln \frac{a_i(T,P,q_i)}{a_i(T,P,q_i^\dagger)}, \]  

in which \( T \) is the temperature, \( P \) the pressure, and \( q_i^\dagger \) any arbitrary reference value of the composition variable \( q_i \) for the \( i \)th species in a uniform mixture; the quantity \( a_i(T,P,q_i) \) is termed the activity of species \( i \) relative to the composition variable \( q_i \) at temperature \( T \) and pressure \( P \). The quantity \( a_i(T,P,q_i) \) is an as yet unknown function of the indicated parameters and variables, whose dependence must be determined later. Equation (3.4.1) specifies the chemical potential \( \mu_i(T,P,q_i) \) relative to \( \mu_i(T,P,q_i^\dagger) \), the reference chemical potential, obtained by substituting \( q_i^\dagger \) for \( q_i \) in the functional dependence of the chemical potential.

Note that Eq. (3.4.1) reduces to an identity when \( q_i = q_i^\dagger \); because of this self-consistency one may choose for \( q_i^\dagger \) any value that happens to be convenient. This flexibility is at once a blessing and a curse: It provides enormous freedom of choice, at the same time that it produces a multitude of seemingly different thermodynamic formulations, all of which must ultimately be shown to be equivalent. The situation is further complicated by the fact that one also has so many choices for specifying the composition variable \( q \).

(b) In this section we begin the thermodynamic analysis by specializing Eq. (3.4.1) in two steps: First we insist that the reference value \( \mu_i(T,P,q_i^\dagger) \) be specified at unit pressure \( P = 1 \) (usually one atmosphere). This may be accomplished by rewriting (3.4.1) as

\[ \mu_i(T,P,q_i) - \mu_i(T,1,q_i^\dagger) + RT \ln \frac{a_i(T,P,q_i)}{a_i(T,1,q_i^\dagger)}, \]

which also reduces to an identity for \( P = 1 \) and \( q_i = q_i^\dagger \). Next, we select as \( q_i^\dagger \) that particular standard value \( q_i^\circ \) which renders \( a_i(T,1,q_i^\circ) = 1 \). These two conditions specify the standard state of the system: here the standard chemical potential \( \mu_i(T,1,q_i^\circ) \) is taken with respect to species \( i \) at unit activity and unit pressure. However, this relation does not suffice to determine
a_i(T,1,q_{i}^{\circ}), since q_i^{\circ} is itself unknown at this point. Therefore, in conformity with the requirement that Raoult's Law must hold for the majority component in exceedingly dilute solutions, we demand that

\[ a_i(T,1,q_{i}^{\circ}) = q_{i}^{\circ}(T,1), \tag{3.4.3} \]

which fixes the scale for a_i; here q_{i}^{\circ}(T,1), given by x^* = 1 or by Eq. (3.5.2) below, is the composition variable for pure i at temperature T and unit pressure. With this choice for q_{i}^{\circ} Eq. (3.4.2) reduces to the \textit{canonical} form:

\[ \mu_i(T,P,q_i) = \mu_i(T,1,q_{i}^{\circ}) + RT \ln a_i(T,P,q_i), \tag{3.4.4} \]

which is clearly patterned after Eqs. (2.4.15)-(2.4.17), and after Eqs. (2.5.1), (2.5.10), and (2.5.11). Note further that when we adopt q_{i}^{\circ} = x_i^* - 1 and x_i = 1 for a pure material, and further employ standard conditions by setting P = 1, then we automatically satisfy the requirement that a_i(T,1,1) = 1. For it is only with this choice that Eq. (3.4.4) reduces to an identity. However, as shown in Section 3.7, a_i(T,P,1) differs from unity, although under normal experimental conditions the deviations from unity are small.

The problem of dimensionality in Eq. (3.4.4) can obviously be disposed of quite readily in the present approach. The specification of the standard chemical potential requires more ingenuity; a consideration of this problem is postponed to later sections.

(c) The next step in the procedure consists of introducing the \textit{activity coefficient} \( \Gamma_i(T,P,q_i) \) through the expression

\[ \Gamma_i(T,P,q_i) = \frac{a_i(T,P,q_i)}{q_i}, \tag{3.4.5} \]

so that Eq. (3.4.4) may be rewritten as
\[ \mu_i(T, P, q_1) = \mu_i(T, 1, q_i^*) + RT \ln \Gamma_i(T, P, q_i) + RT \ln q_i. \]  (3.4.6)

This equation has the drawback that it specifies \( \mu_i(T, P, q_1) \) at pressure \( P \) relative to the standard chemical potential at unit pressure. If desired one may keep the pressure parameter uniform throughout by returning to Eq. (3.4.1) and introducing a second activity coefficient via

\[ \gamma_i(T, P, q_1) = \frac{a_i(T, P, q_1)}{a_i(T, P, q_i^*)} q_1 - \frac{\Gamma_i(T, P, q_i)}{a_i(T, P, q_i^*)}, \]  (3.4.7)

with which Eq. (3.4.1) may be rewritten as

\[ \mu_i(T, P, q_1) = \mu_i(T, P, q_i^*) + RT \ln \gamma_i(T, P, q_1) + RT \ln q_i. \]  (3.4.8)

The quantity \( \mu_i(T, P, q_i^*) \) will be referred to as a reference chemical potential.

Alternatively, Eq. (3.4.6) may be reformulated as

\[ \mu_i(T, P, q_1) = \mu_i(T, 1, q_i^*) + RT \ln (\gamma_i^a(q) q_1), \]  (3.4.9a)

with

\[ A_i^a(q) = a_i(T, P, q_i^*). \]  (3.4.9b)

All three formulations, Eqs. (3.4.4), (3.4.8), and (3.4.9) are encountered in the literature. One should note that \( \gamma_i \) by itself occurs only in equations involving the reference chemical potential \( \mu_i(T, P, q_i^*) \), whereas \( \Gamma_i \) by itself occurs only where the standard chemical potential \( \mu_i(T, 1, q_i^*) \) is involved.

(d) We next specialize to cases where \( q \) refers to mole fraction, molarity, and molality, respectively. For \( q = x \), and \( x^* = 1 \), which holds for pure material, Eqs. (3.4.3) and (3.4.5) reduce to the important relation, applicable for \( q = x \),

\[ a_i(T, 1, 1) = \Gamma_i(T, 1, 1) = 1. \]  (3.4.10a)
Equation (3.4.10a), coupled with the requirement (3.4.3), shows at once that \( x_i^* = x_i^o = x_i = 1 \); i.e., in the present case the standard state of \( i \) is that of the pure substance \( i \) under a pressure of one atmosphere. Furthermore, Eqs. (3.4.7) and (3.4.10a) lead to

\[
\gamma_i(T,P,1) = \frac{a_i(T,P,x_i^o)}{a_i(T,P,x_i^o)} = 1,
\]

or

\[
a_i(T,P,1) = a_i(i,P,x_i^o),
\]

which is a self-consistent result. When \( q = c \) or \( q = m \), Eq. (3.4.3) becomes

\[
a_i(T,l,c_i^*) = c_i^* (T,l) \tag{3.4.11a}
\]

\[
a_i(T,l,m_i^*) = m_i^*, \tag{3.4.11b}
\]

where the quantities on the right are specified by Eq. (3.5.2) below. Also, by definition,

\[
a_i(T,l,c_i^o) = a_i(T,l,m_i^o) = 1. \tag{3.4.12}
\]

The foregoing analysis shows up the advantages of working with mole fractions as composition variables: here \( x_i^o \) is simply unity. By contrast, values of \( c_i^o \) and \( m_i^o \) are yet to be determined; these quantities differ for each solution that is made up. One therefore occasionally encounters schemes whereby \( c_i^o = 1 \) mol/liter or \( m_i^o \) is set at unit molality. This approach may be handled by specializing (3.4.4) to \( P = 1 \), \( q_i = 1 \), so that

\[
\mu_i(T,l,1) = \mu_i(T,l,q_i^o) + RT \ln a_i(T,l,1), \; q = c, m. \tag{3.4.13}
\]

On eliminating \( \mu_i(T,l,q_i^o) \) between (3.4.13) and (3.4.4), we obtain (\( q = c, m \))

\[
\mu_i(T,P,q_i) = \mu_i(T,1,1) + RT \ln \left\{a_i(T,P,q_i)/a_i(T,1,1)\right\}, \tag{3.4.14}
\]
which properly reduces to an identity for \( P - q_i = 1 \). The minor drawback to Eq. (3.4.14) is that it cannot be reduced to a canonical form. In this connection one may introduce the activity coefficient

\[
\Gamma_i'(T,P,q_i) = a_i(T,P,q_i)/a_i(T,l,l)q_i
\]  

(3.4.15)

to find

\[
\mu_i(T,P,q_i) = \mu_i(T,l,l) + RT \ln \Gamma_i'(T,P,q_i) + RT \ln q_i. \tag{3.4.16}
\]

Alternatively, one may now solve Eq. (3.4.4) for \( \mu_1(T,1,q_1^e) \), and substitute in Eq. (3.4.13); this yields

\[
\mu_i(T,l,l) = \mu_1(T,P,1) + RT \ln \left[ a_i(T,l,l)/a_i(T,P,1) \right],\tag{3.4.17}
\]

and when this expression is introduced in (3.4.14) one obtains

\[
\mu_1(T,P,q_i) = \mu_1(T,P,1) + RT \ln \left[ a_i(T,P,q_i)/a_i(T,P,1) \right],
\]

\[q = c, m. \tag{3.4.18}\]

Then, by use of the definition

\[
\gamma_i'(T,P,q_i) = a_i(T,P,q_i)/a_i(T,P,1)q_i, \tag{3.4.19}
\]

one finds

\[
\mu_i(T,P,q_i) = \mu_1(T,P,1) + RT \ln \gamma_i'(T,P,q_i) + RT \ln q_i. \tag{3.4.20}
\]

(d) Perusal of the preceding material shows the flexibility available for specifying the chemical potential of component \( i \) in a uniform mixture. One should note that in every instance it is possible to put the final relations into the general form

\[
\mu_i = \mu_i^0 + RT \ln \beta_1 + RT \ln q_i, \tag{3.4.21}
\]
where $\mu_i^*$ is a standard or reference chemical potential and $\beta_i$ is an appropriate activity coefficient. The various forms in which the preceding expressions have been specified differ from each other solely in the choice of what is considered the appropriate composition variable and the desired reference or standard state.

The foregoing is sufficiently complex that one should seek a simplified approach. This presentation applies if one uses solely the mole fraction $x_i$ as the composition variable and if all thermodynamic characterizations refer only to the standard state at a total pressure of $P = 1$ atm. In such circumstances the self-consistent equation (3.4.1) reduces to

$$\mu_i(T,P,x_i) = \mu_i(T,1,1) + RT \ln \left\{ \frac{a_i(T,P,x_i)}{a_i(T,1,1)} \right\}. \quad (3.4.22)$$

Here again $\mu_i(T,1,1) = \mu_i^*(T,1)$ is the chemical potential for pure $i$ ($x_i^* = 1$) at $P = 1$ atm. According to Raoult's Law, as $x_i \to 1$, the solution approaches ideal behavior, so that $a_i(T,1,1) = x_i \to x_i^* = 1$. Then Eq. (3.4.22) reduces to the canonical form

$$\mu_i(T,P,x_i) = \mu_i^*(T,1) + RT \ln a_i(T,P,x_i). \quad (3.4.23)$$

On now introducing the activity coefficient $\Gamma_i(T,P,x_i) - a_i(T,P,x_i)/x_i$ we write

$$\mu_i(T,P,x_i) = \mu_i^*(T,1) + RT \ln x_i + RT \ln \Gamma_i(T,P,x_i). \quad (3.4.24)$$

Note that $\Gamma_i(T,1,1) = 1$.

However, for pressures other than 1 atm, $\Gamma_i(T,P,1)$ and $a_i(T,P,1)$ deviate from unity. This reflects the fact that a compressed solution experiences greater interactions among its constituents than one at lesser compression. Thus, even though the composition is unaltered the activities do vary with pressure, as does $\Gamma_i(T,P,x_i)$. The discussion surrounding Eqs. (3.4.3)-(3.4.5) shows that there is only one unique set of conditions (here $P = 1$ and $x_i^* = 1$) for which self-consistency
is achieved in Eq. (3.4.22), namely: \( a_i = \Gamma_i = 1 \) only when the mole fraction of the majority component approaches unity and when the solution is under a total pressure of 1 atm.

EXERCISES

3.4.1 Derive explicit expressions which specify \( \mu_i(T,P,m_i) \) relative to (i) \( \mu_i(T,1,m_i=1) \) and (ii) \( \mu_i(T,P,m_i=1) \) in terms of activities and activity coefficients.

3.4.2 Use the Margules formulation \( \Gamma_i = \exp(\beta x_i^2/2) \) for the activity coefficient of species 1 and relate the mole fraction to molarity through the expression \( m_i/x_i = 1000/M_i x_i \) derived in Section 2.10. (a) Specializing to the case of a binary solution, show that it is necessary to invoke an equation of the form (3.4.3) to fix the parameter \( \beta \), determine \( \beta \), and then write down an expression from which \( m_i^\circ \) may be found. (b) Let components 1 and 2 represent water and sucrose respectively; determine \( \beta \) and \( m_i^\circ \) numerically.

3.4.3 Suppose one wishes to specify a chemical potential by the relation \( \mu_i(T,1,x_i^*) = \mu_i(T,1,x_i) + RT \ln a_i(T,1,x_i) \), which reduces to an identity for \( x_i = 1 \). Is it then permissible also to write \( \mu_i(T,P,x_i) = \mu_i(T,P,x_i^*) + RT \ln a_i(T,P,x_i) \), or is one constrained to use the formulation (3.4.2)?

3.4.4 A relation frequently used to represent the activity coefficient for constituent 1 in a binary solution reads (Margules, 1895) \( \Gamma_1 = \exp(\beta x_i^2/2) \). Write out expressions for \( G_1, H_1, S_1, V_1, \) and \( C_{P_1} \), in terms of the parameter \( \beta \).

3.4.5 What is the change in chemical potential for species \( i \) when it is transferred from a pure state at temperature \( T \) to a solution at mole fraction \( x_i \)?

3.4.6 Explain why it is not possible to set up an equation of the form \( \mu_i(T,P,1) = \mu_i(T,1,1) + RT \ln x_i \) for ideal solutions, whereas the corresponding equation for nonideal solutions, with \( x_i \) replaced by \( a_i \), is perfectly appropriate.

3.4.7 Examine the discussion of this section carefully to prove that \( x_i^* = 1 \).

3.5 STANDARDIZATION OF THERMODYNAMIC DESCRIPTIONS OF NONIDEAL SOLUTIONS

In Section 3.4 we have utilized many different modes for characterizing the chemical potential of a given species in a
nonideal solution. While these various descriptions all look different, surely all physical predictions must be independent of the particular standard or reference state which has been chosen, and surely they cannot be allowed to depend on the choice of concentration units. We address ourselves here to restrictions that must be imposed to guarantee that the chemical potential of any species i in any solution relative to the standard potential shall indeed be unique, i.e., invariant under any change in choice of concentration units for a particular choice of standard or reference potentials.

(a) By way of introduction we recall the relations (see Section 2.10)

\[
\frac{x_i}{c_i} = \frac{\sum n_j M_j}{1000 \rho \sum n_j} ; \quad \frac{x_i}{m_i} = \frac{M_i x_i}{1000}. \tag{3.5.1}
\]

From Eq. (3.5.1) we can readily obtain the 'molarity' \(c_i^*\) and 'molality' \(m_i^*\) corresponding to component i in the isolated, pure state, for which \(x_i = x_i^* = 1\). Equation (3.5.1) reduces to the results \((M_i = M_i^*\) in this instance)

\[
c_i^* = 1000 \rho_i^*/M_i ; \quad m_i^* = 1000/M_i. \tag{3.5.2}
\]

From (3.5.1) and (3.5.2) we obtain two relations needed in our later derivations, namely,

\[
\frac{c_i^*(T,P)}{c_i(T,P)} \frac{x_i}{x_i} = \frac{\rho_i^*(T,P)}{\rho(T,P)} \frac{\sum n_j M_j}{M_i \sum n_j} ; \quad \frac{m_i^*}{m_i} x_i = \frac{M_i}{M_i^*} x_i. \tag{3.5.3}
\]

We now recapitulate three different ways of specifying the chemical potential in canonical form, relative to reference chemical potentials. For \(q = x, c, m\) we use Eq. (3.4.8), and we also adopt the special case \(x_i^* = x_i^* = 1\). This leads to the set of relations which appear to be different, but which must ultimately be shown to be equivalent, namely
\[ \mu_i(T,P,x_i) = \mu_i(T,P,x_i^\ast) + RT \ln \gamma_i(T,P,x_i) + RT \ln x_i \]  
(3.5.4a)

\[ \mu_i(T,P,c_i) = \mu_i(T,P,c_i^\ast) + RT \ln \gamma_i(T,P,c_i) + RT \ln c_i(T,P) \]  
(3.5.4b)

\[ \mu_i(T,P,m_i) = \mu_i(T,P,m_i^\ast) + RT \ln \gamma_i(T,P,m_i) + RT \ln m_i. \]  
(3.5.4c)

Analogous developments involving standard states at unit
molarity or molality give rise to complications that are to be
explored in Exercises 3.5.1 and 3.5.3.

(b) In accord with the introductory comments to this
Section we are mandated to equate the three formulations in Eq.
(3.5.4). This leads to the relations

\[ \mu_i(T,P,x_i) + RT \ln \gamma_i(T,P,x_i) + RT \ln x_i \]
\[ = \mu_i(T,P,c_i) + RT \ln \gamma_i(T,P,c_i) + RT \ln c_i(T,P) \]
\[ = \mu_i(T,P,m_i) + RT \ln \gamma_i(T,P,m_i) + RT \ln m_i. \]  
(3.5.4d)

Any formulation that satisfies (3.5.4d) represents an
acceptable expression that guarantees the invariance of \( \mu_i \) under
a change of composition variables. By analogy to other field
theories we shall refer to this process as maintaining the
gauge invariance of the chemical potential. There are
infinitely many ways of maintaining gauge invariance; hence,
some guidance is needed in the methodology of procedure.
Toward this end one should note that (3.5.4d) may sensibly be
broken up into two portions: a part which relates the various
reference chemical potentials \( \mu_i(T,P,q_i^\ast) \) at fixed compositions,
and a part dealing with relations between composition variables
\( RT \ln (\gamma_i q_i) \), in which \( q_i = x_i, c_i(T,P), m_i. \)

Interrelations between the reference chemical potentials
are found by dealing with the \( i \)th species in pure form, for
which composition variables play no role. We specialize Eqs.
(3.5.4a) and (3.5.4b) for pure species \( i \) by setting \( x_i = x_i^\ast = 1 \),
\( c_i = c_i^\ast \), and equating the resulting relations, taking cognizance
of Eq. (3.4.10b), \( \gamma_i(T,P,x_i^\ast) = 1. \) This yields
\[ \mu_1(T,P,c_1^*) = \mu_1(T,P,c_1^0) + RT \ln \gamma_1(T,P,c_1^*) + RT \ln c_1^*(T,P) \]

\[ - \mu_1(T,P,x_1^*) = \mu_1^*(T,P), \quad (3.5.5) \]

where we have also introduced a shorthand notation in the second line for the chemical potential of pure \( i \) at temperature \( T \) and pressure \( P \). The preceding equation may be solved for

\[ \mu_1(T,P,c_1^*) = \mu_1^*(T,P) - RT \ln \gamma_1(T,P,c_1^*) - RT \ln c_1^*(T,P) \]

\[ = \mu_1^*(T,P), \quad (3.5.6) \]

in which the expression on the second line serves as a shorthand notation for the three terms in the middle. Equation (3.5.6) conveys important information: it shows how \( \mu_1(T,P,c_1^*) \) may be determined from the chemical potential of pure \( i \) at temperature \( T \) and pressure \( P \); Eq. (3.5.6) further involves the activity coefficient and concentration of pure \( i \) under the same condition. In Section 3.7 a prescription is provided for determining \( \gamma_1(T,P,c_1^*) \); it will be shown that this quantity ordinarily does not deviate much from unity [as is already evident from Eqs. (3.4.3) and (3.4.7) by which \( \gamma_1(T,1,c_1^*) = 1 \)]. Further, \( c_1^* \) may be determined from Eq. (3.5.2); therefore, \(- RT \ln (\gamma_1 c_1^*) \) in Eq. (3.5.6) is known. Thus, \( \mu_1(T,P,c_1^*) \) is now directly correlated with the quantity \( \mu_1^*(T,P) \); this particular chemical potential will henceforth always be designated by \( \mu_1^*(T,P) \). By the same token we will show in Eq. (3.5.17b) how to determine \( a_1(T,P,c_1^*) \) in terms not involving \( c_1^* \). These particular findings are perhaps among the most important consequences of the invariance requirements imposed on \( \mu_1 \). The awkward term \( \mu_1(T,P,c_1^*) \) has now been eliminated.

(c) As the second step in the process of examining gauge invariance effects, we equate Eqs. (3.5.4a) and (3.5.4b) for any arbitrary concentration \( x_1 \) and \( c_1 \), and introduce Eqs. (3.5.6) and (3.5.5). This immediately yields a relation between activity coefficients,
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\[ RT \ln \left( \frac{\gamma_1(T,P,c_i)}{\gamma_1(T,P,c_1^*)} \right) + RT \ln \left( \frac{c_i(T,P)}{c_1^*(T,P)} \right) = RT \ln \gamma_1(T,P,x_i) \]

\[ + RT \ln x_i. \]  \hspace{1cm} (3.5.7)

or equivalently, in view of (3.5.3),

\[ \frac{\gamma_1(T,P,c_1)}{\gamma_1(T,P,c_1^*)} = \gamma_1(T,P,x_i) \left\{ \frac{c_i^*(T,P)}{c_1(T,P)} x_i \right\} = \gamma_1(T,P,x_i) \left[ \frac{\rho_1^*(T,P)}{\rho(T,P)} \frac{\sum_{j} n_j M_j}{M_i \sum_j n_j} \right]. \]  \hspace{1cm} (3.5.8)

In later sections we show how to determine \( \gamma_1(T,P,c_1^*) \). However, Eq. (3.5.8) is almost never used as such in any computational schemes: It simply demonstrates that \( \gamma_1(T,P,c_i) \) in Eq. (3.5.4b) is directly related to \( \gamma_1(T,P,x_i) \); the interdependence between these two is just a result of the requirement of gauge invariance. The interrelations (3.5.6) and (3.5.8) guarantee that Eqs. (3.5.4a) and (3.5.4b) actually yield physically identical predictions.

(d) A similar set of interrelations is found by equating (3.5.4c) with (3.5.4a); one need merely replace \( c_i \) in Eqs. (3.5.5)-(3.5.8) by \( m_i \), and use the appropriate formula in Eq. (3.5.3). This yields

\[ \mu_1^*(T,P,m_i) = \mu_1^*(T,P) - RT \ln \gamma_1(T,P,m_i) - RT \ln m_i = \mu_1^{*m}(T,P) \]  \hspace{1cm} (3.5.9)

and

\[ \frac{\gamma_1(T,P,m_i)}{\gamma_1(T,P,m_i^*)} = \gamma_1(T,P,x_i) \left\{ \frac{m_i^*}{m_i} x_i \right\} = \gamma_1(T,P,x_i) \left\{ \frac{M_1}{M_i} x_i \right\}. \]  \hspace{1cm} (3.5.10)

Remarks made in conjunction with Eqs. (3.5.6) and (3.5.8) apply to (3.5.9) and (3.5.10) with obvious modifications. In light of the results cited in (3.5.6) and (3.5.9) we rewrite Eq. (3.5.4) as follows [\( \mu_1^*(T,P) = \mu_1(T,P,x_i^*) \)]:
\[
\mu_i = \mu_i^*(T,P) + RT \ln \gamma_i(T,P,x_i) + RT \ln x_i \quad (3.5.11a)
\]
\[
\mu_i = \mu_i^{*c}(T,P) + RT \ln \gamma_i(T,P,c_i) + RT \ln c_i \quad (3.5.11b)
\]
\[
\mu_i = \mu_i^{*m}(T,P) + RT \ln \gamma_i(T,P,m_i) + RT \ln m_i. \quad (3.5.11c)
\]

These relations are a restatement of Eq. (3.4.8) based on Eqs. (3.5.6) and (3.5.9); clearly they involve the reference chemical potential.

(e) So far we have used only reference chemical potentials. Matters are greatly simplified by introducing instead the standard chemical potential; we therefore begin with equations based on Eq. (3.4.6). Let us rewrite \(x_i^* = x_i^\ast = 1\) and \(\mu_i(T,1,x_i^*) = \mu_i^*(T,1)\); then

\[
\mu_i(T,P,x_i) = \mu_i^*(T,1) + RT \ln \Gamma_i(T,P,x_i) + RT \ln x_i \quad (3.5.12a)
\]
\[
\mu_i(T,P,c_i) = \mu_i^*(T,1,c_i^*) + RT \ln \Gamma_i(T,P,c_i) + RT \ln c_i(T,P) \quad (3.5.12b)
\]
\[
\mu_i(T,P,m_i) = \mu_i^*(T,1,m_i^*) + RT \ln \Gamma_i(T,P,m_i) + RT \ln m_i. \quad (3.5.12c)
\]

The procedure used earlier in this section will now be repeated: Specialize (3.5.12a) and (3.5.12b) to pure materials under standard conditions by setting \(P = 1\), \(x_i = 1\), \(c_i = c_i^*\), noting that \(\Gamma_i(T,1,x^*) = 1\) and that \(\Gamma_i(T,1,c_i^*) = a_i(T,1,c_i^*)/c_i^*(T,1) = 1\) on account of Eqs. (3.4.5) and (3.4.11a). Equating the resulting relations, one finds

\[
\mu_i(T,1,c_i^*) = \mu_i^*(T,1) - RT \ln c_i^*(T,1) = \mu_i^{*c}(T,1). \quad (3.5.13)
\]

Equation (3.5.13) bears the important message that \(\mu_i(T,1,c_i^*)\) is related to the chemical potential of pure \(i\), corrected for by a quantity that is readily evaluated by use of (3.5.2); this is a direct consequence of gauge invariance. Equation (3.5.13) also specifies in detail how to evaluate the standard chemical potential referred to molarity.
Next, equate (3.5.12a) with (3.5.12b), taking account of (3.5.13):

\[ RT \ln \Gamma_i(T, P, c_i) + RT \ln \left[ \frac{c_i(T, P)}{c_i^*(T, 1)} \right] = RT \ln \Gamma_i(T, P, x_i) + RT \ln x_i, \]  

which, on account of (3.5.3), may be rearranged to read

\[ \Gamma_i(T, P, c_i) = \Gamma(T, P, x_i) \left[ \frac{c_i^*(T, 1)}{c_i(T, P)} \right] x_i = \Gamma_i(T, P, x_i) \left[ \frac{\rho_i^*(T, 1)}{\rho(T, P)} \sum_{j} \frac{M_j}{n_j} \right]. \]  

Equation (3.5.15) as such is not frequently used. It does demonstrate, however, that because of gauge invariance the activity coefficient expressed in terms of molarity must be related to that expressed in terms of mole fractions.

One other quantity of interest remains to be specified, namely \( a_i(T, P, c_i^*) \). For this purpose we use Eq. (3.4.7) to rewrite (3.5.15) as

\[ \gamma_1(T, P, c_i) a_i(T, P, c_i^*) = \gamma_1(T, P, x_i) a_i(T, P, x_i^*) \left\{ \frac{c_i^*(T, 1)}{c_i(T, P)} x_i \right\}. \]  

We now consider the special case \( x_i = x_i^* = 1, c_i = c_i^* \), noting that \( \gamma_1(T, P, x_i^*) = 1 \), as is to be demonstrated in Exercise 3.5.7. From (3.5.16) we find

\[ a_i(T, P, c_i^*) = \frac{a_i(T, P, x_i^*)}{\gamma_1(T, P, c_i)} \left\{ \frac{c_i^*(T, 1)}{c_i(T, P)} x_i \right\}. \]  

On introducing Eq. (3.5.2) we obtain

\[ a_i(T, P, c_i^*) = \frac{a_i(T, P, x_i^*)}{\gamma_1(T, P, c_i)} \left\{ \frac{\rho_i^*(T, 1)}{\rho_i^*(T, P)} \right\} = a_i^c(T, P). \]  

As shown earlier, the activity of \( i \) in the reference state \( T, P, c_i^* \) may be related to that of pure \( i \) at the same \( T \) and \( P \); this is explicitly indicated by the abbreviated notation on the
right. Eq. (3.5.17b) is another important consequence of gauge invariance. We show later how \( a_i \) and \( \gamma_i \) may be determined experimentally. We therefore at this point have completed the task of specifying the quantity \( a_i(T,P,c_i^0) \) which we had introduced in Eq. (3.4.9b).

