

HETEROGENEOUS EQUILIBRIA: VARIABLE COMPOSITION IN CONDENSED PHASES

6.1 GAS PARTIAL PRESSURE AND FUGACITY

TL analysis of equilibrium systems involving gases has thus far been restricted to consideration of ideal gas behavior. Although such behavior does not exist at higher pressures, many gases do approach ideal behavior at pressures less than approximately 5 atmospheres. Hence, the previous equations developed are reliable for the analysis of gaseous systems at low pressures. If a pure gas or gas mixture deviates from ideal behavior, it is referred to as a *nonideal* or *real gas*. Because the behavior of a real gas cannot be described by [1-1], the equation of state is modified. Real gas behavior implies that the relationship between ΔG_i and $\ln(P_i)$, expressed by [5-7], is no longer valid. In order to retain linearity, a new thermodynamic property, *fugacity*, is substituted for pressure into the differential form of [5-7]. The fugacity, f_i , of gas component i is defined by

$$dG_i = VdP = RTd\ln(f_i) \quad [6-1]$$

where $f_i \rightarrow P_i$ as $P_i \rightarrow 0$. With few exceptions, applications discussed in this book involve low pressures, hence $f = P$ and [5-7] is applicable. For typical discussions of gases at elevated pressures, the reader is referred to Hamill et al. (1966, p. 135–139) and Gaskell (1981, p. 188–205).

6.2 THERMODYNAMIC ACTIVITY

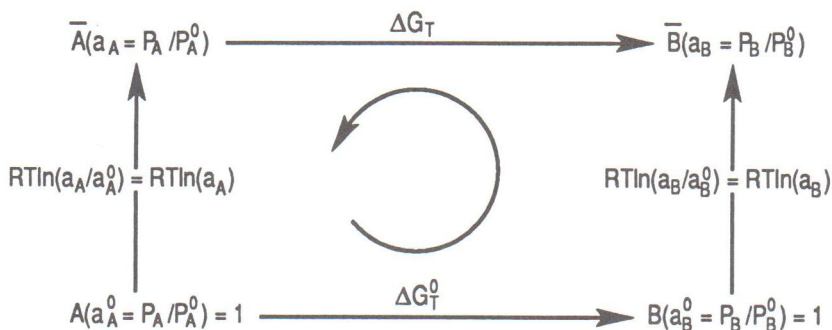
Assuming ideal vapor, the *activity* of a component i is defined by

$$a_i = \frac{f_i}{f_i^0} = \frac{P_i}{P_i^0} \quad [6-2]$$

where P_i is the vapor pressure of i over i in condensed solution and P_i^0 and f_i^0 are the vapor pressure and fugacity, respectively, of i over pure condensed i at the same temperature. Note that P_i^0 is normally defined for i in the same state of aggregation, solid or liquid, as the solution. Substituting [6-2] into [5-5],

$$G_i - G_i^0 = RT \ln(a_i) \quad [6-3]$$

where G_i and G_i^0 are, respectively, the Gibbs free energy of i in condensed solution and the standard state Gibbs free energy of pure condensed i . Note that [6-3] reduces to [5-6] or [5-7] for a mixture of gases only since $P_i^0 = 1.0$ and $a_i = Y_i P_T = P_i$. Incorporating [6-2] into a typical TL involving condensed state components A and B:



where \bar{A} and \bar{B} denote components A and B, respectively, in solution. In addition, a_A^0 and a_B^0 denote the activity of pure A and B respectively. Summing counter-clockwise,

$$\sum \Delta G_{TL} = 0 = \Delta G_T^0 + RT \ln(a_B) - \Delta G_T - RT \ln(a_A)$$

or

$$\Delta G_T = \Delta G_T^0 + RT \ln(a_B/a_A) \quad [6-4]$$

The equilibrium constant follows from [6-4], as will be discussed in Chapter 8.

A review of activity and standard states of gas phases is presented in terms of Systems I and II below. The results are summarized in Figures 6.1 and 6.2 and in Table 6.1.

System I: Gas Insoluble in Condensed Phase

Figure 6.1 characterizes an ideal gas, i , which is insoluble in any condensed phase with which it is in contact. Gas i may be either pure or a component in an ideal gas mixture. Since $P_i^0 = 1$ atm at *any temperature* (Section 5.1), the activity of i from [6-2] is $a_i = P_i/1 = P_i$. Using [5-4], $a_i = P_i/1 = Y_i P_T$. Note that if the total gas pressure in Figure 6.1 is $P_T = 1$ atm, then $a_i = P_i = Y_i$.

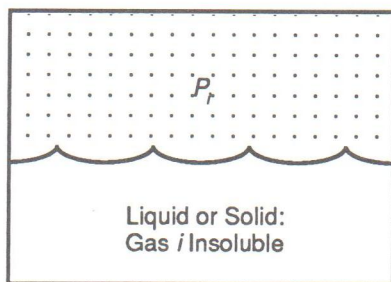


Figure 6.1 Activity of an ideal gas, i , insoluble in the condensed phase. Gas i is either pure or a component in an ideal gas mixture. $P_i^0 = 1$ atm at any temperature, thus $a_i = P_i$

Example Problem 6-1

Sixty moles of an ideal gas mixture at 5 atmospheres pressure contains 15 moles of $S_2(g)$ in contact with microcrystalline quartz, $SiO_2(s)$. If analysis of the quartz reveals that it contains no sulphur impurities, calculate the activity of $S_2(g)$.

Solution

Referring to Table 6.1, $P_{S_2(g)}^0 = 1 \text{ atm}$, since $S_2(g)$ is insoluble in $SiO_2(s)$. Substituting [5-4] into [6-2],

$$a_{S_2(g)} = P_{S_2(g)} / 1 \text{ atm} = Y_{S_2(g)} P_T = (15/60)(5).$$

Hence,

$$a_{S_2(g)} = \underline{1.25}.$$

The reader should note that activity is dimensionless and that $a_{S_2(g)} > 1$.

System II: Vapor Soluble in Condensed Phase

Figure 6.2(a) characterizes a vapor, i , in equilibrium with pure condensed i at temperature T . Since $P_i = P_i^0$, the activity of i in the vapor or condensed state is given by $a_i = P_i^0 / P_i^0 = 1$. It then follows from [5-5] that $\Delta G_i = RT \ln(1) = 0$.

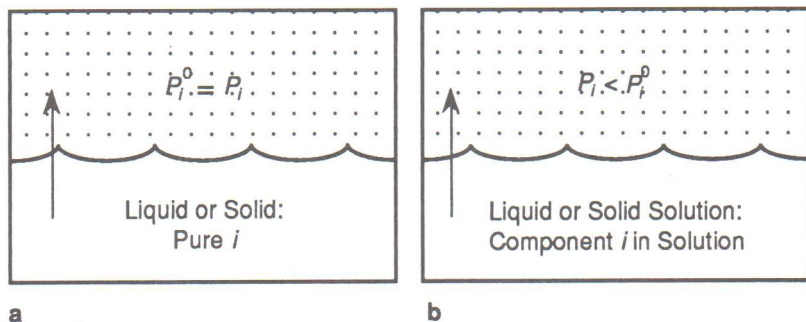


Figure 6.2 Activity of ideal gas component i . (a) Vapor i in equilibrium with pure condensed i at temperature T . (b) Vapor i is soluble in and in equilibrium with a liquid or solid solution which contains i in solution at temperature T .

Figure 6.2(b) characterizes a vapor, i , in equilibrium with component i dissolved in a condensed phase at temperature T . At temperature T , vapor i will exert a pressure less than it would exert if the condensed phase were pure i , hence $P_i < P_i^0$. The activity of i in the vapor, $a_i^v = (P_i / P_i^0)^v$, is equal to the activity of i in the condensed state, hence $a_i^{cond.} = (P_i / P_i^0)^v$. This equality will be formally derived in Section 7.3.

| Table 6.1 Activity in Ideal Gas/Vapor-Condensed Phase Systems | | |
|--|--|--------------------------------------|
| <i>Thermodynamic System</i> | <i>Standard Pressure*</i> | <i>Activity Constant Temperature</i> |
| System I Gas <i>i</i> (pure or in a gas mixture) is insoluble in condensed phase.** | $P_i^0 = 1 \text{ atm}$ (Any Temp.) | $a_i = P_i$ |
| System II Vapor <i>i</i> in equilibrium with pure condensed <i>i</i> . or Vapor <i>i</i> in a gas mixture, <i>i</i> soluble in liquid or solid solution. | $P_i^0 = \text{Vapor Pressure of Pure } i.$ $P_i^0 = \text{Vapor Pressure of Pure } i.$ | $a_i = 1$ $a_i = P_i / P_i^0$ |

* The term vapor pressure refers to the partial pressure exerted by a gas component *i* over a condensed phase containing that component. The term partial pressure refers to a specific component in a gas mixture.

** For gas *i* soluble in condensed phases, see Example Problem 6-9.

Example Problem 6-2

Calculate the activity of zinc in a liquid copper-zinc alloy if the vapor pressure of Zn(g) over the alloy is 1.28 atm at 1060°C. The vapor pressure of Zn(g) over pure liquid zinc is 4 atm at 1060°C (Darken and Gurry, 1953, p. 412).

Solution

Referring to Table 6.1, $a_{\text{Zn}}^l = P_{\text{Zn}(g)} / P_{\text{Zn}(g)}^0$.

Hence, $a_{\text{Zn}}^l = 1.28 \text{ atm} / 4 \text{ atm} = \underline{0.32}$.

Example Problem 6-3

It may be necessary occasionally to convert concentration units to atomic or mole fraction since these are the basic concentration units used in thermodynamic expressions. Develop expressions for the conversion between w/o

and a/o using dimensional consistency. Use m and M to designate mass and molar mass respectively.

