CHAPTER 4

MIXTURES

§4.01 *Introduction*

In this chapter we shall discuss homogeneous mixtures of two or more substances which do not react chemically. Consideration of chemical reactions is postponed to chapter 6. The mixtures may be gaseous, liquid, or solid. So far as possible each of the several component substances of a mixture will be treated on the same basis. The opposite point of view is taken in chapter 5 where one substance is regarded as the solvent and the remaining substances as solutes.

As soon as we turn from single substances to mixtures we introduce the possibility of new degrees of freedom associated with differences of composition. For example we can have two or more liquid phases of different composition in mutual equilibrium.

There are no differences of principle between the treatments of systems of two components on the one hand and of systems of more than two components on the other. Many of the formulae for the former are however more compact than the corresponding formulae for the latter. For this reason we shall in some sections confine ourselves mainly if not entirely, to systems of two substances, i.e. *binary* systems.

§4.02 *Composition of mixture*

The most convenient quantities specifying the relative composition of a mixture are the mole fractions of the several components. These were defined in §1.29. We recall that in a mixture of c components only c−1 of the mole fractions are independent owing to the identity

$$x_1+x_2+\ldots+x_c=1. \qquad 4.02.1$$

When we require independent variables it is convenient to use $x_2, x_3, \ldots x_c$ and regard x_1 as a dependent variable defined by

$$x_1=1-x_2-x_3-\ldots-x_c. \qquad 4.02.2$$

In the simple case of a binary mixture the subscripts may be dropped so that we write x instead of x_2 and $1-x$ instead of x_1.

§4.03 *Partial and proper quantities*

We recall the definitions in §1.26 of partial quantities X_i and proper quantities X_m in terms of an extensive property X, namely

$$X_i = (\partial X/\partial n_i)_{T,P,n_j} \qquad (j \neq i) \qquad 4.03.1$$

$$X_\mathrm{m} = X/\sum_i n_i. \qquad 4.03.2$$

We also recall formula (1.26.3)

$$X = \sum_i n_i X_i. \qquad 4.03.3$$

If we differentiate this we obtain

$$\mathrm{d}X = \sum_i X_i \mathrm{d}n_i + \sum_i n_i \mathrm{d}X_i \qquad 4.03.4$$

while (1) may be rewritten as

$$\mathrm{d}X = \sum_i X_i \mathrm{d}n_i \qquad (\text{const. } T, P). \qquad 4.03.5$$

Subtracting (5) from (4) we obtain

$$\sum_i n_i \mathrm{d}X_i = 0 \qquad (\text{const. } T, P) \qquad 4.03.6$$

or dividing by $\Sigma_i n_i$

$$\sum_i x_i \mathrm{d}X_i = 0 \qquad (\text{const. } T, P). \qquad 4.03.7$$

In particular for a binary mixture

$$(1-x)(\partial X_1/\partial x) + x(\partial X_2/\partial x) = 0 \qquad (\text{const. } T, P). \qquad 4.03.8$$

In the case of a binary mixture we can express X_1 and X_2 in terms of X_m and x. Formula (5) reduces to

$$\mathrm{d}X = X_1 \mathrm{d}n_1 + X_2 \mathrm{d}n_2. \qquad 4.03.9$$

If we apply (9) to unit amount of varying composition, it becomes

$$\mathrm{d}X_\mathrm{m} = (X_2 - X_1)\mathrm{d}x \qquad 4.03.10$$

or

$$(\partial X_\mathrm{m}/\partial x)_{T,P} = X_2 - X_1. \qquad 4.03.11$$

If we apply (3) to unit amount it becomes

$$X_{\mathrm{m}} = (1-x)X_1 + xX_2. \tag{4.03.12}$$

Solving (11) and (12) for X_1 and X_2 we obtain

$$X_1 = X_{\mathrm{m}} - x(\partial X_{\mathrm{m}}/\partial x)_{T,P} \tag{4.03.13}$$

$$X_2 = X_{\mathrm{m}} + (1-x)(\partial X_{\mathrm{m}}/\partial x)_{T,P}. \tag{4.03.14}$$

Formulae (13) and (14) have a simple geometrical interpretation shown in figure 4.1. The abscissa is x, increasing from zero at O representing the pure component 1 to unity at O′ representing the pure component 2. Suppose the curve APB to be a plot of the proper quantity X_{m} as ordinate and P to be any point on it. Let the tangent QPR to this curve at P cut the O and O′ ordinates at Q and R respectively. Then from (13) and (14) we see that the partial quantities X_1 and X_2 for the composition at P are represented by OQ and O′R respectively. It is clear from this construction or otherwise that for either pure component the partial quantity is equal to the proper quantity.

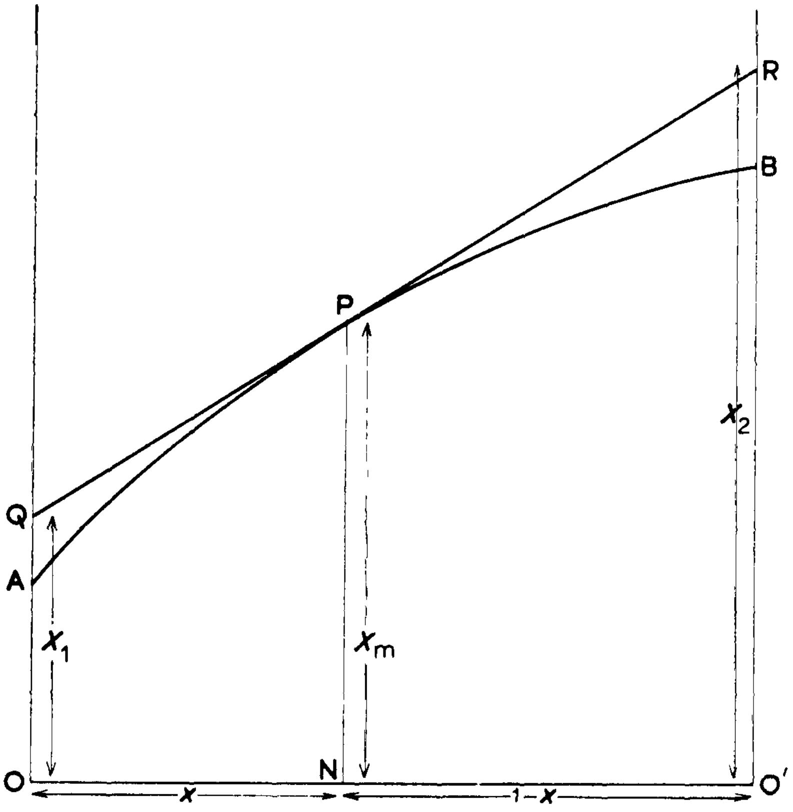

Fig. 4.1. Relation between partial quantities and proper quantity

An especially important example of the pair of formulae (13) and (14) is obtained by setting $X = G$. Taking account of (1.28.11) we obtain

$$\mu_1 = G_1 = G_m - x(\partial G_m/\partial x)_{T,P} \qquad 4.03.15$$

$$\mu_2 = G_2 = G_m + (1-x)(\partial G_m/\partial x)_{T,P}. \qquad 4.03.16$$

§ 4.04 *Relations between partial quantities*

As already mentioned in § 1.26 from every homogeneous relation between extensive properties we obtain by differentiation with respect to n_i a corresponding relation between the partial quantities at a given composition. We now give important examples of such relations taking into account (1.28.11) that

$$\mu_i = G_i. \qquad 4.04.1$$

We have with T, P as independent variables

$$H_i = U_i + PV_i \qquad 4.04.2$$

$$\mu_i = G_i = U_i - TS_i + PV_i \qquad 4.04.3$$

$$S_i = -\partial G_i/\partial T = -\partial\mu_i/\partial T \qquad 4.04.4$$

$$H_i = G_i - T\partial G_i/\partial T = \mu_i - T\partial\mu_i/\partial T \qquad 4.04.5$$

$$V_i = \partial G_i/\partial P = \partial\mu_i/\partial P \qquad 4.04.6$$

$$C_i = T\partial S_i/\partial T = \partial H_i/\partial T. \qquad 4.04.7$$

Relations of precisely the same form hold between proper quantities.