In a similar vein one obtains relations based on the use of Eqs. (3.5.12a) and (3.5.12c),

\[
\mu_i(T,1,m_i^0) = \mu_i^*(T,1) - RT \ln m_i^* = \mu_i^{m*}(T,1) \tag{3.5.18}
\]

\[
\Gamma_i(T,P,m_i) = \Gamma_i(T,P,x_i)[m_i^*x_i/m_i] - \Gamma(T,P,x_i)M_i x_i/M_i \tag{3.5.19}
\]

\[
a_i(T,P,m_i^0) = a_i(T,P,x_i^0)/\gamma_i(T,P,m_i^0) = a_i^{m*}(T,P), \tag{3.5.20}
\]

thereby providing interrelations for \( \mu_i(T,P,m_i^0) \), \( \Gamma_i(T,P,m_i) \), and \( a_i(T,P,m_i^0) \) in terms of corresponding quantities for mole fractions. One should note that in all of the expressions for the chemical potential \( m_i^0 \) has been eliminated.

Equations (3.5.12) may now be rewritten by (i) introducing Eqs. (3.5.13), (3.5.18); (ii) reintroducing the notations \( a_i(T,P,q_i^0) = a_i^q(T,P) \) with \( q = x,c,m; \) (iii) using the relations \( \Gamma_i(T,P,q_i) = \gamma_i(T,P,q_i)a_i^q(T,P) \). Then

\[
\mu_i = \mu_i^{x*}(T,1) + RT \ln [\gamma_i(T,P,x_i)a_i^{x*(T,P)x_i}] - \mu_i^{x*}(T,1) \tag{3.5.21a}
+ RT \ln a_i(T,P,x_i)
\]

\[
\mu_i = \mu_i^{c*}(T,1) + RT \ln [\gamma_i(T,P,c_i)a_i^{c*}(T,P)c_i(T,P)] - \mu_i^{c*}(T,1) \tag{3.5.21b}
+ RT \ln a_i(T,P,c_i)
\]

\[
\mu_i = \mu_i^{m*}(T,1) + RT \ln [\gamma_i(T,P,m_i)a_i^{m*}(T,P)m_i] - \mu_i^{m*}(T,1) \tag{3.5.21c}
+ RT \ln a_i(T,P,m_i).
\]

It should be noted that \( a_i^q(T,1) = 1 \) for all \( q \); hence, the quantities \( a_i^q(T,P) \) in (3.5.21) will ordinarily not differ significantly from unity.

Note that we have now succeeded in specifying the chemical potentials in two different ways: Eqs. (3.5.11)
involve the reference chemical potential, whereas Eqs. (3.5.21) relate $\mu_i$ to standard chemical potentials. In each case, precautions were taken to ensure a unique specification for $\mu_i$.

The reference chemical potentials were specified in terms of $\mu_i^*(T,P) = \mu_i(T,P,x_i^*) = \mu_i^*(T,P)$ for the pure component $i$ through Eqs. (3.5.6) and (3.5.9). If desired the activity coefficients $\gamma_i(T,P,c_i)$ and $\gamma_i(T,P,m_i)$ may be related to $\gamma_i(T,P,x_i)$ via Eqs. (3.5.8) and (3.5.10); the product $\gamma_i(T,P,q_i)a_i^q(T,P)$ may be related to experimental measurements by methods to be discussed in Section 3.7. The standard chemical potentials $\mu_i^*(T,1)$ and $\mu_i^{m}(T,1)$ were specified in terms of $\mu_i^*(T,1) = \mu_i^*(T,1)$ through (3.5.13) and (3.5.18). If desired, $\Gamma_i(T,P,c_i)$, $\Gamma_i(T,P,m_i)$ may be written in terms of $\Gamma_i(T,P,x_i)$, as shown in Eqs. (3.5.15) and (3.5.19); and $a_i^*(T,P)$, $a_i^m(T,P)$ may be specified in terms of $a_i^*(T,P)$ as shown in (3.5.17b) and (3.5.20).

There finally remains the problem of guaranteeing that the chemical potentials specified so far shall actually remain gauge invariant with respect to the use of reference or standard chemical potentials which differ from those adopted in the present section. This matter is to be handled in Exercise 3.5.5. That such invariance can always be maintained should become clear on reflection of the meaning of Eqs. (3.5.5), (3.5.9), (3.5.13), and (3.5.18) in this section, and of Eq. (3.4.14).

EXERCISES

3.5.1 Invoke the invariance principle for chemical potentials by comparing Eq. (3.4.20b) with Eq. (3.5.4a). Find expressions relating $\mu_i(T,P,x_i^*)$ and $\gamma_i(T,P,c_i)$ to $\gamma_i(T,P,x_i)$. How do your results differ from those cited in this section in the text?

3.5.2 Repeat Exercise 3.5.1, by comparing Eq. (3.4.22) with Eq. (3.5.12a). Relate $\mu_i(T,1,c_i-1)$ to $\mu_i(T,1,x_i^*)$ and $\Gamma_i(T,P,c_i)$ to $\Gamma_i(T,P,x_i)$. How do your results differ from those cited in the text?

3.5.3 Repeat Exercise 3.5.1 when molality is used in place of molarity and $\mu_i$ is referred to unit molality as the
reference chemical potential. How do your results differ from those cited in the text?

3.5.4 Repeat Exercise 3.5.2 when molality is used in place of molarity and \( \mu_i \) is referred to unit molality as the standard chemical potential. How do your results differ from those cited in the text?

3.5.5 Discuss the possibility of selecting different gauges in which \( \mu_i^{c}, \mu_i^{m}, \mu_i^{m} \) are interrelated by relations which differ from Eqs. (3.5.5), (3.5.9) and (3.5.18) and show how these alterations may be compensated for in equations interrelating or specifying the \( \gamma_i \) or \( \Gamma_i \).

3.5.6 Derive interrelations involving \( \gamma_i(T,1,c_i), \gamma_i(T,1,m_i) \), and \( \gamma_i(T,1,x_i) \).

3.6 REFORMULATION OF THE THERMODYNAMIC DESCRIPTION OF NONIDEAL SOLUTIONS

The complications of the last section arose from the specification of \( \mu_i \) in terms of the canonical relations (3.5.4), together with the use of the quantity \( \mu_i(T,1,q_i^\Phi) \) as the standard chemical potential; one should recall that \( q_i^\Phi \) had been so chosen that \( a_i(T,1,q_i^\Phi) = 1 \). This treatment is perfectly satisfactory; however, a simpler alternative exists. One may return to the fundamental relation (3.4.2) and select for the concentration variable \( q_i^\Phi \) the reference state \( q_i^* \) for the pure material. With this choice, and in view of the relation (3.4.3), Eq. (3.4.2) becomes

\[
\mu_i(T,P,q_i) = \mu_i(T,1,q_i^*) + RT \ln \left[ a_i(T,P,q_i)/q_i^*(T,1) \right]. \tag{3.6.1}
\]

Note that \( x_i^* = 1 \) and that \( c_i^* \) and \( m_i^* \) are specified by Eq. (3.5.2). Since \( \mu_i(T,1,q_i^*) \) is the chemical potential of pure \( i \) under standard conditions regardless of concentration units, we write

\[
\mu_i(T,P,q_i) = \mu_i^*(T,1) + RT \ln a_i(T,P,q_i), \tag{3.6.2}
\]

in which we have set
\[ a_i(T, P, q_1) = \frac{a_i(T, P, q_1^*)}{q_i^*(T, 1)} \]  
(3.6.3a)

\[ = \frac{\gamma_i(T, P, q_1) a_i^{*q}(T, P) q_i(T, P)}{q_i^*(T, 1)} - \frac{\Gamma_i(T, P, q_1) q_i(T, P)}{q_i^*(T, 1)} \]  
(3.6.3b)

\[ = \frac{\gamma_i(T, P, q_1^*) q_i(T, P)}{q_i^*(T, 1)}, \]  
(3.6.3c)

where we have also reintroduced the definition \( A^{*(q)} = a_i(T, P, q_1^*) = a_i^{*q}(T, P) \).

An alternative derivation of Eq. (3.6.2) is achieved by introducing Eqs. (3.5.13) and (3.5.18) into Eqs. (3.5.21c), respectively.

Written out in full, Eq. (3.6.2) reads

\[ \mu_i = \mu_i^*(T, 1) + RT \ln \left\{ \gamma_i(T, P, x_i) a_i^{*x}(T, P) x_i \right\} - \mu_i^*(T, 1) \]  
(3.6.4a)

\[ = \mu_i^*(T, 1) + RT \ln \left\{ \frac{\gamma_i(T, P, c_i) a_i^{*c}(T, P) c_i(T, P)}{c_i^*(T, 1)} \right\} \]  
(3.6.4b)

\[ = \mu_i^*(T, 1) + RT \ln \left\{ \frac{\gamma_i(T, P, m_i) a_i^{*m}(T, P) m_i}{m_i^*} \right\} \]  
(3.6.4c)

It should be obvious that when \( q = x \), the treatment of this section and that of Section 3.5 leads to identical results.

The formulation provided here has the great advantage that the standard chemical potential is now independent of the mode of specifying the composition of solutions. The standard state in each instance refers to that of pure \( i \) at temperature \( T \) and unit pressure. The price paid for this simplification is that the interrelations between \( a_i(T, P, q_i) \) and \( q_i \) are now slightly more complex than those involving \( a_i(T, P, q_i) \) and \( q_i \) when \( q = c, m \). The \( a_i \) introduced in Eq. (3.6.3) will be termed the relative activity. Note that whereas \( a_i(T, 1, c_i^*) \) and \( a_i(T, 1, m_i^*) \) differ from unity, \( a_i(T, 1, q_i^*) = 1 \) for all \( q_i \). Equations (3.6.3) also show explicitly that \( a_i(T, P, x_i) = a_i(T, P, c_i) = a_i(T, P, m_i) \) all have the same numerical values, independent of the composition units, whereas the corresponding
a_i differ numerically. It seems that relative activities should be more widely adopted in the literature of thermodynamics.

EXERCISES

3.6.1 Determine the choice of gauge by which Eqs. (3.6.2)-(3.6.4) may be directly derived from Eqs. (3.5.3) and (3.5.9).

3.6.2 For a two-component solution, the following equation is often cited: \[ \ln(a_i/A_i) = \ln x_1 + (B/RT)x_2^2; \] \[ B = B(T,P). \] Determine (a) \( \gamma_1(T,P,x_1) \), (b) \( \gamma_2(T,P,x_2) \), (c) \( P_1(T,P,x_1) \).

3.6.3 From the representation that is provided in Exercise 3.6.2 determine \( \ln \left[ a_i(T,P,c_1)/A_i^{(0)} \right] \) and \( \ln \left[ a_i(T,P,m_1)/A_i^{(m)} \right] \), and thence find \( \gamma_1(T,P,c_1) \), \( \gamma_1(T,P,m_1) \), \( \gamma_2(T,P,c_2) \), \( \gamma_2(T,P,m_2) \).

3.6.4 For the representation shown in Exercise 3.6.2 determine \( G_1 \), \( H_1 \), \( S_1 \), \( V_1 \), \( E_1 \), \( F_1 \).

3.7 CHARACTERIZATION OF EQUILIBRIUM IN NONIDEAL SOLUTIONS

In earlier sections we have dealt with a variety of methods for determining the chemical potential of species in nonideal solutions. This now provides the groundwork for the study of equilibrium constants. As might be expected, the large variety of ways in which these chemical potentials may be specified is reflected in many different ways for defining equilibrium constants. As usual, care will have to be taken to ensure that these different specifications will actually lead to identically the same characterization of a given physical system.

(a) In most general terms, one may proceed through the criterion for chemical equilibrium, \( (\sum \nu_i \mu_i)_{eq} = 0 \), developed in Section 2.9. Here again the \( \nu_i \) represent stoichiometry coefficients for the generalized chemical reaction \( \sum _{i} \nu_i A_i = 0 \), where the \( A_i \) represent all of the participating species; \( \nu_i \) is positive or negative according as the corresponding \( A_i \) represents a product or a reagent for the reaction as written. The most straightforward approach involves use of Eqs. (3.4.1)
or (3.4.2), in which, for the time being, \(q^*_f\) is simply some convenient reference value of the composition variable. Starting with Eq. (3.4.1) the equilibrium state is characterized by

\[
\sum_l \nu_l \mu_l (T,P,q^*_f) + \sum_l \nu_l RT \ln \left[ \frac{a_l(T,P,q_f)}{a_l(T,P,q^*_f)} \right]_{eq} = 0, (3.7.1)
\]

which leads to many possibilities. We confine ourselves to the following: (i) One may rewrite the preceding expression as

\[
\ln K(T,P) = - \sum_l \nu_l \mu_l (T,P,q^*_f)/RT
\]

\[
- \sum_l \nu_l \ln \left[ \frac{a_l(T,P,q_f)}{a_l(T,P,q^*_f)} \right]_{eq}, \tag{3.7.2a}
\]

in which an equilibrium 'constant' \(K\) has been introduced that is related exclusively to the reference chemical potential, and that is therefore independent of the composition of the system. Clearly \(K\) depends parametrically on temperature and pressure. Equation (3.7.2a) may be reformulated as

\[
K(T,P) = \prod_l \left[ \frac{a_l(T,P,q_f)}{a_l(T,P,q^*_f)} \right]^{\nu_l}, \tag{3.7.2b}
\]

By contrast, if Eq. (3.4.2) is chosen as the starting point one arrives at the expressions

\[
\ln K(T) = - \sum_l \nu_l \mu_l (T,1,q^*_f)/RT, \text{ or } \tag{3.7.3a}
\]

\[
K(T) = \prod_l \left[ \frac{a_l(T,P,q_f)}{a_l(T,1,q^*_f)} \right]^{\nu_l}_{eq}. \tag{3.7.3b}
\]

On the other hand, one is also free (ii) to return to Eq. (3.7.1) and to define a quantity

\[
\ln K(T,P) = - \sum_l \nu_l [\mu_l(T,P,q^*_f)/RT - \ln a_l(T,P,q^*_f)]
\]

\[
- \sum_l \nu_l \ln \left[ \frac{a_l(T,P,q_f)}{a_l(T,P,q^*_f)} \right]_{eq}, \tag{3.7.4a}
\]

in which the definition of the equilibrium 'constant' \(K\) now
includes the activity of the various species at their reference compositions \( q_i^+ \). Equation (3.7.4a) may be revamped by writing

\[
K(T,P) = \prod_{i} [a_i(T,P,q_i^+)]^{\nu_i^+}.
\] (3.7.4b)

When Eq. (3.4.2) is adapted to this formulation one obtains

\[
\ln K_a(T) = -\sum_{i} \nu_i \left[ \mu_i(T,1,q_i^+)/RT - \ln a_i(T,1,q_i^+) \right] 
\] (3.7.5a)

as well as

\[
K_a(T) = \prod_{i} [a_i(T,P,q_i^+)]^{\nu_i^+}.
\] (3.7.5b)

Comparison of Eqs. (3.7.4b) with (3.7.2b) or of Eq. (3.7.5b) with (3.7.3b) leads immediately to the schematic interrelation

\[
\tilde{K} \prod_{i} (a_i^+)^{\nu_i^+} = K_a,
\] (3.7.5c)

in which the parametric dependences of \( \tilde{K} \), \( K_a \), and \( a_i^+ \) on \( T, P \), and \( q_i^+ \) have been suppressed. Equation (3.7.5b) corresponds to Eqs. (2.10.2), (2.10.11a), and (2.10.12a) for ideal solutions.

Clearly, an enormous variety of equilibrium constants may be constructed, depending on what one chooses as a specification for composition variable, what value is selected for \( q_i^+ \), and whether one elects to refer \( \mu_i \) to a standard or to a reference chemical potential. This indicates that while the equilibrium constant is a useful quantity for characterizing chemical equilibrium, it is not a fundamental concept in the thermodynamic sense, since it cannot be uniquely specified. To prevent proliferation of so many different quantities, we shall henceforth restrict ourselves to equilibrium parameters such as (3.7.3a) or (3.7.5a) that are related to the chemical potentials of the various species in their standard state; this is an almost universally accepted practice.

(b) If one elects to set \( q_i^+ = q_i^* \) in Eq. (3.7.3a), then
a_i(T,1,q_i^*) = q_i^* in (3.7.3b); moreover, \( \mu_i(T,1,q_i^*) \) is the chemical potential of pure \( i \), \( \mu_i(T,1) \), regardless of the choice of \( q_i \) (see Sec. 3.6). One then obtains the result

\[
\ln K(T) = - (RT)^{-1} \sum \nu_i \mu_i^*(T,1) - \sum \ln a_i(T,P,q_i^*) \]_{eq}, \quad (3.7.6a)
\[
K(T) = \prod \frac{[\gamma_i(T,P,q_i^*) a_i^*(T,P) q_i^*/q_i^*]_{eq}^{\nu_i}}{[\Gamma_i(T,P,q_i^*) q_i(T,P)/q_i^*(T,1)]_{eq}^{\nu_i}}, \quad (3.7.6b)
\]

One should note that \( K(T) \) here involves the relative activities. When mole fractions are adopted as composition variables Eq. (3.7.6b) exhibits the special feature that whenever \( q \) indexes a pure condensed phase (denoted by \( s \)) the corresponding factor in the product reduces to the form \( [\gamma_s(T,p,q_s) a_s^*(T,P)]_{eq}^{\nu_s} = [\Gamma_s(T,p,q_s)]_{eq}^{\nu_s} \), which will later be shown not to differ significantly from unity. Thus, the only terms that contribute substantially to (3.7.6b) are factors relating to species actually dissolved in solutions. The above scheme has the further advantage that only a single \( K(T) \) is invoked, regardless of what composition variable is selected, and that according to Eq. (3.7.6a) this quantity varies only with temperature.

(c) The second scheme, which is more generally used, involves a hybrid procedure patterned after the methodology of Section 2.11. Here one distinguishes between pure condensed phases, indexed by the symbol \( s \), and components forming homogeneous mixtures, indexed by the symbol \( j \). For the pure condensed phases one adopts Eq. (3.6.2) in the specification of the chemical potential; for species in solution it is conventional to introduce Eq. (3.5.21). The equilibrium condition for the reaction \( \Sigma \nu_i A_i = 0 \) is now specified by

\[
0 = \sum_s \nu_s \mu_s + \sum_j \nu_j \mu_j \]_{eq} = \sum_s \nu_s \mu_s^*(T,1) + \sum_j \nu_j \mu_j^q(T,1)
+ RT \sum_s \nu_s \ln a_s(T,P,q_s^*) + RT \sum_j \nu_j \ln [a_j(T,P,q_j)]_{eq}, \quad (3.7.7)
\]
which may be rearranged to yield the following definition of an equilibrium constant:

\[- \sum_s \nu_s \mu_s^*(T,1) - \sum_j \nu_j \mu_j^{s*}(T,1) = \ln K_q(T) = \sum_s \nu_s \ln a_s(T,P,q_s^*)
+ \sum_j \nu_j \ln [a_j(T,P,q_j)]_{eq}, \tag{3.7.8a}\]

or alternatively,

\[K_q(T) = \left[ \sum_s a_s(T,P,q_s^*) \right]^{\nu_s} \left[ \sum_j a_j(T,P,q_j) \right]^{\nu_j}_{eq}
- \left[ \sum_s \left[ \gamma_s(T,P,q_s^*)a_s^{*q}(T,P) \right]^{\nu_s} \left[ \sum_j \gamma_j(T,P,q_j)a_j^{*q}(T,P) \right]^{\nu_j}_{eq} \right] \qquad \tag{3.7.8b}\]

where once again for pure condensed phases \(s, (q_s/q_s^*) = 1\).

In this approach every choice of composition variable \(q\) carries with it a different equilibrium constant \(K_q\); these latter quantities depend parametrically on \(T\) alone.

(d) An alternative, equivalent point of view emerges by examination of the interrelation between \(\Delta G_d\) and \(\ln K\). On writing \(\Delta G_d = \Sigma(\nu \mu)\) and utilizing \((3.6.2)\) and \((3.7.6a)\), one finds

\[\Delta G_d = \sum_j \nu_j \mu_j^*(T,1) + RT \sum_j \nu_j \ln a_j(T,P,q_j) \tag{3.7.9a}\]
\[= - RT \ln K(T) + RT \sum_j \nu_j \ln a_j(T,P,q_j) \tag{3.7.9b}\]
\[= - RT \sum_j \nu_j \ln [a_j(T,P,q_j)]_{eq} + RT \sum_j \nu_j \ln a_j(T,P,q_j). \tag{3.7.9c}\]

On introducing the definition \(\Sigma(\nu \mu^*) = \Delta G_d^*\), one obtains the important relation

\[\ln K = - \Delta G_d^*/RT. \tag{3.7.10}\]

From the definition it should be obvious that \(\Delta G_d^*\) is the
differential Gibbs free energy per unit advancement of the reaction $\sum_i \nu_i A_i = 0$ when all components are in their pure state under standard (unit) pressure. That such a system may not be experimentally accessible is not of concern, since one can simply look up tabulated values of $\mu^*_i(T,1)$ for all the pure components and thereby obtain $\Delta G_d^0$. Using Eq. (3.7.10), Eq. (3.7.9b) becomes

$$\Delta G_d = \Delta G_d^0 + RT \sum \nu_i \ln a_i(T,P,q_i). \quad (3.7.11)$$

Let us return to Eq. (3.7.10) to note the very fundamental interrelation between (i) the free energy change per unit advancement of the reaction $\sum_i \nu_i A_i = 0$, when all participating species are isolated and maintained at standard conditions, and (ii) the natural logarithm of the equilibrium constant pertaining to the reaction in question.

One is equally at liberty to make a distinction between pure condensed phases and homogeneous mixtures. In that event one obtains, in view of (3.7.8a),

$$\Delta G_d = \sum_s \nu_s \mu^*_s + \sum_j \nu_j \mu^*_j(T,1) + \sum_s \nu_s \mu^*_s(T,1) + \sum_j \nu_j \mu^*_j(T,1)$$

$$+ RT \sum_s \nu_s \ln a_s(T,P,q_s^*) + RT \sum_j \nu_j \ln a_j(T,P,q_j) = -RT \ln K_q(T)$$

$$+ RT \sum_s \nu_s \ln a_s(T,P,q_s^*) + RT \sum_j \nu_j \ln a_j(T,P,q_j). \quad (3.7.12)$$

If one now sets $\Delta G_d^{eq} = \Sigma_s \nu_s \mu^*_s(T,1) + \Sigma_j \nu_j \mu^*_j(T,1)$, one obtains an analogue of Eq. (3.7.10), namely,

$$\ln K_q(T) = -\Delta G_d^{eq}/RT, \quad (3.7.13)$$

and (3.7.12) may be rewritten as

$$\Delta G_d = \Delta G_d^{eq} + RT \sum_s \nu_s \ln a_s(T,P,q_s^*) + \sum_j \nu_j \ln a_j(T,P,q_j). \quad (3.7.14)$$

Note the distinction between $\Delta G_d^{eq}$ and $\Delta G_d^0$ by referring to Eqs. (3.5.21) and (3.6.2); see also Exercise 3.7.1.
(e) We return to Eq. (3.7.8b) for a discussion of the equilibrium constant which is seen to involve products of factors of the following form: (i) quantities \( \gamma_s(T,P,q_s^*)a_s^q(T,P) \) or, equivalently, \( \Gamma_s(T,P,q_s^*) \), which relate to pure condensed phases, (ii) terms involving the activity coefficients \( \gamma_j(T,P,q_j) \), which correct for gross deviations from ideal properties of species making up homogeneous solutions, (iii) terms involving \( a_j^q(T,P) \), which, by (3.5.17b) or (3.5.20), relate to the activities and activity coefficients of pure \( j \) at pressures other than one atmosphere, and (iv) the usual product \( \prod_j q_j^q \) of concentration units that constitute the equilibrium constant for an ideal solution.

We shall now show that the products in (i) generally differ only slightly from unity, so that for all but the most accurate calculations, the contributions \( \gamma_s a_s^q \) are customarily omitted from the right-hand side of Eqs. (3.7.6b) and (3.7.8b). This step is summarized by the generally cited statement that "the activity of all pure condensed phases is unity." The procedure discussed here also offers a mechanism to determine the activity of condensed phases, which quantity must be experimentally determined in accurate analyses of experimental data.

Toward this goal we now introduce Eqs. (3.4.7), (3.4.5), (3.5.17b), and (3.5.20); in each instance we may write

\[
\gamma_i(T,P,q_i)a_i^q(T,P) = \Gamma_i(T,P,q_i) = a_i(T,P,q_i)/q_i,
\]

with \( q = x, c, m \) and \( a_i^q(T,P) = a_i^q(T,P) \). In the further evaluation we note that for a pure condensed phase at constant temperature \( d\mu_s|_T = \overline{\nu}_s dP|_T = RT d\ln a_s(T,P,q_s^*)|_T \). Therefore,

\[
\ln [a_s(T,P,q_s^*)] - \ln [a_s(T,1,q_s^*)] = (1/RT) \int_1^P \overline{\nu}_s(T,P,q_s^*) \, dp.
\]

Ordinarily, \( \overline{\nu}_s \) changes so little with pressure that it may be regarded as sensibly constant. Furthermore, according to (3.4.3), \( a_s(T,1,q_s^*) = q_s^* \). For \( q = x \), \( x_s^* = 1 \); for \( q = c \), \( q_s^* = c_s^*(T,1) \); and for \( q = m \), \( q_s^* = m_s^* \). Then Eq. (3.7.16) reduces to
\[ \ln \Gamma_s(T, P, q_0^*) = \ln \left( \frac{a_s(T, P, q_0^*)}{q_0^*} \right) \]

\[ = \ln[a_s(T, P, q_0^*)] = \frac{[(P-1)\tilde{V}(T, 1, q_0^*)]}{RT} \]  \hspace{1cm} (3.7.17)

Ordinarily, the ratio \((P-1)\tilde{V}/RT\) is quite small, especially if the total pressure does not deviate greatly from unity. In that event,

\[ \Gamma_s(T, P, q_0^*) = a_s(T, P, q_0^*)/q_0^* = a_s(T, P, q_0^*) \approx 1, \]  \hspace{1cm} (3.7.18)

i.e., the activity coefficients \(\Gamma_s\) and relative activities then differ very little from unity. Moreover, Eqs. (3.7.18) and (3.4.3) show that \(\Gamma_s(T, 1, q_0^*) = a_s(T, 1, q_0^*) = 1\), i.e., \(\) the activity coefficient \(\Gamma_s\) and relative activity of all pure condensed is unity under standard conditions \(P = 1\); in these circumstances the requirement \(a_s(T, 1, q_0^*) = q_0^*\) is automatically recovered. Equations (3.7.17) or (3.7.18) provide a quantitative means for evaluating the product \(\gamma_s(T, P, q_0^*)a_q^*(T, P) = \Gamma_s(T, P, q_0^*)\) appearing in Eq. (3.7.8b). It should now be clear why this product is ordinarily omitted.

The corresponding determination of the products \(\gamma_j(T, P, q_j) a_j^*(T, P)\) for dissolved species is more involved and will be considered in detail beginning with Section 3.11.

For gaseous species the simplest procedure is to substitute fugacities in place of activities. This brings the machinery of Section 3.1 to bear on the present problem. Formally, one may adhere more closely to the methodology of the present Section by writing \(f_i = P_i(f_i/P_i) = \gamma_i(T, P, P_i)P_i\). The quantities \(\gamma_i(T, P, P_i) = f(T, P, P_i)/P\) are specified as shown in Section 3.1.

\(\) At this point the troublesome question arises once more as to the significance of \(K\) or \(K\) or \(K_q\) when its numerical value and even its functional form depends on so many arbitrary choices. Here one must keep in mind that \(K\) or \(K\) or \(K_q\) was
introduced in the process of establishing the differential Gibbs free energy change $\Delta G_d$ accompanying the chemical reaction $\Sigma (\nu_i) \nu_i A_i = 0$. As is evident from (3.7.10) or from (3.7.13) the quantity $\Delta G_d^{q*} = -RT \ln K$, or $\Delta G_d^q = -RT \ln K_q$ has precisely the same functional form as the terms in Eq. (3.7.9c) and as the second and third term on the right of Eq. (3.7.12), except that in $K$, or $K_q$, the $\gamma_i$ and $q_i$ are to be evaluated for the equilibrium state. Thus, the vagaries of choice adopted for $K_q$ or $K$ must be exactly matched in the specification of activities, activity coefficients, and $q_i$'s used in Eqs. (3.7.9) and (3.7.12). It follows that $\Delta G_d$ is indeed invariant under changes in standard states, reference states, or methods of specifying the composition of the system. Since $\Delta G_d$ and other thermodynamic state functions derivable therefrom (such as $\Delta S_d$ or $\Delta H_d$) are the fundamental quantities of interest, the arbitrariness of $K$ or $K_q$ causes no difficulty other than being a nuisance. It should be remembered that, once a choice of units and of standard state has been made, a value of $K$ or $K_q$ $>> 1$ implies that $\Delta G_d^q$ is a large negative quantity, and hence, that $\Delta G_d$ is also likely to be a large negative quantity. Thus, equilibrium will be established after the pertinent reaction has proceeded nearly to completion in the direction as written. Conversely, for values of $K$ or $K_q$ $<< 1$, equilibrium sets in when the reaction is close to completion in the opposite direction. Thus, the equilibrium constant serves as a rough index of how far and in what direction a reaction will proceed, and this prediction does not depend on the arbitrariness discussed earlier. It should also be clear that the equilibrium constants do not in themselves possess the same fundamental importance as the Gibbs free energies. These matters are illustrated by the example worked in Section 3.A.