Solution

For a binary A-B solution,

$$\begin{aligned}(a/o)_A &= X_A \times 100 = [n_A/(n_A + n_B)] \times 100 \\ &= [m_A/M_A/(m_A/M_A + m_B/M_B)] \times 100.\end{aligned}$$

or

$$(a/o)_A = (w/o|_A / M_A) / (w/o|_A / M_A + w/o|_B / M_B) \times 100 \quad [6-5a]$$

Also,

$$\begin{aligned}(w/o)_A &= [m_A/(m_A + m_B)] \times 100 \\ &= [n_A M_A / (n_A M_A + n_B M_B)] \times 100.\end{aligned}$$

Multiplying numerator and denominator by $100/(n_A + n_B)$ and incorporating $a/o|_A$,

$$(w/o)_A = [(a/o|_A \times M_A) / (a/o|_A \times M_A + a/o|_B \times M_B)] \times 100 \quad [6-5b]$$

6.3 SOLUTIONS AND PARTIAL MOLAR PROPERTIES

A *solution* is a combination of two or more components physically combined so as to form a *homogeneous* mixture. Solution components are elements or compounds that constitute the ingredients of the solution. A *homogeneous solution* is a solid, liquid, or gas that exhibits the same physical and chemical properties throughout. Barring chemical reactions, gas mixtures are always homogeneous. In a binary system, the less abundant component in a solution is referred to as the *solute*, while the more abundant component is referred to as the *solvent*.

The concept of *partial molar property** is best described graphically, using volume. The definitions, based on the graphical representations below, apply to all thermodynamic properties in homogeneous binary A-B systems and may be extended to multicomponent systems. However, such systems are not, in general, discussed in this book. As a result, the designation i for component i will be replaced by an A or B in the binary A-B system. Partial molar properties are listed in SYMBOLS FOR MOLAR PROPERTIES: CHARACTERIZED BY VOLUME.

The relationship between the partial molar properties of binary solution components A and B is illustrated in Figure 6.3. As shown, *ideal* and *nonideal solutions* are characterized by linear and non-linear line segments respectively. Consider a homogeneous material of composition W for which there is complete solubility of A and B in the condensed state. Drawing a tangent line through W , a point on the volume curve for a nonideal solution, and using similar triangles as described by Darken and Gurry (1953, p. 240–241):

* The term *partial molal* property is also used, usually by chemists.

component B, the change in the *partial molar volume of B due to mixing*, \bar{V}_B^m , is

$$\bar{V}_B^m = \bar{V}_B - V_B^0 \quad [6-7]$$

where B is in the *same* state of aggregation (liquid or solid). The magnitude of \bar{V}_B^m is a measure of the *state of non-ideality*, as will be discussed later. Note that if $\bar{V}_B = V_B^0$, then $\bar{V}_B^m = 0$ and the addition of A atoms has *no effect on the molar volume* occupied by B atoms in the solution. \bar{V}_B may alternately be defined by

$$\bar{V}_B = (\partial V' / \partial n_B)_{P,T,n_A} \quad [6-8]$$

where \bar{V}_B reflects the change in the total volume of a binary solution of arbitrary mass when an infinitely small amount of component B is added so that the overall composition of the solution is not altered at constant temperature and pressure. By analogy with [6-8], the following expressions apply for binary systems:

$$\bar{G}_A = (\partial G' / \partial n_A)_{P,T,n_B} \quad [6-9]$$

$$\bar{S}_A = (\partial S' / \partial n_A)_{P,T,n_B} \quad [6-10]$$

$$\bar{H}_A = (\partial H' / \partial n_A)_{P,T,n_B} \quad [6-11]$$

Darken and Gurry (1953, p. 242-243) discussed the validity of equations analogous to [4-8] for partial molar properties at constant composition and temperature. Using

$$\Delta G_A = \Delta H_A - T\Delta S_A \quad [6-12]$$

and substituting $\bar{G}_A^m = \Delta G_A$, $\bar{H}_A^m = \Delta H_A$ and $\bar{S}_A^m = \Delta S_A$ into [6-12],

$$\bar{G}_A^m = \bar{H}_A^m - T\bar{S}_A^m \quad [6-13]$$

It should be noted that nearly all of the relationships used to define pure substances can be used to define solution properties, since they are also thermodynamic properties. Substituting $\bar{G}_A^m = \bar{G}_A - G_A^0$ from [6-7] into [6-3],

$$\bar{G}_A^m = RT \ln(a_A) \quad [6-14]$$

Using the differential $d(1/T) = -dT/T^2$, an equivalent form of [4-30] is used to define the enthalpy term in [6-13]:

$$\bar{H}_A^m = \left[\frac{\partial(\bar{G}_A^m / T)}{\partial(1/T)} \right]_{P,x_A} \quad [6-15]$$

Substituting [6-14] into [6-15],

$$\bar{H}_A^m = R \left[\frac{\partial \ln(a_A)}{\partial(1/T)} \right]_{P,x_A} \quad [6-16]$$

Using an equivalent form of [4-27], the entropy term in [6-13] is defined by

$$\bar{S}_A^m = - \left(\frac{\partial \bar{G}_A^m}{\partial T} \right)_{P, X_A} = -R \left[\frac{\partial \ln(a_A)}{\partial T} \right]_{P, X_A}$$

which expanded gives

$$\bar{S}_A^m = -R \ln(a_A) - RT \left[\frac{\partial \ln(a_A)}{\partial T} \right]_{P, X_A} \quad [6-17]$$

Substituting [6-7] and its equivalent for A into [6-6], the *total or integral molar volume of mixing* is

$$V^m = X_A \bar{V}_A^m + X_B \bar{V}_B^m \quad [6-18]$$

By analogy, the following total molar mixing expressions also apply to binary systems:

$$G^m = X_A \bar{G}_A^m + X_B \bar{G}_B^m \quad [6-19]$$

$$H^m = X_A \bar{H}_A^m + X_B \bar{H}_B^m \quad [6-20]$$

$$S^m = X_A \bar{S}_A^m + X_B \bar{S}_B^m \quad [6-21]$$

Substituting expressions for A and B from [6-14] into [6-19],

$$G^m = RT[X_A \ln(a_A) + X_B \ln(a_B)] \quad [6-22]$$

Using an analogous form of [4-8] as in [6-12],

$$G^m = H^m - TS^m \quad [6-23]$$

There are two aspects of solution behavior that should be considered. First, it is common to identify behavior in terms of a specific component. As will be seen, for example, solutions approach ideal behavior at high solvent concentrations as $X_{\text{Solvent}} \rightarrow 1.0$. Second, enthalpy and entropy contributions expressed by [6-13] and defined in general by [6-16] and [6-17] are evaluated separately. The enthalpy contribution is associated with bond energy whereas the entropy contribution is associated with structure, as discussed in Section 3.5. Expressions for \bar{H}_A^m and \bar{S}_A^m are determined from solution models appropriate for the materials system in question. For some systems, \bar{H}_A^m and \bar{S}_A^m are available directly from the literature. However, a trial and error procedure may be useful to extract \bar{H}_A^m and \bar{S}_A^m from solubility data or phase diagrams. Three solution models will now be introduced for use in this and subsequent chapters. Note that the superscript "id" is used to designate an *ideal* solution property.

6.4 SOLUTION MODELS

(1) Ideal Solution: Raoult's Law

Ideal solutions are mixtures in which the bond energy between unlike pairs of atoms is the average of bond energies between like pairs. The ideal solution model is rarely observed in condensed systems over an entire compositional range, hence, an important function of this model is to serve as a reference with which to compare nonideal behavior. These comparisons are

normally expressed quantitatively as *excess thermodynamic properties* and are discussed in Section 6.5.

Ideal or Raoultian solution behavior is stated in terms of *Raoult's law*: the vapor pressure exerted by a dissolved component A, P_A , in a homogeneous condensed solution is equal to the product of the atomic fraction of A in the solution, X_A , and the vapor pressure of pure A, P_A^0 , at the temperature of the solution. Hence,

$$P_A = X_A P_A^0 \quad [6-24]$$

Substituting [6-24] into [6-2],

$$a_A = X_A \quad [6-25]$$

[6-25] is an *alternate form of Raoult's law* and is illustrated for an ideal A-B solution in Figure 6.4. The line labeled A_{Ideal} is a plot of a_A versus X_A , and the line labeled B_{Ideal} is a plot of a_B versus X_B . Note that the slope of each line is $a/X = 1$, in accordance with [6-25].

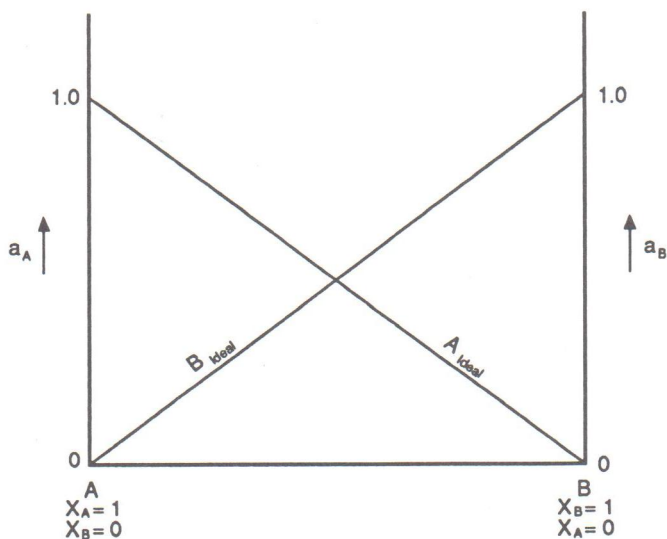


Figure 6.4 Ideal binary A-B solution defined according to Raoult's law, $a_A = X_A$. Solution components A and B are represented by the lines labeled A_{Ideal} and B_{Ideal} respectively. The slopes of these lines are $a_A/X_A = a_B/X_B = 1.0$.