From (5) and (3.15.2) we deduce

$$\partial \ln \lambda_i/\partial T = -H_i/RT^2. \qquad 4.04.8$$

§ 4.05 *Partial quantities at high dilution*

By rewriting (4.03.8) in the form

$$(\partial X_1/\partial x)/(\partial X_2/\partial x) = -x/(1-x) \qquad 4.05.1$$

we make the interesting observation that as $x \to 0$ either $(\partial X_1/\partial x) \to 0$ or $(\partial X_2/\partial x) \to \infty$. Both alternatives occur. We shall find that as $x \to 0$, the quantities $(\partial U_1/\partial x)$, $(\partial H_1/\partial x)$, $(\partial V_1/\partial x)$, $(\partial C_1/\partial x)$ all tend towards zero, while $(\partial S_2/\partial x)$ and $(\partial G_2/\partial x) = (\partial\mu_2/\partial x)$ tend to infinity.

In the limit $x \to 1$ we of course meet the converse behaviour.

§ 4.06 *Perfect gaseous mixture*

In discussing gaseous mixtures, or in discussing single gases, it is expedient

Gaskell

Chapter 10

GIBBS FREE ENERGY COMPOSITION AND PHASE DIAGRAMS OF BINARY SYSTEMS

10.1 INTRODUCTION

It has been seen that, at constant temperature and pressure, the stable state of existence of a system is that which has the minimum possible value of Gibbs free energy. Thus, phase stability in a system, as normally presented on an isobaric phase diagram, can be determined from knowledge of the variations of the Gibbs free energies of the various possible phases with composition and temperature. When a liquid solution is cooled, a liquidus temperature is eventually reached, at which point a solid phase begins to separate from the liquid solution. This solid phase could be a virtually pure component, a solid solution of the same or different composition from the liquid, or a chemical compound formed by reaction between two or more of the components. In all possible cases the composition of the solid phase which is in equilibrium with the liquid solution is that which minimizes the Gibbs free energy. If liquid solutions are stable over the entire range of composition, then the Gibbs free energies of the liquid states are lower than those of any possible solid state, and conversely, if the temperature of the system is lower than the lowest solidus temperature, then the Gibbs free energies of the solid states are everywhere lower than those of liquid states. At intermediate temperatures, the variation of Gibbs free energy with composition will identify ranges of composition over which liquid states are stable, ranges over which solid states are stable, and intermediate ranges in which solid and liquid phases coexist in equilibrium with one another. Thus, by virtue of the facts that (1) the state of lowest Gibbs free energy is the stable state and (2) when phases coexist in equilibrium $\bar{G}_i$ has the same value in all of the coexisting phases, there must exist a quantitative correspondence between Gibbs free energy-composition diagrams and "phase diagrams." This correspondence is examined in this chapter, in which it will be seen that "normal" phase diagrams are generated by, and are simply representations of, Gibbs free energy-composition diagrams.

10.2 GIBBS FREE ENERGY AND THERMODYNAMIC ACTIVITY

The Gibbs free energy of mixing of the components *A* and *B* to form a mole of solution is given by

$$\Delta G^M = RT(X_A \ln a_A + X_B \ln a_B)$$

and ΔG^M is the difference between the Gibbs free energy of a mole of the homogeneous solution and the Gibbs free energy of the corresponding numbers of moles of the unmixed components. As only changes in Gibbs free energy can be measured, the Gibbs free energies of the pure unmixed components are assigned the value of zero. If the solution is ideal, i.e., if $a_i=X_i$, then the molar Gibbs free energy of mixing, given by

$$\Delta G^{M,\mathrm{id}} = RT(X_A \ln X_A + X_B \ln X_B)$$

has the characteristic shape shown, at the temperature T, as curve I in Fig. 10.1. As $\Delta H^{M,\mathrm{id}} = 0$ then $\Delta G^{M,\mathrm{id}} = -T\Delta S^{M,\mathrm{id.}}$ and hence curve I in Fig. 10 1 is obtained as $-T\times$(the curve drawn in Fig. 9.7). It is thus seen that the shape of the variation of $\Delta G^{M,\mathrm{id}}$ with composition depends only on temperature.

If the solution exhibits a slight positive deviation from ideal mixing, i.e., if $\gamma i>1$ and $a_i>X_i$, then, at the temperature T, the Gibbs free energy of mixing curve is typically as shown by curve II in Fig. 10.1; and if the solution shows a slight negative deviation from ideal mixing, i.e., if $\gamma i<1$ and $a_i<X_i$, the Gibbs free energy of mixing curve is typically as shown by curve III in Fig. 10.1. From Eqs. (9.33a and b) the tangent drawn to the ΔG^M curve at any composition intersects the $X_A=1$ and $X_B=1$ axes at $\Delta \bar{G}_A^M$ and $\Delta \bar{G}_B^M$, respectively, and, as $\Delta \bar{G}_i^M = RT$ In a_i, a correspondence is provided between the ΔG^M-composition and activity-composition curves. In Fig. 10.1, at the composition Y, tangents drawn to curves I, II, and III intersect the $X_B=1$ axis at a, b, and c, respectively. Thus

$$\begin{aligned}|Bb = \Delta \bar{G}_B^M = RT \ln a_B \text{ (in system II)}| &< |Ba = \Delta \bar{G}_B^M = RT \ln X_B| \\ &< |\ Bc = \Delta \bar{G}_B^M = RT \ln a_B \text{ (in system III)}|\end{aligned}$$

from which it is seen that

$$\gamma_B \text{ in system II} > 1 > \gamma_B \text{ in system III}$$

The variation, with composition, of the tangential intercepts generates the variations of activity with composition shown in Fig. 10.2.

As $X_i \rightarrow 0$, $a_i \rightarrow 0$, and hence the tangential intercept $\Delta \bar{G}_i^M = RT \ln a_i \rightarrow -\infty$ which indicates that all Gibbs free energy of mixing curves have vertical tangents at their extremities. Similarly, by virtue of being logarithmic, the entropy of the mixing curve shown in Fig. 9.7 has vertical tangents at its extremities.

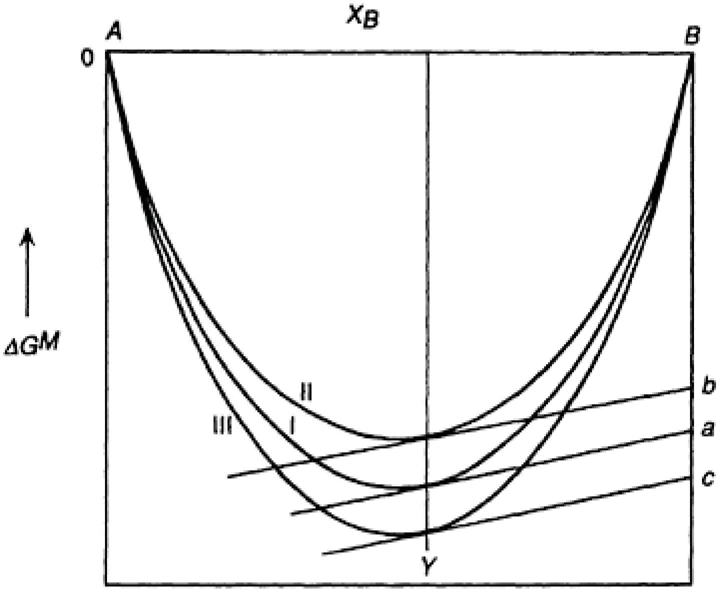

Figure 10.1 The molar Gibbs free energies of mixing in binary systems exhibiting ideal behavior (I), positive deviation from ideal behavior (II), and negative deviation from ideal behavior (III).