(g) It may help to summarize the findings based on the use of Eq. (3.4.23): From the general condition $\Sigma (\nu_i) \nu_i \mu_i = 0$ one finds

$$\sum \nu_i \mu_i^*(T,1) + RT \sum \nu_i \ln a_i(T,p,x_i) \big|_{eq} = 0$$

(3.7.19)
which may be split up into components \( s \) that appear solely as pure condensed phases and components \( f \), that constitute the solution. On rearranging Eq. (3.7.19) according to this pattern one finds (for \( q = x \) only)

\[
- \frac{1}{(RT)^{-1}} \left[ \sum_s \nu_s \mu_s^*(T,1) + \sum_f \nu_f \mu_f^*(T,1) \right] = \sum_s \nu_s \ln a_s(T,P,1) \\
+ \sum_f \nu_f \ln a_f(T,P,x_f) \bigg|_{eq} = \ln K_x(T)
\]

or

\[
K_x(T) = \prod_s a_s(T,P,1)^{\nu_s} \prod_f a_f(T,P,x_f)^{\nu_f} \bigg|_{eq}
\]

Now set

\[
\Delta G_d^{eq} = \sum_s \nu_s \mu_s^*(T,1) + \sum_f \nu_f \mu_f^*(T,1).
\]

Then

\[
\ln K_x(T) = - \frac{\Delta G_d^{eq}}{RT}
\]

and

\[
\Delta G_d = \Delta G_d^{eq} + RT \sum_s \nu_s \ln a_s(T,P,1) + \sum_f \nu_f \ln a_f(T,P,x_f).
\]

**EXERCISES**

3.7.1 Compare and contrast Eqs. (3.7.11) and (3.7.14) and specify the standard or reference state that is associated with Eq. (3.7.14).

3.7.2 Provide estimates showing under what conditions \( \gamma_1(T,P,q)a^aq(T,P) \) will deviate from unity by more than 10%.

3.7.3 Invent a semipractical scheme by which any reaction could in principle be carried out by holding all reagents and products at standard conditions. (Hint: recall van't Hoff's scheme.)

3.7.4 Write out expressions for \( K_x \), \( K_c \), and \( K_p \) for homogeneous gas phase reactions in terms of fugacities or fugacity coefficients, based on derivations analogous to those of Sections 2.9 and 2.11.
3.7.5 Examine the equilibrium state for the system N₂(g) + 3H₂(g) = 2 NH₃(g), introducing the approximation that the fugacity of species i in a gaseous mixture is given by \( f_i = x_i f_i^0 \), where \( f_i^0 \) is the fugacity of pure i at the same temperature. (a) Write out the equilibrium constant in terms of the total pressure, mole fractions, and fugacity coefficients. (b) The standard free energy of formation of NH₃(g) is given by \( \Delta G_m^0 = -9.130 + 7.46T - 24.13T^2 + 3.69 \times 10^{-3}T^3 + 0.235 \times 10^{-7}T^4 \) (in calories). Determine the equilibrium constant for the formation process of NH₃(g) at 450°C.

3.7.6 Consider the reaction CO(g) + 2H₂(g) = CH₃OH(g).
(a) Write down a general expression for \( K_q, q = P, c, x \), for an ideal mixture if \( n \) moles of CO are placed in contact with \( m \) moles of H₂ and the reaction proceeds until the fraction of CO equals \( \alpha \). (b) Assume that all the gases obey an equation of state of the form \( PV = RT + B_iP_i \). Write out the equilibrium constant \( K_q \) in terms of the total pressure, the \( B_i \), and mole fractions.

3.7.7 At 216.6 K the equilibrium pressure of CO₂ over dry ice is 5.1 atm. The equation of state for CO₂(g) is given by \( PV = RT + BP \) where \( B = 42.7 \text{ cm}^3/\text{mol} \). The molar volume of CO₂(s) at 216.6 K is 28.2 \text{ cm}^3/mole and is nearly independent of pressure. Determine \( \Delta G_m^0 \) for the dry ice sublimation process.

3.7.8 Refer to Fig. 3.7.1 for the fugacity coefficients \( \gamma_i = f_i/f_i^0 \) of pure gases and introduce the approximation \( f_i = x_i f_i^0 \), where \( f_i^0 \) is the fugacity of pure i and \( x_i \) is the mole fraction of i in the gaseous mixture. Consider the equilibrium mixture for the reaction CO(g) + H₂O(g) = CO₂(g) + H₂(g) at 600°C and determine the fractional change in equilibrium constant when the pressure over the equilibrium constant is increased from 1/2 to 500 atm. The critical quantities needed for use with Fig. 3.7.1 are \( T_c \) = 304, 41.8, 134, 657 K and \( P_c \) = 72.9, 12.8, 34.6, and 218 atm for CO₂, H₂, CO, and H₂O, respectively.

3.7.9 For the reaction 2H₂(g) + CO(g) = CH₃OH(g), the critical temperatures and pressures read \( T_c = 513.2, 41.2, 134.4 \) K and \( P_c = 98.7, 20.8, 34.6 \) atm for CH₃OH, H₂, and CO, respectively. The heats of formation of CH₃OH(g) and CO(g) are \( \Delta H_{298}^0 = -48.1 \) and \(-26.4 \text{ kcal/mol} \), respectively. Furthermore,

\[
\begin{align*}
C_p(\text{CH}_3\text{OH}) & = 4.394 + 24.274 \times 10^{-3}T - 68.55 \times 10^{-7}T^2 \text{ cal/mol-deg} \\
C_p(H_2) & = 6.947 - 0.200 \times 10^{-3}T + 4.81 \times 10^{-7}T^2 \text{ cal/mol-deg} \\
C_p(CO) & = 6.342 + 1.836 \times 10^{-3}T + 2.80 \times 10^{-7}T^2 \text{ cal/mol-deg}.
\end{align*}
\]

The standard entropies are \( S_{298}^0 = 56.63, 31.21, \) and \( 47.30 \text{ eu/mol} \) for CH₃OH(g), H₂(g), and CO(g), respectively. In conjunction with Fig. 3.7.1 and with the aid of the approximation \( f_i = x_i f_i^0 \) determine the equilibrium constant at 600 K when the mixture
is held at a total pressure of 25 and of 250 atm, respectively. If a mixture of 2 mole of H₂ and 3 mol of CO are equilibrated, determine the extent of conversion at each pressure.

3.7.10 (a) For \( \text{H}_2\text{O(\ell)} \rightarrow \text{H}_2\text{O(g)} \), \( \Delta G_{298}^\circ = 2.0545 \text{ kcal} \) and 
\[ \Delta H^\circ = 13,644 - 10.84T + 1.187x(10^{-3})T^2 + 0.89x(10^{-7})T^3. \]
Find \( \Delta G_{380}^\circ \). (b) For the change \( 2\text{Ag(s)} + \text{Hg}_2\text{Br}_2(s) \rightarrow 2\text{AgBr(s)} + 2\text{Hg(\ell)} \), \( \Delta G_{298}^\circ = -3.138 \text{ kcal} \) and the temperature coefficient of this change, \( \left( \frac{\partial \Delta G_{298}^\circ}{\partial T} \right)_P \), is -14.39 cal deg\(^{-1} \). Find \( \Delta H_{298}^\circ \).

3.7.11 For the reaction \( \text{CaCO}_3(s) \rightarrow \text{CaO(s)} + \text{CO}_2(g) \), the following empirical expression is found to be applicable for the partial pressure of \( \text{CO}_2 \) in equilibrium with the condensed phases:
\[ \log P = -9140/T + 0.382 \log T - 0.668 x 10^{-3}T + 7.4363 \]
(P in atm). The equation of state for \( \text{CO}_2 \) is given by \( PV = RT + BP \), where \( B = 42.7 \text{ cm}^3/\text{mol} \). The densities of \( \text{CaCO}_3(s) \) and \( \text{CaO(s)} \) are, respectively, 2.93 and 3.346 g/cm\(^3 \). (a) Determine the activity of \( \text{CO}_2 \) relative to its pressure. (b) Determine the activity ratio \( a_{\text{CaO}}/a_{\text{CaCO}_3} \) and check on the validity of the approximation of replacing this ratio by unity. What is the percentage error when the total pressure is \( \frac{1}{2} \text{ atm} \) and \( T = 500\text{°C} \)? (c) Write out an exact expression for \( K_P \) as a function of \( P \) and \( T \) and check how well this result agrees with the relation \( K_P = P_{\text{CO}_2} \) when the total pressure over the system is \( \frac{1}{2} \text{ atm} \) and \( T = 500 \text{ K} \). (d) Derive an expression for \( \Delta H_0 \) as a function of the
temperature. (e) By how much does $a_{CO_2}$ change at 500°C when the total pressure on the system is changed from 1 to 101 atm? (f) What is the numerical value of $\Delta G_{d1000}$, $\Delta S_{d1000}$, $\Delta H_{d1000}$. $\Delta C_{dp}$ (at 1000 K)?

3.7.12 For the reaction $3Si(s) + 2N_2(g) = Si_3N_4(g)$, $\Delta G^o = -1.77 \times 10^5 - 5.76T \log_{10} T + 96.3T$ (cal) (valid over the range 500-1670 K). (a) Calculate $\Delta G^o_{1000}$ and $\Delta H^o_{1000}$ of $Si_3N_4(g)$ at 1000 K. (b) Derive expression for $\Delta S^o$ and $\Delta C_{dp}$ for the reaction. (c) Suppose excess Si(s) is subjected to 1 atm of $N_2(g)$ in a closed vessel at 1000 K and the system is allowed to come to equilibrium. Compute the partial fugacities of $Si_3N_4$ gas at equilibrium.

3.7.13 Consider the reaction $2Fe_3O_4(s) + CO_2(g) = 3Fe_2O_3(s) + CO(g)$ and the values listed below:

<table>
<thead>
<tr>
<th></th>
<th>$G_{1000} - H_{298}^o$/1000 (cal/deg-mol)</th>
<th>$H_{2,298}^o$ (cal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Fe_3O_4(s)$</td>
<td>-58.970</td>
<td>-267,800</td>
</tr>
<tr>
<td>$Fe_2O_3(s)$</td>
<td>-36.430</td>
<td>-196,800</td>
</tr>
<tr>
<td>$CO(g)$</td>
<td>-50.843</td>
<td>-26,616</td>
</tr>
<tr>
<td>$CO_2(g)$</td>
<td>-56.348</td>
<td>-94,052</td>
</tr>
</tbody>
</table>

(a) Obtain the ratio $a_{CO}/a_{CO_2}$ at 1000 K when the total pressure is 1 atm. (b) Obtain the ratio $a_{CO}/a_{CO_2}$ at 1000 K at a total pressure of 1000 atm. Here the molar volume of $Fe_3O_4$ under standard conditions is 44.7 cm$^3$ and that of $Fe_2O_3$ is 30.5 cm$^3$.

3.7.14 Determine the activity of pure water at 25°C and at a pressure of 1000 atm, given that its density is $\rho = 0.99707$ g/cc and that its isothermal compressibility at 25°C is $\beta = -45.5 \times 10^{-6}$ atm$^{-1}$.

3.7.15 For $H_2O$, $H_2$, $O_2$ the critical values read $T_c = 374.2°C$, -240°C, -118°C and $P_c = 218.3$, 13, 50.2 atm, respectively. Using Fig. 3.7.1, determine $K_p$, $K_c$, $K_x$ for the reaction $H_2(g) + (1/2)O_2(g) = H_2O(g)$, given that $AG_{298}^o = -54.634$ kcal.

3.7.16 Refer to Fig. 3.7.1 for the reaction $SO_2(g) + (1/2)O_2(g) = SO_3(g)$, in which the critical temperatures and pressures are given by $T_c = 157.4$, -118.5 218.3°C and $P_c = 78.6$, 50.5, 83.6 atm for $SO_2$, $O_2$, $SO_3$, respectively. (a) Determine $K_p$, $K_c$, and $K_x$ for this reaction under a total pressure of 200 atm and 25°C given that $AG_{298}^o = -70.88$ kJ. (b) Find the fractional degree of conversion to $SO_3$ if 1 mol of $SO_2$ and 1/2 mole $O_2$ are equilibrated under a total pressure of 200 atm and at 25°C.

3.7.17 It has often been stated that $\Delta \ln K/\Delta T \rho = \Delta H_{d}/RT^2$. Accordingly, if $\Delta H_d$ is independent of $T$, a plot of $\ln K$ versus $1/T$ should yield a straight line with slope $\Delta H_{d}/R$. (If $\Delta H_d$ depends on $T$ such a plot will produce a curve.) On the other hand, it is often stated that $\Delta G_d^o = -RT \ln K$. Accordingly, a plot of $\ln K$ versus $1/T$ should result in a straight line of slope $\Delta G_d^o/R$. Thus, one concludes that one and
the same plot provides information on $\Delta H_d^o$ and on $\Delta G_d^o$. Show the origin of this paradox, state which alternative is correct, and demonstrate why it is correct.

3.7.18 For the reaction $\text{SO}_2(g) + (1/2)\text{O}_2(g) \rightarrow \text{SO}_3(g)$ one finds as standard Gibbs free energies of formation at 25°C of $-71.7$, $0$, and $88.5$ kcal/mol for $\text{SO}_2$, $\text{O}_2$, and $\text{SO}_3$. The variation of heat capacity is given by $C_p = A + BT + CT^2$ cal/deg·mole in which

<table>
<thead>
<tr>
<th></th>
<th>$\text{SO}_2$</th>
<th>$\text{O}_2$</th>
<th>$\text{SO}_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$</td>
<td>6.147</td>
<td>6.148</td>
<td>6.077</td>
</tr>
<tr>
<td>$B \times 10^3$</td>
<td>13.844</td>
<td>3.102</td>
<td>23.537</td>
</tr>
<tr>
<td>$C \times 10^6$</td>
<td>-9.103</td>
<td>-0.923</td>
<td>-9.687</td>
</tr>
</tbody>
</table>

Determine $\Delta G_d^o$ for this reaction at 500°C.

3.7.19 At 1100 and 1200 K the equilibrium pressure of $\text{CO}_2$ above $\text{CaCO}_3/\text{CaO}$ mixtures is 0.423 and 1.924 atm respectively. Determine whether the reaction $\text{CaCO}_3(s) = \text{CaO}(s) + \text{CO}_2(g)$ is feasible at 1100 and at 1200 K under conditions where $P_{\text{CO}_2}$ is maintained at 1 atm.

3.7.20 For the reaction $(1/2)\text{N}_2 + (3/2)\text{H}_2 \rightarrow \text{NH}_3$ at 475°C, gas analysis of a mixture initially of composition $x_{\text{N}_2}^0 = 1/4x_{\text{H}_2}^0 = 3/4$ yielded the following data as a function of the total pressure $P$:

<p>| | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$x_{\text{NH}_3}$</td>
<td>0.0161</td>
<td>0.453</td>
<td>0.1298</td>
<td>0.475</td>
</tr>
<tr>
<td>$P$(atm)</td>
<td>10</td>
<td>30</td>
<td>100</td>
<td>600</td>
</tr>
</tbody>
</table>

Assume that the gases are ideal at $P = 10$ atm; determine $K_p$ for the system, and the apparent variation of $K_p$ as a function of $P$ when $P$ assumes the values cited in the tabulation.

3.7.21 For the equilibrium constant for the reaction $\text{CO}_2(g) + \text{H}_2(g) \rightarrow \text{CO}(g) + \text{H}_2\text{O}(g)$, one finds the following values:

<table>
<thead>
<tr>
<th>$t$(°C)</th>
<th>600</th>
<th>700</th>
<th>800</th>
<th>900</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K$</td>
<td>0.39</td>
<td>0.64</td>
<td>0.95</td>
<td>1.30</td>
</tr>
</tbody>
</table>

The following relation is found to hold for these gases: $C_p = A + BT + CT^2$ (cal/mol·deg), with

<table>
<thead>
<tr>
<th></th>
<th>$\text{CO}_2$</th>
<th>$\text{H}_2$</th>
<th>$\text{CO}$</th>
<th>$\text{H}_2\text{O}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B \times 10^3$</td>
<td>10.396</td>
<td>-0.200</td>
<td>1.836</td>
<td>2.374</td>
</tr>
<tr>
<td>$C \times 10^6$</td>
<td>-3.545</td>
<td>0.4808</td>
<td>-0.2801</td>
<td>0.257</td>
</tr>
</tbody>
</table>

Determine $\Delta G_d^o$, $\Delta S_d^o$, $\Delta H_d^o$ at 25°C for this reaction.

3.7.22 The composition of a saturated solution of oxygen in water is given by the expression $\log_{10} x_2 = 4271.1/T + 29.1918 \log T - 88.72463$. Determine $\Delta G_d^o$, $\Delta H_d^o$, $\Delta S_d^o$, and $\Delta G_d^{iP}$ for the solution process.

3.7.23 Determine the equilibrium constant for the reaction $\text{CH}_4(g) \rightarrow \text{C}(s) + 2\text{H}_2(g)$, neglecting deviations from ideality, given the fact that the pressure in a vessel of pure methane sealed in a capsule rises from 1/3 to 1.525 atm when the temperature is increased from 300 to 800 K.

3.7.24 For the reaction $\text{B}_4\text{C}(s) = 4 \text{B}(g) + \text{C}(s)$ the
equilibrium vapor pressure in the temperature range 2350–2615 K is given by \( \log_{10} P \) (atm) = 7.506 – 29.630/T. (a) What is the equilibrium constant at 2350 K? (b) What is the equilibrium constant at 2350 K for the reaction \((1/4)B_4C(s) = B(g) + (1/4)C(s)\)? (c) 5 g of \(B_4C\) are enclosed in a 10 cc crucible and equilibrated at 2350 K. What are the equilibrium numbers of moles of \(B_4C\), C, and B in the system? The density of \(B_4C\) is 2.5 g/cc. (d) 1.0 \(x\ 10^{-10}\) mole of B gas is added to the system described in (c). What is the equilibrium pressure of B and what are the mole numbers of \(B_4C\), C, and B at equilibrium? (e) 4.29 \(x\ 10^{-10}\) mol of B gas is added to the system described in (c). What is the equilibrium pressure of B and what are the mole numbers of \(B_4C\), C, and B at equilibrium? (f) 5 \(x\ 10^{-10}\) mole of Ar is added to the system described in (c). What is the total pressure of the system at equilibrium? What are the mole numbers of all components of the system at equilibrium?

3.7.25 For the reaction \(CaCO_3 = CaO + CO_2\) the dissociation pressure in atm is given by \(\log_{10} P_{CO_2} = -11.355/T - 5.388 \log_{10} T + 25.238\). Determine \(\Delta H^\circ\) for the reaction as a function of T.

3.7.26 (a) For \(H_2O(\ell) = H_2O(g)\), \(\Delta G^\circ = 2.0545\) kcal at 298.2 K, and \(\Delta H^\circ(\text{cal}) = 13,644 - 10.84T + 1.187(10^{-3})T^2 + 0.89(10^{-5})T^3\). Find \(\Delta G^\circ\) at 400 K. (b) For the change \(2Ag(s) + Hg_2Br_2(s) = 2AgBr(s) + 2Hg(\ell)\), \(\Delta G^\circ = -3.138\) kcal at 298 K and the temperature coefficient of this change, \((\partial \Delta G^\circ/\partial T)_p\), is -14.39 cal deg\(^{-1}\). Find \(\Delta H^\circ\) at 298 K.

3.7.27 Examine the consequences of defining an equilibrium constant analogous to Eq. (3.7.3d) but with \(\mu_i(T,1,q^\dagger)\) replaced by \(\mu_i(T,P,q^\dagger)\). How is the revised equilibrium constant related to Eq. (3.7.3a)?

3.7.28 Examine the consequences of defining an equilibrium constant obtained by replacement of \(\mu_i^q(T,1)\) in Eq. (3.7.8a) with \(\mu_i^q(T,P)\). How does the equilibrium constant so obtained differ from \(K_q(T)\)?

3.7.29 What happens if \(\mu_i^q(T,1)\) in Eq. (3.7.12) is replaced by \(\mu_i^q(T,P)\)? How is this \(\Delta G^\circ\) related to Eq. (3.7.13)?

3.A THE OXIDATION BOUNDARY FOR MAGNETITE–ZINC FERRITE SOLID SOLUTIONS

(a) We analyze the thermodynamics of the \(Fe_2O_3–ZnFe_2O_4–Fe_3O_4\) system at the oxidation boundary separating hematite \((Fe_2O_3)\) from the magnetite–based \(ZnFe_2O_4–Fe_3O_4\) solid solution. This sample calculation illustrates one method of dealing with unspecified standard chemical potentials.
(b) Step 1 involves writing down the chemical oxidation process

\[
(\text{Fe}_3\text{O}_4)_{1-x} \cdot (\text{ZnFe}_2\text{O}_4)_x + \frac{1-x}{4} \text{O}_2(\text{g}) \rightleftharpoons \frac{3(1-x)}{2} \text{Fe}_2\text{O}_3(\text{s}) + x\text{ZnFe}_2\text{O}_4.
\]

(3.A.1)

Note how the solid solution has been represented schematically on the left, as being composed of a mole fraction 1-x of undoped (pure) Fe\(_3\)O\(_4\) and a mole fraction x of zinc ferrite. It is supposed that the latter moiety remains passive.

(c) We now write out the Gibbs free energy change accompanying Reaction (3.A.1) at constant T and P:

\[
\Delta G(1) = - \mu[(\text{Fe}_3\text{O}_4)_{1-x} \cdot (\text{ZnFe}_2\text{O}_4)_x] - \frac{1-x}{4} \mu[\text{O}_2(\text{g})] + \frac{3(1-x)}{2} \mu[\text{Fe}_2\text{O}_3(\text{s})] + x\mu[\text{ZnFe}_2\text{O}_4(\text{s})].
\]

(3.A.2)

As usual, for solids we set \(\mu_i(T,1) = \mu_i^*(-T,1) + RT \ln a_i(T,P,x_i)\), and for gases we set \(\mu_i(T,1) = \mu_i^{\text{gop}}(T) + RT \ln P\).

For simplicity we assume further that we may write

\[
\mu[(\text{Fe}_3\text{O}_4)_{1-x} \cdot (\text{ZnFe}_2\text{O}_4)_x] = x\mu[\text{ZnFe}_2\text{O}_4(\text{s})] + (1-x)\mu[\text{Fe}_3\text{O}_4(\text{sss})],
\]

(3.A.3)

where \(\mu[\text{Fe}_2\text{O}_4(\text{sss})]\) signifies the chemical potential of the Fe\(_3\)O\(_4\) component that forms the spinel solid solution (sss) with ZnFe\(_2\)O\(_4\); this quantity must be carefully distinguished from the chemical potential \(\mu^*[\text{Fe}_3\text{O}_4(\text{s})]\) for pure solid magnetite. On applying Eq. (3.A.3) to (3.A.2) one obtains

\[
\Delta G(1) = - (1-x)\mu[\text{Fe}_3\text{O}_4(\text{sss})] - \frac{1-x}{4} \mu[\text{O}_2(\text{g})] + \frac{3(1-x)}{2} \mu[\text{Fe}_2\text{O}_3(\text{s})]
\]

\[
= - (1-x)\mu^*[\text{Fe}_3\text{O}_4(\text{s})] - \frac{1-x}{4} \mu^*[\text{O}_2(\text{g})] + \frac{3(1-x)}{2} \mu^*[\text{Fe}_2\text{O}_3(\text{s})]
\]

\[
- (1-x)RT \ln a[\text{Fe}_3\text{O}_4(\text{sss})] - \frac{1-x}{4} RT \ln f[\text{O}_2(\text{g})] = 0.
\]

(3.A.4)

Note that at equilibrium \(\Delta G(1)\) vanishes.
(d) Next, consider the following oxidation step to be executed under standard conditions:

\[ 2\text{Fe}_3\text{O}_4(s) + \frac{1}{2} \text{O}_2(g) \rightarrow 3\text{Fe}_2\text{O}_3(s), \quad (3.\text{A}.5) \]

for which

\[ \Delta G(5) = -2\mu^*[\text{Fe}_3\text{O}_4(s)] - \frac{1}{2} \mu^*[\text{O}_2(g)] - \frac{1}{2} RT \ln f[\text{O}_2(\text{M-H})] 
+ 3\mu^*[\text{Fe}_2\text{O}_3(s)] = 0, \quad (3.\text{A}.6) \]

where \( f[\text{O}_2(\text{M-H})] \) is the oxygen equilibrium fugacity at the magnetite-hematite boundary. The latter is cited in the literature in the functional form \( \log f[\text{O}_2(\text{M-H})] = -24,634/T + 13.96 \) (atm). Use of this expression in (3.\text{A}.6) immediately leads to

\[ -\mu^*[\text{Fe}_3\text{O}_4(s)] - \frac{1}{4} \mu^*[\text{O}_2(g)] + \frac{3}{2} \mu^*[\text{Fe}_2\text{O}_3(s)] 
= (2.303)[-24,634/T + 13.96]/4. \quad (3.\text{A}.7) \]

This relation shows explicitly how the combination of \( \mu^* \) quantities in Eq. (3.\text{A}.4) may be determined experimentally and thereby eliminated. Such procedures are in common use when it is necessary to deal explicitly with standard chemical potentials.

(e) The remaining steps are elementary. We use Eq. (3.\text{A}.7) in (3.\text{A}.4) and solve for

\[ \log f[\text{O}_2(\text{M-H})] \text{ (atm)} = -4 \ln a[\text{Fe}_3\text{O}_4(\text{sss})] 
- 24,634/T + 13.96. \quad (3.\text{A}.8) \]

It remains to determine the first term on the right. Under pressures normally prevailing at the M-H boundary one may drop this term in zero order, since \( a \approx 1 \). The remaining terms then specify \( f[\text{O}_2(\text{M-H})] \) at the particular temperature of interest. The fugacity so determined may then be used in Eq. (3.7.16) to obtain a first order value for \( a[\text{Fe}_3\text{O}_4(\text{sss})] \) that can then be
used in Eq. (3.A.8) for a first order improvement on the oxygen fugacity. The process may be iterated if necessary.

Note that Eq. (3.A.8) specifies the oxygen fugacity prevailing at the oxidation boundary for the Fe$_3$O$_4$(ss) phase boundary at temperature T. As a typical value one finds that $f(O_2) = 5.8$ atm.

3.8 THERMOCHEMISTRY

Thermochemistry pertains to changes in energy or enthalpy that accompany chemical reactions; generally one deals with the heat of reaction which refers to the quantity of heat $Q$ that must be absorbed or released at the end of a process in order that the temperature at the conclusion of the reaction shall be the same as at the outset. As follows from the discussion of Section 1.19, at constant volume $Q_v = \Delta E_d$, whereas at constant pressure $Q_p = \Delta H_d$. Here, $\Delta E_d = \Sigma (i) \nu_i E_i$ and $\Delta H_d = \Sigma (i) \nu_i H_i$, wherein, as before, the $\nu_i$ are the stoichiometry coefficients in the chemical reaction $\Sigma (i) \nu_i A_i = 0$, and $\nu_i < 0$ or $\nu_i > 0$ according to whether one deals with reagents or products. It is customary to provide all information normalized to $25^\circ$C and $P = 1$ atm. Where experimental data are taken under other conditions the data are corrected for standard conditions as discussed in Section 1.18; see also Exercise 3.8.1.

Thermochemical equations represent ordinary chemical equations also containing information on the heats of reaction, the temperature, pressure, and state of aggregation of the substance participating in the reaction. Examples are given by

(1) $C_2H_4(g) = 2CO_2(g) + 2H_2O(l)$ : $\Delta H_d = -337.3$ kcal

(2) $H_2(g) + \frac{1}{2} O_2(g) = H_2O(l)$ : $\Delta H_d = -68.3$ kcal

(3) $C_2H_6(g) + \frac{7}{2} O_2(g) = 2CO_2(g) + 3H_2O(l)$ : $\Delta H_d = -372.8$ kcal

which means, for example, that in the reaction of $7/2$ moles of
gaseous oxygen with one mole of gaseous ethylene to form two moles of gaseous carbon dioxide and three moles of liquid water the enthalpy (heat of reaction, presumably at 298 K and at one atmosphere total pressure, in the absence of other information) given off per unit advancement of reaction is 372.8 kcal. The unit of advancement may be considered infinitesimal for a finite system, or on a per mole basis in an infinite copy of the system. In either case the experimental conditions of the system remain undisturbed by the reaction.