Substituting [6-25] into [6-14],

$$\bar{G}_A^m = RT \ln(X_A) \quad [6-26]$$

Substituting [6-25] into [6-16],

$$\bar{H}_A^m = R \left[\frac{\partial \ln(X_A)}{\partial (1/T)} \right]_{P, X_A} \quad 0$$

or

$$\bar{H}_A^m = 0 \quad [6-27]$$

Substituting [6-25] into [6-17],

$$\bar{S}_A^m = -R \ln(X_A) - RT \left[\frac{\partial \ln(X_A)}{\partial T} \right]_{P, X_A} \quad 0$$

or

$$\bar{S}_A^m = -R \ln(X_A) \quad [6-28]$$

Substituting expressions for both A and B from [6-26], [6-27], and [6-28] into [6-19], [6-20], and [6-21] respectively,

$$G^m = RT[X_A \ln(X_A) + X_B \ln(X_B)] \quad [6-29]$$

$$H^m = 0 \quad [6-30]$$

$$S^m = -R[X_A \ln(X_A) + X_B \ln(X_B)] \quad [6-31]$$

A graphical concept of ideality is illustrated in Figure 6.3. If the binary A-B solution of composition W shown were ideal, the curve $E'W-D'$ would be linear and would follow the trace of the tangent line through $W, E-W-D$. Note that in such a case, $\bar{V}_A^m = \bar{V}_B^m = 0$.

Example Problem 6-4

Consider a solid solution of components A and B. Assume both components behave ideally. Plot Gibbs partial molar free energy of mixing for both components as well as the total molar free energy of mixing versus mole fraction. Show maxima, minima, and slopes at critical points.

Solution

\bar{G}_A^m and \bar{G}_B^m :

At $X_A = 1$ and $X_B = 0$ and from [6-26]:

$$\bar{G}_A^m = RT \ln(X_A) = RT \ln(1) = 0,$$

$$\frac{d\bar{G}_A^m}{dX_A} = \frac{d[RT \ln(X_A)]}{dX_A} = \frac{RT}{X_A} = \frac{RT}{1} = \text{finite slope};$$

$$\bar{G}_B^m = RT \ln(X_B) = RT \ln(0) = -\infty.$$

At $X_B = 1$ and $X_A = 0$:

$$\bar{G}_B^m = RT \ln(1) = 0,$$

$$\frac{d\bar{G}_B^m}{dX_B} = \frac{d[RT \ln(X_B)]}{dX_B} = \frac{RT}{X_B} = \frac{RT}{1} = \text{finite slope};$$

$$\bar{G}_A^m = RT \ln(0) = -\infty.$$

The limiting slopes are approximated on Figure 6.5.

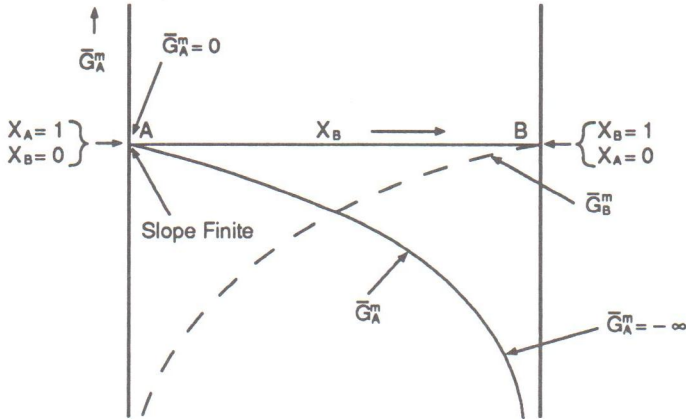


Figure 6.5 \bar{G}_A^m and \bar{G}_B^m versus X_A and X_B , respectively, for a homogeneous ideal binary A-B solution.

G^m :

At $X_A = 1$ and $X_B = 0$ and from [6-29]:

$$G^m = RT[X_A \ln(X_A) + X_B \ln(X_B)] = RT[(1)\ln(1) + 0 \ln(0)] = 0 \ln(0).$$

Since $0 \cdot \ln(0) = 0 \cdot (-\infty)$ is indeterminate, L'Hopital's rule (Protter and Morrey, 1970, p. 632-635) is used to evaluate G^m :

$$\text{Let } Y = \frac{G^m}{RT} = X_B \ln(X_B) = \frac{\ln(X_B)}{1/X_B} = \frac{f(X_B)}{F(X_B)}$$

where $f(X_B) = \ln(X_B)$ and $F(X_B) = 1/X_B$. Then

$$\lim_{X_B \rightarrow 0} \frac{f(X_B)}{F(X_B)} = \lim_{X_B \rightarrow 0} \frac{f'(X_B)}{F'(X_B)} = \lim_{X_B \rightarrow 0} \frac{(1/X_B)}{(-1/X_B^2)} = \lim_{X_B \rightarrow 0} (-X_B) = 0.$$

Consequently, at $X_B = 0$, $G^m = 0 \cdot \ln(0) = 0$. Taking the derivative of [6-29],

$$\frac{dG^m}{dX_A} = RT[\ln(X_A) - \ln(X_B)] = RT[\ln(1) - \ln(0)] = \infty.$$

At $X_B = 1$ and $X_A = 0$:

The calculations are analogous to those immediately above:

$$G^m = 0 \text{ and } dG^m/dX_B = -\infty.$$

The limiting slopes are approximated on Figure 6.6.

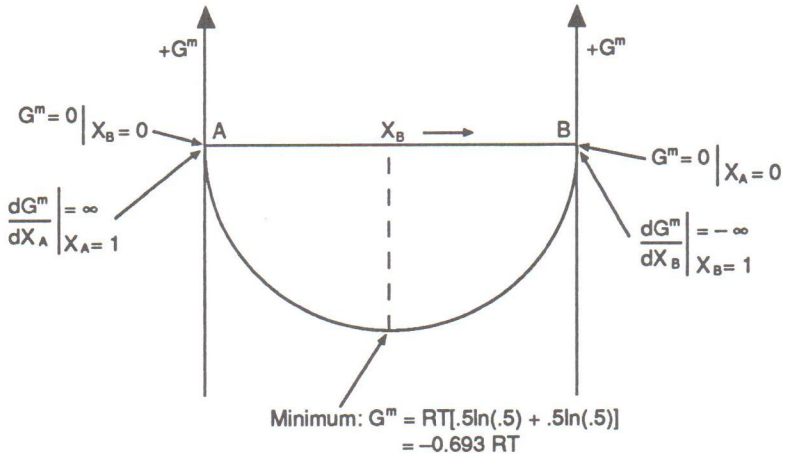


Figure 6.6 G^m versus X_A and X_B for a homogeneous ideal binary A-B solution.

(2) Nonideal Solutions

Nonideal solutions are mixtures in which the attraction between like pairs of atoms is greater than the attraction between unlike pairs (*positive deviation from ideality*) or less than the attraction between unlike pairs (*negative deviation from ideality*). The arrangement of atoms may or may not be random and substitutional. Non-ideality is introduced into [6-25] by inserting the thermodynamic *activity coefficient*, γ , into the expression. Hence, [6-25] becomes

$$a_A = \gamma_A X_A \quad [6-32]$$

For ideal solutions, $\gamma_A = 1.0$. In general, γ_A is a function of both temperature and composition, hence

$$[\partial \ln(a_A) / \partial T]_{P, X_A} \neq 0.$$

For $\gamma_A = (\text{constant})$,

$$[\partial \ln(a_A) / \partial T]_{P, X_A} = 0.$$

(a) *Henrian Solution Model:*

The *Henrian solution model* applies to mixtures in which a solute, A, is at low concentration, usually $X_A < 1$ a/o. The distance between solute atoms at such concentrations is large, hence thermodynamic properties are additive and in direct proportion to solute concentration. At low solute concentrations, solute behavior in a dilute solution is expressed by *Henry's Law*:

$$X_A = k_A P_A \quad [6-33]$$

where X_A and P_A have the usual meaning and k_A is a temperature dependent constant. Substituting [6-32] and [6-33] into [6-2],

$$\gamma_A = \frac{1}{(P_A^0 k_A)} = b \text{ (constant).}$$

Substituting into [6-32],

$$a_A = bX_A \quad [6-34]$$

(b) *Dilute Solution Model-Modified Henrian Solution:*

The *dilute solution model* is essentially identical to the Henrian model and applies to low concentration solutes. The difference relates to how the non-ideality, γ_A , is expressed. For example, substituting [6-34] into [6-14],

$$\bar{G}_A^m = RT \ln(bX_A).$$

Substituting this expression into [6-15] and [6-17],

$$\bar{H}_A^m = \left[\frac{\partial RT \ln(bX_A)}{\partial(1/T)} \right]_{P, X_A} = 0;$$

$$\bar{S}_A^m = -R \ln(bX_A) - RT \left[\frac{\partial \ln(bX_A)}{\partial T} \right]_{P, X_A}$$

$$\begin{aligned} &= -R \ln(b) - R \ln(X_A) \\ &= (\text{constant}) - R \ln(X_A). \end{aligned}$$

From the above analysis, it is observed that non-ideality, according to Henry's law, is identified only with the entropy term since enthalpy is zero. Kubaschewski and Alcock (1979, p. 47) comment on the increased accuracy that is achieved when non-ideality is distributed between both enthalpy and entropy terms. Parameters incorporating both terms define the dilute solution model.