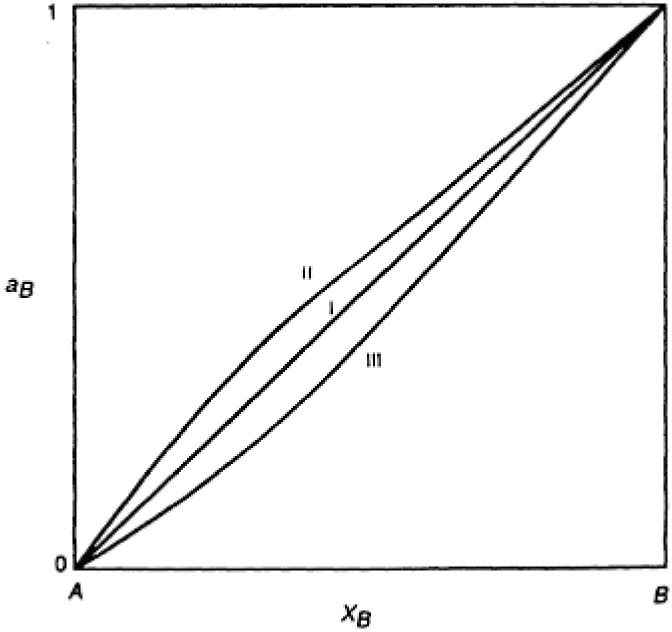

Figure 10.2 The activities of component *B* obtained from lines I, II, and III in Fig. 10.1.

10.3 THE GIBBS FREE ENERGY OF FORMATION OF REGULAR SOLUTIONS

If curves II and III in Fig. 10.1 are drawn for regular solutions, then deviation of ΔG^M from $\Delta G^{M,\mathrm{id}}$ is due only to the nonzero heat of mixing and the difference between the two curves, $\Delta G^M - \Delta G^{M,\mathrm{id}}$

$$= G^{xs} = RT\alpha X_A X_B = \Omega X_A X_B = \Delta H^M$$

For curve II, $|\Delta G^M| < |\Delta G^{M,\mathrm{id}}|$, and thus ΔH^M is a positive quantity (α and Ω are positive quantities). It is of interest to consider the effect of increasingly positive values of α on the shape of the Gibbs free energy of mixing curve for a regular solution. In Fig. 10.3, curve I is drawn as—$\Delta S^{M,\mathrm{id}}/R = X_A \ln X_A + X_B \ln X_B$. This curve represents $\Delta G^{M,\mathrm{id}}$/RT. Curves for $\Delta H^M/RT = \alpha X_A X_B$ are drawn for $\alpha=0$, $+0.5$, $+1.0$, $+1.5$, $+2.0$, $+2.5$, and $+3.0$, and the corresponding $\Delta G^M/RT$ curves are drawn as the sum of the particular $\Delta H^M/RT$ and $-\Delta S^{M,\mathrm{id}}/R$ curves. As the magnitude of α is increased it is seen that the shape of the $\Delta G^M/RT$ curve continuously changes from a shape typified by $\alpha=0$ to a form typified by $\alpha=3$. Before discussing the consequences of this change of shape on the

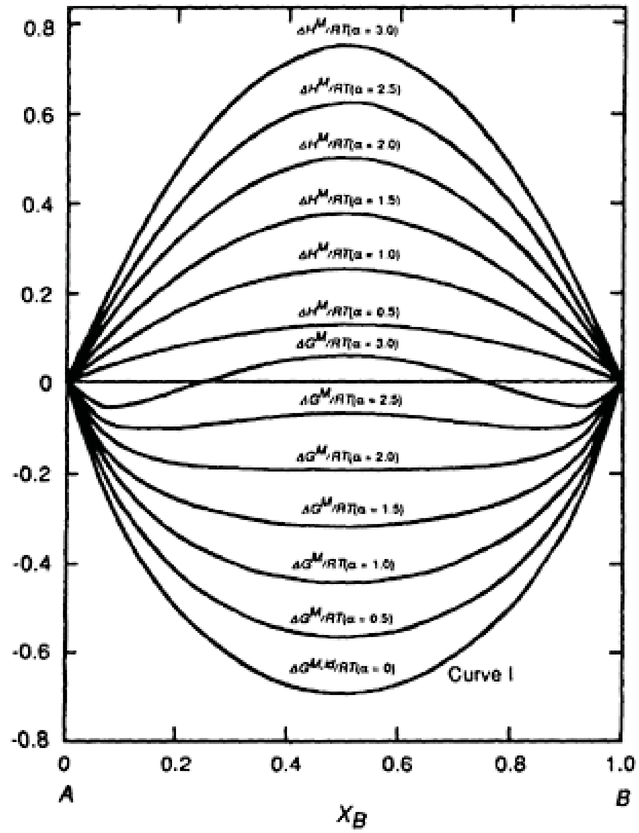

Figure 10.3 The effect of the magnitude of a on the integral molar heats and integral molar Gibbs free energies of formation of a binary regular solution.

behavior of the solutions, it is pertinent to examine the significance of the shape of the curve. Curve I from Fig. 10.1 is reproduced in Fig. 10.4*a*. This curve is "convex downwards" at all compositions. Thus the homogeneous solution formed from any mixture of *A* and *B* is the stable state, as this state has the lowest possible Gibbs free energy. Consider, further, two separate solutions, say, *a* and *b* in Fig. 10.4*a*. Before mixing of these two solutions, the Gibbs free energy of the two-solution system, with respect to pure *A* and pure *B,* lies on the straight line joining *a* and *b,* with the exact position being determined, via the lever rule, by the relative proportions of the separate solutions. If the solutions *a* and *b* are present in equal amounts then the Gibbs free energy of the system is given by the point *c*. When mixed, the two solutions form a new homogeneous solution, as thereby the Gibbs free energy of the system is decreased from *c* and *d,* the minimum Gibbs free energy which it can have. Consider now Fig. 10.4*b* in which the $\Delta G^M/RT$ curve for α=+3.0 is reproduced from Fig. 10.3. This curve is "convex downwards” only between *a* and *n* and between *p* and *B* and is “convex upwards” between *n* and *p*. The Gibbs free energy of a system of composition between *m* and *q* is minimized when the system occurs as two solutions, one of composition *m* and the other of composition *q;* e.g., if the homogeneous solution of composition *r* separates into the two coexisting solutions *m* and *q,* the Gibbs free energy of the system is decreased from *r* to *s*. The equilibrium coexistence of two separate solutions at the temperature *T* and pressure *P* requires that

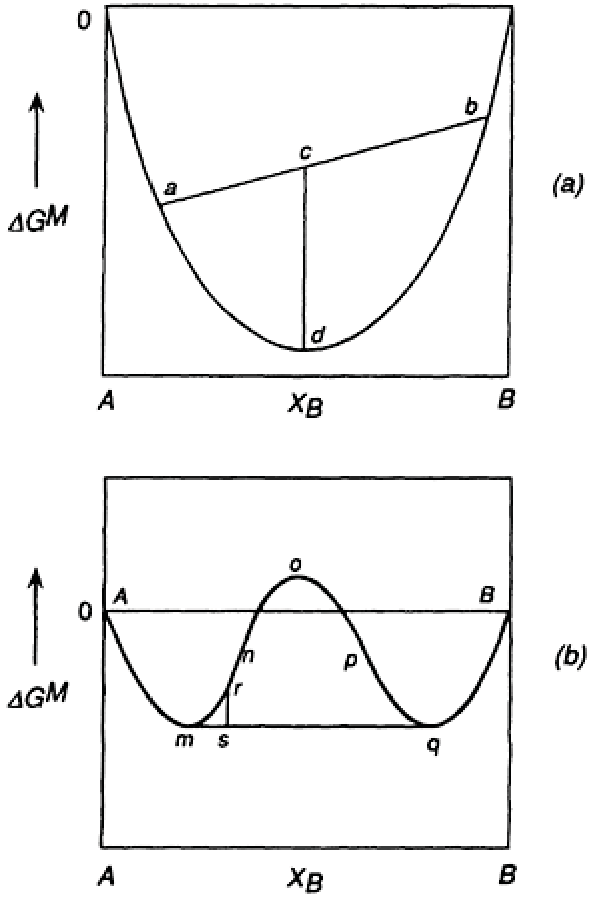

Figure 10.4 *(a)* The molar Gibbs free energies of mixing of binary components which form a complete range of solutions. *(b)* The molar Gibbs free energies of mixing of binary components in a system which exhibits a miscibility gap.

