Chap. 9 Binary Phase Equilibria – Phase Diagrams

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9.1 Scope

The preceding chapter (with the exception of Section 8.3) dealt with the chemical properties of individual phases, in particular the Gibbs free energy of a solution and the chemical potentials of its constituents. In the present chapter, these properties are applied to determine the phases present and their compositions when a two-component system, or binary system, achieves equilibrium. The two components, denoted by A and B, distribute between two phases labeled I and II. This system, shown in Fig. 9.1, is at thermal, mechanical, and chemical equilibrium. The first two of these conditions means that the two phases have the same temperature and pressure. The consequence of the last condition is developed in the following section.



Fig. 9.1 Components A and B equilibrated in two phases I and II at specified pressure and temperature

Phases I and II can be solid, liquid or gas in any combination except two gases. Chemical reaction between components A and B is not permitted; the two species retain the same molecular form in the two phases they occupy (with the exception of the dissolution of a diatomic gas in some solids).

Practically important examples of two-component, two-phase equilibria include the following:

<u>Gas-liquid:</u> example: oxygen solubility in water. Although the solubility is small, the effect on corrosion of metals is profound.

<u>Gas-solid</u>: example: dissolution of hydrogen in metals. The special feature of this process is the dissociation of molecular hydrogen into atoms in the metal

<u>Liquid-liquid:</u> example: distribution of a solute between two immiscible solvents, such as acetic acid between water and a hydrocarbon. This example contains three components, but because the solvents are immiscible (meaning no mutual solubility), the thermodynamics governing the distribution of the solute is formally identical to the two-

component case. Liquid-liquid extraction is a basic unit operation in the chemical process industry.

<u>Two condensed phases</u>: solids and liquids are collectively known as condensed phases. Analysis of equilibria between condensed phases usually ignores the gas phase. The condensed phase combinations include liquid-solid and solid-solid. The many crystallographic forms of solids are each regarded as distinct phases, so these equilibria show considerable variety. The subject is known as binary phase diagram representation.

In each of the above examples, the objective is to determine the concentrations of components A and B in the two coexisting phases. In condensed-phase equilibria, identification of the stable phases I and II is also an objective.

9.2 Condition of Interphase Equilibrium

The two-headed arrows in Fig. 9.1 indicate chemical equilibrium of components A and B between phases I and II. According to the discussion in Sect. 5.4, the criterion of chemical equilibrium at fixed T and p is the minimization of the total Gibbs free energy of the contents of the cylinder-piston in the figure. Since the total Gibbs free energy is the sum of those of the two phases, this criterion is:

$$dG = dG_I + dG_{II} = 0 \tag{9.1}$$

The free energy of a phase is related to the chemical potentials of its components by Eqs (8.31) and (8.32). Using the latter for components A and B in Eq (9.1) gives:

$$\mu_{AI}dn_{AI} + \mu_{BI}dn_{BI} + \mu_{AII}dn_{AII} + \mu_{BII}dn_{BII} = 0$$

where $n_{AI} \dots n_{BII}$ are the numbers of moles of each constituent in each phase and $\mu_{AI} \dots \mu_{BII}$ are their chemical potentials.

The change in the state of the system implied by the differentials in Eq (9.1) is the movement of a small quantity of one of the two components from phase I to phase II without altering the other component. Thus, if dn_{AI} moles of A are transferred from I to II, the change in n_{AII} is $dn_{AII} = -dn_{AI}$. Because component B is not moved, $dn_{BI} = dn_{BII} = 0$. Inserting these mole relations into the preceding equation yields the result $\mu_{AI} = \mu_{AII}$. Applying the same argument to component B yields $\mu_{BI} = \mu_{BII}$. In general, for any number of components in the two-phase system, the condition for chemical equilibrium is:

$$\mu_{iI} = \mu_{iII} \quad \text{for all } i \tag{9.2}$$

The chemical potentials are seen to be analogous to the thermal and mechanical potentials which provide the equilibrium conditions $T_I = T_{II}$ and $p_I = p_{II}$. Equation (9.2) is the multicomponent generalization of the equilibrium condition for two coexisting phases of a pure substance, namely $g_I = g_{II}$, where g is the molar Gibbs free energy (Eq (6.2)).