The enthalpy and entropy contributions of solute A in the dilute solution model (personal communication, 1959, R. Schuhmann, Jr., Department of Metallurgical Engineering, Purdue University, West Lafayette, Indiana) are described by

$$\bar{H}_A^m = h (\text{constant}) \quad [6-35]$$

$$\bar{S}_A^m = s (\text{constant}) - R \ln(X_A) \quad [6-36]$$

Substituting [6-35] and [6-36] into [6-13],

$$\begin{aligned} \bar{G}_A^m &= h - T[s - R \ln(X_A)] \\ &= RT \ln(X_A) + h - Ts \end{aligned} \quad [6-37]$$

Inserting [6-32] into [6-14] and comparing with [6-37] term by term, $RT \ln(\gamma_A) = h - Ts$. Solving for γ_A ,

$$\gamma_A = b = \exp\left(\frac{h - Ts}{RT}\right) \quad [6-38]$$

where b is constant at constant temperature. The Henrian and modified Henrian (dilute) solution models are summarized in Table 6.2.

Table 6.2 Henrian and Modified Henrian (Dilute) Solution Models*

| Solution Model | \bar{H}_A^m | \bar{S}_A^m |
|---------------------------------------|---------------|------------------|
| Henrian Solution | 0 | $s - R \ln(X_A)$ |
| Dilute Solution (Modified Henrian) | h | $s - R \ln(X_A)$ |

* h and s are temperature dependent constants but over small temperature intervals may be assumed constant, as in Chapter 7.

Where specific interest is focused at a low concentration to one component, it is convenient to introduce an alternative to the pure component standard state. This alternative defines b such that $b \rightarrow 1.0$ at infinite dilution. For the purposes of this book, the pure component standard state will be used in all calculations.

(3) Regular Solution Model

Regular solutions are comprised of components at intermediate concentrations. Interactions between like and unlike atoms vary with solution composition, hence, γ_i is *variable* with X_i . An example of a regular solution is a binary A-B substitutional solid solution with random arrangement of A and B atoms on A and B sites.

The *quasi-chemical theory* (Swalin, 1964, p. 109-116) relates chemical effects to energetics rather than mechanical or valence effects and demonstrates that the enthalpy associated with a regular solution is *nonideal*. Vibrational effects are unchanged during the solution process, hence, entropy is *ideal*. The *nonideal* partial molar enthalpy of mixing for a binary A-B solution component A is

$$\bar{H}_A^m = \Omega(1 - X_A)^2 \quad [6-39]$$

where

$$\Omega = zN_{AV}[h_{AB} - (h_{AA} + h_{BB})/2] \quad [6-40]$$

z is the number of bonds (coordination number) per atom and N_{AV} is Avogadro's number. The enthalpies per A-A, B-B, and A-B bond are designated h_{AA} , h_{BB} , and h_{AB} respectively. Ω is *constant and independent of temperature*. Substituting [6-39] into [6-20],

$$H^m = \Omega X_A(1 - X_A)^2 + \Omega X_B(1 - X_B)^2.$$

Since $(1 - X_A) = X_B$ and $(1 - X_B) = X_A$,

$$H^m = \Omega X_A X_B^2 + \Omega X_B X_A^2$$

or

$$H^m = \Omega X_A X_B \quad [6-41]$$

Since a regular solution is ideal with respect to entropy,

$$\bar{S}_A^m = -R \ln(X_A) \quad [6-42]$$

Substituting [6-39] and [6-42] into [6-13],

$$\bar{G}_A^m = \Omega(1 - X_A)^2 + RT \ln(X_A) \quad [6-43]$$

Consider now a plot of H^m versus composition according to [6-41] and shown in Figure 6.7. If $\Omega > 0$, $H^m > 0$, mixing is endothermic, the solution exhibits a positive deviation from ideality, and like pairs of atoms attract. If $\Omega = 0$, the solution is ideal. If $\Omega < 0$, $H^m < 0$, mixing is exothermic, the solution exhibits a negative deviation from ideality, and unlike pairs of atoms attract. For further reading refer to DeHoff (1993, p. 196-203) and Gaskell (1981, p. 366-373).

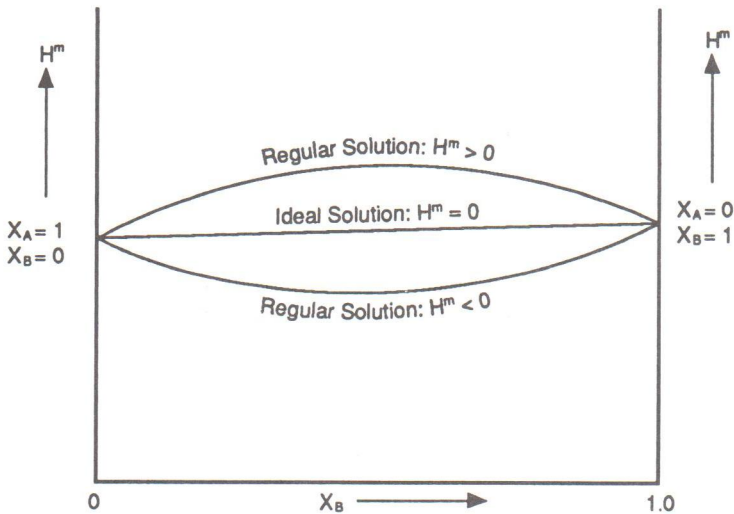


Figure 6.7 Positive ($H^m > 0$) and negative ($H^m < 0$) departures from ideality ($H^m = 0$) for ideal and regular binary A-B solutions. Note that positive and negative deviations apply in general to all nonideal solutions.

6.5 EXCESS THERMODYNAMIC PROPERTIES AND ALTERNATE SOLUTION MODELS

The difference between a nonideal and ideal thermodynamic property is defined as an *excess* of that property. Excess properties, sometimes referred to as *residuals*, are point functions and can be treated as exact differentials. There are occasions in which excess properties are easier to analyze mathematically than the properties themselves. Superscript "XS" is used to designate an excess property. Hence, for component A,

$$\bar{G}_A^{XS} = \bar{G}_A^m - \bar{G}_A^{m,id} \quad [6-44]$$

$$\bar{H}_A^{XS} = \bar{H}_A^m - \bar{H}_A^{m,id} \quad [6-45]$$

$$\bar{S}_A^{XS} = \bar{S}_A^m - \bar{S}_A^{m,id} \quad [6-46]$$

where superscript "id" refers to the ideal solution. Using an analogous form of [4-8] as in [6-12],

$$\bar{G}_A^{XS} = \bar{H}_A^{XS} - T\bar{S}_A^{XS} \quad [6-47]$$

Substituting [6-32] and [6-25] into [6-44],

$$\bar{G}_A^{XS} = RT \ln(\gamma_A) + RT \ln(X_A) - RT \ln(X_A)$$

or

$$\bar{G}_A^{XS} = RT \ln(\gamma_A) \quad [6-48]$$

Additional relationships can now be developed for each of the solution models discussed.

(1) Ideal Solution ($\gamma_A = 1$)

From [6-26] and [6-44] or from [6-48],

$$\bar{G}_A^{XS} = RT \ln(X_A) - RT \ln(X_A) = RT \ln(1) = 0.$$

Substituting [6-27] into [6-45] and [6-28] into [6-46],

$$\bar{H}_A^{XS} = 0;$$

$$\bar{S}_A^{XS} = 0.$$

In general, any excess thermodynamic property for a solution component exhibiting ideal behavior is zero.

(2) Dilute Solution (γ_A is constant $\neq 1$)

Substituting [6-26] and [6-37] into [6-44] and comparing the result with [6-47],

$$\bar{H}_A^{XS} = h;$$

$$\bar{S}_A^{XS} = s.$$

(3) Regular Solution (γ_A is variable)

Substituting [6-26], [6-43], and [6-48] into [6-44],

$$\begin{aligned} \bar{G}_A^{XS} &= \Omega(1 - X_A)^2 + RT \ln(X_A) - RT \ln(X_A) = \Omega(1 - X_A)^2 = RT \ln(\gamma_A); \\ \gamma_A &= \exp[\Omega(1 - X_A)^2/RT] \end{aligned} \quad [6-49]$$

Note that if Ω is positive, $\gamma_A > 1$ and like pairs of atoms attract. If Ω is negative, $\gamma_A < 1$ and unlike pairs attract.

(4) Alternate Solution Models

In this book, ideal, dilute, and regular solution models are applied analytically. Variations in these models incorporate excess entropy. Two alternate models are introduced here but are not used in any problem solutions.

(a) Athermal Solution:

These solutions are characterized by large size differences between component atoms. Solutions containing Fe and Na approach this type of behavior, as noted by Johnson (1964). Internal energy in athermal solutions is governed

almost entirely by excess entropy. Hence, the following expressions define enthalpy and entropy contributions:

$$\begin{aligned}\bar{H}_A^{XS} &= 0; \\ \bar{S}_A^{XS} &= s \text{ (constant)}\end{aligned}$$

or

$$\bar{S}_A^{XS} = \delta(1 - X_A)^2$$

where δ is constant.