$$\overline{G}_A \text{ (in solution } m) = \overline{G}_A \text{ (in solution } q) \qquad \text{(i)}$$

and

$$\bar{G}_B \text{ (in solution } m) = \bar{G}_B \text{ (in solution } q) \tag{ii}$$

Subtracting G_A° from both sides of Eq. (i) gives

$$RT \ln a_{A(\text{in solution } m)} = RT \ln a_{A(\text{in solution } q)}$$

or

$$a_{A(\text{in solution } m)} = a_{A(\text{in solution } q)}$$

Similarly

$$a_{B(\text{in solution } m)} = a_{B(\text{in solution } q)} \tag{iv}$$

Equations (iii) and (iv) are the criteria for equilibrium coexistence of two solutions (or phases) at constant *T* and *P*. As $\Delta\bar{G}_A^M$ (in m)=$\Delta\bar{G}_A^M$ (in *q*), and $\Delta\bar{G}_B^M$ (in *m*)= $\Delta\bar{G}_B^M$ (in *q*), then it is seen that the tangent to the curve at the point *m* is also the tangent to the curve at the point *q*. The positioning of this double tangent defines the positions of the points *m* and *q* on the Gibbs free energy of mixing curve.

The *A-B* system, as represented in Fig. 10.4*b*, is one in which, at the temperature *T,* the value of α is sufficiently positive that the consequent tendency toward clustering of like atoms is great enough to cause phase separation. A homogeneous solution (phase I) is formed when *B* is initially added to *A* and saturation of phase I with *B* occurs at the composition *m*. Further addition of *B* causes the appearance of a second solution (phase II) of composition *q* (which is phase II saturated with A), and continued addition of *B* causes an increase in the ratio of phase II to phase I occurring, until the overall composition of the two-phase system reaches *q,* at which point phase I disappears. A homogeneous solution (phase II) occurs between the compositions *q* and *B*. The curve *mn* represents the Gibbs free energy of phase I supersaturated with *B,* and the curve *qp* represents the Gibbs free energy of phase II supersaturated with *B.* As the line *AmqB* represents the equilibrium states of the system, then this line alone has physical significance, and the line is the isobaric, isothermal section of the system as it occurs in *G-T-P*-composition space.

10.4 CRITERIA FOR PHASE STABILITY IN REGULAR SOLUTIONS

For a given temperature it is obvious that a critical value of a occurs below which a homogeneous solution is stable over the entire range of composition and above which phase separation occurs. The criteria used to determine this critical value are illustrated in Fig. 10.5. Fig. 10.5*a, b,* and *c* show the variations of ΔG^M, $\partial \Delta G^M/\partial X_B$, $\partial^3 \Delta G^M/\partial X_B^3$, and $\partial^3 \Delta G^M/\partial X_B^3$ with composition for $\alpha<\alpha_{\text{critical}}$, $\alpha=\alpha_{\text{critical}}$, and $\alpha>\alpha_{\text{critical}}$ respectively. The critical value of α is seen to be that which makes $\partial^2 \Delta G^M/\partial X_B^2$ and $\partial^3 \Delta G^M/\partial X_B^3$ simultaneously equal to zero at that composition at which immiscibility becomes imminent. For a regular solution,

$$\Delta G^M = RT(X_A \ln X_A + X_B \ln X_B) + RT\alpha X_A X_B$$

$$\frac{\partial \Delta G^M}{\partial X_B} = RT\left[\ln \frac{X_B}{X_A} + \alpha(X_A - X_B)\right]$$

$$\frac{\partial^2 \Delta G^M}{\partial X_B^2} = RT\left(\frac{1}{X_A} + \frac{1}{X_B} - 2\alpha\right)$$

and

$$\frac{\partial^3 \Delta G^M}{\partial X_B^3} = RT\left(\frac{1}{X_A^2} - \frac{1}{X_B^2}\right)$$

The third derivative, $\partial^3 \Delta G^M/\partial X_B^3 = 0 \text{ at } X_A = X_B = 0.5$ and thus the second derivative, $\partial^3 \Delta G^M/\partial X_B^3 = 0 \text{ at } X_A = X_B = 0.5$ when α=2, which is thus the critical value of α above which phase separation occurs. As a is an inverse function of temperature, given by

$$\Omega = RT\alpha$$

a critical temperature occurs in any regular system with a positive value of Ω, above which α<2 and below which α>2. The critical temperature, T_{cr}, is

$$T_{\text{cr}} = \frac{\Omega}{2R} \tag{10.1}$$

Fig. 10.6*a* shows the variation, with temperature, of the Gibbs free energy of mixing curve for a regular solution which has a positive molar heat of mixing (Ω=16,630 joules) and a critical temperature of T_{cr}=16,630/2*R*=1000 K. The Gibbs free energy expression contains a negative logarithmic term, the magnitude of which is proportional to temperature, and a positive parabolic term which is independent of temperature. At high enough temperature, the logarithmic contribution predominates and the Gibbs free energy of mixing is convex downwards at all compositions. However, with decreasing temperature, the contribution of the logarithmic term decreases, and eventually the positive parabolic term predominates and produces a range of composition centered on X_B=0.5 over which the Gibbs free energy curve is convex upwards. The logarithmic term still requires that the tangents to the curve at X_A=1 and X_B=1 be vertical. Fig. 10.6*b* shows the phase diagram for the system, in which the miscibility curve bounding the two-phase region is simply the locus of the double tangent compositions in Fig. 10.6*a*. The influence of temperature on the variations of the activity of component *B* with composition is shown in Fig. 10.6*c*. The activities are obtained from the intercepts, with the X_B=1 axis,

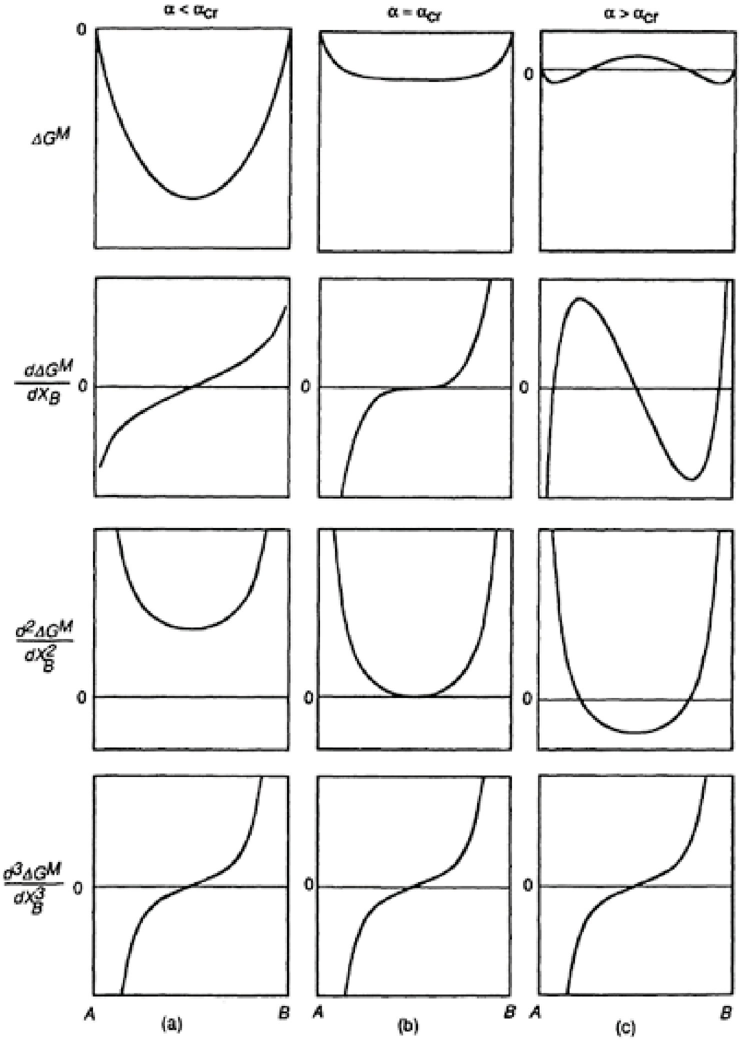

Figure 10.5 The effect of the magnitude of a on the first, second, and third derivatives of the integral Gibbs free energy of mixing with respect to composition.