9.3 Raoult's and Henry's Laws

These two thermodynamic laws deal with the partitioning of the components A and B between a gas phase and a condensed phase. They are limiting cases of a general vapor-liquid or vapor-solid distribution expression relating the partial pressures of A and B in the gas, p_A and p_B , to the mole fractions of these components in the condensed phase, x_A and x_B . We will assume that the condensed phase contains only A and B (although this is not required) and that the total pressures p is fixed, as is the temperature. The gas phase may contain an inert diluent that does not enter the liquid phase, such as the rare gas helium. As long as the total pressure is not very large, its value does not affect the distributions of A and B between the two phases. We derive the distribution laws for component A only; those for component B are determined in the same manner as for A.

From Eq (9.2) the equilibrium condition for component A is $\mu_A(g) = \mu_A(s \text{ or } l)$, where g denotes the gas phase and s and l denote solid and liquid, respectively. The relationships between the chemical potential and the partial pressure in the gas phase and between the chemical potential and the mole fraction in the condensed phase were derived in Sects 8.7 and 8.10. For the solid or liquid, combination of Eqs (8.34) and (8.35) yields:

$$\mathbf{m}_{A}(s \text{ or } l) = g_{A}(s \text{ or } l) + RT \ln(\mathbf{g}_{A}x_{A})$$
(9.3)

where g_A is the molar free energy of pure A and γ_A is the activity coefficient of A in the A-B solution. The chemical potential of A in the gas phase is given by Eq (8.47):

$$\boldsymbol{m}_{A}(g) = g_{A}^{o}(g) + RT \ln p_{A} \tag{9.4}$$

where $g_A^o(g)$ is the molar Gibbs free energy of pure gaseous A at one atm pressure (indicated by the superscript o). The corresponding quantity for the condensed phase, g_A , does not need an indication of 1 atm because it is essentially pressure-insensitive. Both molar free energies are at the same temperature T.

Equating the right hand sides of Eqs (9.3) and (9.4) as required by the equilibrium criterion yields:

$$\frac{p_A}{g_A x_A} = \exp\left(-\frac{g_A^o(g) - g_A(s \text{ or } l)}{RT}\right)$$

For pure component A, the terms on the left hand side of the above equation are: $\gamma_A = 1$, $x_A = 1$, and $p_A = p_{sat,A}$, the vapor pressure. Therefore, the right hand side of the above equation is the vapor pressure of pure A, and the formula can be written as:

$$p_A = \mathbf{g}_A x_A p_{sat,A} \tag{9.5}$$

A similar equation applies to component B:

$$p_B = g_B x_B p_{sat,B} \tag{9.6}$$

Equations (9.5) and (9.6) are the general relations between the concentrations of a component in the condensed phase and the equilibrium partial pressures in the gas phase. The latter depend on the composition of the condensed phase and on the deviations of the components from ideality, as represented by the activity coefficients. These two quantities are not independent, however; if γ_A is known as a function of composition, γ_B follows from application of the Gibbs-Duhem equation (see Eq (8.36b)).

The activity coefficients can be greater or less than unity, depending on the strength of the bonds between A and B molecules compared to the mean of the A-A and B-B bond strengths. The curves in Fig. 9.2 illustrate these two cases; activity coefficients greater than unity give positive deviations from ideal behavior and activity coefficients less than unity result in negative deviations. This figure illustrates the type of measurement (i.e., partial pressure as a function of solution composition) that, in conjunction with Eq (9.5), provides experimental values of activity coefficients of components in solution.



Fig. 9.2 Equilibrium partial pressures of component A over A-B solutions that exhibit positive and negative deviations from ideality. The temperature is fixed.

The line labeled "Raoult's law" represents ideality. For systems that obey this law, the activity coefficients of both A and B are unity over the entire composition range. The equilibrium partial pressures are lower than the pure-component vapor pressures by factors exactly equal to the corresponding mole fraction in the solution.

$$p_A(ideal \ solution) = x_A p_{sat,A}$$
 $p_B(ideal \ solution) = x_B p_{sat,B}$ (9.7)

Such solutions are the exception rather than the rule. For Raoult's law to be followed, the two components must be chemically very similar (e.g., A = benzene and B = toluene – see problem 9.1). Even metals as similar as nickel and iron exhibit nonideal behavior when in solution with each other.