The handling of thermochemical equations is facilitated by two thermochemical laws: The first, enunciated by Lavoisier and Laplace (1780), reads as follows (in slightly generalized form): The heat change accompanying a chemical reaction in one direction is exactly equal in magnitude but opposite in sign to the heat change for the reverse reaction under the same conditions. The second law of constant heat summation was enunciated by Hess in 1840: The heat change accompanying a given chemical reaction under a given set of conditions is the same whether the process is carried out in one stage or in several steps. The relation of these laws to the First Law of Thermodynamics is explored in Exercise 3.8.4; both laws allow us to treat thermochemical equations as quantities that may be manipulated by ordinary rules of algebra.

For example: (i) if Eq. (1) were written in reverse one would have to set $\Delta H_d = +337.3$ kcal. (ii) If Eq. (2) were doubled to read $2H_2(g) + O_2(g) = 2H_2O(l)$, one would have to set $\Delta H_d = -2(68.3)$ kcal $= -136.6$ kcal. (iii) If Eqs. (1)-(3) were combined to yield $C_2H_2(g) + H_2(g) = C_2H_6(g)$, by adding (1) and (2) and subtracting (3), one would obtain $\Delta H_d = \Delta H_d(1) + \Delta H_d(2) - \Delta H_d(3) = -32.8$ kcal. (iv) If one were interested in the reaction $H_2(g) + \frac{1}{2}O_2(g) = H_2O(g)$ one would have to adjoin to $\Delta H_d(2)$ the enthalpy for conversion of water to steam at 1 atm and 25°C, $\Delta H_d = 10.52$ kcal. These illustrative examples show how to proceed in a large variety of cases.

Several different types of 'heats' are commonly referred to in thermochemistry. The most important of these is the heat of formation of a substance, which represents the $\Delta H_d$ value when
one mole of a compound is formed from its elements. Once again, the use of a specific set of conditions helps to standardize an enormous amount of information. Accordingly, we take as standard states for elements their stable forms at 25°C and at P = 1 atm; the $\Delta H^\circ$ value obtained under these conditions is the standard heat of formation. For example, for the reaction

$$\text{(4) } C(g) + O_2(g) = CO_2(g)$$

(note the use of the superscript zero) the standard heat of formation (298 K, 1 atm) is $-94.05 \text{ kcal}$ per degree of advancement of reaction (4). That is, the stable form of solid carbon, namely graphite, must be used, and the gases oxygen and carbon dioxide are to be separately maintained at a pressure of 1 atm. Finally, we note that since energies or enthalpies are known only to within an arbitrary constant, we violate no principles by postulating that the enthalpy of any element in its standard state shall be zero; then the enthalpy of any compound from elements in their standard state is equal to its heat of formation. Some of the preceding concepts are illustrated by the examples worked in the next section.

Other 'heats' in common use are the following: (i) the heat of combustion, which refers to the $\Delta H_d$ values for the complete oxidation of hydrocarbons to form CO$_2$(g) and H$_2$O(g), (ii) the heats of hydrogenation, which are the $\Delta H_d$ values for the hydrogenation of unsaturated hydrocarbons, (iii) heats of transition which involve $\Delta H_d$ values for phase changes (see Section 1.20), i.e., latent heats involved in transforming a given material from one state of matter or allotropic modification from one form to another, and (iv) heats of solution, which are discussed next.

When a reaction occurs in solution the heat of reaction is different compared to that for the same reaction involving components in the pure state. This is so because the process whereby a material goes into solution is characterized by heat evolution or absorption. This heat of solution is not constant
even at fixed $T$, but depends on the concentration of the solution. As the solute dissolves in a given solvent in increasing amounts, the heat of solution per mole of solvent changes with concentration. One must therefore distinguish between (i) the **integral heat of solution**, which is represented by the value of $\Delta H/m$, where $\Delta H$ is the enthalpy change when $m$ moles of solute are dissolved in a fixed amount (say 1000 g) of solvent, and (ii) the **differential heat of solution**, which is the quantity $(\partial \Delta H/\partial m)_{T,P}$ when an infinitesimal amount of solute is added to a solution at a certain molality $m$. The need for such a differentiation is demonstrated when it is realized, for example, that for HCl in water $\Delta H/m$ changes from $-17.9$ to $-17.4$ kcal/mole as one proceeds from infinite dilution to a molality of 1.1.

Let $H$, $H^*_1$, $H^*_2$ be the enthalpies of a binary solution and of one mole of components 1 and 2 in pure form; let 1 represent the solvent and 2, the solute. Then the enthalpy change in admixing $n_1$ moles of 1 with $n_2$ moles of 2 is

$$\Delta H = H - (n_1H^*_1 + n_2H^*_2), \quad (3.8.1)$$

and the differential heat of solution is

$$(\partial \Delta H/\partial n_2)_{T,P,n_1} = (\partial H/\partial n_2)_{T,P,n_1} - H^*_2 - H^*_2 - H^*_2. \quad (3.8.2a)$$

It is customary to reexpress this in terms of the partial molar enthalpy of the solute at infinite dilution, $H^*_2$. Then

$$(\partial \Delta H/\partial n_2)_{T,P,n_1} = (H^*_2 - H^*_2) - (H^*_2 - H^*_2) = \bar{L}_2 - \bar{L}_2. \quad (3.8.2b)$$

For the solvent one finds similarly

$$(\partial \Delta H/\partial n_1)_{T,P,n_2} = H - H^*_1. \quad (3.8.3)$$

The quantities $H/m$ and $(\partial \Delta H/m_1)$ are known as **integral and differential heats of dilution**, since they relate to the solvent.
Before concluding three items should be noted: First, $\Delta H_d$ values may be correlated with equilibrium constants and activity coefficients of solutions as shown later in Eq. (3.10.3), for example. Second, to convert $\Delta H_d$ values from one temperature to another one uses the Kirchhoff relation, Eq. (1.18.30) (see also Exercise 3.8.3). Third, to convert $\Delta H_d$ values from one pressure to another, the integrated form of Eq. (1.18.13b) may be used.

EXERCISES

3.8.1 One mole of liquid benzene is completely oxidized under 1 atm of oxygen gas to form CO$_2$(g) and H$_2$O(ℓ); for this process, $\Delta H^o_d = -780,980$ cal at 300 K. The process is now repeated by adding the requisite amount of oxygen gas to 1 mol of benzene and adjusting the volume of the chamber until the initial oxygen pressure is 1 atm. The standard entropies of Φ₆H₆(ℓ), O₂(g), CO₂(g), and H₂O(ℓ) at 300°K are 41.30, 49.00, 51.06, and 16.72 cal/deg·mol respectively. (a) Calculate $\Delta F^o_d$ at 300 K for the ensuing oxidation at constant volume. State all assumptions made. (b) Calculate $\Delta F^o_d$ at 300 K for the original process at constant pressure and compare the results.

3.8.2 Given the following data:

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta H^o_d$ (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(s) + O₂(g) → CO₂(g)</td>
<td>-94.05</td>
</tr>
<tr>
<td>H₂(g) + (1/2)O₂(g) → H₂O(ℓ)</td>
<td>-68.32</td>
</tr>
<tr>
<td>CH₂N₂(s) + (3/2)O₂(g) → CO₂(g) + H₂O(ℓ) + N₂(g)</td>
<td>-177.20</td>
</tr>
</tbody>
</table>

Compute the standard enthalpy of formation for cyanamide, CH₂N₂(s).

3.8.3 Given that the heat of formation of water vapor at 100°C is -57.8 kcal/mol H₂O and that the gases are assumed to be ideal: (a) Calculate the heat of formation of water vapor at 300°C using average heat capacities: $C_p$(H₂O,g) = 8 cal/mol·deg, $C_p$(O₂,g) = 7 cal/mol·deg. (b) Calculate the heat of formation of water at 300°C, given the temperature-dependent heat capacities:

<table>
<thead>
<tr>
<th>Substance</th>
<th>Heat Capacity (cal/mol·°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O(g)</td>
<td>7.2 + (2.8 x 10⁻³)T + (0.27 x 10⁻⁶)T²</td>
</tr>
<tr>
<td>H₂(g)</td>
<td>7.0 - (0.2 x 10⁻³)T + (0.5 x 10⁻⁶)T²</td>
</tr>
<tr>
<td>O₂(g)</td>
<td>6.1 + (3.3 x 10⁻³)T - (1.0 x 10⁻⁶)T²</td>
</tr>
</tbody>
</table>

3.8.4 Discuss the derivation of the two thermochemical laws from the First Law of Thermodynamics.

3.8.5 Review the distinction between the differential free energy change accompanying a slight displacement of a
chemical reaction from equilibrium and the overall free energy change accompanying a chemical reaction per mole of advancement. Compare this to the heats of solutions discussed in this section.

3. B EQUILIBRIUM CALCULATIONS

The examples cited below illustrate some of the important features of equilibrium which one tends to encounter in various applications.

(a) The dissociation of water vapor, neglecting deviations from ideality. Let $\alpha$ be the degree of dissociation. Then the following scheme may be devised for the determination of equilibrium properties:

\[
\begin{align*}
2\text{H}_2\text{O}(g) & \rightleftharpoons 2\text{H}_2(g) + \text{O}_2(g) \\
\text{Relative Mole Numbers} & \quad 1 - \alpha \quad \alpha \quad \alpha/2 \\
\text{Total:} & \quad 1 + \alpha/2 \\
\text{Mole Fractions} & \quad \frac{1-\alpha}{1+\alpha/2} \quad \frac{\alpha}{1+\alpha/2} \quad \frac{\alpha}{1+\alpha/2} \\
\text{Partial Pressure} & \quad \frac{1-\alpha}{1+\alpha/2} P \quad \frac{\alpha}{1+\alpha/2} P \quad \frac{\alpha}{2(1+\alpha/2)} P
\end{align*}
\]

In this table $P$ is the total pressure. The equilibrium 'constant' for the reaction as written is given by

\[
K_p = \frac{P_{\text{O}_2}^2 P_{\text{H}_2}}{P_{\text{H}_2}^2} = \frac{\alpha^3 P}{2(1-\alpha)^2(1+\alpha/2)}. \quad (3.B.1)
\]

Experimental values of $\alpha = 0.504\%$, 1.21\% at $P = 1$ atm and $T = 2000$ K, 2200 K have been cited in the literature. Insertion in (3.B.1) yields $K_p = 6.45 \times 10^{-8}$, $9.02 \times 10^{-7}$ atm at 2000 K, 2200 K respectively. The average enthalpy of dissociation is given as $\Delta H_d = \frac{RT_1 T_2}{(T_2 - T_1)} \ln \left[ \frac{K_p^2}{K_{p_1}} \right] = 115,300 \text{ cal/mol}$; also, $\Delta G_d = -RT \ln K_p = 65,800 \text{ cal/mol}$ at $T = 2000$ K for the reaction as written.
(b) Gaseous equilibrium involving ammonia. We cite the \( \frac{1}{2} \, \text{N}_2(g) + \frac{3}{2} \, \text{H}_2(g) \rightleftharpoons \text{NH}_3(g) \) reaction as an example of how equilibrium states are characterized self consistently. Experimental studies have shown that at 450°C and at \( P = 300 \) atm the equilibrium concentration of \( \text{NH}_3 \) stands at 35.82 mol \%, starting with a 3:1 mixture of \( \text{H}_2: \text{N}_2 \). The fugacity coefficients are given as \( \gamma(\text{H}_2) = 1.08 \), \( \gamma(\text{N}_2) = 1.14 \), and \( \gamma(\text{NH}_3) = 0.91 \) at the prevailing temperature and pressure. The equilibrium constant may be specified as

\[
K_p = \frac{f(\text{NH}_3)}{f^{1/2}(\text{N}_2)f^{3/2}(\text{H}_2)} = \frac{\gamma(\text{NH}_3)}{\gamma^{1/2}(\text{N}_2)\gamma^{3/2}(\text{H}_2)} \cdot \frac{n(\text{NH}_3)}{n^{1/2}(\text{N}_2)n^{3/2}(\text{H}_2)} \cdot \frac{n}{P}
\]

(3.8.2)

for the reaction as written. Here \( n(X) \) is the relative mole number of the indicated species and \( n \) is the total mole number of all gaseous species. Initially, \( n_0(\text{N}_2) = 1/2 \), \( n_0(\text{H}_2) = 3/2 \), \( n_0(\text{NH}_3) = 0 \). Let \( x \) be the fraction of \( \text{NH}_3 \) generated by the reaction proceeding to equilibrium. The final relative mole numbers of equilibrium are \( n(\text{N}_2) = \frac{1}{2}(1 - x) \), \( n(\text{H}_2) = \frac{3}{2}(1 - x) \), \( n(\text{NH}_3) = x \), \( n = 2 - x \). Accordingly,

\[
K_x = \frac{0.91}{(1.14)^{1/2}(1.08)^{3/2}} \cdot \frac{x}{\left[ \frac{1}{2} \right]^{1/2}(1-x)^{1/2} \left[ \frac{3}{2} \right]^{3/2}(1-x)^{3/2}} \cdot \frac{2-x}{300}
\]

(3.8.3)

Experimental analysis has shown that under the prevailing conditions, \( n(\text{NH}_3)/n = 0.3582 \); one thus obtains \( x = 0.5275 \), and \( K_x = 6.79 \times 10^{-3} \text{ atm}^{-1} \).

This procedure illustrates the arbitrariness in the specification of \( K_x \). The numerical value of the equilibrium constant would have been different if some other sets of units had been employed. However, once the \( K_x \) value is determined for a particular physical situation, this quantity can be used to determine \( x \) under any other set of conditions, provided \( P \) is expressed in atmospheres and the same temperature prevails. It is this feature that renders the equilibrium constant such a useful quantity.
3.9 REDUCTION TO IDEAL CASES

By definition, ideal solutions are mixtures that obey Raoult's Law over the entire composition range, so that \(a_i(T,P,x_i) = x_i\) for all \(x_i\). From Eq. (3.4.5) and (3.4.7) it follows that 
\[
\Gamma_i(T,P,x_i) = 1
\]
and that 
\[
\gamma_i(T,P,x_i)a_i^*(T,P) = 1
\]
for ideal solutions: On setting \(q_1 = x_i\) one finds that 
\[
a_i(T,P,x_i) = \gamma_i(T,P,x_i)a_i^*(T,P)x_i = x_i,
\]
so that in this case Eq. (3.6.2) reduces to
\[
\mu_i = \mu_i^*(T,1) + RT \ln x_i,
\]
as expected. On the other hand, Eqs. (3.5.15), (3.5.17b), and (3.4.7) with \(q = c\) show that
\[
\Gamma(T,P,c_i) = \gamma_i(T,P,c_i)a_i^*(T,P) = \frac{\rho_i^*(T,1)}{\rho(T,P)} \left( \frac{\sum j n_j m_j}{M_i \Sigma n_j} \right),
\]
(ideal solution)
which product is not necessarily close to unity. In Exercise 3.9.1 we examine requirements under which the right side is close to unity. It follows that even for an ideal solution the factors \(\ln (\gamma_i a_i^*)\) do not necessarily drop out, so that the full equation in the form (3.6.4b) must be used. The only distinction between ideal and nonideal cases is that in the latter situation Eq. (3.9.2) may be introduced.

Similar arguments hold for the case involving molalities; according to Eqs. (3.5.19), (3.5.20), and (3.4.7) with \(q = m\),
\[
\Gamma_i(T,P,m_i) = \gamma_i(T,P,m_i)a_i^*(m)(T,P) = x_i M_i / M_i
\]
(ideal solution),
which again may differ considerably from unity.

As a consequence the equilibrium constants Eq. (3.7.5b) for ideal solutions may assume three different forms as shown in the following:
\[
K'_x = \left[ \sum j (x_j)_{eq}^\nu_j \right],
\]
(ideal solution) (3.9.4a)
REDUCTION TO IDEAL CASES

\[
K'_m = \prod_l \left\{ \rho^*_T(T,1) \left( \frac{\Sigma_j n_j M_j}{M \Sigma n_j} \right) \left( \frac{c_i^*}{c_i^*} \right) \right\}_{eq}^{\nu'} \quad \text{(ideal solution) (3.9.4b)}
\]

\[
K'_c = \prod_l \left\{ \frac{x_l M_l}{m_l} \left( \frac{m_l^*}{m_l^*} \right) \right\}_{eq}^{\nu'} \quad \text{(ideal solution). (3.9.4c)}
\]

The preceding may be brought into correspondence with the results of Section 2.11 in a two-step process. Let us introduce the quantities

\[
F_c(T,P) = \prod_l \left[ \rho^*_T(T,1) \Sigma n_j M_j / \rho(T,P) M \Sigma n_j \right]^{\nu'},
\]

and

\[
F_m = \prod_l \left( x_l m_l / M_l \right)^{\nu'}.
\]

Then, with \( K'_c = K_c / F_c \), \( K'_m = K_m / F_m \), \( K'_x = K_x \),

\[
K'_x(T) = \prod_l (x_l)^{\nu'}_{eq} \quad \text{(ideal solution) (3.9.5a)}
\]

\[
K'_c(T,P) = K'_c F_c^{-1}(T,P) = \prod_l (c_l^* / c_l^*)^{\nu'}_{eq} \quad \text{(ideal solution) (3.9.5b)}
\]

\[
K'_m(T) = K'_m F_m^{-1} = \prod_l (m_l^* / m_l^*)^{\nu'}_{eq} \quad \text{(ideal solution). (3.9.5c)}
\]

These forms are convenient because of their simplicity, and because of their utility for ideal heterogeneous solutions. Whenever \( l \) indexes a pure condensed phase the corresponding factor on the right-hand side is unity; this latter feature was stressed in Section 2.11. To be consistent with earlier discussions we will also restrict ourselves to the case \( P = 1 \ atm \) in Eq. (3.9.5b). A further simplification is possible through the definition \( K'_x = K_x \)

\[
K_x = \prod_i (x_i)^{\nu'}_{eq} \quad \text{(ideal solution) (3.9.6a)}
\]

\[
K_c = K'_c \prod_i (c_i^*)^{\nu_1} = \prod_i (c_i^*)^{\nu_1}_{eq} \quad \text{(ideal solution) (3.9.6b)}
\]

\[
K_m = K'_m \prod_i (m_i^*)^{\nu_1} = \prod_i (m_i^*)^{\nu_1}_{eq} \quad \text{(ideal solution). (3.9.6c)}
\]
In these relations the primes on the multiplication symbols explicitly designate the fact that pure materials are to be excluded from the product. This is accomplished by dropping such factor of unity out from Eq. (3.9.5) before taking the next step of converting (3.9.5) into (3.9.6). The quantities $K_x, K_c, K_m$ correspond to the three equilibrium constants defined in Section 2.11.

EXERCISES

3.9.1 By a careful examination of Eq. (3.9.2) show what conditions must be met in order that the product $\gamma_1(T,P,c_1)a_1^0(T,P)$ have values close to unity.

3.9.2 Repeat Exercise 3.9.1 for Eq. (3.9.3).

3.9.3 Derive Eqs. (3.9.6) directly from the hybrid equilibrium constants specified by Eqs. (3.7.3b) and (3.7.5b).

3.C ENERGETICS OF CHEMICAL PROCESSES

Here we illustrate the type of calculations required to characterize the energetics of chemical processes. Recall that the standard state for a solid or for a liquid is the pure material in its most stable form at one atmosphere at the temperature of interest. For a gas the standard state is the hypothetical ideal gas at one atmosphere and at the temperature of interest.

(a) Example 1: Find the 'heat of formation' of CO$_2$ gas from the reaction of the elements according to the equation $C(s) + O_2(g) = CO_2(g)$. By convention we set $\Delta H_f^0[C(s),\text{graphite}] = \Delta H_f^0[O_2(g),\text{ideal}] = 0$, where $\Delta H_f^0$ is the molar enthalpy of formation under standard conditions.

According to the reaction we set $\Delta H_f^0[CO_2(g)] = \Delta H_{Rx}, 298.15 - \Delta H_f^0[C(s)] - \Delta H_f^0[O_2(g)]$. Experimental measurements yield $\Delta H_f^0[CO_2(g)] = -393.5 \text{ kJ/mol at } 298.15 \text{ K}$; note the sign. The enthalpy of one mole of CO$_2$ gas is thus lower than that of one mole of graphite and one mole of oxygen under standard conditions by 393.5 kJ at 298.15 K.
(b) Example 2: Characterize the dissociation of oxygen gas. We consider the process \( \text{O}_2(g) \rightarrow 2\text{O}(g) \) for which the experimentally determined molar enthalpy change under standard conditions is \( \Delta H_{\text{rxn}}^\circ = 494 \text{ kJ/mol} \) at 300 K. Accordingly, the standard enthalpy change for the reaction is given by \( \Delta H_{\text{rxn}}^\circ = 2\Delta H_{\text{f}}^\circ[\text{O}(g)] - \Delta H_{\text{f}}^\circ[\text{O}_2(g)] \), which yields \( \Delta H_{\text{f}}^\circ[\text{O}(g)] = 494/2 = 247 \text{ kJ/mol} \).

(c) Example 3: Characterize the energetics of the isomerization reaction \( \text{n-butane (n.b.,g)} \rightarrow \text{i-butane (i.b.,2-methyl propane,g)} \). This conversion cannot be readily achieved under normal laboratory conditions. However, it is easy to carry out and monitor the following combustion steps:

\[
\text{n-C}_4\text{H}_{10}(g) + \frac{13}{2} \text{O}_2(g) \rightarrow 4\text{CO}_2(g) + 5\text{H}_2\text{O}(g) \quad \Delta H_1^\circ \\
\text{i-C}_4\text{H}_{10}(g) + \frac{13}{2} \text{O}_2(g) \rightarrow 4\text{CO}_2(g) + 5\text{H}_2\text{O}(g) \quad \Delta H_2^\circ
\]

from which, by Hess’s law, one determines \( \Delta H_{\text{isom}}^\circ = \Delta H_1^\circ - \Delta H_2^\circ \).

(d) Example 4: Determine the enthalpy of dilution for the process

\[
\text{HNO}_3(\ell) + \text{nH}_2\text{O(solvent)} = \text{HNO}_3 \text{ in nH}_2\text{O(solution)}
\]

for which \( \Delta H_{298}^\circ (\text{sol'n}) = \Delta H_{298}^\circ (\text{sol'n}) - \Delta H_{298}^\circ (\text{HNO}_3) - n\Delta H_{298}^\circ (\text{H}_2\text{O, }\ell) \). For \( n = 100 \), which represents almost infinite dilution, one finds from the literature

\[
\Delta H_{298}^\circ (\text{sol'n}) = -206.85 - (-174.10) - 0 = -32.76 \text{ kJ/mol}.
\]

(d) Example 5: Characterize the energetics of the adiabatic combustion of methane. The reaction of interest is written as

\[
\text{CH}_4(g) + 2\text{O}_2(g) = \text{CO}_2(g) + 2\text{H}_2\text{O}(g) \quad \Delta H_{298}^\circ = -165.2 \text{ kcal/mol}.
\]
Prior to initiation the CH$_4$(g) is heated in air to a temperature of 200°C. Assume that the reaction then proceeds to completion. Given the values cited in the literature of $\bar{C}_p[CH_4(g)] = 7.5 + 5 \times 10^{-3}T$; $\bar{C}_p[O_2(g)] = 6.5 \times 10^{-3}T$; $\bar{C}_p[H_2O(g)] = 8.15 \times 10^{-4}T$; $\bar{C}_p[CO_2(g)] = 7.7 + 5.3 \times 10^{-3}T$ (in cal/mol), determine the final temperature of the reaction products.

Since the enthalpy is a function of state, we can set up a suitable sequence of steps for which the enthalpy change may readily be determined. (i) Cool the products from the final temperature $T_f$ to 298.15 K. (ii) Cool the reagents from the starting temperature of 473.15 K to 298.15 K. (iii) Carry out the hypothetical reaction at 298.15 K. Then $\Delta H = \Delta H_i + \Delta H_{i1} + \Delta H_{i1} = 0$ for an adiabatic process. This may be translated into the equation

$$n[CO_2] \int_{298}^{T_f} \bar{C}_p[CO_2]dT + n[N_2] \int_{298}^{T_f} \bar{C}_p[N_2]dT - n[CH_4] \int_{473}^{298} \bar{C}_p[CH_4]dT - n[O_2] \int_{473}^{298} \bar{C}_p[O_2]dT - n[N_2] \int_{473}^{298} \bar{C}_p[N_2]dT,$$

where account was taken of the fact that all the oxygen was used up at the termination of the reaction, whereas at the beginning $n[N_2] = 2(0.79/0.21)$ is the approximate N$_2$:O$_2$ molecular ratio in air, taking account of the stoichiometry requirements. On inserting the expressions for $\bar{C}_p$ and the tabulated value of $\Delta H^o_{298}$ for the reaction at 298.15 K, one can determine the unknown $T_f = 2265$ K. This is obviously an upper limit since the reaction is never totally adiabatic and because it is not 100% complete; there also is some dissociation of the products at the elevated temperature achieved at the final stages of the reaction.

3.10 VARIATIONS OF ACTIVITY, ACTIVITY COEFFICIENTS AND EQUILIBRIUM CONSTANTS WITH TEMPERATURE AND PRESSURE

(a) The manner in which various activities and activity coefficients vary with the temperature and the pressure may be
investigated by the techniques repeatedly used earlier. For simplicity of notation, we now abbreviate \( \Gamma_i(T,P,q) \) as \( \Gamma_i^{(q)} \) and \( a_i(T,P,q) \) by \( a_i^{(q)} \). The reader should have no difficulty in verifying the following: According to (3.5.19) and (3.4.5), with \( q = x \) or \( m \), we find for constant temperature and composition

\[
[\partial \ln \Gamma_i^{(m)}/\partial P]_{T,m_i} = [\partial \ln a_i^{(m)}/\partial P]_{T,m_i} - [\partial \ln \Gamma_i^{(x)}/\partial P]_{T,x_i}
\]

\[
= [\partial \ln a_i^{(x)}/\partial P]_{T,x_i} - \bar{V}_i/RT - \bar{V}_i^*/RT,
\]

(3.10.1)

where use was made of (3.5.12a) and of \((\partial \mu_i/\partial P)_{T,x_i} = \bar{V}_i \) to arrive at the final result; note that \( \mu_i(T,P,x_i) \) is referred to the standard chemical potential. Here one must be very careful in the differentiation with respect to \( P \): as discussed in Section 3.7(a), \( \bar{V}_i = \bar{V}_i(T,P) \), whereas \( \bar{V}_i^* = \bar{V}_i^*(T,1) \).

According to Eq. (3.5.15) and (3.4.5) with \( q = c \) and (3.4.2), we find at constant \( x_i \)

\[
[\partial \ln \Gamma_i^{(c)}/\partial P]_{T,c_i} = [\partial \ln a_i^{(c)}/\partial P]_{T,c_i} - [\partial \ln a_i^{(x)}/\partial P]_{T,x_i}
\]

\[
- [\partial \ln \rho/\partial P]_{T,x_i} - \bar{V}_i/RT - \bar{V}_i^*/RT - [\partial \ln \rho/\partial P]_{T,x_i}
\]

\[
+ \lim_{P \to 1} [\partial \ln \rho_i(T,P)/\partial P]_{T,x_i},
\]

(3.10.2)

where we have also used Eq. (3.10.1). Similarly, we find

\[
[\partial \ln \Gamma_i^{(m)}/\partial T]_{P,m_i} = [\partial \ln a_i^{(m)}/\partial T]_{P,m_i} - [\partial \ln \Gamma_i^{(x)}/\partial T]_{P,x_i}
\]

\[
= [\partial \ln a_i^{(x)}/\partial T]_{P,x_i} = - (\bar{H}_i - \bar{H}_i^*)/RT^2
\]

(3.10.3)

\[
[\partial \ln \Gamma_i^{(c)}/\partial T]_{P,c_i} = [\partial \ln a_i^{(c)}/\partial T]_{P,c_i} - [\partial \ln a_i^{(x)}/\partial T]_{P,x_i}
\]

\[
+ [\partial \ln (\rho_i^*/\rho)/\partial T]_{P,x_i} = - (\bar{H}_i - \bar{H}_i^*)/RT^2 + [\partial \ln (\rho_i^*/\rho)/\partial T]_{P,x_i}.
\]

(3.10.4)

Note here that \( \bar{H}_i^* \), derived from \( \mu_i(T,1,x_i^*) \), is the molar enthalpy of pure \( i \) at unit pressure, while \( \bar{V}_i \) and \( \bar{H}_i \), derived from \( \mu_i(T,P,x_i) \), refer to the partial molar quantities in solution at pressure \( P \).
(b) The variation of the different equilibrium constants with temperature and pressure may be determined as follows: Since \( \mathcal{K}_x(T) \), as determined in terms of the chemical potentials in Eq. (3.7.8a), is identical to \( K(T) \) as specified by the \( \mu_i^* \) in Eq. (3.7.6a), these two quantities may be considered as a unit. One obtains

\[
\frac{d \ln K(T)}{dT} = \frac{d \ln \mathcal{K}_x(T)}{dT} - \sum_j \nu_j \frac{d}{dT} \left[ \frac{\mu_j^*(T,1)}{RT} \right]
\]

It should be clear that \( \Delta H_d^* \) refers to the (differential) enthalpy change accompanying unit advancement of the reaction \( \Sigma \nu_i \nu_i A_i = 0 \) when all pure species \( A_i \) are maintained at unit pressure (usually, 1 atm). How this reaction could be accomplished in principle is the subject matter of Exercise 3.7.3. Equation (3.10.5) is the fundamental relation of interest; this expression is known as the van't Hoff equation (1879).