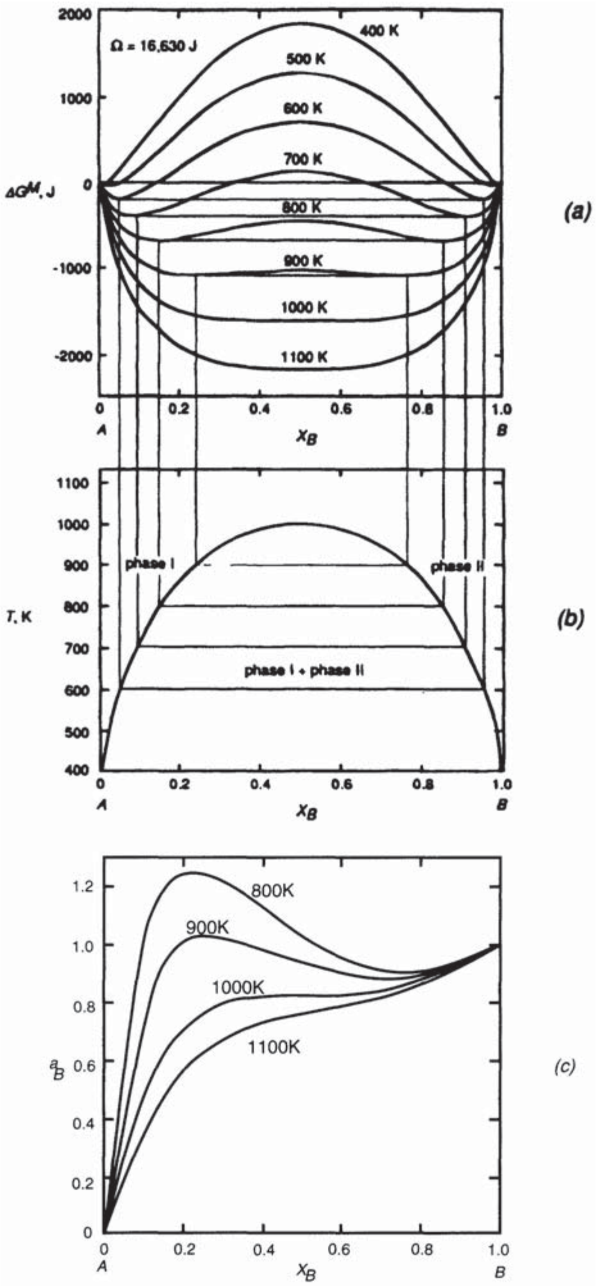

Figure 10.6 *(a)* The effect of temperature on the molar Gibbs free energy of mixing a binary regular solution for which Ω=16,630 joules, *(b)* The loci of the double tangent points in *(a),* which generate the phase diagram for the system, *(c)* The activities of component *B* derived from *(a)*.

of tangents drawn to the free energy $\Delta\bar{G}_B^M = RT \ln a_B$. At T_{cr} the activity exhibits a horizontal inflexion at X_B=0.5, as is seen from the following. From Eq. (9.33b),

$$\Delta\bar{G}_B^M = \Delta G^M + X_A\left(\frac{\partial\Delta G^M}{\partial X_B}\right) = RT\ln a_B$$

Thus

$$\frac{\partial\Delta\bar{G}_B^M}{\partial X_B} = X_A\frac{\partial^2\Delta G^M}{\partial X_B^2} = \frac{RT}{a_B}\frac{\partial a_B}{\partial X_B} \tag{10.2}$$

and

$$\frac{\partial^2\Delta\bar{G}_B^M}{\partial X_B^2} = X_A\left(\frac{\partial^3\Delta G^M}{\partial X_B^3}\right) - \left(\frac{\partial^2\Delta G^M}{\partial X_B^2}\right) = \frac{RT\partial^2 a_B}{a_B\partial X_B^2} - \frac{RT}{a_B^2}\left(\frac{\partial a_B}{\partial X_B}\right)^2 \tag{10.3}$$

At T_{cr} and X_B=0.5 both the second and third derivatives of ΔG^M with respect to X_B are zero, and thus, from Eqs. (10.2) and (10.3), the first and second derivatives of a_B with respect to X_B are zero, which produces a horizontal inflexion point on the activity curve at X_B=0.5 and T_{cr}. At $T<T_{cr}$ the activity curve has a maximum and a minimum, which occur at the spinodal compositions (where $\partial^2\Delta G^M/\partial X_B^2$, and hence $\partial a_B/\partial X_B$, are zero), e.g., the points *n* and *p* in Fig. 10.4*b* and the points *b* and *c* on the activity curve at 800 K shown in Fig. 10.7. The portion of the curve given by *ab* in Fig. 10.7 represents the activity of *B* in phase I which is supersaturated with *B* and the portion of the activity curve given by *cd* represents the activity of *B* in phase II which is supersaturated with *A*.

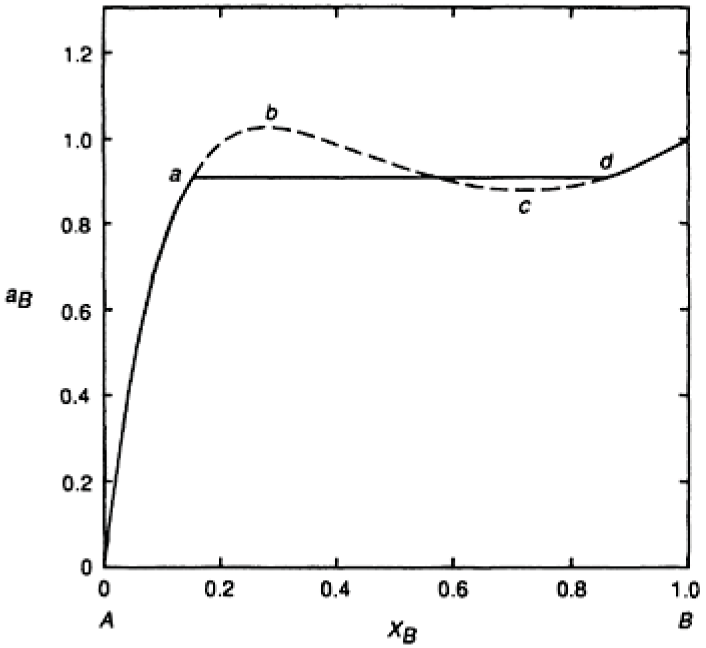

Figure 10.7 The activity of *B* at 800 K derived from Fig. 10.6*a*.