In Fig. 9.2, the partial pressure curve joins the Raoult's law line as x_A approaches unity. In this limit, the activity coefficient of A approaches unity. Less expected is the approach of the partial pressure curve and the Raoult's law line well before x_A reaches one. That is, not only is $\gamma_A = 1$ as $x_A = 1$, but $d\gamma_A/dx_A = 0$ in the same limit.

At the other limit, as the solution becomes dilute in component A, the partial pressure curve turns into the straight line labeled Henry's law in Fig. 9.2. For this functional dependence, Eq (9.5) shows that the activity coefficient must be constant, although not equal to unity. This dilute solution behavior of a constant activity coefficient reduces Eq (9.5) to:

$$p_A(\text{dilute A}) = \gamma_A(x_A \rightarrow 0) p_{\text{sat},A} x_A = k_{\text{HA}} x_A \qquad (9.8)$$

The product of the activity coefficient and the vapor pressure, k_{HA} , is termed the Henry's law constant. Physically, Henry's law behavior in dilute solutions simply reflects the fact that all A molecules are surrounded by B molecules, irrespective of the concentration of A (as long as it is low). In the Henry's law limit for component A, component B obeys Raoult's law.

Exercises that apply the general partial pressure-composition formulas of Eqs (9.5) and (9.6) are part of problems 9.2, 9.10, 9.15, 9.18 and 9.19. In some of these problems, the activity coefficient is expressed by the regular-solution formulas of Eqs (8.44). The remaining exercises involve nonideal solutions with nonregular activity coefficients. Problem 9.4 provides the thermodynamic basis for an everyday phenomenon: the boiling point of water containing dissolved salts is higher than that of pure water.

Two other common phase distribution systems are consequences of the physical situation that leads to Henry's law in vapor-condensed phase equilibria. The first is the partitioning of a small quantity of a solute species A between two immiscible solvents, designated as phases I and II. At equilibrium, the chemical potentials of A in the two phases, as given by Eq (9.3), are equal. The common pure-A molar free energy cancels, leading to the equilibrium relation:

$$\frac{x_A^{II}}{x_A^I} = \frac{\mathbf{g}_A^I}{\mathbf{g}_A^{II}} = D_A \tag{9.9}$$

The ratio of the activity coefficients of A in the two solvents is called the distribution coefficient of A, D_A . As long as A is dilute in both solvents, the activity coefficients are independent of the concentration of A, but in general are not equal.

The second example of the application of Henry's law involves the dissolution of the so-called permanent gases in condensed phases. Examples are helium solution in glass and oxygen dissolution in water. To describe this equilibrium situation, the chemical potentials of the gas (species A) in the two phases are equated. In the gas phase, the chemical potential of A is given by Eq (9.4). In applying Eq (9.3) to A in the condensed phase, however, the assignment of the reference free energy $g_A(s \text{ or } l)$ poses a difficulty. It cannot refer to pure A as a solid or liquid because A is gaseous at all temperatures of interest. Consequently, $g_A(s \text{ or } l)$ in Eq (9.3) is replaced by the molar free energy of A in its normal gaseous state at 1 atm pressure. That is, $g_A(s \text{ or } l)$ is replaced by $g_A^{\circ}(g)$. In so doing, the characteristic behavior $\gamma_A \rightarrow 1$ as $x_A \rightarrow 1$ is lost, but this is of no practical consequence because high concentrations of the permanent gases in the condensed phases cannot be attained. With this modification in Eq (9.3), equating with Eq (9.4) yields:

$$\frac{x_A}{p_A} = \frac{1}{g_A} = k_{HA} \tag{9.10}$$

where k_{HA} is the Henry's law constant for the gas in the solid or liquid. Note that the definition of k_{HA} in Eq (9.10) is the inverse of that defined in Eq (9.8) for condensable vapors.

In arriving at Eq (9.10), the activity coefficient has lost its original meaning as a deviation from solution ideality. In the end, all that thermodynamics has been able to elucidate for this case is the proportionality of x_A and p_A

The preceding application of Henry's law does not apply to the very important case of the dissolution of diatomic gases such as H_2 , O_2 , and N_2 in metals. These gases dissociate into atoms upon entering a metal, and the dissolution process is best treated as a chemical reaction rather than as a physical distribution between phases. This process is deferred until the next chapter.