Combining [6-13], [6-45], and [6-46] and substituting for \bar{S}_A^{XS} ,

$$\bar{G}_A^m = T[R \ln(X_A) - \delta(1 - X_A)^2] \quad [6-50]$$

(b) *Subregular Solutions:*

Internal energy is governed by both size and chemical bond effects, hence characteristics of both athermal and regular solutions are incorporated into the model. The following expressions define enthalpy and entropy contributions where Ω and ω are constants. Substituting as above,

$$\begin{aligned}\bar{H}_A^{XS} &= \Omega(1 - X_A)^2; \\ \bar{S}_A^{XS} &= \omega(1 - X_A)^2.\end{aligned}$$

The Gibbs partial molar free energy of mixing of A becomes

$$\bar{G}_A^m = \Omega(1 - X_A)^2 - T[\omega(1 - X_A)^2 - R \ln(X_A)] \quad [6-51]$$

6.6 TL ANALYSIS OF SOLUTIONS IN HETEROGENEOUS REACTIONS

Example Problem 6-5

The following enthalpy data are given for Au-Cu alloys at a temperature of 500°C (Swalin, 1964, p. 329). H^m is in cal/mol.

| X_{Cu} | 0.1 | 0.2 | 0.3 | 0.4 | 0.5 | 0.6 | 0.7 | 0.8 | 0.9 |
|----------|------|------|------|-------|-------|-------|-------|------|------|
| H^m | -355 | -655 | -910 | -1120 | -1280 | -1240 | -1130 | -860 | -460 |

(a) Examine the data and identify the solution model most appropriate for this system.

Solution

The solution is not ideal in the range of compositions given since $H^m \neq 0$. Because of the wide range of compositions for X_{Cu} , the data is best analyzed using the regular solution model.

(b) Find expressions for H^m and \bar{H}_{Cu}^m .

Solution

Using [6-41], values of Ω are computed at each composition. The results are recorded in the table below:

| | | | | | | | | | |
|------------------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| X_{Cu} | 0.1 | 0.2 | 0.3 | 0.4 | 0.5 | 0.6 | 0.7 | 0.8 | 0.9 |
| X_{Au} | 0.9 | 0.8 | 0.7 | 0.6 | 0.5 | 0.4 | 0.3 | 0.2 | 0.1 |
| $X_{\text{Cu}}X_{\text{Au}}$ | 0.09 | 0.16 | 0.21 | 0.24 | 0.25 | 0.24 | 0.21 | 0.16 | 0.09 |
| H^m | -355 | -655 | -910 | -1120 | -1280 | -1240 | -1130 | -860 | -460 |
| Ω | -3944 | -4094 | -4333 | -4667 | -5120 | -5167 | -5381 | -5375 | -5111 |

Rigorous application of [6-41] would require that Ω remain constant. A random variation would be acceptable for engineering applications. Noting that Ω increases to $X_{\text{Cu}} = 0.7$ and then decreases, assume an average $\Omega = -4800$ cal/mol \times (4.184 J/cal) = -20,083 J/mol. Hence, from [6-41],

$$\begin{aligned} H^m &= -4800 X_{\text{Cu}}X_{\text{Au}} \text{ cal/mol} \\ &= \underline{-20,083 X_{\text{Cu}}X_{\text{Au}} \text{ J/mol.}} \end{aligned}$$

From [6-39],

$$\begin{aligned} \bar{H}_{\text{Cu}}^m &= -4800(1 - X_{\text{Cu}})^2 \text{ cal/mol} \\ &= \underline{-20,083(1 - X_{\text{Cu}})^2 \text{ J/mol.}} \end{aligned}$$

(c) Determine G^m at $X_{\text{Cu}} = 0.45$.

Solution

Using [6-41],

$$\begin{aligned} H^m &= -20,083 X_{\text{Cu}}X_{\text{Au}} = -20,083 \times 0.45 \times 0.55 \\ &= -4971 \text{ J/mol.} \end{aligned}$$

Substituting [6-42] for both components into [6-21],

$$\begin{aligned} S^m &= -R[X_A \ln(X_A) + X_B \ln(X_B)] & [6-52] \\ S^m &= -8.3144[0.45 \ln(0.45) + 0.55 \ln(0.55)] = 5.72 \text{ J/(mol}\cdot\text{K).} \\ G^m &= -4971 - (773)(5.72) \Rightarrow G^m = \underline{-9393 \text{ J/mol.}} \end{aligned}$$

(d) Determine the activity coefficient of Cu, γ_{Cu} , at $X_{\text{Cu}} = 0.45$.

Solution

From [6-49],

$$\gamma_{\text{Cu}} = \exp[-20,083(1 - 0.45)^2/8.3144 \times 773] \Rightarrow \gamma_{\text{Cu}} = \underline{0.389}.$$

(e) Find the partial pressure of Cu, P_{Cu} , at $X_{\text{Cu}} = 0.45$.

Solution

From [6-2] and [6-32],

$$a_{\text{Cu}} = P_{\text{Cu}}/P_{\text{Cu}}^0 = \gamma_{\text{Cu}}X_{\text{Cu}} \Rightarrow P_{\text{Cu}} = P_{\text{Cu}}^0 \gamma_{\text{Cu}}X_{\text{Cu}}.$$

Hence,

$$P_{\text{Cu}} = 0.389 \times 0.45 P_{\text{Cu}}^0 = 0.175 P_{\text{Cu}}^0.$$

From Appendix A, Table A.5,

$$\begin{aligned} \log_{10}[P_{\text{Cu}(s)}^0 (\text{mm Hg})] &= (-17,770/773) - 0.86 \log_{10}(773) + 12.29 \\ &= -13.182 \Rightarrow P_{\text{Cu}}^0 = 6.58 \times 10^{-14} \text{ mm Hg.} \end{aligned}$$

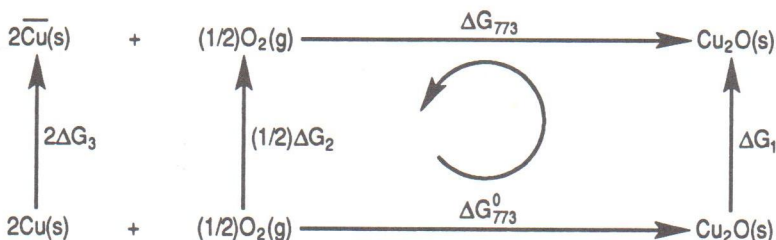
Therefore,

$$\begin{aligned} P_{\text{Cu}} &= 0.175 \times 6.58 \times 10^{-14} \\ &= \underline{1.15 \times 10^{-14} \text{ mmHg.}} \end{aligned}$$

(f) Calculate the $P_{\text{O}_2(g)}$ in equilibrium with the Cu-Au alloy for $X_{\text{Cu}} = 0.45$ at 500°C . Assume $a_{\text{Cu}_2\text{O}(s)} = 1.0$ [pure cuprite, $\text{Cu}_2\text{O}(s)$].

Solution

(1) **Set Up.** A horizontal line above a condensed phase is used to indicate that the component is in solution.



(2) **Sum.**

$$\sum \Delta G_{\text{TL}} = 0 = \Delta G_{773}^0 + \Delta G_1 - \Delta G_{773} - (1/2)\Delta G_2 - 2\Delta G_3.$$

(3) **Substitute.**

$\Delta G_1 = RT \ln(1) = 0$ and $\Delta G_{773} = 0$ at equilibrium.

From Table A.4,

$$\Delta G_T^0 = -169,470 - 16.40T \log(T) + 123.44(T) \text{ from } 298 \text{ to } 1356 \text{ K} \Rightarrow$$

$$\Delta G_{773}^0 = -169,470 - 16.40(773)\log(773) + 123.44(773)$$

$$= -110,665 \text{ J/mol.}$$

$$(1/2)\Delta G_2 = (1/2)RT \ln(P_{\text{O}_2}).$$

$$2\Delta G_3 = 2\bar{G}_{\text{Cu}}^m = 2RT \ln(a_{\text{Cu}}) = 2(8.3144)(773)\ln(0.389 \times 0.45)$$

$$= -22,401 \text{ J/mol.}$$

Substituting the above data into $\sum \Delta G_{\text{TL}} = 0$,

$$0 = -110,665 - (1/2)RT \ln(P_{\text{O}_2}) - (-22,401).$$

(4) **Solve.**

$$(1/2)RT \ln(P_{\text{O}_2}) = -110,665 + 22,401 = -88,264.$$

$$\ln(P_{\text{O}_2}) = 2(-88,264)/(8.3144 \times 773) \Rightarrow$$

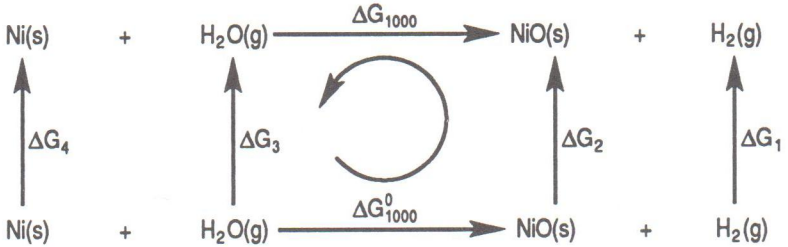
$$P_{\text{O}_2(g)} = \underline{1.18 \times 10^{-12} \text{ atm.}}$$

Example Problem 6-6

(a) Will a gas mixture containing 97 v/o H₂O vapor and 3 v/o H₂(g) deoxidize nickel oxide over pure nickel at 1000 K? Assume P_T = 1 atm (Darken and Gurry, 1953, p. 513).

Solution

(1) Set Up.