The value of $\partial a_B/\partial X_B$ is negative between *b* and *c,* and this violates an intrinsic criterion for stability which requires that $\partial a_i/\partial X_i$ always be positive [cf. $(\partial P/\partial V)_T>0$ over the portion *JHF* in Fig. 8.7]. Thus the derived activity curve between *b* and *c,* and, consequently, the Gibbs free energy of mixing curve between the spinodal compositions, have no physical significance. The horizontal line drawn between *a* and *d* in Fig. 10.7 represents the actual constant activity of *B* in the two-phase region, and the compositions *a* and *d* are those of the double tangents to the Gibbs free energy of mixing curve.

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7.5.1 Overview of the Phase Diagram

The phase diagram for a regular solution is shown schematically in Figure 7.9. It has the following important features, which we will see how to calculate:

1. A *critical point* (T_c, x_c) such that for $T > T_c$ a one-phase solution is formed for all compositions.
2. A *coexistence curve*, or *binodal*, which describes the compositions of the two phases x_1' and x_1'' that coexist at equilibrium, after liquid–liquid separation at some fixed $T < T_c$. Any solution prepared such that (T, x_1) lies under the binodal will be out of equilibrium until it has undergone phase separation.
3. A *stability limit*, or *spinodal*, which divides the two-phase region into a *metastable* window, between the binodal and the spinodal, and an *unstable* region, below the spinodal. The significance of the terms metastable and unstable will be explained subsequently. Note that the binodal and spinodal curves meet at the critical point.

Qualitatively, of course, we should expect one-phase behavior at high T because $\Delta S_m > 0$, and therefore $-T\Delta S_m$ contributes an increasingly negative term to ΔG_m. However, although $\Delta G_m < 0$ is the criterion for spontaneous mixing, it by no means guarantees a *single* mixed phase, as we shall

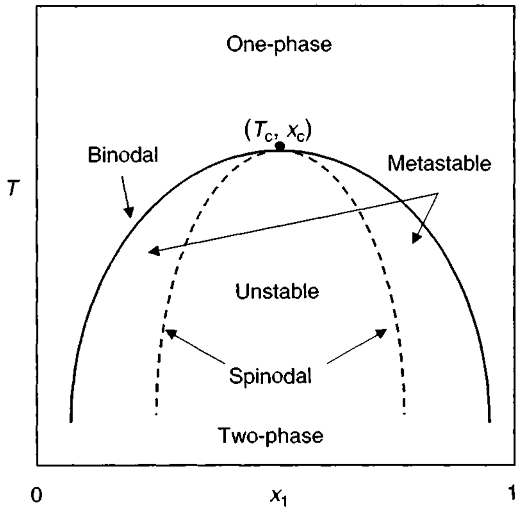

Figure 7.9 Phase diagram (temperature versus mole fraction of component 1) for regular solution theory. The binodal (coexistence curve) separates the one-phase region at high temperature from the two-phase region at low temperature. The spinodal curve (stability limit) separates the unstable and metastable windows within the two-phase region. The binodal and spinodal curves meet at a critical point.

see. To begin the analysis, we resolve the two contributions to $\Delta G_m/RT$ from regular solution theory (Equation 7.2.11):

$$\begin{aligned} -\frac{\Delta S_m}{R} &= x_1 \ln x_1 + x_2 \ln x_2 \\ \frac{\Delta H_m}{RT} &= x_1 x_2 \chi \end{aligned} \tag{7.5.1}$$

and recall from its definition (Equation 7.2.9) that $\chi \sim 1/T$. These two functions are plotted in Figure 7.10a and Figure 7.10b, respectively. Note that both are symmetric about $x_1 = 1/2$, and that in this format the entropy term is independent of T, whereas the enthalpy term is not (due to χ). Furthermore, we take $\chi > 0$, as expected by the theory. In Figure 7.10c we combine the two terms, at two generic temperatures, one "high" and one "low." At the higher T, χ is so small that ΔG_m looks much like the ΔS_m term; it is always concave up. However, at the lower T, the larger χ in the enthalpy term produces a "bump," or local maximum in the free energy. This will turn out to have profound consequences. Note that even at the lower T, $\Delta G_m < 0$ for all compositions considered in this example.

Phase separation will occur whenever the system can lower its total free energy by dividing into two phases. If we prepare a solution with overall composition $\langle x_1 \rangle$, and then ask will it prefer to separate into phases with compositions x_1' and x_1'', we can find the answer simply by drawing a line connecting the corresponding points on the ΔG_m curve (i.e., $\Delta G_m(x_1')$ to $\Delta G_m(x_1'')$), as shown in Figure 7.11a. Because ΔG_m is an extensive property, this line represents the hypothetical free energy of a combination of two phases, x_1' and x_1'', for any overall composition $\langle x_1 \rangle$ that lies in between. (Note that the relative proportions of the two phases with compositions x_1' and x_1'' are determined once $\langle x_1 \rangle$ is selected, by the so-called lever rule.)

What we now realize is that, so long as ΔG_m is concave up, this straight line will lie *above* ΔG_m at $\langle x_1 \rangle$ for any choice of x_1' and x_1'', and therefore phase separation would *increase* the free energy.

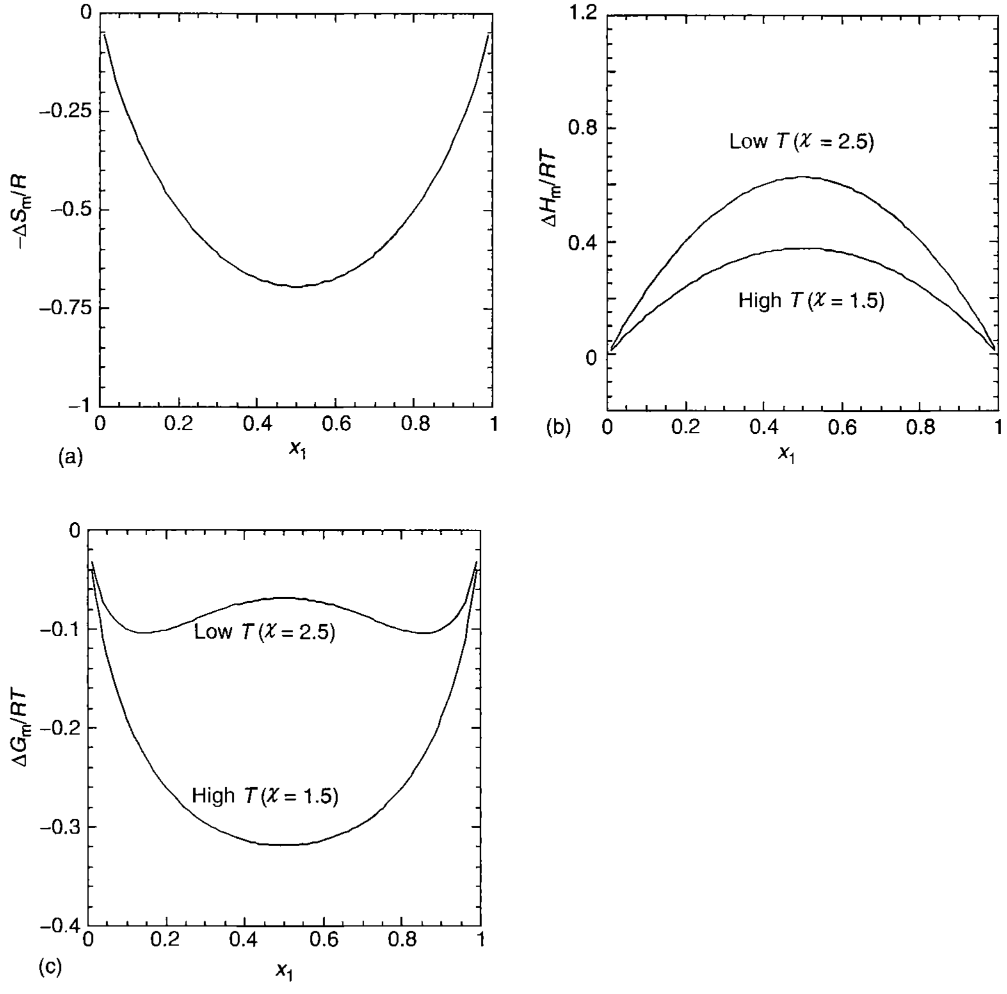

Figure 7.10 Predictions of regular solution theory for (a) entropy of mixing, plotted as $-\Delta S_m/R$; (b) enthalpy of mixing, plotted as $\Delta H_m/RT$, for two temperatures; (c) free energy of mixing obtained by combining panels (a) and (b), plotted as $\Delta G_m/RT$.