9.4 Binary Solid-Liquid and Solid-Solid Equilibria (Phase diagrams)

Binary phase diagrams depict the stable condensed phase (or phases) formed by a two-component system as a function of temperature and overall composition. The ordinate of a phase diagram is the temperature and the overall composition is the abscissa.

The composition of the gas phase in equilibrium with the solid or liquid (as given by Eqs (9.5) and (9.6)) is ignored in this representation. In order to graphically depict the equilibrium partial pressures as functions of temperature and composition would require a third dimension on the plot, which makes the representation unwieldy.

The phase rule (see Eq (1.23)) for a two component system permits $\mathbf{F} = 4 - \mathbf{P}$ degrees of freedom for a two-component system. Since the diagrams deal only with

condensed phases, they are minimally affected by total pressure^{*}. Ignoring the total pressure reduces the number of degrees of freedom by one, thereby allowing $3 - \mathbf{P}$ properties to be independently varied. In a single phase ($\mathbf{P} = 1$) portion of the phase diagram, two degrees of freedom are permitted. These are the temperature T and the composition, represented by the mole fraction of one of the constituents, say x_B . Single-phase regions appear as areas in the phase diagram.

In two-phase zones ($\mathbf{P} = 2$), only one system property can be specified. Fixing the temperature, for example, determines the compositions of the two coexisting condensed phases. These temperature-composition relationships appear in the phase diagram as lines (or curves) called *phase boundaries*. A three-phase system ($\mathbf{P} = 3$) has no degrees of freedom and is represented by a point on the phase diagram.

The distinction between overall compositions and the compositions of individual phases is essential to understanding phase diagrams. For single-phase zones, the two are identical. When two phases coexist, the compositions of the phases are different from the overall composition. The latter is the quantity-weighted average of the compositions of the two phases (i.e., the lever rule).

The structure of a phase diagram is determined by the condition of chemical equilibrium. As shown in Sect. 9.2, this condition can be expressed in one of two ways: either the total Gibbs free energy of the system (Eq (8.38)) is minimized or the chemical potentials of the each component (Eq(9.3)) in coexisting phases are equated. The choice of the manner of expressing equilibrium is a matter of convenience and varies with the particular application.

9.5 Melting of Two-Component Ideal Systems

A pure substance melts at a fixed temperature. A binary solution changes from solid to liquid over a range of temperatures. In the melting range, components A and B in the solid phase are in equilibrium with A and B in the coexisting liquid phase. The equilibrium conditions are:

$$\mu_A(L) = \mu_A(S)$$
 and $\mu_B(L) = \mu_B(S)$

The chemical potentials are related to mole fractions by Eq (9.3). Assuming that the A-B solutions are ideal in both the solid and liquid phases, the above conditions become:

$$g_A(L) + RT \ln x_{AL} = g_A(S) + RT \ln x_{AS}$$
(9.11a)

$$g_{B}(L) + RT \ln x_{BL} = g_{B}(S) + RT \ln x_{BS}$$
(9.11b)

Since $x_{AL} + x_{BL} = 1$ and $x_{AS} + x_{BS} = 1$, the above equations contain two unknowns. Solution gives the composition of the solid and liquid as functions of temperature, the

^{*} The total pressure is independent of the equilibrium partial pressures of the components of the condensed phase. For example, an inert gas can be added to the gas phase without affecting the thermodynamics.

plot of which is a *binary* phase *diagram*. Eliminating the mole fractions of component A gives the following solutions of Eqs (9.11):

$$x_{BL} = \frac{1 - e^a}{e^b - e^a}$$
 and $x_{BS} = e^{\beta} \left(\frac{1 - e^{\alpha}}{e^{\beta} - e^{\alpha}} \right)$ (9.12)

 α and β are the temperature functions:

$$\boldsymbol{a} = \frac{g_A(L) - g_A(S)}{RT}$$
 $\boldsymbol{b} = \frac{g_B(L) - g_B(S)}{RT}$

The temperature dependence of the Gibbs free energy of a pure phase was derived in Sect. 6.7. To a good approximation, the Gibbs free energy difference between liquid and solid is given by Eq (6.12):

$$g(L) - g(S) = \left(1 - \frac{T}{T_M}\right) \Delta h_M \tag{9.13}$$

where T_M is the melting temperature of the pure substance and Δh_M is its heat of fusion. Combining the above two equations gives α and β as explicit functions of temperature:

$$\boldsymbol{a} = \left(1 - \frac{T}{T_{MA}}\right) \frac{\Delta h_{MA}}{RT} \qquad \boldsymbol{b} = \left(1 - \frac{T}{T_{MB}}\right) \frac{\Delta h_{MB}}{RT} \qquad (9.14)$$