(2) Sum.

$$\sum \Delta G_{\text{TL}} = 0 = \Delta G_{1000}^0 + \Delta G_1 + \Delta G_2 - \Delta G_{1000} - \Delta G_3 - \Delta G_4.$$

(3) Substitute. From [4-9],

$$\Delta G_{1000}^0 = \sum n \Delta G_{1000}^0(\text{Products}) - \sum n \Delta G_{1000}^0(\text{Reactants}).$$

$$\Delta G_{1000}^0 = \Delta G_{1000}^0, \text{NiO(s)} - \Delta G_{1000}^0, \text{H}_2\text{O(g)}. \text{ From Table A.4,}$$

$$\Delta G_{1000}^0 = -244,580 + 98.54(1000) - [-246,460 + 54.82(1000)] = 45,600 \text{ J/mol.}$$

$$\Delta G_1 = RT \ln(P_{\text{H}_2}) = 8.3144(1000) \ln(P_{\text{H}_2}) = 8314.4 \ln(P_{\text{H}_2}).$$

$$\text{From [5-4], } P_{\text{H}_2} = Y_{\text{H}_2} P_T = 0.03(1 \text{ atm}) = 0.03 \text{ atm.}$$

$$\text{Hence, } \Delta G_1 = 8314.4 \ln(0.03).$$

$$\Delta G_2 = RT \ln(1) = 0.$$

$$\Delta G_3 = RT \ln(P_{\text{H}_2\text{O}}) = 8.3144(1000) \ln(P_{\text{H}_2\text{O}}) = 8314.4 \ln(P_{\text{H}_2\text{O}}).$$

$$\text{From [5-4], } P_{\text{H}_2\text{O}} = 0.97(1 \text{ atm}) = 0.97 \text{ atm. Hence,}$$

$$\Delta G_3 = 8314.4 \ln(0.97).$$

$$\Delta G_4 = \bar{G}_{\text{Ni}}^m = 0 \text{ (pure solid).}$$

$$\text{Substituting the above data into } \sum \Delta G_{\text{TL}} = 0,$$

$$0 = 45,600 + 8314.4 \ln(0.03) - \Delta G_{1000} - 8314.4 \ln(0.97).$$

(4) Solve.

$$\Delta G_{1000} = 45,600 + 8314.4 \ln(0.03/0.97) = 16,698 \text{ J/mol.}$$

Since $\Delta G_{1000} > 0$, NiO(s) will tend to deoxidize.

Figure 6.8, a simplified portion of Figure E.2, can be used to confirm that the reaction will be deoxidizing. From the nomograph, $P_{\text{H}_2}/P_{\text{H}_2\text{O}} \approx 10^{-2} = 0.02$. Since the actual ratio $P_{\text{H}_2}/P_{\text{H}_2\text{O}} = 0.03/0.97 = 0.031$, the reaction will tend to shift from right to left.

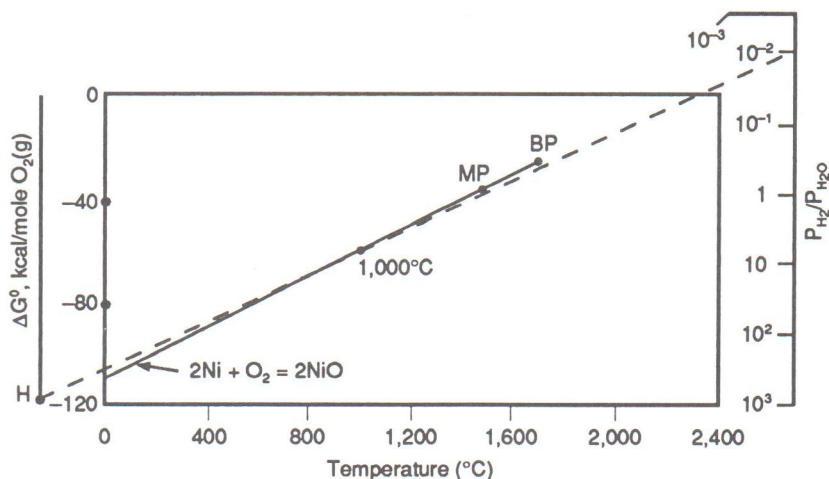
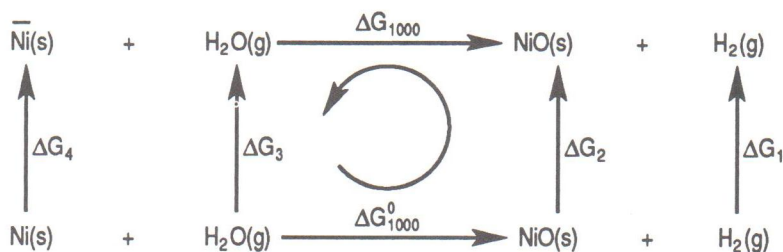


Figure 6.8 Ellingham diagram for Ni oxidation. ΔG^0 versus T ($^{\circ}\text{C}$) is shown by the solid line. M.P. and B.P. represent the melting and boiling points of Ni(s) respectively. The dashed line, drawn from point H on the vertical line at the left side of the diagram through the 1000°C point to the vertical scale at the right, graphically determines the $P_{\text{H}_2}/P_{\text{H}_2\text{O}}$ ratio. The result is $P_{\text{H}_2}/P_{\text{H}_2\text{O}} \approx 10^{-2}$.

- (b) An alloy contains 20 a/o Ni and 80 a/o Au in solid solution at 1000 K. This alloy reacts with water vapor to form NiO(s). Experimental measurement indicates the reaction reaches equilibrium when the H_2O - H_2 mixture contains 0.35 v/o H_2 . Find the activity coefficient of Ni in the alloy. Assume NiO(s) is pure oxide. How does alloying affect the result obtained in part (a)?

Solution

(1) Set Up.



(2) Sum.

$$\sum \Delta G_{\text{TL}} = 0 = \Delta G_{1000}^0 + \Delta G_1 + \Delta G_2 - \Delta G_{1000} - \Delta G_3 - \Delta G_4.$$

(3) Substitute.

$$\Delta G_{1000}^0 = 45,600 \text{ J/mol, from part (a) above.}$$

$$\Delta G_1 = RT \ln(P_{H_2}) = 8.3144(1000) \ln(0.0035).$$

$$\Delta G_2 = RT \ln(1) = \Delta G_{1000} \text{ (equilibrium)} = 0.$$

$$\Delta G_3 = RT \ln(P_{H_2O}) = 8.3144(1000) \ln(1 - 0.0035).$$

$$\Delta G_4 = \bar{G}_{Ni}^m = RT \ln(a_{Ni}) = 8.3144(1000) \ln(a_{Ni}).$$

$$\text{Substituting the above data into } \Sigma \Delta G_{TL} = 0,$$

$$0 = 45,600 + 8314.4 \ln(0.0035) - 8314.4 \ln(0.9965) - 8314.4 \ln(a_{Ni}).$$

(4) Solve.

$$a_{Ni} = 0.846 = \gamma_{Ni} X_{Ni} \Rightarrow \gamma_{Ni} = 0.846/0.2 = 4.23.$$

If the effect of alloying is incorporated into part (a),

$$\Delta G_4 = \bar{G}_{Ni}^m = 8.3144(1000) \ln(0.846).$$

Therefore,

$$\Sigma \Delta G_{TL} = 0 = 45,600 + 8314.4 \ln(0.03/0.97) + 1390 - \Delta G_{1000}$$

or

$$\Delta G_{1000} = 18,088 \text{ J/mol.}$$

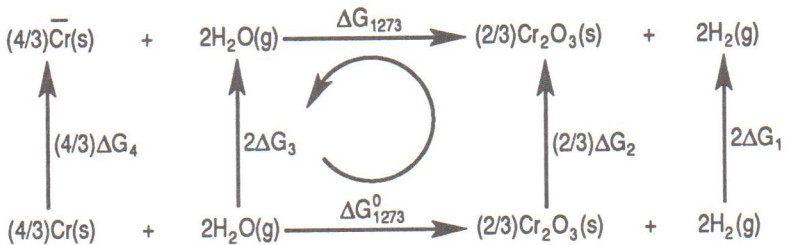
The tendency to deoxidize is increased when Ni is in solid solution with Au since ΔG_{1000} increases.

Example Problem 6-7

Repeat Example Problem 5-2 for the case where Cr forms a 15 a/o solid solution with a metal, M. Assume Cr is more readily oxidized than M and that Cr_2O_3 is insoluble in solution. Assume an ideal Cr-M solid solution. (Darken and Gurry, 1953, p. 513).

Solution

(1) Set Up.



(2) Sum.

$$\Sigma \Delta G_{TL} = 0 = \Delta G_{1273}^0 + 2\Delta G_1 + (2/3)\Delta G_2 - \Delta G_{1273} - 2\Delta G_3 - (4/3)\Delta G_4.$$

(3) Substitute.

$$\Delta G_{1273}^0 = -173,039 \text{ J, from Example Problem 5-2.}$$

$$\Delta G_{1273} = 0 \text{ at equilibrium.}$$

$$2\Delta G_1 = 2R(1273)\ln(P_{\text{H}_2}) \text{ and } 2\Delta G_3 = 2R(1273)\ln(P_{\text{H}_2\text{O}}).$$

$$2/3\Delta G_2 = 2/3RT \ln(1) = 0.$$

$$4/3\Delta G_4 = 4/3\bar{G}_{\text{Cr}}^m = 4/3R(1273)\ln(X_{\text{Cr}}) = 4/3R(1273)\ln(0.15).$$

Substituting the above data into $\sum \Delta G_{\text{TL}} = 0$,

$$0 = -173,039 + 2(8.3144)(1273)\ln(P_{\text{H}_2}) - 2(8.3144)(1273)\ln(P_{\text{H}_2\text{O}}) - 4/3(8.3144)(1273)\ln(0.15).$$

(4) Solve.

$$P_{\text{H}_2} / P_{\text{H}_2\text{O}} = \underline{1002}.$$

Comparing this result with that of Example Problem 5-2 for which $P_{\text{H}_2} / P_{\text{H}_2\text{O}} = 3.55 \times 10^3$, alloying reduces the ratio of partial pressures by a factor of nearly 3.5.