Thus "concave up" gives us the criterion for *stability* of the one-phase solution; the mathematical expression of concave up is

$$\left(\frac{\partial^2 \Delta G_m}{\partial x_i^2}\right)_{T,p} > 0 \tag{7.5.2}$$

where the second derivative can be taken with respect to the mole fraction of any component. The meaning of stability is this: In any mixture at a finite temperature, there will be spontaneous, small local fluctuations in concentration δx, such that there are small regions that have x_1 bigger than the average, and some regions where it is smaller. Now, by the argument given above, any such fluctuation will actually *increase* the free energy; the straight line connecting $\langle x_1 \rangle - \delta x_1$ and $\langle x_1 \rangle + \delta x_1$ will fall above $\Delta G_m(x_1)$. Consequently all these fluctuations will relax back to $\langle x_1 \rangle$. The importance of these spontaneous fluctuations will be taken up again in Chapter 8, where we will show how they are the origin of light scattering.

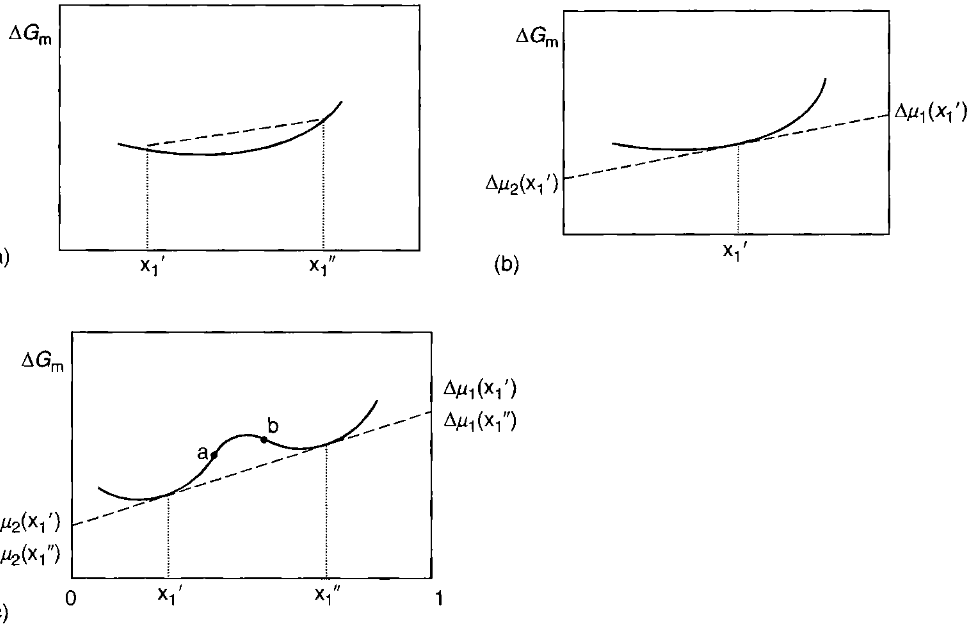

Figure 7.11 Generic free energy of mixing versus composition curves. (a) If a solution with overall composition between x_1' and x_1'' were to separate into two phases with compositions x_1' and x_1'', the resulting free energy (the dashed line) would lie above the one-phase case (smooth curve). (b) Tangent construction showing how the chemical potentials of the two components may be obtained for a given composition x_1'. (c) Tangent construction finds the compositions of the two phases x_1' and x_1'' that would coexist at equilibrium, for a system with overall composition between x_1' and x_1''. Points a and b denote the inflection points of ΔG_m, which separate the metastable ($x_1' < x_1 < a, b < x_1 < x_1''$) and unstable regions ($a < x_1 < b$).

7.5.2 Finding the Binodal

Now consider the lower T curve in Figure 7.10c, where ΔG_m shows the bump. Here we can see that if we prepared a solution with $\langle x_1 \rangle$ somewhere near the local maximum of ΔG_m, we could find an x_1' and x_1'' such that the straight line between them would fall below the ΔG_m curve for our $\langle x_1 \rangle$, and phase separation should occur. In fact, there are many such pairs x_1' and x_1'' that would lower ΔG_m, so which pair is chosen? We recall the criteria for phase equilibria: T and p must be identical in the two phases, and

$$\mu_1(x_1') = \mu_1(x_1''), \quad \mu_2(x_1') = \mu_2(x_1'') \tag{7.5.3}$$

The chemical potential of component 1 is the same in both phases and the chemical potential of component 2 is equal in both phases. (Be careful with this; both relations must be satisfied simultaneously, but it is *not* an equality between μ_1 and μ_2.) It turns out that there will be only one solution (x_1', x_1'') for both of these relations at a particular T, which we can identify by the *common tangent* construction. We can write the free energy as the mole-weighted sum of the chemical potentials (which are the partial molar free energies, Equation 7.1.5):

$$\Delta G_m = n_1 \Delta\mu_1 + n_2 \Delta\mu_2$$

or (7.5.4)

$$\Delta G_m = x_1 \Delta\mu_1 + (1 - x_1)\Delta\mu_2 = \Delta\mu_2 + x_1(\Delta\mu_1 - \Delta\mu_2)$$

where we have divided by the total number of moles to get to mole fractions, and where $\Delta\mu_i = \mu_i - \mu_i^o$. Now imagine we draw a straight line that is tangent to ΔG_m at some composition, x_1', as shown in Figure 7.11b. This line can be written generically as

$$y = kx_1 + b \tag{7.5.5}$$

where k is the slope and b is the $x_1 = 0$ intercept. But we chose $y = \Delta G_m$ for $x_1 = x'_1$, so inserting Equation 7.5.4 into Equation 7.5.5 we find

$$kx'_1 + b = \Delta\mu_2(x'_1) + x'_1\left[\Delta\mu_1(x'_1) - \Delta\mu_2(x'_1)\right] \tag{7.5.6}$$

But this relation holds whatever x'_1 we choose, so we can match the intercepts and slopes to obtain

$$\begin{aligned} b &= \Delta\mu_2(x'_1) \\ k &= \Delta\mu_1(x'_1) - \Delta\mu_2(x'_1) \end{aligned} \tag{7.5.7}$$

In other words, if we follow the tangent to the $x_1 = 0$ intercept, we obtain $b = \Delta\mu_2(x'_1)$, and if we follow it to the $x_1 = 1$ intercept, $k + b = \Delta\mu_1(x'_1)$.

The argument so far applies for any ΔG_m curve. Now if we have a ΔG_m curve with a bump as in Figure 7.11c, we can draw one straight line that is tangent to ΔG_m at *two* particular points, call them x'_1 and x''_1. From the argument above, the $x_1 = 0$ intercept gives us *both* $\Delta\mu_2(x'_1)$ and $\Delta\mu_2(x''_1)$, so these two chemical potentials must be equal. By the same reasoning the other intercept gives $\Delta\mu_1(x'_1) = \Delta\mu_1(x''_1)$, and therefore we have shown that x'_1 and x''_1 defined by the common tangent are indeed the compositions of the two coexisting phases. (Warning: for regular solution theory, where the ΔG_m curve is symmetric, x'_1 and x''_1 coincide with the local minima in the ΔG_m curve, but this is not generally true.) So, in summary, one can locate the coexistence concentrations by geometrical construction on a plot of ΔG_m versus composition, or one could do it from the analytical expressions for the two chemical potentials. However, the latter is algebraically a little tricky, particularly because of the natural logarithm terms (see, for example, Equation 7.4.14).