Eq. (3.7.8a) serves as a basis for determining the variation of \( K_c \) and of \( K_m \) with \( T \). By using Eqs. (3.5.13), (3.5.18), and (3.5.2), one finds \( \mu_j^c(T,1) = \mu_j^x(T,1) - RT \ln [1000 \rho_j^c(T,1)/M_j] \) and \( \mu_j^m(T,1) = \mu_j^x(T,1) - RT \ln (1000/M_j) \). On inserting these relations into (3.7.8a) and noting that \( \mu_j^x(T,1) = \mu_j^*(T,1) \) one finds

\[
\ln K_c(T) = \ln K(T) + \sum_j \nu_j \ln [1000 \rho_j^*(T,1)/M_j]
\]

\[
\ln K_m(T) = \ln K(T) + \sum_j \nu_j \ln (1000/M_j).
\]

Thus, in view of (3.10.5),
\[
\frac{d\ln K_j(T)}{dT} = \frac{\Delta H^*_j}{RT^2} + \sum_j \nu_j \left( \frac{d\ln \rho_j^*(T,1)}{dT} \right)
\]  
(3.10.7a)

\[
\frac{d\ln K_x(T)}{dT} = \frac{d\ln K_x(T)}{dT} - \frac{\Delta H^*_x}{RT^2}.
\]  
(3.10.7b)

One should note very carefully that the quantities entering the sum on the right hand side of Eq. (3.10.7a) relate the density, \(\rho_j\), of pure \(j\) at one atmosphere, and that the summation over \(j\) involves only those quantities which form homogeneous mixtures in the system under study.

Equation (3.10.5) or (3.10.7) is the fundamental relation of interest, the van't Hoff equation; it is evident that from the enthalpy change accompanying a unit advancement of the reaction of interest under standard conditions, one can obtain the rate of change of the equilibrium constants \(K_q\) with alterations in temperature.

By now the point has repeatedly been made (see Sections 2.10(a), 3.7(d)) that the convention that relates equilibrium constants to chemical potentials in their standard states does not imply that \(K\) or \(K_q\) is independent of \(P\). Rather, one finds in conformity with Section 3.7(d) from Eqs. (3.7.6a) and (3.7.8a) that

\[
\left( \frac{\partial \ln K}{\partial P} \right)_T = \left( \frac{\partial \ln K_x}{\partial P} \right)_T = -\sum_j \nu_j \frac{\overline{\nu}_j^*(T,1)}{RT}.
\]  
(3.10.8)

The reader is asked in Exercise 3.10.5 to obtain the corresponding expression for \(K_c\) and \(K_m\).

(c) We summarize briefly the situation that applies when one deals with standard states involving pure materials and with mole fractions as concentration units.

We begin with the equilibrium condition for chemical reactions \(\Sigma_{i(i)} \nu_i \mu_i(T,P,x_i) = 0\) and invoke Eq. (3.7.19) with \(a_i(T,P,x_i) = a_i(T,P,x_i)\)
and rewrite the above as

\[- (RT)^{-1} \sum \nu l \mu_l^*(T,1) = \ln K_x - \sum \nu_l \ln a_l(T,P,x_l)|_{eq}, \quad (3.10.10)\]

where the equilibrium 'constant' is specified by

\[K_x(T) = \prod \frac{\nu_l}{a_l(T,P,x_l)|_{eq}}. \quad \text{(3.10.11)}\]

Furthermore, for nonequilibrium conditions

\[\Delta G_d = \sum \nu_l \mu_l(T,P,x_l) = \sum \nu l \mu_l^*(T,1) + RT \sum \nu_l \ln a_l(T,P,x_l)\]

\[= \Delta G_d^* + RT \sum \nu_l \ln a_l(T,P,x_l), \quad (3.10.12)\]

wherein \(\Delta G_d^* = \Sigma_l \nu_l \mu_l^*(T,1)\) is the differential free energy change involving the species \(l\) in the pure state under standard conditions, and

\[K_x = \exp (- \Delta G_d^*/RT). \quad (3.10.13)\]

Lastly, van't Hoff's Law assumes the form

\[\frac{d \ln K_x}{dT} = \sum \left(\frac{\nu_l \mu_l^*}{RT^2}\right) = \frac{\Delta H_d^*}{RT^2}. \quad (3.10.14)\]

**EXERCISES**

3.10.1 Derive expressions for \((\partial \ln \gamma_l^q/\partial z)\) where \(q = x,c,m\) and \(z = T,P\), and compare the results with Eqs. (3.10.1) - (3.10.4).

3.10.2 Having defined \(\Delta H_d = \Sigma_l \nu_l \mu_l^*\), obtain an expression for \((\partial \Delta H_d/\partial T)_{P,x}\).

3.10.3 For a dilute aqueous solution determine the change of activity with respect to mole fraction at 27°C when
the pressure over the solution is changed from 1 atm to 27 mm Hg, which is the vapor pressure of pure water at that temperature. The molar volume of H₂O is 18.0 cc.

3.10.4 The dissociation pressures of Ag₂O are given by the following tabulation:

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Dissociation Pressure (torr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>173.0</td>
<td>422</td>
</tr>
<tr>
<td>183.1</td>
<td>605</td>
</tr>
<tr>
<td>188.2</td>
<td>717</td>
</tr>
</tbody>
</table>

The heat capacities vary with T according to the relations

- \( C_p(Ag) = 5.60 + 1.5 \times 10^{-3}T \) cal/mol-deg
- \( C_p(Ag_2O) = 13.87 + 8.9 \times 10^{-3}T \) cal/mol-deg
- \( C_p(O_2) = 6.50 + 1.0 \times 10^{-3}T \) cal/mol-deg.

Determine \( \Delta H^0 \), \( \Delta S^0 \), and \( \Delta G^0 \) for the reaction \( Ag_2O \rightarrow Ag + (1/2)O_2 \) at 25°C.

3.10.5 Derive expression analogous to Eq. (3.10.8) for \( K_c \) and \( K_m \).

3.11 DETERMINATION OF ACTIVITY COEFFICIENTS BY MEASUREMENT OF VAPOR Pressures

The mathematical treatment of Sections 3.4–3.10 has been largely formal so far because only the activity or activity coefficients of pure condensed phases has been discussed up to this point: In Eqs. (3.7.16) through (3.7.18) a procedure was set up for their determination by experiment. No method has yet been provided by which the activity coefficients or activities of species in solution can be determined experimentally. We now turn our attention to these matters.

(a) One of the common procedures is to equilibrate a binary solution with its vapor, so that the chemical potential of each species is the same in the condensed and gaseous phases. For simplicity we choose the representations (3.6.4a), (3.6.2) with \( a_1 = a_1 \), and (3.1.4a); at equilibrium,

\[
\mu_i^P(T) - \mu_i^{\ast \ast}(T,1) = RT \ln \left\{ \gamma_i(T,P,x) a_i^{\ast \ast}(T,P) x_i \right\}
\]

\[
= RT \ln f_i(T,P,P_1) - RT \ln \left\{ a_i(T,P,x) / f_i(T,P,P_1) \right\}. \quad (3.11.1)
\]

In conjunction with (3.11.1) let us next consider the equilibrium between pure \( i \) in the liquid phase and pure \( i \) in
the vapor phase. We now set $x_i = 1$ and correspondingly, $P_i = P_i^* = P$. Then the relation analogous to (3.11.1) reads

$$\mu_i^{op}(T) - \mu_i^{xx}(T,1) = RT \ln \left[ \gamma_i(T,P_i^*,1)a_i^{*x}(T,P_i^*) \right] - RT \ln f_i(T,P_i^*,P_i^*)$$

$$- RT \ln \left\{ a_i(T,P_i^*,1)/f_i(T,P_i^*,P_i^*) \right\}. \quad (3.11.2)$$

Elimination of the quantities on the left hand side of Eqs. (3.11.1) and (3.11.2) now yields

$$a_i(T,P,x_i) = a_i(T,P_i^*,1) \frac{f_i(T,P,P_i)}{f_i(T,P_i^*,P_i^*)}. \quad (3.11.3a)$$

Alternatively, on introducing (3.4.7), with $q_i^0 = x_i^* = 1$ and on setting $a_i(T,P,1) = a_i^{*x}(T,P)$, $a_i(T,P_i^*,1) = a_i^{*x}(T,P_i^*)$, we find

$$\gamma_i(T,P,x_i) = \gamma_i(T,P,x_i)a_i^{*x}(T,P) = a_i^{*x}(T,P_i^*) \left( \frac{f_i(T,P,P_i)}{x_i f_i(T,P_i^*,P_i^*)} \right). \quad (3.11.3b)$$

As discussed earlier, the activity for a pure condensed component and hence, the ratio $a_i^{*x}(T,P_i^*)/a_i^{*x}(T,P)$, is ordinarily very close to unity; also, the ratio of fugacilities usually may be replaced by the ratio of vapor pressures. In that case one obtains the approximate relations

$$a_i(T,P,x_i) \approx P_i/P_i^* \quad (3.11.4a)$$

as well as

$$\gamma_i(T,P,x_i) \approx P_i/x_iP_i^*, \quad (3.11.4b)$$

which are cited in all elementary texts on the subject. The physical significance of the procedure is perhaps better appreciated with reference to Fig. 3.11.1. We see that the quantity $x_iP_i^*$ is given by the length of the arrow $\overline{AC}$ in that
FIGURE 3.11.1 Diagram for calculation of activity coefficients relative to the pure solvent (ACB)$_r$ and to infinite dilution (DFE)$_h$, using Eqs. (3.11.4b) and (3.11.7b).

figure; this represents the vapor pressure of $i$ if the solution were ideal. By contrast, $P_i$ is represented by the arrow $AB$, so that $\gamma_i$ is given as the ratio $AB/AC$.

In more exact work one would have to calculate the fugacities in (3.11.3) by the methods of Section 3.1 and the activities for pure $i$ according to Eqs. (3.7.16) and (3.7.17); then $a_i(T,P,x_i)$ may be obtained by calculation. The procedure developed so far is useful in cases where the species of interest may be considered to be the solvent, i.e., when $x_i$ approaches unity.

(b) An alternative procedure is to take as a reference the solution in infinite dilution. This is a useful procedure for cases where the component under study is considered to be the solute.

As already stated in Section 3.3, it is known from innumerable experimental investigations that at very great dilution the vapor pressure of the solution is given by the relation $P_i = K_i x_i$. In the range $x_i$ close to zero, where this
relationship is found to hold, the solution is said to obey Henry’s Law; $K_H$ is known as the Henry’s Law constant. The straight line $OP_i$ in Fig. 3.11.1 shows the vapor pressure of $i$ if this component were to obey Henry’s Law over the entire composition range. Based on this scheme one selects as a standard the hypothetical material $i$ in pure form, as obtained by extrapolation of Henry’s Law to $x_i = 1$. The vapor pressure of this hypothetical substance will be designated as $P_i$. The fact that actual solutions do not obey Henry’s Law beyond the dilute solution range should not be a deterrent to the use of the hypothetical standard state in which the vapor pressure of the pure solvent is $P^*$ rather than $P_i$. What is selected is a matter of convenience rather than an absurd procedure.

Equation (3.11.1) remains applicable as before. However, the chemical potential of the hypothetical material in the gas phase now reads $\mu_i^p(T) + RT \ln \gamma_i(T,P_i,P_i)$ and for the pure condensed phase it has the form (3.5.21a), with $P$ replaced by $P_i$ and with $x_i = 1$. Accordingly, Eq. (3.11.2) is replaced by

$$\mu_i^g(T) - \mu_i^e(T,1) = RT \ln \gamma_i(T,P_i,P_i) - RT \ln \phi_i(T,P_i,P_i)$$

$$= RT \ln \left( \frac{\gamma_i(T,P_i,1)a_i^e(T,P_i)}{\phi_i(T,P_i,P_i)} \right).$$

When account is taken of Eq. (3.11.1) one may eliminate the left-hand side to obtain either

$$a_1(T,P,x_i) = a_1(T,P_i,1) \left( \frac{\phi_i(T,P,P_i)}{\phi_i(T,P_i,P_i)} \right)$$

$$or, in light of the fact that $\gamma_1(T,P,x_i=1) = 1$, as was shown in Section 3.6:

$$\Gamma_i(T,P,k) = \gamma_i(T,P,x_i)a_i^e(T,P) = a_i^e(T,P_i) \left( \frac{\phi_i(T,P,P_i)}{x_i\phi_i(T,P_i,P_i)} \right).$$

To a good degree of approximation these relations reduce to
\[ a_1(T,P,x_1) \approx \frac{P_i}{P_i^\parallel} \]  

(3.11.7a)

and to

\[ \gamma_1(T,P,x_1) \approx \frac{P_i}{x_iP_i^\parallel}. \]  

(3.11.7b)

To calculate activities in the present scheme one determines the vapor pressures of solutions for various \( x_1 \), with special emphasis on the range where Henry's Law holds. Extrapolation of the straight line to \( x_1 = 1 \) yields \( P_i^\parallel \). Then \( x_iP_i^\parallel \) corresponds to the vector \( \overrightarrow{DE} \) and \( P_i \), to the vector \( \overrightarrow{DF} \) in Fig. 3.11.1. A measurement of \( P_i \) corresponding to \( x_1 \) then yields \( a_1 \) and \( \gamma_1 \). For more precise work, Eq. (3.11.6) must be employed.

One should not adhere to the mistaken notion that the analysis of subsection (a) can be used in the upper range of \( x_1 \) values and that the analysis of subsection (b) for the same solution can then be used in the lower range. The two approaches are based on different standard states (i.e. \( P^* \) versus \( P_i^\parallel \), as discussed earlier) and therefore are not interchangeable or interrelated. Further, one must stay with one scheme or the other to obtain internally consistent results. It is just more convenient to apply methodology (b) if one is interested primarily in the thermodynamic characterization of solutes in dilute solution, and methodology (a) if one wishes to analyze the properties of solvents. This discussion again points to the fact (see also subsection (e) below) that it is only the differences in the chemical potential themselves that are unique in value; all other quantities must be determined self-consistently.

(c) In principle, one can use Eq. (3.11.6b) in Eqs. (3.5.8) and (3.5.10) to obtain \( \gamma_i(T,p,c_i) \) and \( \gamma_i(T,p,m_i) \). However, it is also possible to determine activities and activity coefficients relative to \( c_i \) or \( m_i \) directly from experiment. This involves the use of Eq. (3.5.21b) as the equation specifying \( \mu_i \) for the \( i \)th species in the condensed
phase, and correlating this with Eq. (3.1.4a) for the gas phase. This yields

\[
\mu_i^\text{op}(T) - \mu_i^*(T,1) = RT \ln \left[ \gamma_i(T,P,c_i)a_i^*(T,P)c_i(T,P) \right] \\
- RT \ln f_i(T,P,P_i^D).
\] (3.11.8)

Here we have adopted as a reference state the hypothetical solution in which the Henry's Law region is extrapolated to the value \( c_i = 1 \), as indicated in Fig. 3.11.2. Let the corresponding value pressure be designated as \( P_i = P_i^D \). Then for such a hypothetical solution at a total pressure \( P' \)

\[
\mu_i^\text{op}(T) - \mu_i^*(T,1) = RT \ln \left[ \gamma_i(T,P',1)a_i^*(T,P') \right] \\
- RT \ln f_i(T,P',P_i^D).
\] (3.11.9)

The juxtaposition of (3.11.8) and (3.11.9) yields the relation

\[
\Gamma_i(T,P,c_i) = \gamma_i(T,P,c_i)a_i^*(T,P) \\
= \gamma_i(T,P',1)a_i^*(T,P') \left( \frac{f_i(T,P,P_i)}{c_i f_i(T,P',P_i^D)} \right),
\] (3.11.10)

which simplifies to the following very approximate relationship:

![Diagram for the calculation of the activity coefficient \( \gamma_i(T,P',c_i) \).](image)
\[ \gamma_i(T, P, c_i) = \frac{P_i}{c_i P_i^0}. \]  

(3.11.11)

The calculations are illustrated in Fig. 3.11.2 by vectors \( GI/\overline{GH} \).

(d) Finally, it should be evident that the activity coefficient with respect to molality may be determined in precisely the same manner as sketched in (c). One equates (3.5.21c) with (3.1.4a) to obtain the analogue of (3.11.8), with \( c \) replaced by \( m \). One then chooses as a reference solution the hypothetical Henry's Law case in which the straight line region of the \( P \) versus \( m_i \) curve at low \( m_i \) is extrapolated to \( m_i = 1 \). Let the corresponding hypothetical vapor pressure be \( P_i^0 \). This leads to an equation of the form (3.11.10), (3.11.11) and to the relations

\[ \Gamma_i(T, P, m_i) = \gamma_i(T, P, m_i) a_i^{\text{m}}(T, P) \]

\[ = \gamma_i(T, P', 1) a_i^{\text{m}}(T, P') \left[ \frac{f_i(T, P, P_i)}{m_i f_i(T, P', P_i^0)} \right] \]  

(3.11.12)

and

\[ \gamma_i(T, P, m_i) \approx \frac{P_i}{m_i P_i^0}. \]  

(3.11.13)

The calculations are illustrated in Fig. 3.11.3 by the vectors \( JL/\overline{JK} \).

In passing from (3.11.10) to (3.11.11) or from (3.11.12) to (3.11.13) one is forced to set \( P = P' \) (which is not a very restrictive assumption), and to assume that \( \gamma_i(T, P, 1) = 1 \) when \( c_i = 1 \) or \( m_i = 1 \). The latter assumptions are extremely questionable, because at unit molarity or molality one is generally far removed from ideality. However, one can improve the procedure by an iterative technique, employing (3.11.11) or (3.11.13) to determine \( \gamma_i(T, P, 1) \), and then substituting this value in (3.11.10) or (3.11.12) respectively. Using the condition \( P = P' \) and replacing the terms in braces with \( P_i/c_i P_i^0 \) or \( P_i/m_i P_i^0 \), respectively, yields a better value of \( \gamma_i(T, P, c_i) \) or...
of $\gamma_1(T,P,m_i)$. If desired, further iterations may be performed, by concentrating on measurements near unit molarity or molality that yield new values of $\gamma_1(T,P,1)$, which may then be used on the right-hand side of (3.11.10) or (3.11.12) for improved determinations of $\gamma_1(T,P,q_1)$.

(e) After the welter of different reference states, activity coefficients, activities, methods of specifying compositions, and deviations from ideal behavior, the reader may be excused for wondering whether a unified description of physical phenomena has in fact been achieved. The acid test involves a check on whether, given any process, the change in chemical potential is indeed independent of all arbitrary features that have been introduced in Sections 3.4–3.10. We shall employ a simple numerical example to check on the overall consistency of our approach, employing well established data relating to the Br$_2$–CCl$_4$ system at room temperature.

The vapor pressure of Br$_2$, corresponding to various compositions of the liquid phase, as read off from a published graph, is shown in Table 3.11.1; also included is the value of
### Table 3.11.1
Tabulation of Br₂ Vapor Pressure as Function of Br₂ Mole Fraction in Br₂-Cl₄ Solutions at Room Temperature*

<table>
<thead>
<tr>
<th>x</th>
<th>0</th>
<th>0.2</th>
<th>0.4</th>
<th>0.6</th>
<th>0.8</th>
<th>1.0</th>
<th>(1.0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(atm)</td>
<td>0</td>
<td>0.095</td>
<td>0.145</td>
<td>0.183</td>
<td>0.220</td>
<td>0.280</td>
<td>(0.539 = P₆)</td>
</tr>
</tbody>
</table>


### Table 3.11.2
Tabulation of Activities and Activity Coefficients for Br₂ in Br₂-CCl₄ Solutions at Room Temperature

<table>
<thead>
<tr>
<th>x</th>
<th>P (atm)</th>
<th>γ</th>
<th>a - P/P₆</th>
<th>γ</th>
<th>a - P/P₇</th>
<th>γ</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>1.92*</td>
<td>0</td>
<td>1.00</td>
</tr>
<tr>
<td>0.2</td>
<td>0.095</td>
<td>1</td>
<td>0.339</td>
<td>1.69</td>
<td>0.185</td>
<td>0.925</td>
</tr>
<tr>
<td>0.4</td>
<td>0.145</td>
<td>1</td>
<td>0.517</td>
<td>1.29</td>
<td>0.269</td>
<td>0.672</td>
</tr>
<tr>
<td>0.6</td>
<td>0.183</td>
<td>1</td>
<td>0.653</td>
<td>1.09</td>
<td>0.339</td>
<td>0.564</td>
</tr>
<tr>
<td>0.8</td>
<td>0.217</td>
<td>1</td>
<td>0.775</td>
<td>0.97</td>
<td>0.408</td>
<td>0.510</td>
</tr>
<tr>
<td>1.0</td>
<td>0.280 = P₆</td>
<td>1</td>
<td>1.00</td>
<td>1.00</td>
<td>0.520</td>
<td>0.520‡‡</td>
</tr>
<tr>
<td>1.0</td>
<td>0.539 = P₇</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Calculated as 0.539/0.280
‡‡Calculated as 0.280/0.539
the vapor pressure $P^*$ attained by extrapolation of the Henry's Law region to $x = x_{Br_2} = 1$. Shown in Table 3.11.2 are corresponding activities and activity coefficients based on Raoult's Law, when $Br_2$ is considered as the solvent, or based on Henry's Law, when $Br_2$ is considered as the solute. The calculations were carried out in conformity with Eqs. (3.11.4a) and (3.11.7a), which involve the assumption that $Br_2$ is an ideal gas and that the deviations of $a^*(T,P)$ from unity may be neglected. One should carefully note that the activities and activity coefficients in schemes (a), (b), and (c) are widely different.

Suppose now that one wishes to determine $\Delta \mu$ for the process of altering the mole fraction of $Br_2$ from $x_1 = 0.8$ to $x_2 = 0.4$ at constant temperature. Then, according to Table 3.11.2, for the gas phase $\Delta \mu = RT \ln \frac{P_2}{P_1} = RT \ln \frac{0.145}{0.217} = RT \ln 0.668$. For case (b) where $Br_2$ is considered as the solvent, $\Delta \mu = RT \ln \left(\frac{a_2}{a_1}\right)_b = RT \ln \frac{0.517}{0.775} = RT \ln 0.668$. For case (c) where $Br_2$ is considered the solute $\Delta \mu = RT \ln \left(\frac{a_2}{a_1}\right)_c = RT \ln \frac{0.269}{0.402} = RT \ln 0.688$.

The preceding calculations illustrate explicitly that although the numerical values of $a$ and of $\gamma$ in Table 3.11.2 differ for the different cases, the values obtained for $\Delta \mu$ are identical: This shows that only $\Delta \mu$ is of fundamental significance; activities or activity coefficients have only a relative significance. Thus, in conjunction with the foregoing, it is of interest that if deviations from ideality had been ignored the value $\Delta \mu = - \ln \left(\frac{x_2}{x_1}\right) = RT \ln \frac{0.4}{0.8} = RT \ln 0.500$ would have been obtained, which is appreciably off the mark. One should also note that whereas for case (b) $\gamma$ tends to be greater than unity, $\gamma$ is less than unity for case (c).

(f) Frequently it is more convenient to measure activities or activity coefficients for a component which differ from that in which one is really interested. In that case it is expedient to use the Gibbs-Duhem equation for a
DETERMINATION OF ACTIVITY COEFFICIENTS

binary mixture. For a two-component system at constant T and P, we find \( n_1 \, d \mu_1 = - n_2 \, d \mu_2 \). On account of Eq. (3.6.2) this may be rewritten as

\[
\mathrm{d} \ln a_1(T, P, q_1) = (n_2/n_1) \, \mathrm{d} \ln a_2(T, P, q_2),
\]

(3.11.14)

where \( q = x, c, m \). Integration then yields

\[
\ln \left( \frac{a_1(T, P, q_1)}{a_1(T, P, q)} \right) = - \int_{q_0}^{q} (n_2/n_1) \, \mathrm{d} \ln a_2(T, P, q_2).
\]

(3.11.15)

As a special case we may consider the specification of composition via mole fraction:

\[
\ln \left( \frac{a_1(T, P, x_1)}{a_1(T, P, 1)} \right) = - \int_{0}^{x_2} [x_2/(1 - x_2)] \, \mathrm{d} \ln a_2(T, P, x_2).
\]

(3.11.16)

Thus, if \( a_2 \) is known as a function of \( x_2 \), the definite integral may be evaluated by numerical methods, yielding \( a_1 \).

EXERCISES

3.11.1 (a) Rewrite Eq. (3.11.4) in terms of the activity coefficient \( \Gamma_1 \). (b) Write out an explicit relation when the Margules relation \( \gamma_2 = x_2^2 \mathcal{B}/RT \) is used.

3.11.2 Given the following data for water - ethanol solutions at 250°C, calculate \( \gamma_{\text{H}_2\text{O}} \) and \( \gamma_{\text{C}_2\text{H}_5\text{OH}} \) relative to the solvent standard states for each component at \( x_{\text{H}_2\text{O}} = 0.1, 0.2, \ldots, 1.0 \) and plot \( \gamma_{\text{H}_2\text{O}} \) and \( \gamma_{\text{C}_2\text{H}_5\text{OH}} \) vs. \( x_{\text{H}_2\text{O}} \) over the entire composition range.

<table>
<thead>
<tr>
<th>wt%</th>
<th>( P_{\text{C}_2\text{H}_5\text{OH}} ) (torr)</th>
<th>( P_{\text{H}_2\text{O}} ) (torr)</th>
<th>wt%</th>
<th>( P_{\text{C}_2\text{H}_5\text{OH}} ) (torr)</th>
<th>( P_{\text{H}_2\text{O}} ) (torr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H}_2\text{O}(\ell) )</td>
<td></td>
<td></td>
<td>( \text{H}_2\text{O}(\ell) )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>23.7</td>
<td>54.85</td>
<td>37.7</td>
<td>12.9</td>
</tr>
<tr>
<td>5.30</td>
<td>10.3</td>
<td>17.6</td>
<td>65.53</td>
<td>40.5</td>
<td>12.0</td>
</tr>
<tr>
<td>13.74</td>
<td>19.6</td>
<td>14.6</td>
<td>72.25</td>
<td>43.3</td>
<td>11.1</td>
</tr>
<tr>
<td>25.32</td>
<td>27.7</td>
<td>13.5</td>
<td>92.30</td>
<td>50.7</td>
<td>7.7</td>
</tr>
<tr>
<td>34.38</td>
<td>32.2</td>
<td>13.4</td>
<td>94.96</td>
<td>52.4</td>
<td>5.4</td>
</tr>
<tr>
<td>46.21</td>
<td>35.4</td>
<td>13.3</td>
<td>100</td>
<td>58.8</td>
<td>0</td>
</tr>
</tbody>
</table>

3.11.3 Suppose a diatomic gas dissolves as atoms in a solid. What is the relation between the activity of the gas in the solid and the vapor pressure of the diatomic species?
3.11.4 The tabulation shown below lists the mole fraction and the quantities \( P_1/P_1^* \) for the vapor pressure of mercury \( P_1 \) in equilibrium with bismuth amalgams at 321°C:

\[
\begin{array}{cccccccc}
x_2(Bi) & 0.1486 & 0.247 & 0.347 & 0.463 & 0.563 & 0.670 & 0.793 & 0.937 \\
\frac{P_1}{P_1^*} & 0.908 & 0.840 & 0.765 & 0.650 & 0.542 & 0.432 & 0.278 & 0.092
\end{array}
\]

Determine the activity coefficient of mercury and of bismuth at the mole fractions \( x_2 = 0.25, 0.50, 0.75 \).