6.7 THE GIBBS-DUHEM EQUATION

For a binary A-B solution at constant pressure and temperature,

$$G' = f(n_A, n_B)$$

where n_A and n_B are the number of moles of components A and B respectively. Applying the chain rule and [6-9],

$$dG' = \left(\frac{\partial G'}{\partial n_A} \right)_{P,T,n_B} dn_A + \left(\frac{\partial G'}{\partial n_B} \right)_{P,T,n_A} dn_B$$

or

$$dG' = \bar{G}_A dn_A + \bar{G}_B dn_B \quad [6-53]$$

Replacing V in [6-6] with G and multiplying through by $(n_A + n_B)$,

$$G(n_A + n_B) = X_A(n_A + n_B)\bar{G}_A + X_B(n_A + n_B)\bar{G}_B$$

or

$$G' = \frac{n_A}{(n_A + n_B)}(n_A + n_B)\bar{G}_A + \frac{n_B}{(n_A + n_B)}(n_A + n_B)\bar{G}_B.$$

Hence,

$$G' = n_A \bar{G}_A + n_B \bar{G}_B.$$

Taking the total derivative of this expression,

$$dG' = n_A d\bar{G}_A + \bar{G}_A dn_A + n_B d\bar{G}_B + \bar{G}_B dn_B \quad [6-54]$$

Equating [6-53] and [6-54],

$$n_A d\bar{G}_A + n_B d\bar{G}_B = 0 \quad [6-55]$$

Dividing [6-55] by $(n_A + n_B)$,

$$X_A d\bar{G}_A + X_B d\bar{G}_B = 0 \quad [6-56]$$

Similarly,

$$X_A d\bar{H}_A + X_B d\bar{H}_B = 0 \quad [6-57]$$

and

$$X_A d\bar{S}_A + X_B d\bar{S}_B = 0 \quad [6-58]$$

In general, for a solution containing any number of components at constant pressure and temperature,

$$\sum X_i d\bar{\theta}_i = 0 \quad [6-59]$$

or

$$\sum n_i d\bar{\theta}_i = 0 \quad [6-60]$$

where $\bar{\theta}_i$ is any partial molar thermodynamic property of component i . Both [6-59] and [6-60] are equivalent forms of the Gibbs-Duhem equation.

Example Problem 6-8

If the solute in a binary A-B condensed solution obeys Henry's law, show that the solvent obeys Raoult's law. Let component A be the solvent and B be the solute. Sketch the result for A_{solvent} , B_{solute} and A_{solute} , B_{solvent} .

Solution

Substituting the differential form of [6-14], $d\bar{G}_A^m = RT d\ln(a_A)$ and $d\bar{G}_B^m = RT d\ln(a_B)$, into [6-56] and dividing through by RT ,

$$X_A d\ln(a_A) + X_B d\ln(a_B) = 0 \quad [6-61]$$

Substituting [6-34] (component B) into [6-61] and solving for a_A ,

$$\begin{aligned} d\ln(a_A) &= -\frac{X_B}{X_A} d\ln(bX_B) = -\frac{X_B}{X_A} [d\ln(b) + d\ln(X_B)] \\ &= -\frac{X_B}{X_A} d\ln(X_B). \end{aligned}$$

Substituting $X_A = (1 - X_B)$ and integrating over limits that yield $\ln(a_A)$ directly,

$$\int_1^{a_A} d\ln(a_A) = -\int_0^{X_B} \frac{X_B d\ln(X_B)}{1 - X_B}$$

or

$$\ln(a_A) - \ln(1) = \ln(1 - X_B) - \ln(1) \Rightarrow \ln(a_A) = \ln(X_A).$$

Therefore,

$$\underline{a_A = X_A \Rightarrow \text{A is ideal.}}$$

Figure 6.9 is a plot of activity versus composition for both components. As illustrated in the figure, both Raoultian and Henrian behavior are approached at high concentration and dilution respectively. In this sense, Raoult's and

Henry's law are limiting laws (Lupis, 1983, p. 158–163). The activity (slope) of each line in mid-range compositions is variable and compositionally dependent. The regular solution model is often applicable in this range.

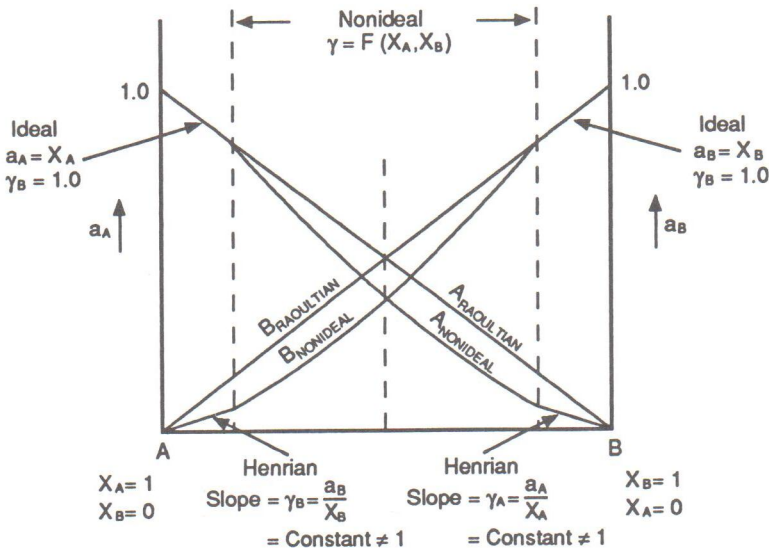


Figure 6.9 Nonideal binary solutions of A and B are represented by the line segments labeled A_{Nonideal} and B_{Nonideal} . Solutes A and B exhibit Henrian behavior at low concentrations, while solvents A and B exhibit ideal behavior at high concentrations. At intermediate concentrations, A and B exhibit nonideal solution behavior.

6.8 CHEMICAL POTENTIAL

Recalling the four Maxwell equations for *closed systems* presented in Chapter Four, *total thermodynamic properties* for each equation can be expressed as follows:

$$U' = U'(S', V') \quad [3-6]$$

$$H' = H'(S', P) \quad [3-7]$$

$$G' = G'(T, P) \quad [4-14]$$

$$A' = A'(T, V') \quad [4-20]$$

Rewriting these equations for an *open* binary A-B system,

$$U' = U'(S', V', n_A, n_B)$$

$$H' = H'(S', P, n_A, n_B)$$

$$G' = G'(T, P, n_A, n_B)$$

$$A' = A'(T, V', n_A, n_B).$$

Using the chain rule to expand each expression for an *open system*,

$$dU' = \left(\frac{\partial U'}{\partial S'} \right)_{V', n_A, n_B} dS' + \left(\frac{\partial U'}{\partial V'} \right)_{S', n_A, n_B} dV' + \left(\frac{\partial U'}{\partial n_A} \right)_{S', V', n_B} dn_A + \left(\frac{\partial U'}{\partial n_B} \right)_{S', V', n_A} dn_B \quad [6-62]$$

$$dH' = \left(\frac{\partial H'}{\partial S'} \right)_{P, n_A, n_B} dS' + \left(\frac{\partial H'}{\partial P} \right)_{S', n_A, n_B} dP + \left(\frac{\partial H'}{\partial n_A} \right)_{S', P, n_B} dn_A + \left(\frac{\partial H'}{\partial n_B} \right)_{S', P, n_A} dn_B \quad [6-63]$$

$$dG' = \left(\frac{\partial G'}{\partial T} \right)_{P, n_A, n_B} dT + \left(\frac{\partial G'}{\partial P} \right)_{T, n_A, n_B} dP + \left(\frac{\partial G'}{\partial n_A} \right)_{T, P, n_B} dn_A + \left(\frac{\partial G'}{\partial n_B} \right)_{T, P, n_A} dn_B \quad [6-64]$$

$$dA' = \left(\frac{\partial A'}{\partial T} \right)_{V', n_A, n_B} dT + \left(\frac{\partial A'}{\partial V'} \right)_{T, n_A, n_B} dV' + \left(\frac{\partial A'}{\partial n_A} \right)_{T, V', n_B} dn_A + \left(\frac{\partial A'}{\partial n_B} \right)_{T, V', n_A} dn_B \quad [6-65]$$

By definition, μ_A , the *chemical potential* of component A is

$$\mu_A \equiv \left(\frac{\partial U'}{\partial n_A} \right)_{S', V', n_B} = \left(\frac{\partial H'}{\partial n_A} \right)_{S', P, n_B} = \left(\frac{\partial A'}{\partial n_A} \right)_{T, V', n_B} = \left(\frac{\partial G'}{\partial n_A} \right)_{T, P, n_B}$$

Since pressure and temperature are simplest to control during an experiment, the most useful of these expressions is

$$\mu_A = \left(\frac{\partial G'}{\partial n_A} \right)_{T, P, n_B} \quad [6-66]$$

Substituting [6-9] into [6-66],

$$\mu_A = \bar{G}_A \quad [6-67]$$

Equations [6-62] through [6-65] may be expressed in alternate form by incorporating the definitions of chemical potential into the extensive forms of [3-6], [3-7], [4-14], and [4-20]:

$$dU' = TdS' - PdV' + \mu_A dn_A + \mu_B dn_B \quad [6-68]$$

$$dH' = TdS' + VdP + \mu_A dn_A + \mu_B dn_B \quad [6-69]$$

$$dG' = VdP - SdT + \mu_A dn_A + \mu_B dn_B \quad [6-70]$$

$$dA' = -SdT - PdV' + \mu_A dn_A + \mu_B dn_B \quad [6-71]$$

Example Problem 6-9

Gases dissolve in metals monatomically and normally in dilute concentrations. Using TL analysis, derive *Sievert's law* relating the partial pressure of hydrogen in a gas phase to the concentration of hydrogen dissolved in a coex-

where C_H is the concentration of H in solution, C_H^0 is the concentration at $P_{H_2}^0 = 1$ atm, and ΔH_s^0 and ΔS_s^0 are the enthalpy and entropy of solution relative to gaseous hydrogen. In [6-72b], Sievert's law, C_H has arbitrary units consistent with constant k .