Figure 9.3 shows the phase diagram for an ideal binary system calculated from Eqs (9.12) using specific values of the melting properties of metals A and B (chosen as U and Zr, see Table 9.1). The upper line (representing T Vs x_{BL}) is called the *liquidus*. All points lying above this line are completely liquid. Similarly, all points below the lower curve (the *solidus*, or T Vs x_{BS}) are completely solid, which in this case is an ideal solid solution.



Fig. 9.3 Phase diagram of a binary system with ideal behavior in both liquid and solid

In the region bounded by the solidus and the liquidus, two phases coexist. The left-hand panel of Fig. 9.3 represents the actual phase diagram. In the right-hand panel, the horizontal and vertical lines are superimposed on the phase diagram in order to illustrate important characteristics of the melting process. If the solid solution with a composition $x_B = 0.4$ is heated, the intersection of the vertical line with the liquidus (at point A) shows that the first liquid appears at 1630 K and has a composition $x_{BL} = 0.21$ (at point B). As the temperature is increased to 1700 K, the system lies at point P. Here a liquid phase with composition $x_{BL} = 0.31$ (point C) and a solid phase with $x_{BS} = 0.49$ (point D) coexist. The fraction of the mixture present as liquid at point P is obtained from the mole balance known as the *lever rule*^{*}:

Fraction liquid at point P =
$$\frac{\overline{PB}}{\overline{CB}} = \frac{x_{BS} - x_B}{x_{BS} - x_{BL}} = \frac{0.49 - 0.4}{0.49 - 0.31} = 0.50$$

Upon heating from point P, the last solid disappears at T = 1790 K (Point E on the liquidus). Melting of this binary system at this particular overall composition is spread over a 160 K temperature range.

Problem 9.6 provides additional practice in applying ideal-melting theory to the MnO-FeO binary system. The effect of even slight deviations from ideal solution behavior can result in phase diagrams that are distorted or qualitatively different from the diagram shown in Fig. 9.3. Problems 9.8, 9.9 and 9.16 explore the nonideality effect on this type of phase diagram using regular solution theory for the solid and liquid phases.

9.6 Phase Separation

The single-phase solid and liquid phase regions in Fig. 9.3 exhibit no structure because the A-B solutions were assumed to be ideal. However, if the components exhibit positive deviations from ideality (i.e., if the A-B molecular interaction is weaker than the average of the A-A and the B-B interactions), the single-phase solutions separate into two distinct phases, either both liquid or both solid. The system in which phase separation has occurred is termed *partially miscible* because the B-rich phase contains some dissolved A and the A-rich phase contains some dissolved B.

The phase diagram for a binary system exhibiting phase separation can be deduced in one of two equivalent ways: analytically, starting from the equilibrium criterion in terms of chemical potentials (Eq (9.2)); or graphically, based on minimizing the system's total Gibbs free energy, as suggested by Eq (9.1). In both methods, nonideality is assumed (for simplicity) to be represented by the regular solution model (Sect. 8.9), in which the excess Gibbs free energy is approximated by the excess enthalpy. This latter property is a symmetric function of composition:

^{*} See p. 13 of Chap. 2 for application of the lever rule in single-component vapor-liquid systems Sect, 9.9 presents a more detailed discussion of the levery rule for binary condensed-phase systems.

$$\mathbf{h}^{\mathrm{ex}} = \mathbf{\Omega} \mathbf{x}_{\mathrm{A}} \mathbf{x}_{\mathrm{B}} \tag{9.15}$$

where Ω is the interaction energy. If this property is negative, the stability of the A-B solution is greater than that of the ideal solution, and no phase separation occurs. If $\Omega > 0$, the solution is energetically less stable than an ideal solution. When the destabilizing effect of the excess enthalpy overcomes the stabilizing influence of the entropy of mixing, phase separation occurs.