3.11.5 The following data were obtained at 50°C for the vapor pressures of \( \text{CCl}_4(A) \), \( \text{C}_2\text{H}_5\text{OCH}_3(B) \) solutions:

<table>
<thead>
<tr>
<th>( x_B )</th>
<th>( P_A )(mm)</th>
<th>( P_B )(mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>306</td>
<td>0</td>
</tr>
<tr>
<td>0.096</td>
<td>277</td>
<td>34.4</td>
</tr>
<tr>
<td>0.120</td>
<td>269</td>
<td>42.6</td>
</tr>
<tr>
<td>0.198</td>
<td>250</td>
<td>67.0</td>
</tr>
<tr>
<td>0.215</td>
<td>246</td>
<td>72.3</td>
</tr>
<tr>
<td>0.326</td>
<td>215</td>
<td>104</td>
</tr>
<tr>
<td>0.425</td>
<td>190</td>
<td>126</td>
</tr>
<tr>
<td>0.598</td>
<td>136</td>
<td>175</td>
</tr>
<tr>
<td>0.684</td>
<td>110</td>
<td>196</td>
</tr>
<tr>
<td>0.748</td>
<td>90.1</td>
<td>213</td>
</tr>
<tr>
<td>0.806</td>
<td>70.7</td>
<td>228</td>
</tr>
<tr>
<td>0.849</td>
<td>56.2</td>
<td>240</td>
</tr>
<tr>
<td>0.950</td>
<td>18.6</td>
<td>266</td>
</tr>
<tr>
<td>1.00</td>
<td>0</td>
<td>280</td>
</tr>
</tbody>
</table>

Assume the vapor phase to be characterized as an ideal gas. Determine the activity coefficients for components A and B at \( x_1 = 1/4, 1/2, 3/4 \) at 500°C relative to the solvent and the solute reference states involving mole fractions.

3.11.6 The partial pressures of \( \text{C}_2\text{H}_5\text{OH}(A) \) and \( \text{CCl}_4(B) \) over \( \text{C}_2\text{H}_5\text{OH}-\text{CCl}_4 \) are found to be as follows:

<table>
<thead>
<tr>
<th>( x_V )</th>
<th>( P_A )(mm)</th>
<th>( P_B )(mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>173.09</td>
<td>0</td>
</tr>
<tr>
<td>0.0212</td>
<td>169.0</td>
<td>38.31</td>
</tr>
<tr>
<td>0.035</td>
<td>167.04</td>
<td>95.32</td>
</tr>
<tr>
<td>0.1016</td>
<td>158.45</td>
<td>135.56</td>
</tr>
<tr>
<td>0.1638</td>
<td>150.97</td>
<td>158.45</td>
</tr>
<tr>
<td>1.000</td>
<td>0</td>
<td>258.84</td>
</tr>
</tbody>
</table>

(a) Does this system show positive or negative deviations from ideality? (b) Show the approach to (i) Raoult’s Law for A and (ii) Henry’s Law for B as \( x_B \) approaches zero. (c) Assuming a Henry’s Law constant for B of 1135 mm and ideal behavior in the vapor phase, what is the fugacity of B in the hypothetical standard state? (d) Assuming Henry’s Law to hold for \( x_B < 0.025 \), find

(i) \( \Delta G_{318.2} \) for \( B(x_B = 0.1016) \rightarrow B(x_B = 0.0356) \)
(ii) \( \Delta G_{318.1} \) for \( B(x_B = 0.0212) \rightarrow B \) (hypothetical standard state)
(iii) \( \Delta H_{318.2} \) and \( \Delta S_{318.2} \) for the transfer in (ii).
(iv) \( \Delta H_{318.2} \) for B (hypothetical standard state) \rightarrow B(x_B = 0).

(e) Find \( \Delta G_{318.2} \) for the transfer in (d) if Henry’s Law were valid up to \( x_B = 0.1016 \).

3.11.7 The following data for the system \( \text{H}_2\text{O}(A)-n-\text{C}_3\text{H}_7\text{OH}(B) \) at 25°C are cited below:
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3.11.8 The activity coefficients for solid solutions of \( p-C_6H_4Cl_2(A) \) in \( p-C_6H_4BrCl(B) \) at 50°C were measured.

| \( x_A \) | 0.056 | 0.312 | 0.409 | 0.660 | 0.841 | 0.949 |
| \( \gamma_A \) | 0.87 | 0.98 | 1.01 | 1.04 | 1.02 | 1.00 |
| \( \gamma_B \) | 1.00 | 0.97 | 0.95 | 0.93 | 1.01 | 1.14 |

Pure \( A(s) \) and \( B(s) \) were taken as the standard states for \( A \) and \( B \) respectively. (a) If \( P_A^* \) and \( P_B^* \) are 7.48 and 2.36 mm, respectively, at this temperature, find the total pressure of the vapor in equilibrium with the solution for which \( x_A = 0.660 \). (b) What unusual feature does this system exhibit?

3.11.9 For the \( HNO_3-H_2O \) system, the following vapor pressure data have been reported at 25°C:

<table>
<thead>
<tr>
<th>wt % ( HNO_3 )</th>
<th>( P_{HNO_3} ) (torr)</th>
<th>( P_{H_2O} ) (torr)</th>
<th>wt % ( HNO_3 )</th>
<th>( P_{HNO_3} ) (torr)</th>
<th>( P_{H_2O} ) (torr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>20.6</td>
<td>55</td>
<td>25</td>
<td>19.2</td>
<td>60</td>
</tr>
<tr>
<td>30</td>
<td>17.8</td>
<td>65</td>
<td>35</td>
<td>16.2</td>
<td>70</td>
</tr>
<tr>
<td>40</td>
<td>14.6</td>
<td>80</td>
<td>45</td>
<td>12.7</td>
<td>90</td>
</tr>
<tr>
<td>50</td>
<td>10.7</td>
<td>100</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(a) Determine the activity coefficients at \( x_{HNO_3} = 0.2, 0.4, 0.6, 0.8 \). (b) Determine the composition of the vapor phases at the above compositions of the solutions. (c) Estimate the Henry’s Law constants for both components.

3.11.10 (a) For \( O_2(l)-N_2(l) \) solutions, the vapor pressure of pure \( O_2(l) \) at 81.1 K is 263.2 torr. The liquid and vapor phase compositions correspond to \( x_{O_2} = 0.445 \) and 0.181 when the total pressure is 1 atm. Determine the activity coefficient of oxygen. (b) The equilibrium vapor pressure of \( N_2(l) \) at 84.3 K is 1591 torr, and the mole fraction of \( N_2 \) in the liquid and vapor phases is 0.610 and 0.320 respectively. Determine the activity coefficient of \( N_2 \) in the solution.

3.11.11 The following results pertain to chloroform \( (A) \) -ethanol \( (B) \) mixtures at 55°C:

| \( x_B \) | 0 | 0.0100 | 0.0200 | 0.0500 | 0.1000 | 0.2000 |
| \( \gamma_B \) | 12.5 | 12.3 | 11.6 | 9.92 | 6.05 | 3.12 |

(a) Find \( \gamma_A \) in the solution for which \( x_B = 0.1000 \) assuming the reference state for \( A \) to be also the pure liquid. (b) What value of \( \gamma_A \) is approached as \( x_A \) approaches unity? Why? (c) What can be said about the limit of \( \gamma_A \)?
where \( x \) and \( y \) are the mole fractions in the liquid and vapor phases. (a) Find \( \gamma_A \) for each solution when \( A \) is considered to be the solvent and the reference state is pure liquid \( A \). (b) Find \( \gamma_B \) for \( x_B = 0.9288 \) when the standard state for \( B \) is pure liquid \( B \). (c) Find \( \gamma_A \) for \( x_B = 0.9288 \) when the standard state for \( A \) is the hypothetical Henry's Law solution.

3.11.12 At 35°C the activity coefficients of \( \text{CCl}_4 \) in \( \text{CH}_3\text{OH} \) read as follows:

<table>
<thead>
<tr>
<th>( x_{\text{CH}_3\text{OH}} )</th>
<th>1</th>
<th>0.91</th>
<th>0.79</th>
<th>0.66</th>
<th>0.49</th>
<th>0.36</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \gamma_{\text{CH}_3\text{OH}} )</td>
<td>1</td>
<td>1.04</td>
<td>1.11</td>
<td>1.27</td>
<td>1.63</td>
<td>2.16</td>
</tr>
</tbody>
</table>

What is the change in activity coefficient for \( \text{Cl}_4 \) when the composition of the solution is altered from \( x_{\text{CCl}_4} = 0.50 \) to \( x_{\text{CCl}_4} = 0.25 \)?

3.11.13 At 0°C the following data apply to a solution of sucrose in water:

<table>
<thead>
<tr>
<th>Molality</th>
<th>0</th>
<th>0.2</th>
<th>0.5</th>
<th>1.0</th>
<th>3.5</th>
<th>4.5</th>
<th>5.0</th>
<th>6.0</th>
</tr>
</thead>
</table>

Find the activity of water and of sucrose for each composition.

3.11.14 The following data have been reported for the total vapor pressure and vapor composition in equilibrium with solutions of carbon tetrachloride and acetonitrile at 45°C:

<table>
<thead>
<tr>
<th>( x_{\text{CCl}_4} ) (liquid)</th>
<th>( x_{\text{CCl}_4} ) (vapor)</th>
<th>Vapor pressure (torr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>204.8</td>
</tr>
<tr>
<td>0.0347</td>
<td>0.1801</td>
<td>248.0</td>
</tr>
<tr>
<td>0.1914</td>
<td>0.4603</td>
<td>336.0</td>
</tr>
<tr>
<td>0.3752</td>
<td>0.6429</td>
<td>364.6</td>
</tr>
<tr>
<td>0.4790</td>
<td>0.5684</td>
<td>369.6</td>
</tr>
<tr>
<td>0.6049</td>
<td>0.5936</td>
<td>371.1</td>
</tr>
<tr>
<td>0.8069</td>
<td>0.6470</td>
<td>362.8</td>
</tr>
<tr>
<td>0.9609</td>
<td>0.8001</td>
<td>314.4</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>258.8</td>
</tr>
</tbody>
</table>

Calculate the activity and activity coefficient for each component relative to the standard state of the pure materials.

3.11.15 For the \( \text{N}_2\text{H}_4-\text{N}_2\text{H}_2(\text{CH}_3)_3 \) system the following data have been cited at 20°C (\( x_1 \) and \( y_1 \) refer, respectively, to the mole fractions of \( \text{N}_2\text{H}_4 \) in the liquid and vapor phases):

<table>
<thead>
<tr>
<th>( x_2 )</th>
<th>( y_2 )</th>
<th>( P ) (torr)</th>
<th>( x_2 )</th>
<th>( y_2 )</th>
<th>( P ) (torr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>10.7</td>
<td>0.6</td>
<td>0.960</td>
<td>106.0</td>
</tr>
<tr>
<td>0.1</td>
<td>0.836</td>
<td>70.1</td>
<td>0.7</td>
<td>0.970</td>
<td>112.7</td>
</tr>
<tr>
<td>0.2</td>
<td>0.900</td>
<td>82.5</td>
<td>0.8</td>
<td>0.978</td>
<td>120.4</td>
</tr>
<tr>
<td>0.3</td>
<td>0.922</td>
<td>89.9</td>
<td>0.9</td>
<td>0.989</td>
<td>128.2</td>
</tr>
<tr>
<td>0.4</td>
<td>0.941</td>
<td>95.5</td>
<td>1</td>
<td>1</td>
<td>135.9</td>
</tr>
<tr>
<td>0.5</td>
<td>0.950</td>
<td>99.9</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
(a) Determine \(a_2\) from these data at each cited value of \(x_2\).
(b) Determine \(a\) from these data for \(x_2 = 0.2, 0.4, 0.6, 0.8\). Discuss any difficulties you may encounter at this step.

3.11.16 Write down a complete set of equations specifying \(\mu_i\) and its temperature and pressure derivatives for nonideal solutions in which the reference state is: (a) a solution saturated with respect to component \(i\), (b) a solution which is infinitely dilute with respect to all components save the solvent. What is the advantage of each of these reference states relative to those introduced in the text? Introduce appropriate activity coefficients and obtain expressions showing how these quantities vary with \(T\) and \(P\).

3.12 ACTIVITY OF SOLVENT AND SOLUTE FROM LOWERING OF FREEZING POINT DATA

(a) In an extension of the results derived earlier (Section 2.8) we relate the activity \(a_i^{(x)}\) to the lowering of the freezing point \(\theta\) of a binary solution through the expression

\[
- \ln a_i^{(x)} = \frac{L_1 \theta}{RT^2} + \left(\frac{\theta}{T}\right)^2 \left(\frac{L_1}{RT_0} - \frac{C_p}{2R}\right) = - \ln \Gamma_i^{(x)} - \ln x_1
\]

where \(\theta = T_o - T_f\), \(L_1\) is the molar heat of fusion of the pure solvent; all other symbols retain their standard significance. Strictly speaking we should have included the term \(- \ln a_i^{(x)}\) on the second line, but as long as operating conditions remain at or close to one atmosphere, the omission of this term is justifiable. Similar remarks apply to \(\gamma_2\) introduced here and in later sections. We see immediately that \(\Gamma_1\) may be found by a determination of the \(\theta\) value which corresponds to the composition \(x_1\) of the solution under study; in addition \(L_1\), \(C_p\), and \(\tilde{C}_p\) must be specified.

(b) The difficulty with Eq. (3.12.1) is that it yields \(\gamma_i^{(x)}\) at the freezing point \(T_f\) of the solution. One is usually interested in the value of \(\gamma_1 = \gamma_i^{(x)}\) at a standard temperature
The specification of \( \gamma_1(T_s) \) in terms of \( \gamma_1(T_f) \) may be accomplished through the general relation (\( \partial \ln \Gamma_1/\partial T \))_{x_1, P} = - (\bar{H}_1 - \bar{H}_1^*)/RT^2 \) cited in Eq. (3.10.3). Accordingly,

\[
\ln \frac{\Gamma_1(T_s)}{\Gamma_1(T_f)} = \ln \frac{\gamma_1(T_s)}{\gamma_1(T_f)} = \ln \frac{a_1(T_s)}{a_1(T_f)} = - \int_{T_f}^{T_s} \frac{\bar{H}_1 - \bar{H}_1^*}{RT^2} \, dT
\]

\[(P, x_1 \text{ constant}) \] (3.12.2)

Here \( \bar{H}_1 - \bar{H}_1^* \) is the enthalpy difference involved in changing the solution from a mole fraction value \( x_1^* - 1 \) to a final composition specified by \( x_1 \). This difference must be known as a function of \( T \) before the integration may be carried out. Using Kirchhoff's law we write

\[
(H_1 - H_1^*)_T = (H_1 - H_1^*)_{T_f} + (\bar{C}_{1P} - \bar{C}_{1P}^*)(T - T_f),
\]

whence

\[
\ln \left[ \frac{\Gamma_1(T_s)}{\Gamma_1(T_f)} \right] = \ln \left[ \frac{\gamma_1(T_s)}{\gamma_1(T_f)} \right] = - \left( \frac{\bar{H}_1 - \bar{H}_1^*}{RT} \right)_{T_f} \left( T_s - T_f \right)
\]

\[
+ \left( \frac{\bar{C}_{1P} - \bar{C}_{1P}^*}{R} \right) \left[ (T_s - T_f)/T_s - \ln (T_s/T_f) \right].
\]

This solves the problem at hand; note that the parameters \( T_s, T_f \) and the thermodynamic state functions \( \bar{H}_1, \bar{H}_1^*, \bar{C}_{1P}, \) and \( \bar{C}_{1P} \) must be specified.

(c) The foregoing may be used to determine the activity of the second component, i.e., the solute in the experiment on the lowering of the freezing point. Here we employ the Gibbs-Duhem relation \( [a_i = a_i(x^*)] \):

\[
d\ln a_2^{(m)} = d\ln a_2 = - \left( \frac{x_1}{x_2} \right) d\ln a_1.
\]

In principle, one may integrate Eq. (3.12.5) numerically, using computer fits to experimental data; this method nowadays
is the preferred methodology. However, it may not be out of place to discuss procedures in use before computerized calculations became possible. Such methods are interesting in their own right and not just historical artifacts.

We reintroduce Eq. (3.5.1) to write

$$\frac{x_1}{x_2} = \frac{1000}{m M_1} = b_1/m,$$  \hspace{1cm} (3.12.6)

where $m = m_2$ is the molality, $M_1$ the gram molecular mass of the solvent, and $b_1 = 1000/M_1$. Equation (3.12.1) may be rewritten as

$$-\ln a_1 = -\ln a_1^{(m)} = b_2\theta + b_3\theta^2,$$  \hspace{1cm} (3.12.7)

where $b_2$ and $b_3$ are appropriate parameters involving the multipliers of $\theta$ and $\theta^2$ in (3.12.1). On differentiation one finds

$$-\frac{d\ln a_1^{(m)}}{m} = (b_2 + 2b_3\theta)d\theta,$$  \hspace{1cm} (3.12.8)

so that (3.12.5) may be revamped to read

$$\frac{d\ln a_1^{(m)}}{m} = \frac{b_1}{m} (b_2 + 2b_3\theta)d\theta = \frac{d\theta}{\lambda m} + c\frac{\theta}{m} d\theta,$$  \hspace{1cm} (3.12.9)

where $\lambda^{-1} = b_1b_2$, $c = 2b_1b_3$.

One can now carry the necessary integrations numerically. However, before computers were available a different strategy was used. One may define a quantity $j$ by

$$j = 1 - \theta/\lambda m.$$  \hspace{1cm} (3.12.10)

Then

$$dj = -\frac{d\theta}{\lambda m} + (\theta/\lambda m^2)dm = -\frac{d\theta}{\lambda m} + (\theta/\lambda m)d\ln m$$

$$-\frac{d\theta}{\lambda m} + (1 - j)d\ln m,$$  \hspace{1cm} (3.12.11)
which may be solved for

\[ \frac{d\theta}{\lambda m} = (1 - j) \ln m - dj. \quad (3.12.12) \]

Using (3.12.12) in (3.12.9) yields

\[ \ln a_i^{(m)} = (1 - j) \ln m - dj + c \frac{\theta}{m} d\theta. \quad (3.12.13a) \]

\[ \ln \Gamma_2^{(m)} = \ln a_i^{(m)} - \ln m = - j \frac{dm}{m} - dj + c \frac{\theta}{m} d\theta. \quad (3.12.13b) \]

Now integrate \( m \) from 0 to a final value \( m \). For very dilute solutions Eq. (3.12.7) reduces to

\[ - \ln x_1 = b_2 \theta - \ln (1 - x_2) = x_2 x_1 = m/b_1, \]

whence \( \theta = m/b_2 - \lambda m \). Thus, according to (3.12.10), for \( m = 0, j = 0 \). Then Eq. (3.12.13b) becomes

\[ \ln \Gamma_2^{(m)}(T_f) = - j - \int_0^m (j/m) dm + c \int_0^m (\theta/m) d\theta. \quad (3.12.14) \]

Note that by our procedure \( \Gamma_2^{(m)} \) is evaluated at the freezing temperature of the solution \( T_f = T_0 - \theta \). The first term on the right is easily found from (3.12.10). The second term is found from a plot of \( - m^{-1}(1 - \theta/\lambda m) \) versus \( m \), and the third term is found from a plot of \( c\theta/m \) versus \( \theta \), taking the area under the resulting curve in both cases. This requires measurements of a series of \( \theta \) values corresponding to a set of closely spaced solutions for different molalities \( m_i \). \( \Gamma_2^{(m)}(T_f) \) is now known; note that

\[ \lambda^{-1} = 1000 \frac{\bar{L}_1}{M_1 R T_o^2}, \quad c = \frac{2000}{M_1 T_o^2} \left[ \frac{\bar{L}_1}{RT_o} - \frac{\bar{C}_p - \bar{C}_p}{2R} \right]. \quad (3.12.15a) \]

(d) There is still the troublesome problem of finding \( \Gamma_2^{(m)} \) at a standard temperature \( T_s \) other than \( T_f \). To accomplish this we set

\[ y = \ln \left[ \frac{a_1(T_s)}{a_1(T_f)} \right], \quad (3.12.15b) \]

whence
We set \( \frac{x_1}{x_2} = \frac{b_1}{m} \), and we turn to the determination of

\[
d\ln \Gamma_a^m(T_s) = d\ln \Gamma_a^m(T_f) - d\ln \Gamma_a^m(T) - (b_1/m)\, dy - d\ln m. \tag{3.12.17}
\]

Note how by the use of \( dy \), the quantity \( \Gamma_a^m \) at the standard temperature \( T_s \) is correlated with \( \Gamma_a^m \) at the freezing point of the solution. Since \( - (b_1/m) \, d\ln \Gamma_a^m = d\ln \Gamma_a^m \) we have

\[
d\ln \Gamma_a^m(T_s) = d\ln \Gamma_a^m(T_f) - d\ln \Gamma_a^m(T) - (b_1/m)\, dy
\]

Now integrate from \( m = 0 \) to \( m \). At the lower limit, \( \Gamma_a^m = 1 \) and \( \ln \Gamma_a^m = 0 \) (\( m \to 0 \)). Hence

\[
\ln \Gamma_a^m(T_s) = \ln \Gamma_a^m(T_f) - b_1 \int_0^y \frac{1}{m} \, dy, \tag{3.12.19}
\]

which is the final desired relation. For, \( \ln \Gamma_a^m(T_f) \) is known from Eq. (3.12.14) at \( T_f = T_o - \theta \). We also require a plot of \( - b_1/m \) vs. \( y \). The latter quantity is given by (3.12.15); but the logarithm of the ratio of activities is identical with \( \ln \left( \Gamma_a^m(T_s)/\Gamma_a^m(T_f) \right) \), and this latter quantity is found from (3.12.4). At the lower limit \( T_f = T_s \), \( y = 0 \).

Analogous procedures hold with respect to the boiling point elevation.

**EXERCISES**

3.12.1 The following freezing-point data are reported for aqueous solutions of cane sugar:

<table>
<thead>
<tr>
<th>( m ) (molal)</th>
<th>0.100</th>
<th>0.200</th>
<th>0.400</th>
<th>0.500</th>
<th>0.700</th>
<th>1.000</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.200</td>
<td>1.500</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \theta/m ) (deg/molal)</td>
<td>1.883</td>
<td>0.904</td>
<td>1.946</td>
<td>0.967</td>
<td>2.003</td>
<td>2.067</td>
</tr>
<tr>
<td></td>
<td>2.104</td>
<td>2.173</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
3. CHARACTERIZATION OF NONIDEAL SYSTEMS

Calculate the molal activity coefficients of the cane sugar in each of the solutions.

3.12.2 The following freezing-point data are reported for aqueous solutions of formic acid:

<table>
<thead>
<tr>
<th>m (molal)</th>
<th>1.0</th>
<th>2.0</th>
<th>3.0</th>
<th>4.0</th>
<th>5.0</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>θ/m (deg/molal)</td>
<td>1.83</td>
<td>1.78</td>
<td>1.75</td>
<td>1.71</td>
<td>1.69</td>
<td>1.5</td>
</tr>
</tbody>
</table>

Calculate j and j/m for each of the solutions. Assuming j/m to be constant and equal to the average of the six calculated values, determine the molal and the rational activity coefficients of formic acid in the solutions for which m = 3, 5, 10.

3.12.3 The following data pertain to the lowering of the freezing point of aqueous urea solutions:

<table>
<thead>
<tr>
<th>m (mol)</th>
<th>0.3241</th>
<th>0.6458</th>
<th>3.3601</th>
<th>5.2848</th>
<th>8.0828</th>
</tr>
</thead>
<tbody>
<tr>
<td>θ (deg)</td>
<td>0.5953</td>
<td>1.1698</td>
<td>5.3897</td>
<td>8.0825</td>
<td>11.4142</td>
</tr>
</tbody>
</table>

(a) Determine the activity coefficient of water γ_w(m) at the indicated molalities. (b) Determine how well the data may be fitted to the Margules equation \( \ln γ_i(m) = Bx_i^2 \) (see also Eq. (3.13.12a)) and determine B. (c) Find γ_0(x) for urea in solution. (d) The enthalpy change for formation of aqueous urea solution is given by \( 1.548m^2 - 0.246m^3 + 2.36 \times 10^{-2}m^4 - 1.06 \times 10^{-2}m^5 \). Determine γ_w(m) at 298 K for m = 0.3, 1, and 3.

3.13 MIXING IN NONIDEAL SOLUTIONS

In this section we provide the basis for later discussions pertaining to phase diagrams; the results are also of intrinsic interest. We consider the process of generating a nonideal solution from its pure constituents; the formulation obtained here should be contrasted with that of Section 2.5.

As usual, all thermodynamic properties of interest may be derived from the expression for the free energy. Here we shall be concerned with the free energy of mixing, defined as

\[
\Delta G_m = \sum_{i=1}^{n} n_i [\mu_i(T,P,x_i) - \mu_i^*(T,P)],
\]

in which \( \mu_i \) is the chemical potential of constituent \( i \) in the nonideal solution, whose composition is specified by the mole fraction \( x_i \), and \( \mu_i^* \) is the corresponding chemical potential of
each constituent in its pure form at the same temperature and pressure. For simplicity all subsequent manipulations will be based on the use of mole fractions for prescribing compositions. Corresponding analyses based on molarity or molality are called for in Exercise 3.13.1.

We begin with Eqs. (3.6.3a), (3.6.4a), and revert to the abbreviation $\Gamma_i(T,P,x_i) = \Gamma_i$. As stated in Section 3.4, for pure materials $\Gamma_i(T,P,1) = 1$, so that for pure components $\mu_i^*(T,P) = \mu_i^*(T,1) + RT \ln a_i$. On inserting this relation and Eq. (3.6.4a) into (3.13.1) we find

$$\Delta G_m = RT \sum_i n_i \ln (x_i \Gamma_i). \tag{3.13.2}$$

From (3.13.2) we readily obtain

$$\Delta S_m = -(\partial \Delta G_m / \partial T)_{P,x_1} = -R \sum_i n_i \ln (x_i \Gamma_i)$$

$$-RT \sum_i n_i (\partial \ln \Gamma_i / \partial T)_{P,x_1} \tag{3.13.3}$$

$$\Delta H_m = -T^2 [\partial (\Delta G_m / T) / \partial T]_{P,x_1} = -RT^2 \sum_i n_i (\partial \ln \Gamma_i / \partial T)_{P,x_1} \tag{3.13.4}$$

$$\Delta V_m = [\partial (\Delta G_m) / \partial P]_{T,x_1} = RT \sum_i n_i (\partial \ln \Gamma_i / \partial P)_{T,x_1} \tag{3.13.5}$$

$$\Delta E_m = \Delta H_m - P \Delta V_m \tag{3.13.6}$$

$$(\Delta C_P)_m = -RT \sum_i n_i [2(\partial \ln \Gamma_i / \partial T)_{P,x_1} + T(\partial^2 \ln \Gamma_i / \partial T^2)_{P,x_1}] \tag{3.13.7}$$

A corresponding equation is obtained for $(\Delta C_v)_m$. The various partial derivatives called for in Eqs. (3.13.3)–(3.13.7) may be determined via Eqs. (3.10.1) and (3.10.3). The above expressions all correctly reduce to the results of Sec. 2.5 for ideal solutions.

It is worth examining Eq. (3.13.2) in greater detail for a binary solution. Defining $\Delta G_m = \Delta G_m / (n_1 + n_2)$ we have the symmetric formulation, obtained when specializing to standard states at unit pressure:
\[
\Delta \tilde{G}_m^{\text{RT}} = x_1 \ln x_1 + x_2 \ln x_2 + x_1 \ln \Gamma_1 + x_2 \ln \Gamma_2. \tag{3.13.8}
\]

For further progress we require explicit relations for \(\Gamma_1\) and \(\Gamma_2\). The simplest useful formulation is an expansion of \(\ln \Gamma_1\) and \(\ln \Gamma_2\) in a power series in \(x_1\) and \(x_2\) as shown below,

\[
\ln \Gamma_1 = \ln a_1 - \ln x_1 - D_1 x_2 + B_1 x_2^2 + \ldots \tag{3.13.9a}
\]

\[
\ln \Gamma_2 = \ln a_2 - \ln x_2 - D_2 x_1 + B_2 x_1^2 + \ldots. \tag{3.13.9b}
\]

Note that \(\ln \Gamma_1\) is expanded as an ascending power series in \(x_2\) and \(\ln \Gamma_2\), in an ascending series in \(x_1\). This ensures that as \(x_2 \to 0\), \(\Gamma_1 \to 1\) and as \(x_1 \to 0\), \(\Gamma_2 \to 1\), as required. The series (3.13.9) as written will be useful if, for successive members \(C_i x_2^i + F_i x_2^i + \ldots\), the inequality \(|C_i|, |F_i|, \ldots \ll |B_i|\) applies.