6.9 DISCUSSION QUESTIONS

- (6.1) A component in a condensed solution is in equilibrium with its vapor. How is the Gibbs free energy change of the condensed component related to the vapor? What assumption is made about the vapor?
- (6.2) At what relative solution concentrations (low, intermediate, or high) will a solution component exhibit:
- Ideal behavior?
 - Dilute (Henrian) behavior?
 - Regular behavior?
- (6.3) Using a plot of H^m vs. X_A , show that $\bar{H}_A^m = 0$ for a solution ideal with respect to A over the entire composition from $X_A = 0$ to $X_A = 1.0$.
- (6.4) Referring to (6.3), describe how to determine that component B is also ideal over the entire composition from $X_B = 0$ to $X_B = 1.0$.
- (6.5) If $\bar{G}_i^m \rightarrow -\infty$ as $X_i \rightarrow 0$, what can be said about the stability of component i in solution as $X_i \rightarrow 0$? What does this imply about purification processes?
- (6.6) Comment on the thermodynamic validity of the following expressions for a binary alloy:
- $\sigma = X_A \bar{\sigma}_A + X_B \bar{\sigma}_B$
where σ is stress and $\bar{\sigma}_A$ and $\bar{\sigma}_B$ are partial stresses.
What restriction is placed on σ ?
 - $C_p = X_A \bar{C}_p^A + X_B \bar{C}_p^B$
where C_p is constant pressure heat capacity and \bar{C}_p^A and \bar{C}_p^B are partial heat capacities at constant pressure.
 - $\alpha = X_A \bar{\alpha}_A + X_B \bar{\alpha}_B$
where α is the thermal expansion coefficient and $\bar{\alpha}_A$ and $\bar{\alpha}_B$ are partial thermal expansion coefficients.
- (6.7) The expression \bar{G}_A^m only holds if the standard state is in the same state of aggregation as the solution. Explain.
- (6.8) Excess Gibbs free energy of solution for a binary alloy is $G^{XS} = X_A \bar{G}_A^{XS} + X_B \bar{G}_B^{XS}$.
Express G^{XS} for a solution that is subregular with respect to both A and B.
- (6.9) Show that $\mu_A - \mu_A^0 = \bar{G}_A^m$.
- (6.10) Is $\bar{H}_A = \mu_A$? Explain.

6.10 EXERCISE PROBLEMS

- [6.1] Derive an expression equivalent to Sievert's law, [6-72b], for solution of hydrogen gas in an aqueous solution. Assume Henry's law.
Ans: $C_{H_2} = k P_{H_2}$.
- [6.2] Sievert's constant for solution of oxygen in liquid silver is $k \approx 193.6 \text{ cm}^3 \cdot \text{atm}^{-0.5} / 100 \text{ gm Ag}$ at 1075°C (Darken and Gurry, 1953, p. 513). Calculate the solubility of Ag at the same temperature if $P_{O_2} = 50 \text{ mm Hg}$.
Ans: $C_{Ag} = 49.7 \text{ cm}^3 / 100 \text{ gm Ag}$.
- [6.3] Referring to Example Problem 6-5, show from the Gibbs-Duhem equation that $\bar{H}_{Au}^m = -20,083(1 - X_{Au})^2 \text{ J/mol}$.
- [6.4] Calculate the composition (a/o) of a binary A-B alloy in equilibrium with oxides A_2O and BO at 627°C . Given $\Delta G_{A_2O}^0 = -15,000 \text{ cal/mol}$ and $\Delta G_{BO}^0 = -25,000 \text{ cal/mol}$. Assume solvent A is ideal. Solute B is Henrian with $\gamma_B = \text{constant} = 1.15$. The metallic phases are completely soluble in each other, whereas the oxides are insoluble.
Ans: 99.7 a/o A; 0.3 a/o B.
- [6.5] For the binary liquid alloy system Cu-Zn, the zinc vapor pressure at 1060°C is given as a function of composition in the following partially completed table (Darken and Gurry, 1953, p. 512):

| | | | | | | | |
|------------------------|--------|--------|--------|--------|--------|--------|--------|
| X_{Zn} | 0.05 | 0.10 | 0.15 | 0.20 | 0.30 | 0.45 | 1.0 |
| $P_{Zn} \text{ (atm)}$ | 0.0289 | 0.0592 | 0.1184 | 0.2368 | 0.6000 | 1.2763 | 4.000* |
| a_{Zn} | | | | | | | |
| γ_{Zn} | | | | | | | |
| \bar{G}_{Zn}^m | | | | | | | |
| $\bar{G}_{Zn}^{m, XS}$ | | | | | | | |
| $\bar{G}_{Zn}^{m, id}$ | | | | | | | |
| Ω_{Zn} | | | | | | | |

* Value is high compared to data in Appendix A, Table A.5.

- (a) Complete the table (use metric units).
 (b) Does the system obey the ideal, Henrian, or regular solution model?

Ans: Ideal behavior with respect to zinc as $X_{Zn} \rightarrow 1$, regular for approximately $0.05 < X_{Zn} < 0.30$, and Henrian for approximately $X_{Zn} < 0.05$.

- [6.6] One mole of solid A at 1200°C is added to a large quantity of a liquid solution comprised of components A and B ($X_A = 0.8$). The liquid solution is also at 1200°C . If A and B form ideal solutions, calculate the Gibbs free energy change resulting from the addition of solid A to

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the mixture. Assume C_p^A (liquid) $\approx C_p^A$ (solid) and C_p^A is independent of temperature. $\Delta H_A^f = 24,000$ J/mol at 1800°C .

Ans: $\bar{G}_A^l - \bar{G}_A^{s*} = 4210$ J/mol.

- [6.7] The molar heat of formation of liquid brass according to the reaction $(1 - X)\text{Cu} + X\text{Zn} \rightarrow \text{CuZn}$ is given by $H^m = -7100X(1 - X)$ cal/mol (Upadhyaya and Dube, 1977, p. 139). Determine the expressions relating the partial molar heats of mixing of copper and zinc in liquid brass to the alloy composition.

Ans: $\bar{H}_{\text{Cu}}^m = -7100(1 - X_{\text{Cu}})^2$; $\bar{H}_{\text{Zn}}^m = -7100(1 - X_{\text{Zn}})^2$.

- [6.8] The solubility limit of component A in B is 1.5 w/o at 760°C . If an alloy contains 0.5 w/o A, calculate the activity of A. Assume Henrian solution behavior in the composition range.

Ans: $a_A = 0.33$.

- [6.9] Antimony is removed from lead during the refining process by selective oxidation (Darken and Gurry, 1953, p. 513). Estimate the Sb content obtained for air agitation of the bath at 1173 K. State assumptions and use the following data: $\Delta G_{1100}^{0,f} = -417,600$ J/mol Sb_2O_3 and $\Delta G_{1200}^{0,f} = -395,000$ J/mol Sb_2O_3 (Wicks and Block, 1963, p. 13).

Ans: Applying two methods: Method 1 – antimony (ppb) ≈ 2 and Method 2 – (more realistic) Sb (ppm) ≈ 8000 .

- [6.10] Show for a regular binary solution that

$$\Omega_i = \frac{RT \ln(\gamma_i)}{(1 - X_i)^2}.$$

- [6.11] Show that if a solution component i exhibits ideal behavior at constant temperature, $\bar{V}_i^{m,\text{id}} = 0$.

- [6.12] During low temperature-high pressure metamorphism, the albite component in the mineral plagioclase breaks down to form the mineral quartz and jadeite, a component in the mineral omphacite. Quartz occurs as a separate phase during metamorphism, hence $a_{\text{SiO}_2} = 1$. Referring to Exercise Problem [4.22]:

- (a) Calculate ΔG_T as a function of temperature, activity of albite, a_{Ab} , in plagioclase, and activity of jadeite, a_{Jd} , in omphacite.

Ans: ΔG_T (J/mol) = $53.21 \times 10^3 - 2000.4T + 238.217 \ln(T) - 70.349 \times 10^{-3}T^2 + 3.791 \times 10^{-6}T^3 + 17.478 \times 10^3T^{0.5} + 2460.4 \times 10^3T^{-1} + RT \ln(a_{\text{Jd}}/a_{\text{Ab}})$.

- (b) Assuming ideal mixing, determine ΔG_T as a function of temperature, X_{Ab} , and X_{Jd} .

Ans: ΔG_T (J/mol) = $53.21 \times 10^3 - 2000.4T + 238.217 \ln(T) - 70.349 \times 10^{-3}T^2 + 3.791 \times 10^{-6}T^3 + 17.478 \times 10^3T^{0.5} + 2460.4 \times 10^3T^{-1} + RT \ln(X_{\text{Jd}}/X_{\text{Ab}})$.

- [6.13] Plagioclase feldspar, one of the most common rock forming minerals, exhibits complete solid solution between the pure end members albite (Ab), $\text{NaAlSi}_3\text{O}_8$, and anorthite (An), $\text{CaAl}_2\text{Si}_2\text{O}_8$. Solid solution min-

eral compositions are usually given in abbreviated form, such as $\text{Ab}_{40}\text{An}_{60}$, which denotes a plagioclase of composition 40 w/o albite and 60 w/o anorthite. Show that the partial pressure of anorthite over a homogeneous liquid solution of $\text{Ab}_{20}\text{An}_{80}$ at 1350°C is:

$$P_{\text{An}} = \exp\left(\frac{-\Delta G_{1623}^0 - 383R}{1623R}\right)$$

where ΔG_{1623}^0 is the standard Gibbs free energy change at 1623 K for the phase transformation $\text{An}(l) \rightarrow \text{An}(g)$. The molecular weights of albite and anorthite are 262.23 and 278.21 respectively. State assumptions.