7.5.3 Finding the Spinodal

The next issue to address is the location of the spinodal, or *stability limit*. We have already indicated the condition for stability, namely Equation 7.5.2. The stability limit, then, is found where the second derivative of ΔG_m changes sign, which defines an *inflection point*:

$$\left(\frac{\partial^2 \Delta G_m}{\partial x_i^2}\right)_{T,p} = 0 \quad \text{on the spinodal} \tag{7.5.8}$$

Returning to Figure 7.11c, we see that there are two inflection points, marked a and b, on each side of the bump. Between these two compositions, the free energy is concave down, and we say the solution for that (x_1, T) is *unstable*. What does this mean? For any small local fluctuation in concentration δx_1, the straight line connecting $x_1 - \delta x_1$ and $x_1 + \delta x_1$ will fall below $\Delta G_m(x_1)$. These fluctuations will therefore grow in amplitude and spatial extent; the mixture will spontaneously phase separate into two phases with compositions x'_1 and x''_1. Thus in a region where the ΔG_m curve is concave down, the solution is unstable with respect to any fluctuation in concentration. The mechanism by which this phase separation occurs is called *spinodal decomposition*, and it is quite interesting in its own right. However, in this chapter we are concerned with thermodynamics, not kinetics, so we will not pursue this here.

You may have noticed that there are two regions on the curve in Figure 7.11c, between x'_1 and a, and between b and x''_1, where the curve is locally concave up, indicating stability, yet we already know that the equilibrium state in these intervals should be liquid–liquid coexistence with concentrations x'_1 and x''_1. What does this mean? These regions fall between the binodal and spinodal, and are termed *metastable*. They are stable against small, spontaneous fluctuations, but not globally stable against phase separation. Consequently, a system in the metastable region may remain there indefinitely; it requires *nucleation* of a region of the new phase before separation

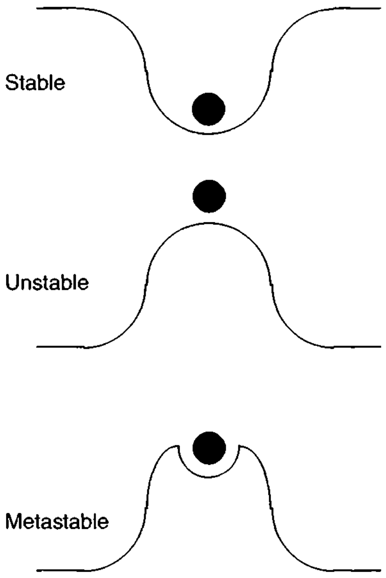

Figure 7.12 Schematic illustration of the difference between stable, unstable, and metastable states.

proceeds. Nucleation, and the ensuing process of domain growth, is another interesting kinetic process that we will not discuss here. However, metastability can be a wonderful thing; diamond is metastable with respect to graphite, the equilibrium phase of carbon at room T and p, but no one worries about diamonds transforming to graphite in their lifetime. A mechanical analogy is helpful in distinguishing among stable, metastable, and unstable systems, as shown in Figure 7.12. The ball in panel (a) may rattle around near the bottom of the bowl, but it will never come out; the system is stable. The ball in panel (b) is precariously perched on top of the inverted bowl, and the slightest breeze or vibration will knock it off; the system is unstable. The ball in panel (c) can rattle around in the small depression, and may appear to be stable for long periods of time, but with a sufficiently large impulse it will roll over the barrier and downhill to a lower energy state; the system is metastable. Only state (a) is an equilibrium state, but state (c) might not change in our lifetime.

7.5.4 Finding the Critical Point

The final feature to locate in the phase diagram is the critical point. We know it lies on the spinodal, so it must satisfy Equation 7.5.8. But, we need another condition to make it a single, special point. The easiest way to visualize this is to return to Figure 7.10c and the plots of ΔG_m at different temperatures. Phase separation occurs only when we have the bump in ΔG_m, so the critical point marks the temperature where the bump first appears. This also corresponds to the temperature where the two inflection points merge into one and this is determined by

$$\left(\frac{\partial^3 \Delta G_m}{\partial x_i^3}\right)_{T,p} = 0 \quad \text{at the critical point} \qquad (7.5.9)$$

We can understand this by realizing that as T approaches T_c from below, one inflection point moves to the right, and one to the left. The rate of change of the inflection point, $\partial/\partial x_i(\partial^2 \Delta G_m/\partial x_i^2)$, vanishes when the two meet.

Algebraic expressions for the spinodal and the critical point of regular solution theory can be directly obtained as follows. The chemical potential for component 1 (and of course, by symmetry, we could equally well use component 2) comes from differentiating ΔG_m:

$$\begin{aligned}\frac{\mu_1}{RT} &= \frac{\partial}{\partial n_1}\{n_1 \ln x_1 + n_2 \ln(1-x_1) + n_1(1-x_1)\chi\} \\ &= \ln x_1 + \frac{n_1}{x_1}\frac{\partial x_1}{\partial n_1} - \frac{n_2}{1-x_1}\frac{\partial x_1}{\partial n_1} + (1-x_1)\chi - n_1\frac{\partial x_1}{\partial n_1}\chi \end{aligned} \tag{7.5.10}$$

Now

$$\frac{\partial x_1}{\partial n_1} = \frac{n_1 + n_2 - n_1}{(n_1+n_2)^2} = \frac{x_1 x_2}{n_1} = \frac{x_2^2}{n_2} \tag{7.5.11}$$

so

$$\begin{aligned}\frac{\mu_1}{RT} &= \ln x_1 + (1-x_1) - (1-x_1) + \chi(1-x_1)^2 \\ &= \ln x_1 + \chi(1-x_1)^2 \end{aligned} \tag{7.5.12}$$

The stability limit can now be obtained by taking the derivative with respect to x_1:

$$\frac{\partial}{\partial x_1}\left(\frac{\mu_1}{RT}\right) = \frac{1}{x_1} - 2\chi_s(1-x_1) = 0 \tag{7.5.13}$$

where the subscript s denotes the value of χ on the spinodal. (You should convince yourself that if we followed the prescription for the stability limit given by Equation 7.5.8, and took the second derivative of $\Delta G_m/kT$ from Equation 7.2.11b with respect to x_1 instead of first obtaining μ_1, we would get the same relation.) This equation is a quadratic in x_1:

$$x_1^2 - x_1 + \frac{1}{2\chi_s} = 0 \tag{7.5.14a}$$

Note that this relation can be rewritten in the appealingly symmetric form

$$\frac{1}{x_1} + \frac{1}{x_2} - 2\chi_s = 0 \tag{7.5.14b}$$

The critical point requires that we differentiate Equation 7.5.13 once more:

$$\frac{\partial}{\partial x_1}\left(\frac{1}{x_1} - 2\chi(1-x_1)\right) = -\frac{1}{x_1^2} + 2\chi_c = 0 \tag{7.5.15}$$

Equation 7.5.14a and Equation 7.5.15 constitute two simultaneous equations that can be solved to obtain the critical point (see Problem 9): The result is $x_{1,c} = 1/2$ (which we could have guessed from the outset, due to symmetry) and $\chi_c = 2$. This means that unless it costs at least $2kT$ to exchange one molecule of type 1 with one molecule of type 2, there will be no phase separation. To obtain the critical temperature for a particular system, T_c, we need to know the value of χ (i.e., $z\Delta w$):

$$T_c = \frac{z\Delta w}{k\chi_c} = \frac{z\Delta w}{2k} \tag{7.5.16}$$

Generically, however, we can see that the larger Δw, the larger T_c will be, and therefore the larger the two-phase window. If, perhaps due to some specific interactions, Δw happens to be negative, there will be no critical point according to regular solution theory; the system will be completely miscible at all temperatures and in all proportions.