The coefficients on the right of (3.13.9) are not arbitrarily adjustable. This may be shown by solving (3.13.9) for \(2n a_i - 2n x_i + D_i(I - x_i) + B_i(I - x_i)^2\) with \(i = 1, 2\), and then constructing the expression

\[
x_1 \frac{d\ln a_1}{dx_1} = x_1 \frac{d\ln x_1}{dx_1} - (D_1 + 2B_1)x_1 dx_1 + 2B_1 x_1^2 dx_1. \tag{3.13.10}
\]

Next, from (3.13.10) form the sum \(x_1 \frac{d\ln a_1}{dx_1} + x_2 \frac{d\ln a_2}{dx_2}\), which vanishes because of the Gibbs-Duhem relation. Moreover, \(x_1 \frac{d\ln x_1}{dx_1} + x_2 \frac{d\ln x_2}{dx_2} = dx_1 + dx_2\). Thus,

\[
0 = dx_1 + dx_2 - (D_1 + 2B_1)x_1 dx_1 - (D_2 + 2B_2)x_2 dx_2
\]

\[
+ 2B_1 x_1^2 dx_1 + 2B_2 x_2^2 dx_2. \tag{3.13.11a}
\]

Next, set \(x_2 = 1 - x_1\), \(dx_2 = -dx_1\), cancel out the common multiplier \(dx_1\), and rearrange the resulting term in ascending powers of \(x_1\). This yields

\[
D_2 - (D_1 + D_2)x_1 + 2(B_1 - B_2)x_1^2 = 0. \tag{3.13.11b}
\]
The coefficients of \(x_0^2\), \(x_1^2\), \(x_2^2\) must vanish separately if (3.13.11) is to hold for arbitrary \(x_1\) in the interval \(0 \leq x_1 \leq 1\). Similar considerations apply to the expansion in \(x_2\). This leads to the requirements \(D_1 - D_2 = 0\) and \(B_2 - B_1 = B\), so that finally one obtains the Margules (1889) equations:

\[
\ln \Gamma_1 = Bx_2^2; \quad \ln \Gamma_2 = Bx_1^2, \tag{3.13.12a}
\]

or

\[
\Gamma_1 = \exp(Bx_2^2); \quad \Gamma_2 = \exp(Bx_1^2). \tag{3.13.12b}
\]

Equation (3.13.8) now reads

\[
\frac{\Delta G_m}{RT} = x_1 \ln x_1 + x_2 \ln x_2 + Bx_1x_2. \tag{3.13.13}
\]

We note that for ideal solutions, \(B = 0\). The variation of \(\Delta G_m/RT\) with \(x_2\) is represented by curve 1 in the accompanying diagram, Figure 3.13.1. Since \(x_1, x_2 < 1\), \(\Delta G_m\) is necessarily negative: thus, the mixing of components to form a solution occurs spontaneously. For \(B < 0\), the term \(Bx_1x_2\) renders \(\Delta G_m\) even more negative than for the ideal case; this situation is represented by Curve 5 in the diagram. However, a very interesting situation arises for \(B > 0\); for, when \(B\) becomes sufficiently large, the simple monotonic variation \(\Delta G_m\) with \(x_2 = x\) gives way to a more complex behavior in which there is first a local minimum and ultimately, an absolute maximum in \(\Delta G_m\) at \(x = 1/2\). This situation is depicted by Curve 4 on the diagram. Curve 3 is discussed later.

We now touch on a point that will be much more extensively taken up in Section 3.14. Reference is made to curve 4 of Fig. 3.13.1, which is redrawn in Fig. 3.13.2, where we set \(x = x_2\). Let \(x'\) and \(x''\) represent the values of \(x_2\) where the local minima in \(\Delta G_m\) occur. Clearly, an attempt to make up a homogeneous solution of composition \(x\) in the range \(x' < x < x''\) at fixed \(T\) and \(P\) will result in a more positive value of \(\Delta G_m\) than formation of a heterogeneous mixture of composition \(x'\) and
FIGURE 3.13.1 The Gibbs free energy of mixing for a nonideal solution according to Eq. (3.13.13), for various values of the parameter $B$.

$x''$ (present in appropriate quantities to preserve the overall composition $x$ of the hypothetical homogeneous solution from which these two phases are derived). Since $\Delta G_m$ is reduced by splitting of the solution into two distinct phases for which $\Delta G_m$ is as small as possible, such a process will occur spontaneously. Thus, under the specified conditions one cannot obtain a single phase solution of composition in the range $x' \leq x \leq x''$. Instead the solution splits into two components, $x'$ and $x''$, whose compositions correspond to the minima of the curve; the two distinct phases $x = x'$ and $x = x''$ are at equilibrium with each other.

The compositions $x'$ and $x''$ of the heterogeneous phases are determined through the requirement $(\partial \Delta G_m/\partial x) = 0$; because of the symmetry inherent in Eq. (3.13.13), $x'' = 1 - x'$. On setting $x_2 = x = 1 - x_1$ in (3.13.13) and carrying out the differentiation, one arrives at the result
FIGURE 3.13.2 Diagram illustrating the reduction in $\Delta \tilde{G}_m/RT$ when a homogeneous solution of composition $x'''$ splits into two phases of composition $x'$ and $x''$, respectively.

\[ \ln \left[ \frac{x''}{(1 - x'')} \right] = B(2x'' - 1), \quad (3.13.14) \]

which is a transcendental equation that must be solved numerically for $x = x''$ once $B$ is specified. As $B$ is increased $x'$ and $x''$ are found symmetrically to move away from the value $1/2$ toward the values $0$ and $1$ respectively.

As is seen from Fig. 3.13.1, there exists a critical $B$ value, $B_c$, for which $x' = x'' = 1/2$; for $B < B_c$ no phase separation is encountered. The critical value, $B_c$, which separates the U-shaped curves from those that have minima away from $x = 1/2$, is determined from the requirements

\[ \frac{\partial^2 \Delta \tilde{G}_m}{\partial x^2} = 0 = 1/(1 - x_c) + 1/x_c - 2B_c \quad (3.13.15a) \]

and

\[ \frac{\partial^3 \Delta \tilde{G}_m}{\partial x^3} = 0 = 1/(1 - x_c)^2 - 1/x_c^2, \quad (3.13.15b) \]

whose solution leads to the values
\[ x_c = \frac{1}{2}, \quad B_c = 2. \]  \hspace{1cm} (3.13.15c)

The corresponding variation of \( \Delta G_m/RT \) with \( x_2 \) is shown as curve 3 in Fig. 3.13.1.

We return briefly to Eq. (3.13.9) which becomes \( (D = 0, \quad B_1 = B_2 = B) \)

\[ \ln a_1 = \ln x_1 + Bx_2^2. \]  \hspace{1cm} (3.13.16)

Plots of \( a_1 \) versus \( x_1 \) are shown in Fig. 3.13.3 for \( B = 0, \ 1.15, \ 2, \ 2.88 \). One notes that for \( B > B_c = 2 \) there exist two values of \( x_1 \), namely \( x_1' \) and \( x_1'' \), which are associated with the same activity. Since \( \mu_1 = \mu_1^* + RT \ln a_1 \), the equality \( a_1(x_1') = a_1(x_1'') \) implies an equality of chemical potentials: \( \mu_1(x_1') = \mu_1(x_1'') \), that is again an indication that there are two discrete phases.

FIGURE 3.13.3 Activity of component 1 versus mole fraction \( x_1 \) in a binary solution. Computation according to Eq. (3.13.16).
of composition $x'_1$ and $x''_1$ that are in mutual equilibrium.

To summarize the foregoing, it has been shown by very elementary methods involving an expansion of the form (3.13.9) that one can specify a set of activity coefficients (3.13.12) which lead to an equation of the form (3.13.13) for the Gibbs free energy change of mixing. For $B$ sufficiently large and positive, the term $Bx_1x_2$ gives rise to a phase separation.

Entropies, enthalpies, and volume changes arising from the mixing process may be readily deduced from Eqs. (3.13.3)-(3.13.7), and are left as an exercise (Exercise 3.13.3).

Next, it should be noted that Fig. 3.13.3 is also representable as a vapor pressure diagram of $P_1/P_1^*$ versus $x_1$. This is so because at equilibrium $\mu_1 + RT \ln a_1 = \mu_1^{pp} + RT \ln P_1$; on rearranging one finds $x_1 \Gamma_1/P_1 = a_1/P_1 = \exp[(\mu_1^{pp} - \mu_1^*)/RT] = C$. For pure liquid 1, $\Gamma_1 = 1$, $a_1 = 1$, $P_1 - P_1^*$, thereby rendering $C = 1/P_1^*$, so that finally $P_1/P_1^* = a_1$, which proves the assertion. Thus, Fig. 3.13.3 is equivalent to diagrams that show departures from Raoult's Law. The interpretation of Curve 4 on the diagram now runs as follows: As the solution is rendered increasingly rich in component 1, the partial pressure of component 1 in the vapor phase rises much more rapidly than would be the case for an ideal solution. For $x'_1 \leq x_1 \leq x''_1$, $P_1/P_1^*$ remains fixed, corresponding to the fact that there now exist three phases in mutual equilibrium, i.e., two liquids and the vapor. As the solution is made increasingly rich in component 1, the phase of composition $x''_1$ grows at the expense of the phase at composition $x'_1$. Ultimately, when the mixture is characterized by $x_1 > x''_1$, one reverts back to a single liquid phase, and $P_1$ again varies with $x_1$ until the value $P_1 - P_1^*$ is reached for $x_1 = 1$.

Note further that as $x_1 \rightarrow 1$, all curves in Fig. 3.13.3 merge with the one for which $B = 0$; this agrees with the experimental fact that Raoult’s Law always holds in this range. Similarly, as $x_1 \rightarrow 0$ one obtains a straight line region consistent with Henry’s Law; here the slope as $x_1 \rightarrow 0$ varies with each solution. For $B < 0$ negative deviations from Raoult’s Law are encountered, but for $B > 0$ one finds positive
deviations with slopes that become steeper, the greater the positive departure from ideality.

Finally, we should note that in Eq. (3.13.13) the terms \( R(x_1 \ln x_1 + x_2 \ln x_2) \) represent the entropy of mixing, which, in the present approximation scheme, is the same as for an ideal solution. The term \( Bx_1x_2 \) is then to be identified with \( \Delta H - \Delta G + T\Delta S \). We may rewrite Eq. (3.13.13) as

\[
\Delta G_m = RT\{x_1 \ln x_1 + x_2 \ln x_2\} + wx_1x_2, \tag{3.13.17}
\]

in which \( B = w/RT \) and \( \Delta H = RTBx_1x_2 = wx_1x_2 \). On introducing the definitions for mole fraction we find \([\Delta G = n\Delta G = (n_1 + n_2)\Delta G]\)

\[
\Delta G_m = RT(n_1 \ln x_1 + n_2 \ln x_2) + w(n_1n_2/n). \tag{3.13.18}
\]

It is quite remarkable how many firm deductions are based on a single hypothesis. Beginning with the Margules formulation (3.13.12) for \( \Gamma_1 \), thermodynamics leads directly to the specification of \( \Delta G_m \), as shown in (3.13.13). All other mixing functions are then found from (3.13.3)-(3.13.7). When phase separation does occur the composition of the two phases in equilibrium is specified by Eq. (3.13.14). The critical value of \( B \) required for incipient phase separation and the critical composition of the mixture are specified by Eq. (3.13.15c). Finally, one may construct diagrams such as shown in Fig. 3.13.3 by which deviations from Raoult's Law are predicted. The foregoing is a beautiful illustration of the power of thermodynamic methodology.

**EXERCISES**

3.13.1 Sketch out derivations by which \( \Delta G_m \) and other mixing functions may be specified in terms of \( \gamma_1(T,p,c) \) and \( \gamma_1(T,p,m) \).

3.13.2 (a) Derive Eq. (3.13.11) and (3.13.12) in detail, proving that \( D_1 = D_2 = 0 \) and \( B_1 = B_2 = B \) as stated in the text. (b) Expand on the derivation by adding terms in \( x^3 \) and \( x^4 \) to Eqs. (3.13.9). Obtain expanded relations for \( \ln \gamma_1 \) and \( \Delta G_m \).
3.13.3 (a) Starting with Eq. (3.13.13) derive expressions for $\Delta S_m/RT$, $\Delta H_m/RT$, $\Delta V_m/RT$, $\Delta E_m/RT$, $(\Delta C_p)_m/RT$ on the assumption that $B$ depends on $T$ via $B = w/RT$, $w$ being constant. (b) Make sketches showing the dependence of each of these on $x_2 = x$ for $B = -1, 0, 1.5, 3$, at $T = 300$ K. (c) Comment on the nature of each of the curves.

3.13.4 (a) Determine the Henry's Law constant in terms of $B$ for a binary solution to which Eq. (3.13.13) applies. (b) Discuss negative departures from Raoult's Law in terms of Eq. (3.13.13).

3.13.5 The normal isotopic abundances for Li are 92.48 mole % for $^7$Li and 7.52 mole % for $^6$Li. Making reasonable approximations, determine the entropy, enthalpy, and Gibbs free energy changes on mixing the pure isotopes. Discuss your results in terms of the statements made in Section 1.21 in conjunction with the Third Law of Thermodynamics.

3.13.6 For some kinds of high-polymer solutions, the chemical potentials of solvent and solute are given by the approximate equations

$$\bar{\mu}_1 = \bar{\mu}_1^0(T,P) + RT \left\{ \ln \phi_1 + \left(1 - \frac{1}{r}\right) \ln (1 - \phi_1) \right\} + w(1 - \phi_1)^2,$$

$$\bar{\mu}_2 = \bar{\mu}_2^0(T,P) + RT \left\{ \ln \phi_2 - \left(r - 1\right) \ln (1 - \phi_2) \right\} + rw(1 - \phi_2)^2,$$

where $r$ stands for the degree of polymerization and $\phi_1$, for the volume fractions

$$\phi_1 = N_1/(N_1 + rN_2), \quad \phi_2 = rN_2/(N_1 + rN_2).$$

Here $N_1$ and $N_2$ are the number of solvent molecules and of solute high-polymer molecules, respectively. It is assumed that each polymer molecule consists of $r$ monomers, and that the volume of a monomer approximately equals the volume of a solvent molecule. (a) Determine $\phi_1$ and $\phi_2$ in terms of $x_1$ and $x_2$, and $x_1$ and $x_2$ in terms of $\phi_1$ and $\phi_2$. (b) Compare the entropy of mixing of this solution with that of an ideal solution. (c) Derive the relation of the enthalpy of mixing to the concentration of this solution.

3.13.7 The following expression has been proposed for the activity coefficient of component 1 in a two component solution: $\ln \Gamma_1 = \bar{\mu}_1^*/\phi_2^*/RT$, where $V_1^*$ is the molar volume of pure 1, at temperature $T$ and total pressure $P$, and $A$ is a constant. The volume fraction $\phi_2$ is given by

$$\phi_2 = n_2 V_2^* / [n_1 V_1^* + n_2 V_2^*].$$

On the basis of elementary theories one finds that

$$A = \frac{[(\Delta \bar{E}_{vap})_1/\sqrt{V_1^*}]^{1/2} - [(\Delta \bar{E}_{vap})_2/\sqrt{V_2^*}]^{1/2}}{V_2^*}.$$

(a) Derive a relation for $\ln \Gamma_2$. (b) Prove that the free energy of mixing is given by

$$\Delta G_m = RT \left[ n_1 \ln x_1 + n_2 \ln x_2 \right] + A(n_1 V_1^* + n_2 V_2^*) \phi_1 \phi_2.$$

(c) Let the second term on the right of the expression for $\Delta G_m$ be the excess free energy of mixing $G_e$. Obtain expressions for
S., H., V.; the final relations should include the functions
\[ \alpha_1 = (\bar{V}_1^*)^{-1}(\partial \bar{V}_1^*/\partial T)_T; \beta_1 = (\bar{V}_1^*)^{-1}(\partial \bar{V}_1^*/\partial P)_T. \]

(d) Simplify the expressions in (c) by neglecting terms in \((\phi_1 - \phi_2)(\alpha_1 - \alpha_2)\) and \((\phi_1 - \phi_2)(\beta_1 - \beta_2)\). Provide arguments to show why these quantities should be small.

3.13.8 It is found empirically that, for many systems, the equilibrium vapor pressure of component 2 in a nonideal solution is given by \(P_2 = (2x_2 - x_2^2)P_2^*\). (a) Obtain an expression for \(\gamma_2\) relative to the solvent standard state for component 1 and determine \(\gamma_2\) at \(x_2 = 1/2\). (b) Obtain an analytic expression for \(P_1\) in terms of \(x_1\). (c) Does one obtain positive or negative deviations from Raoult's Law? For what range is \(dP_T/dx_2 > 0\)? For what value of \(x_2\) is a maximum encountered in \(P_T\), the total pressure in the system?

3.13.9 Let the 'unsymmetrical' Gibbs free energy of a mixture be given by the expression
\[
G = n_1\mu_1^* + n_2\mu_2^* + RT\ln \left(n_1/(n_1 + n_2)\right) + RT\ln \left(n_2/(n_1 + n_2)\right) + Bn_1n_2,
\]
where \(B = B(T,P), \mu_1^* = \mu_1^*(T,P)\). (a) Obtain the relation for the molar Gibbs free energy of the mixture solely in terms of mole fractions. (b) Obtain \(S, H, V, E, C_P, C_v\) in terms of \(x_1, x_2\) and parameters. (c) Determine the vapor pressures \(P_1\) and \(P_2\) in terms of a modified Raoult's Law. (d) Plot \(\Delta S_m/R, \Delta H_m/RT, \Delta G_m/RT, P_2\) as functions of \(x_2\) for \(r = 1/2, 2, 1/5, 5\); assume constant \(T\) and \(P\). Here \(\Delta G_m\) refers to the molar free energy of mixing. Comment on the nature of the curves you obtain.

3.13.10 For the acetone-carbon disulfide system the following activities have been reported at 35.17°C (subscript 2 refers to CS₂)

<table>
<thead>
<tr>
<th>(x_2)</th>
<th>(a_2)</th>
<th>(a_1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.24 x 10^{-2}</td>
<td>0.216</td>
<td>0.963</td>
</tr>
<tr>
<td>0.1330</td>
<td>0.405</td>
<td>0.896</td>
</tr>
<tr>
<td>0.2761</td>
<td>0.631</td>
<td>0.800</td>
</tr>
<tr>
<td>0.4533</td>
<td>0.770</td>
<td>0.720</td>
</tr>
<tr>
<td>0.6161</td>
<td>0.835</td>
<td>0.656</td>
</tr>
<tr>
<td>0.828</td>
<td>0.908</td>
<td>0.524</td>
</tr>
<tr>
<td>0.935</td>
<td>0.960</td>
<td>0.318</td>
</tr>
<tr>
<td>0.9692</td>
<td>0.970</td>
<td>0.1803</td>
</tr>
</tbody>
</table>

Determine \(\Delta G_m, \Delta H_m, \Delta S_m\) for the system and plot the results. Do you detect any evidence for phase separation?

3.13.11 Let the excess molar and partial molal Gibbs free energy for a two-component mixture relative to an ideal mixture be given by \(\Delta G_1 = x_2^2[A - BT + C(x_2 - x_1)], \Delta G = x_1x_2(A - BT + Cx_2)\), in which \(A, B,\) and \(C\) are constants. Determine \(\bar{H}, \bar{S}, \bar{G}_2, \bar{H}_1, \bar{H}_2, \bar{S}_1, \bar{S}_2\) for this system.

3.13.12 The following type of equation is frequently used in the empirical representation of data in a binary solution:
PHASE STABILITY

\[ \ln \gamma_1 = A_1(T)x_1^2 + B_1(T)x_1^3 + C_1(T)x_1^4 + D_1(T)x_1^5, \]
where \( A_1 \) through \( D_1 \) are independent of composition. Determine \( \Delta G_m \), \( \Delta H_m \), and \( \Delta S_m \) for the binary solution from this relation.

3.13.13 The heats of mixing have been reported for various solutions of carbon tetrachloride and acetonitrile at 45°C, as summarized below:

<table>
<thead>
<tr>
<th>( x_{CCl_4} )</th>
<th>0.128</th>
<th>0.317</th>
<th>0.407</th>
<th>0.419</th>
<th>0.631</th>
<th>0.821</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Delta H(\text{sol'n}) )</td>
<td>99</td>
<td>179</td>
<td>206</td>
<td>235</td>
<td>222</td>
<td>176</td>
</tr>
</tbody>
</table>

Cal / mol solution

(a) Using these data and the tabulations in Exercise 3.11.14, determine \( \Delta H_m \), \( \Delta G_m \), \( \Delta S_m \) for \( x_{CCl_4} = 0.1, 0.2, \ldots, 0.9 \), and plot the results. (b) Assuming that \( \Delta S_m \) may be approximated by the relation that applies to an ideal solution, use these data to calculate the activity coefficients of \( CCl_4 \) at \( x = 0.128, 0.317, 0.419, \) and 0.631, and compare these with the values that are interpolated from Exercise 3.11.14.

3.14 PHASE STABILITY: GENERAL CONSEQUENCES OF DEVIATIONS FROM IDEALITY

(a) We had earlier encountered specific examples where deviations from ideal behavior of binary solutions led to the phenomenon of phase separation. We now introduce several generalizations on the basis of qualitative sketches introduced later.

In ideal solutions the mixing process is rendered spontaneous through the positive entropy of mixing \( \Delta S/R = x_1 \ln x_1 + x_2 \ln x_2 > 0 \); here \( \Delta H = 0 \). The molar free energy for ideal solutions reads

\[
\bar{G} = RT \left\{ x_1 \ln x_1 + x_2 \ln x_2 \right\} + (x_1\mu_1^* + x_2\mu_2^*)
\]

(3.14.1a)

\[
\bar{G} = -T\Delta S_0 + \bar{G}^*.
\]

(3.14.1b)

Qualitatively, Eq. (3.14.1) may be represented as shown in Fig. 3.14.1(b), where energy is plotted schematically versus \( x_2 = x \). The plot shows \( T\Delta S_0 \) versus \( x \) as the bottom curve; the sloping baseline (top curve) for \( \bar{G}^* \) is obtained from the sum \( x_1\mu_1^* + x_2\mu_2^* \) in which \( \mu_1^* \) and \( \mu_2^* \) are held constant. The resultant graph, shown in the middle, \( \bar{G} = -T\Delta S_0 + \bar{G}^* \), is a skewed U-shaped
FIGURE 3.14.1 Free energies $\tilde{G}$ of binary solutions. (a) $\Delta \tilde{H} < 0$, (b) $\Delta \tilde{H} = 0$, (c) $\Delta \tilde{H} > 0$.

For nonideal solutions there occur two corrections: (i) There exists in general an excess entropy term $\tilde{S}_e$ that must be added to $\Delta \tilde{S}_o$; the resulting sum may be simulated by the expression $\Delta \tilde{S} = x_1 \ln x_1 + x_2 \ln (rx_2)$, where $r$ is a suitable parameter. One now obtains a skewed $-T\Delta \tilde{S}$ curve of the type shown in Figs. 3.14.1, parts (a) and (c). (ii) The enthalpy of mixing no longer vanishes but is a function of $x_2 = x$, such as given by $\Delta \tilde{H} = wx(1 - xr)$; this relation reduces to the last term of Eq. (3.13.17) when $r = 1$. On introducing these corrections one obtains a new curve as in part (a) where $w < 0$, and in part (c) where $w > 0$. The resultants obtained on adding up the sloping baselines, the entropy, and the enthalpy contributions are indicated by the curve $\tilde{G}$. In part (a) $\tilde{G}$ is simply more negative and more skewed than for part (b), but in part (c) a nonmonotonic variation of $\tilde{G}$ with $x$ is obtained, because over certain ranges of $x$ the large positive $\Delta \tilde{H}$ values outweigh the negative contributions associated with $-T\Delta \tilde{S}$. As will be shown shortly, such a situation signals the onset of phase separation.

(b) In this connection it is of some interest to establish how much of each phase must be present to form a heterogeneous
mixture of average mole fraction \( x \). The reader may consult Table 3.16.1, p. 377, in deriving Eqs. (3.14.2).

Consider \( n = n_A + n_B \) moles of A and B with an overall mole fraction \( 1 - x = n_A/n \). Let a two-phase mixture be formed such that the mole fraction of A in the first phase and in the second phase is given by \( l - x' = n'_A/(n'_A + n'_B) \) and by \( 1 - x'' = n''_A/(n''_A + n''_B) \), respectively. Let the fraction of the total mole numbers in the first phase be \( 1 - f = (n'_A + n'_B)/n \). Then one finds that \( n_A = n(1 - x) \), \( n'_A = n(1 - f)(1 - x') \), and \( n''_A = nf(1 - x'') \). Conservation of mole numbers requires that \( n_A = n'_A + n''_A \). On substituting and solving for \( f \) one obtains

\[
f = \frac{(x - x')/(x'' - x')}{(3.14.2a)}
\]

\[
1 - f = \frac{(x'' - x)/(x'' - x')} \tag{3.14.2b}
\]

which results are known as the Lever Rule.

(c) For a given set of conditions, can one predict whether a given alloy is homogeneous or not? Consider a solution of mole fraction \( x_0 \) for a system for which Fig. 3.14.2 is relevant. If the alloy were simply a mechanical mixture of the pure

![FIGURE 3.14.2 Diagram of \( \tilde{G} \) vs. \( x \), showing how the homogeneous phase has a lower free energy than any biphasic mixture.](image-url)
components A and B, then according to the Lever Rule the free energy of the system would be given by the intersection of the straight line joining $\bar{G}_A$ to $\bar{G}_B$ with the vertical line at $x = x_o$, labeled $\bar{G}^*$ in the diagram. If instead the phase mixture involved two solutions of compositions $x_a'$ and $x_a''$, then the same Lever Rule yields the free energy of the alloy designated as $\bar{G}_a$. Since $\bar{G}_a < \bar{G}^*$, this new state is more stable than the original one. Analogous remarks apply to another heterogeneous alloy whose two compositions are represented by $x_b'$ and $x_b''$; the corresponding free energy, $\bar{G}_b$, is still lower. Continuing this process it is found that at the composition $x$ where the two phases merge into a single homogeneous solution of composition $x_o$, the free energy attains its lowest possible value, $\bar{G}_o$. This is the stable configuration. For the type of free energy displayed in Fig. 3.14.2, $\partial^2 G/\partial x^2 > 0$ for all $x$; hence, any straight line joining two points on the curve always lies above the curve between these points. When the free energy versus composition curve is U-shaped the homogeneous solution always has the lowest free energy.

By contrast, consider the free energy curve as a function of composition as sketched in Fig. 3.14.3, which reproduces curve $\bar{G}$ in Fig. 3.14.1(c). If an alloy of composition $x_o$ were

![Diagram](https://via.placeholder.com/150)

**FIGURE 3.14.3** Diagram of $\bar{G}$ versus $x$, illustrating a condition in which a biphasic mixture of relative composition $x'$ and $x''$ with respect to the second component is the most stable configuration for a solution; here $x' \leq x \leq x''$. For $0 \leq x < x'$ and for $x'' < x \leq 1$, a homogeneous phase is stable.
to exist as a homogeneous solution, its free energy would be given by the point \( G_0 \) on the diagram. On the other hand, if the alloy were a heterogeneous mixture of composition \( x' \) and \( x'' \) for component 2, the free energy of the system would be lowered to \( G_a \). By choosing \( x' \) and \( x'' \) to be more widely separated in composition one progressively lowers the free energy until a minimal value \( G \) is reached when the two phases are of composition \( x' \) and \( x'' \); here the straight line forms a tangent to the two curves near the local minima. Any attempt to spread the composition of the two phases further will lead to a rise in free energy, as is illustrated for \( x_b \) and \( x_b'' \), with a corresponding value for \( G_b \).

The stable state of the system under study is thus a heterogeneous mixture of composition \( x' \) and \( x'' \). For \( x' < x < x'' \), the alloy consists of two phases of composition \( x' \) and \( x'' \) in the proportions \( (x - x')/(x'' - x') \) and \( (x'' - x)/ (x'' - x') \) given by the Lever Rule. Note that the proportions change linearly with composition. In the ranges \( x < x' \) or \( x > x'' \), the homogeneous solution is stable, as is seen by inspection of Fig. 3.14.3.

(d) The change in the alloy system with composition at fixed temperature is easily visualized with the aid of Fig. 3.14.4. As pure B is added to pure A, the B atoms form a homogeneous solution in A; when the composition \( x \) reaches the value \( x' \) the solution is saturated. Any further addition of B atoms results in the formation of a second phase for which \( x = x'' \), in which atoms of type A are considered dissolved in B. With further addition of B the proportion of the second phase at fixed composition \( x'' \) increases at the expense of the first until the phase boundary at \( x = x'' \) is reached. For \( x > x'' \) only the homogeneous solution of A in B is stable. Thus, in the heterogeneous region the compositions of the two phases of the mechanical mixture remain constant, but the relative amounts of material in each phase changes with alterations in x.

(e) The presentation may readily be generalized to a system
FIGURE 3.14.4 Variation of the makeup of a binary system with relative composition (mole fraction), shown as a plot of $1 - f$ and of $f$ versus $x$. 

in which more than two phases appear. A typical example is shown in Fig. 3.14.5; here the homogeneous and heterogeneous composition ranges are delineated by use of an imaginary string

FIGURE 3.14.5 Gibbs free energy as a function of $x$ when several mixtures of intermediates are formed. Stable single phases are indicated by cross-hatching on the $x$ scale.
that is tightly wound around the curves between points A' and B' in the diagram to exhibit all possible common tangent constructions. It is customary to designate phases consecutively by Greek lowercase letters in alphabetical order. The various phases and their composition ranges are indicated on the diagram. In general, if ΔH is small, as is likely to be the case for homogeneous solutions, the free energy plotted as a function of composition forms a broad, shallow U-shaped curve, and the ranges of composition over which the single phases are stable are large. However, when a compound is formed, deviations from the appropriate stoichiometric ratio remain very small. This is reflected in the very sharp rise of the free energy as the composition is changed even slightly from the stoichiometric ratio. A situation of this type is depicted in Fig. 3.14.6; it is seen that the composition \( x = x_1 \) is stable over only a narrow range. The composition of the compound does not necessarily coincide with an ideal stoichiometric value; for example, the compound CuAl\(_2\) does not

![Figure 3.14.6](image)

**FIGURE 3.14.6** Gibbs free energy as a function of mole fraction for a binary mixture involving formation of a compound corresponding to the phase with stoichiometry \( A_{1-x_1}B_{x_1} \). Cross-hatched composition ranges indicate stable monophasic regions.
exist, but a compound on the Al-rich side of this value is stable.

EXERCISES

3.14.1 Discuss in terms of chemical potentials why phase equilibrium requires the tangent constructions described in this section.

3.14.2 Prove that the common tangent construction is equivalent to the equality of chemical potentials of the phases whose compositions are given by the points of tangency.

3.15 DISCUSSION OF SEVERAL TYPES OF PHASE DIAGRAMS

The general features of standard phase diagrams will now be correlated with the free energy curves depicted in Section 3.14. For simplicity we immediately specialize to systems where the liquid phase is homogeneous throughout its composition range; the corresponding free energy curve is then U-shaped, as depicted in Fig. 3.14.2. In our first example, Fig. 3.15.1, the solid state also exists only as a homogeneous solution. Quite generally, as the temperature is lowered the free energy curve of the solid moves past that of the liquid, and the shape of each curve (i.e., the skewness of the U shapes) will also be altered. Thus, with diminishing temperature the two free energy curves will intersect and give rise to situations where the common tangent construction indicates the existence of biphasic mixtures. In Fig. 3.15.1a the temperature $T_1$ is sufficiently high that the entire free energy curve for the liquid, $G_l(x)$, lies below that for the solid, $G_s(x)$; at any composition $x$, the system is stable in the liquid state. As the temperature is lowered to a value $T_A$ (part (b)), the two free energy curves touch at the composition $x = 0$; solid and liquid now coexist for the pure phase, and $T_A$ is the melting point of pure A. However, for $x > 0$ the free energy of the liquid remains below that of the solid. As $T$ is reduced further to the value $T_2$ (part (c)), the $G_l(x)$ and $G_s(x)$
types of phase diagrams

---

FIGURE 3.15.1 Derivation of a phase diagram from free energy curves of liquid and solid phases. $T_1 > T_A > T_2 > T_B > T_3$.

curves intersect, such that in the composition regions $0 \leq x < x^*_B$ or $x^*_B < x \leq 1$ a single homogeneous solid or homogeneous liquid phase is stable; in the intermediate range the common tangent construction indicates that the system divides into a phase mixture involving a solid of composition $x^*_B$ and a liquid of composition $x^*_B$. With a further decrease in temperature to the value $T_B$ (part (d)), the curves $G_t$ and $G_s$ touch at $x = 1$; this is the melting point of pure B. For $T < T_B$ (part (e)), $G_s < G_t$ for all $x$; the homogeneous solid phase is now the stable one.

The preceding information may be assembled into an equilibrium phase diagram shown in part (f), which is typical for the type of system under study. The diagram shows the $T$-$x$ regions in which the homogeneous solid or liquid is stable; the two corresponding boundary lines are known as the solidus and liquidus; the $T$-$x$ region between these represents an unstable or forbidden range called a miscibility gap. A tie-line connects the solid of composition $x^*_B$ with the liquid of different composition $x^*_B$ with which it is in equilibrium. The Ag-Au, Cu-Ni, Au-Pt, and U-Zr alloys are representative examples of such systems.
Variants of this scheme are encountered for alloys where \( G_s(x) \) has a significantly smaller curvature than \( G_t(x) \). As shown in Fig. 3.15.2, with diminishing temperature the intersections between the two curves move from \( x = 0 \) and \( x = 1 \) inward until they meet at a common point. In the intermediate regions a common tangent construction is called for. The relationship between the free energy curves and the phase diagram on the right should be clear; again, the region between areas c and d or between e and f in part (c) represent miscibility gaps. The inverse situation is depicted in Fig. 3.15.3; it arises when the curvature of \( G_s(x) \) significantly exceeds that of \( G(x) \).

In the preceding cases the solidus and liquidus curves meet tangentially to an isothermal line at a congruent point; the solution freezes at this temperature without any change in composition. Au-Ni alloys exhibit the behavior depicted in Fig. 3.15.2. Inasmuch as \( \Delta H_c > 0 \) for this case, the solid solution for \( T < T_c \) is less stable than a mixture of phases; this is indicated by the dotted curve at the bottom of the diagram.

**FIGURE 3.15.2** Derivation of a phase diagram with a minimum, obtained from free energy curves of liquid and solid phases. \( T_A > T_B > T_1 > T_2 > T_3 > T_c \).
A second case frequently encountered involves a solid for which the components are only partially miscible and in which no intermediate phases are formed. The relevant free energy curves are shown in Fig. 3.15.4. At temperature $T = T_1$, $G_s(x) < G_l(x)$ for all $x$; the homogeneous liquid phase is stable over the entire composition range. At a particular value $T = T_2$, somewhat below the melting point of pure A, the free energy curves for solid and liquid intersect, as shown in part (b). By the common tangent construction, we see that for $0 < x < x'$ the homogeneous solid alloy is stable; for $x' < x < x''$ solid of composition $x'$ is in equilibrium with liquid of composition $x''$; for $x > x''$ the homogeneous liquid phase is stable. Part (c) is typical of a temperature $T_3$ at which $G_s$ and $G_l$ intersect both at the A-rich and at the B-rich ends of the diagram. Here, homogeneous solid alloys exist for the composition ranges $0 < x < x'$ and $x'''' < x < 1$; solid of composition $x'$ is in equilibrium with liquid of composition $x''$, and liquid of composition $x''''$ is in equilibrium with solid of composition $x''''$;
3. CHARACTERIZATION OF NONIDEAL SYSTEMS

FIGURE 3.15.4 Derivation of phase diagram (f) from free energy curves of a liquid and a solid which are only partially miscible.

in the range $x'' < x < x'''$ the homogeneous liquid phase is stable. Further cooling narrows the homogeneous $x'' - x'''$ range until it vanishes at temperature $T_4$ where $x'' = x'''$. This point, known as the **eutectic temperature**, is the lowest temperature at which an alloy still remains liquid. This liquid of composition $x''$ is in equilibrium with two solid phases of composition $x'$ and $x'''$. The **eutectic** is a heterogeneous mixture of two solid phases of composition $x'$, $x'''$. For $T = T_5 < T_4$, only the solid is stable, but in the composition range $x' < x < x'''$ of part (e) one encounters a heterogeneous mixture of two phases of composition $x'$ and $x'''$ in mutual equilibrium. The corresponding phase diagram is shown in part (f). Ag–Cu, Pb–Sn, Pb–Sb, Al–Si, and Cr–Ni are examples of systems exhibiting those properties which arise when the end members crystallize in the same structure. One also encounters such a system for two materials A and B which crystallize in different habits; the construction of the corresponding phase diagram is shown in Fig. 3.15.5. Conventionally, the solid solution occupying the left portion of a phase diagram is labeled as the $\alpha$-phase. Subsequent homogeneous phases occurring to the right
are labeled by successive lowercase letters of the Greek alphabet, \( \beta, \gamma, \delta \), etc.

The reader should be able to construct and interpret the phase diagram in Fig. 3.15.6 on a similar basis. This situation arises mainly when the melting points of pure A and B differ considerably. Diagrams of this type are classified as

FIGURE 3.15.5 Derivation of phase diagram (e) from free energy curves of a liquid and two solids.

FIGURE 3.15.6 Derivation of phase diagram (e) from free energy curves of a liquid and a solid.
belonging to the peritectic type; the temperature $T_p$ is the peritectic temperature; above it no solid $\alpha_2$ phase is formed for any alloy composition; below it there is a wide composition range over which the homogeneous solid $\alpha_2$ alloy system is stable.

We next turn to more complex cases involving formation of intermediate compounds. In Fig. 3.15.7, the relative positions of the free energy curves for $\alpha$, $\beta$, and $\gamma$, and of liquid phases are such that an initial intersection of the $G$ curve occurs with the $G_s$ curve for phase $\beta$, as shown in part (b). On further cooling, more intersections arise as shown in parts (c) and (d); this leads to the appearance of the $\alpha$ and $\gamma$ alloys. At still lower temperatures, two eutectics are formed, first one between $\beta$ and $\alpha$ and then, a second between $\beta$ and $\gamma$. Finally, for $T = T_5$, one obtains three homogeneous alloys phases in three composition ranges near $x = 0$, $x \approx 1/3$, and $x = 1$, as well as

![Figure 3.15.7 Derivation of phase diagram (f) from free energy curves for a liquid and three solids.](image)
two-phase regions in the intermediate composition ranges. In Ex. 3.15.5 the reader is asked to construct free energy curves whose gradual intersection leads to a peritectic diagram of the type illustrated in Fig. 3.15.8. Phase diagrams of this type are commonly encountered in the literature; they tend to arise when the melting points of the pure components are very different. The reader should carefully note the very distinct domains in which monophasic and biphasic regions are encountered.

A general feature of the phase diagrams explored in Figs. 3.15.7 and 3.15.8 is the existence of a maximum in the solidus and liquidus curves, corresponding to the composition of the intermediate $\beta$ phase. This reflects the composition at which $G_\alpha$ and $G_{\beta}$ first become tangent to each other. However, this point generally does not coincide exactly with the minimum in $G$; the composition of the intermediate phase then does not agree precisely with the ideal stoichiometric formula for the phase.

Finally, we refer the reader to Fig. 3.15.9 for a study on how the diagram of part (f) arises. More complex types of phase diagrams will not be explored here, but the general methodology should be clear from the preceding examples.

FIGURE 3.15.8 Compound peritectic phase diagram.
FIGURE 3.15.9 Derivation of phase diagram (f) from the free energy curves for a liquid and three solids.

EXERCISES

3.15.1 Corresponding to the phase diagram shown in Fig. 3.15.10a, answer the following questions: (a) Describe briefly the meaning of areas labelled 1 to 6. (b) Describe briefly the
meaning of the various curves separating these areas. (c) Provide an interpretation of the temperatures $T_A$, $T_B$, $T_C$. (d) Using approximate values of $x_B$ as read off from the diagram, discuss what happens to binary alloys of composition L, M, and N as the temperature is lowered from $T > T_A$ to $T_D$.

3.15.2 Label all parts of the peritectic phase diagram (Fig. 3.15.10b) for solid–liquid equilibria at constant pressure. State what happens as liquids of compositions a, b, c, d, and e are cooled from temperature $T_1$ to temperature $T_2$. Read approximate values of $T$ and $x$ off the graph.

3.15.3 On phase diagram Fig. 3.15.10c identify regions 1–5.

3.15.4 (a) Identify the regions 1–11 on phase diagram Fig. 3.15.10d. (b) Describe what happens as a liquid solution for which $x_B = 2/5$ is cooled from temperature $T_1$, to temperature $T_2$.

3.15.5 Sketch out free energy curves leading to a phase diagram of the type shown in Fig. 3.15.8.

### 3.16 VARIATION OF MUTUAL SOLUBILITY WITH TEMPERATURE

As a rule of thumb, a rise in temperature generally broadens the homogeneity range of a solution that is heterogeneous at low temperatures. This is so because at higher $T$ the negative contribution to the free energy arising from $-T\Delta S$ will begin to compete with and ultimately outweigh the positive contribution arising from $\Delta H$ which was responsible for the initial phase separation. The net effect is to bring the local minima in Fig. 3.16.1 together until they merge for $x = 1/2$ at a critical temperature, above which the solution is homogeneous throughout the entire composition range.

(a) These matters may be verified quantitatively in the so-called Bragg–Williams approximation. On temporarily ignoring the variation of $G^*$ with $x$ in Eq. (3.13.13) one obtains the relation ($B = w/RT$)

$$
\Delta G_m/RT = (\bar{G}_m - \bar{G})/RT = (1 - x) \ln (1 - x) + x \ln x + (w/RT)x(1 - x).
$$

(3.16.1)
Plots of \((\Delta G_m/RT)\) versus \(x\) obtained with a variety of values for the dimensionless parameter \(RT/w\) are exhibited in Fig. 3.16.1. We note that either at very low temperatures or for very large positive \(w\) the last term outweighs the entropy term, except near the end points \(x \to 0\) or \(x \to 1\). Correspondingly, the major portion of the top curve in Fig. 3.16.1 is positive, but there are two minima symmetrically disposed along the negative portion of the curve. For \(RT/w > 1/3\) the curve lies entirely in the negative domain, and for \(RT/w > 1/2\), it no longer exhibits local minima away from \(x = 1/2\). In the latter case \(\Delta G_m/RT > 0\) for all \(x\), so that the alloy remains homogeneous over the entire composition range below the critical value of \((RT/w)_c = 1/2\).

**FIGURE 3.16.1** Variation of Gibbs free energy of mixing with composition of a mixture for which \(w > 0\). Different curves correspond to different values of \(w/RT\). Dashed curve shows the locus of the local minima.
When account is taken of the variation of $\tilde{G}$ with $x$, the curves in Fig. 3.16.1 become skewed with respect to $x$, as was illustrated in Figs. 3.14.1.

The locus of the minima is shown as a dotted curve in Fig. 3.16.1. Any horizontal line within its boundaries represents the composition range over which the mixture is heterogeneous for a fixed value of $RT/w$. The plot of $RT/w$ versus $x$ obtained from the dotted curve is shown in Fig. 3.16.2. For constant $w$ this figure traces the variation of the immiscibility range with temperature. As $T$ is lowered the two phases approach the pure limiting compositions $x = 0$ and $x = 1$, which would be attained, if the system could be equilibrated, at $T = 0$.

(b) For a quantitative assessment concerning the variations of $\tilde{G}$ with temperature at fixed overall composition, one must deal with Eq. (3.16.1), which is satisfactory as it stands for the $T$ range $RT/w > 1/2$. However, for temperatures such that $RT/w < 1/2$ a splitting of the solution into two phases of composition $x'$ and $x''$ occurs. The relative amounts are specified by the lever rule, Eq. (3.14.2). This phase separation introduces complications because $x'$ and $x''$ are no

Fig. 3.16.2 Separation of phases for a binary mixture. Region inside curve represents the domain of heterogeneous phases.
longer variables; instead, they are now fixed by the solution temperature. In the subsequent analysis it is important to keep track of quite a few quantities that are listed in Table 3.16.1 for easy reference.

For a two-phase heterogeneous mixture we write

$$G = G' + G''$$  \hspace{1cm} (3.16.2)

in which $G'$ and $G''$ are the Gibbs free energies for the two phases of composition $x_B$ and $x_S$. According to Eq. (3.13.18),

$$G' = n_A G_A^* + n_B G_B^* + RT \left\{ n_A \ln x_A' + n_B \ln x_B' \right\} + w(T) \frac{n_A n_B}{n'},$$  \hspace{1cm} (3.16.3)

with a corresponding expression for $G''$.

Referring to lines 2 and 8 of Table 3.16.1, and introducing the definition of $n'G' = G'$ on the left of Eq. (3.16.3), we find

$$n'G' = n'_A G_A^* + n'_B G_B^* + RT n' \left\{ (1 - x') \ln (1 - x') + x' \ln x' \right\}$$

$$+ w(T)n'x'(1 - x'),$$  \hspace{1cm} (3.16.4a)

$$n''G'' = n''_A G_A^* + n''_B G_B^* + RT n'' \left\{ (1 - x'') \ln (1 - x'') + x'' \ln x'' \right\}$$

$$+ w(T)n''x''(1 - x'').$$  \hspace{1cm} (3.16.4b)

Here we have assumed that $w(T)$ is the same function for both phases. This is probably a rather poor approximation which has been introduced to keep the subsequent operations manageable. Accordingly, the total free energy reads $G = n'G' + n''G'' = nG$, so that by lines 6 and 8 of Table 3.16.1,

$$G = (n'/n)G' + (n''/n)G'' = x_A G_A^* + x_B G_B^*$$

$$+ RT(1 - f) \left\{ (1 - x') \ln (1 - x') + x' \ln x' \right\}$$

$$+ RT f(1 - x'') \ln (1 - x'') + x'' \ln x''$$

$$+ w(T)\left( (1 - f)x'(1 - x') + fx''(1 - x'') \right).$$  \hspace{1cm} (3.16.5)
Table 3.16.1

Tabulation of Compositional Relations Pertaining to Binary Phase Mixtures

<table>
<thead>
<tr>
<th>Phase'</th>
<th>Phase''</th>
</tr>
</thead>
<tbody>
<tr>
<td>n'a, n'b</td>
<td>n'a, n'b</td>
</tr>
</tbody>
</table>

1. Mole number

2. Mole fractions

\[
x' = \frac{n'a}{n'a + n'b} = 1 - x'
\]

\[
x'' = \frac{n'a}{n'a + n'b} = 1 - x''
\]

\[
x' = \frac{n'b}{n'a + n'b} = x'
\]

\[
x'' = \frac{n'b}{n'a + n'b} = x''
\]

3. Total mole numbers per phase

\[
n' = n'a + n'b
\]

\[
n'' = n'a + n'b
\]

4. Mole fraction for each phase

\[
1 - f = \frac{n'}{n' + n''} = \frac{n'}{n}
\]

\[
f = \frac{n''}{n' + n''} = \frac{n''}{n}
\]

5. Overall composition of system

\[
x_A = \frac{n_a}{n_a + n_b} = 1 - x = \frac{n_a}{n}
\]

\[
x_B = \frac{n_b}{n_a + n_b} = x = \frac{n_b}{n}
\]

6. Conservation of mole numbers

\[
n_a = n'a + n''
\]

\[
n_b = n'b + n''
\]

7. Interrelation mole fractions

\[
(1 - x)n' = (1 - x')n + (1 - x'')n''
\]

\[
xn = x'n' + x''n''
\]

\[
+ (1 - x'')n'' = x'(1 - f)n
\]

\[
+ (1 - x')n' = x''fn
\]

\[
+ (1 - x')n = x''fn
\]

8. Final interrelations

\[
n_a = n(1 - x)
\]

\[
n_b = nx
\]

\[
n' = n(1 - f)
\]

\[
n'' = nf
\]

\[
n'a = n'(1 - x')
\]

\[
n'' = n''(1 - x'')
\]

\[
n_b = n'x'
\]

\[
n'' = n''x''
\]
Since the minima in Fig. 3.16.1 are symmetrically displaced with respect to $x = 0$ and $x = 1$, we now set $x' = 1 - x''$ and $1 - x' = x''$. This rather drastic assumption has been introduced to keep subsequent mathematical manipulations simple. Equation (3.16.5) then reduces to

$$
\tilde{G}/RT = \tilde{G}*/RT + \left\{ (1 - x'') \ln (1 - x'') + x'' \ln x' \right\} + (w(T)/RT) x''(1 - x'').
$$

Equation (3.16.6) can now be used to show how $\tilde{G}/RT$ varies with temperature by numerical solution of the transcendental equation (3.13.14). This variation is not of particularly great interest. Rather more to the point is a study of the enthalpy changes with temperature. Proceeding by standard methodology, one obtains the enthalpy as $H = - T^2 \left[ \beta(G/T)/\beta T \right]$. Here one must be careful to recognize that for $RT/w < 1/2$, $x'' = x''(T)$ is an implicit function of temperature. Accordingly, the differentiation process yields

$$
- (\tilde{H}/RT^2) = - (\tilde{H}*/RT^2) + \left\{ \ln \left[ x''/(1-x'') \right] + (w(T)/RT)(1-2x'') \right\} (dx''/dT)
$$

$$
+ x''(1-x'') \left[ \left( \frac{1}{RT} \right) \frac{dw(T)}{RT^2} - \frac{w(T)}{RT^2} \right].
$$

On account of Eq. (3.13.14) the central term in braces drops out; Eq. (3.16.7a) may be rearranged to read
\[ \tilde{H} = x_A \tilde{H}_A^* + x_B \tilde{H}_B^* + \left[ w(T) - T \frac{dw(T)}{dT} \right] x''(1 - x''). \] (3.16.7b)

In the literature on the subject it is conventional to introduce a quantity termed the degree of order, or order parameter, \( s_p \), defined by

\[ s_p = 2x'' - 1 \quad \text{or} \quad x'' = (1/2)(1 + s_p); \quad (0 \leq s_p \leq 1), \] (3.16.8)

with which the equilibrium condition (3.13.14) assumes the simpler form

\[ \ln \left[ \frac{(1 + s_p)}{(1 - s_p)} \right] = \frac{w}{RT} s_p. \] (3.16.9)

Equations (3.16.6) and (3.16.7) now read

\[ \Delta G_m = RT \left[ \frac{1}{2} (1 + s_p) \ln (1 + s_p) + \frac{1}{2} (1 - s_p) \ln (1 - s_p) - \ln 2 \right] \]
\[ + \left( \frac{w}{4RT} \right) (1 - s_p^2) \] (3.16.10)

and

\[ \Delta \tilde{H}_m = \left[ w(T) - T \frac{dw(T)}{dT} \right] \frac{1}{4} (1 - s_p^2). \] (3.16.11)

Equation (3.16.9) is frequently written out in the equivalent form

\[ \tanh \left( \frac{ws_p}{2RT} \right) = s_p, \] (3.16.12)

and one conventionally defines a characteristic temperature \( T_\lambda \) by \( T_\lambda = \frac{w}{2R} \), on the assumption that \( w \) is constant. Equation (3.16.12) then reads

\[ \frac{T_\lambda}{T} = (\tanh^{-1}s_p) s_p. \] (3.16.13)

(c) It should be noted that Eq. (3.16.12) is a function of temperature alone; we next ascertain precisely how \( \Delta \tilde{H}_m \) varies
with $T$. For this purpose it is first necessary to determine $s_p(T)/T_\lambda$ by numerical solution of Eq. (3.16.13); the resulting universal functional relationship is shown in Fig. 3.16.3. One notes that the value of $s_p$ changes very little in the range $0 \leq T/T_\lambda \leq 0.3$; $x'' \approx 1$ in this range. As $T/T_\lambda$ is increased there is a gradually accelerating dropoff in $s_p$, until for $T/T_\lambda \to 1$, $s_p$ drops abruptly to zero, corresponding to $x'' = 1/2$.

Using the $s_p(T)$ relation embodied in Fig. 3.16.3 one can now determine $\Delta H_m$ via Eq. (3.16.11). The result is shown in Fig. 3.16.4 as a plot of $\Delta H_m/(1/4)w$ versus $T/T_\lambda$, on neglect of the term $dw(T)/dT$. One notes that at first $\Delta H_m$ is close to zero, but as $T/T_\lambda$ increases beyond 0.3 the enthalpy of mixing increases rapidly to its final value of $(1/4)w$ at $T = T_\lambda$.

The heat capacity at constant pressure is now found through the relation $(C_m)_P = (\delta \Delta H_m/\delta T)_P$. The result, shown as $(\Delta C_m)_P/R$ versus $T/T_\lambda$ in Fig. 3.16.5, is proportional to the slope of the curve in Fig. 3.16.4.

Inspection of Fig. 3.16.5, where we have set $w = 2RT_\lambda$, shows that as the temperature rises there is a marked increase in heat capacity, with a sharp drop off back to zero at $T = T_\lambda$. This figure has approximately the shape of the Greek capital letter $\Lambda$ and hence is frequently called a $\Lambda$ anomaly; $T_\lambda$ is known as the lambda point. What Fig. 3.16.5 once more illustrates is

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure3.16.3}
\caption{Variation of $s_p = 2x'' - 1$ versus $T/T_\lambda$ in accordance with Eq. (3.16.13); $T_\lambda = w/2R$.}
\end{figure}
that the transition from the biphasic to the monophasic regime occurs over a considerable range of temperature. As the temperature is raised, continually increasing amounts of energy are required to achieve a further rise in $T$ while the system moves close to the region of homogeneous stability, the onset of which abruptly halts the heat capacity anomaly.

We briefly consider the physical interpretation of the foregoing analysis in which the order parameter plays a central role. At $T = 0$ $s_p = 1$, so that $x'' = 1$ and $x' = 0$. This signals the separation of the AB mixture into pure A and pure B – the completely ordered state of the system. With rising $T$ $s_p$ drops slightly; $x'$ and $x''$ move away from 0 and 1, respectively: some
B has dissolved into A and vice versa. The system has now become slightly disordered. With an additional increase in T, s_p becomes still smaller; x' and x'' move further away from their end points, so that the two phases are now characterized by a greater degree of mixing and disorder. Finally, at T_lambda, s_p = 0 and x' = x'' = 1/2. The two phases have merged into one and the mixing of the two components is complete. The system now displays the maximum degree of disorder. Thus, the decline in s_p from 1 to 0 is a measure of the degree of disorder attendant to the increasing intermixing of components A and B in the two phases. Correspondingly, ΔG_m, ΔH_m, ΔC_m, indicate the changes in Gibbs free energy, enthalpy, and heat capacity at constant pressure that are associated with each stage of the gradual transition from complete order at T = 0 to complete disorder at T = T_lambda.

Although these results were derived in the context of the mixing process for binary solutions, the formulation just provided is of much more general applicability. As an example, consider a ferromagnetic domain in a specimen held at T = 0. All spins are aligned in one specific direction, with spins 'up'. States with spin 'down' do not exist. With rising temperature some spin reversals are encountered; the system has become somewhat disordered. There is a progressive shift of this type with increasing T until, at the Curie temperature, there are an equal number of spins in either alignment; the material has entered the paramagnetic state, with the spins completely disordered. Another illustration is furnished by the adsorption of N atoms of Hg on 2N surface sites of an inert solid. At T = 0 the N Hg atoms are congregated on N adjacent sites as a cluster; the remaining N sites form an empty cluster. With a progressive rise in temperature Hg atoms start to move onto previously empty sites, thereby diminishing the degree of ordering. Beyond a certain characteristic temperature the Hg atoms are randomly distributed, corresponding to complete disordering of the distribution of occupied sites.

These examples suffice to show that a variety of physical situations can be treated by the approach of the present section, namely cases where one encounters an individual state
of a system in one of two possible configurations: A or B, full or empty, up or down, plus or minus, and so on.

These results again follow in a straightforward manner as an inescapable consequence from very modest beginnings: the Margules formulation for activity coefficients in binary solutions. However, as with any elementary approach involving the use of many simplifying assumptions, one cannot expect quantitative agreement with experiment. Rather, the semiquantitative correctness of the theory is an indication that the overall approach taken here is basically sound.

EXERCISES

3.16.1 Provide a physical interpretation for the significance of Fig. 3.16.3 and discuss its correlation with Fig. 3.16.2.

3.16.2 Why is $\Delta H_m$ almost zero at low temperatures (Fig. 3.16.4) and what is the physical significance of the rapid rise in $\Delta H_m$ with $T$ as $T \to T_\lambda$?

3.16.3 Provide graphs analogous to Figs. 3.16.2–3.16.5, which show how the entropy of mixing $\Delta S_m/R$ varies with temperature in the region where the binary phase system is stable.

3.16.4. Estimate the value of $\Delta C_p^m$ as $T \to T_\lambda$ from below: Set $a = 2RT_\lambda$, derive the proper relationship for $\Delta T_m$ from Eq. (3.16.11), using the simplifying assumption that $w$ is constant, then estimate $s_p$ and $ds_p/dT$ and $T_\lambda$ numerically.

3.16.5. Derive a plot showing how the entropy of mixing changes with $T/T_\lambda$. 