Analytical Method

Labeling the partially-miscible phases as I and II, use of Eq (9.3) in Eq (9.2) with i = A yields the following:

$$g_A + RT \ln \gamma_{AI} x_{AI} = g_A + RT \ln \gamma_{AII} x_{AII}$$
(9.16a)

The analogous equation for component B is:

$$g_{B} + RT \ln \gamma_{BI} x_{BI} = g_{B} + RT \ln \gamma_{BII} x_{BII}$$
(9.16b)

The activity coefficients derived from h^{ex} of Eq (9.15) are given by Eq (8.44). Substituting these into Eq (9.16) and replacing x_A by $1 - x_B$ for both phases gives:

$$C(x_{BI}^2 - x_{BII}^2) = ln\left(\frac{1 - x_{BII}}{1 - x_{BI}}\right)$$
 (9.17a)

$$C[(1 - x_{BI})^2 - (1 - x_{BII})^2] = ln\left(\frac{x_{BII}}{x_{BI}}\right)$$
 (9.17b)

where

$$C = \Omega/RT \tag{9.18}$$

is a dimensionless (but temperature-dependent) form of the interaction parameter.

Equation (9.17b) can be obtained from Eq (9.17a) by replacing x_{BI} and x_{BII} by $1-x_{BI}$ and $1-x_{BII}$, respectively. This mathematical feature implies that the two equations are mirror-image branches of a function that is symmetric about $x_B = 0.5$. Using the mathematical property $x_{BII} = 1 - x_{BI}$ of such a symmetric function, Eqs (9.17a) and (9.17b) are seen to be identical, and can be represented by the function:

$$C = \frac{\ln\left(\frac{1 - x_B}{x_B}\right)}{1 - 2x_B}$$
(9.19)

This function passes through a minimum at $x_B = 0.5$, at which point, l'Hopital's rule shows that C = 2. No mathematical solutions exist for C < 2, which physically means that the system is a single phase solution for all compositions. For C > 2, the same value of C is obtained for x_B and $1 - x_B$.

To convert Eq (9.19) to the equation for the phase diagram (i.e., T Vs x_B), we note that the maximum C = 2 can be converted to a unique temperature T* by using Eq (9.18):

$$T^* = \Omega/2R \tag{9.20}$$

T* is called the *critical solution temperature*. It is a property of the A-B binary system that reflects its nonideal behavior, as represented in the regular solution approximation.

With the help of Eqs (9.18) and (9.20), Eq (9.19) becomes:

$$\frac{T}{T^*} = \frac{2(1 - 2x_B)}{\ln\left(\frac{1 - x_B}{x_B}\right)}$$
(9.21)

Equation (9.21) is graphed in Fig. 9.4. For $T > T^*$ only a single solution exists. Below T^{*}, the system spits into two phases. In this range, the compositions of phase I follow the curve up to $x_B = x_{BI} = 0.5$. The remaining portion of the curve represents the compositions x_{BII} of the second phase.



Fig. 9.4 Phase diagram of a binary system exhibiting phase separation

Graphical Method

An alternative to the analytical method for determining the phase diagrams of a binary system exhibiting phase separation is a graphical procedure based on minimizing the Gibbs free energy of the system at a fixed temperature (and total pressure). Per mole of solution, the free energy is given by Eq (8.38) with g^{ex} approximated by h^{ex} for a regular solution:

$$g = g_{\rm comp} + h^{\rm ex} - Ts_{\rm mix} \tag{9.22}$$

Where g_{comp} is the sum of the free energies of the pure (unmixed) components:

$$g_{\rm comp} = x_{\rm A}g_{\rm A} + x_{\rm B}g_{\rm B} \tag{9.23}$$

where x_B and $x_A = 1-x_B$ represent the overall composition of the two-phase mixture, not the composition of either of the individual phases. h^{ex} is the excess enthalpy according to regular solution theory (Eq (9.15)), and s_{mix} is the entropy of mixing:

$$s_{mix} = -R(x_A ln x_A + x_B ln x_B)$$
(9.24)

The phase diagram depends on the last two terms in Eq (9.22). They represent the change in the Gibbs free energy of the system when the pure components are mixed. To aid in visualizing the interplay of these terms, Eq (9.22) is divided by RT: the entropy of mixing term becomes s_{mix}/R , which is independent of temperature; the excess enthalpy becomes Cx_Ax_B , where C is the dimensionless form of the interaction parameter in regular solution theory. According to Eq (9.18), C can be varied either by changing the interaction energy Ω or by changing the temperature.

Figure 9.5 shows how the excess enthalpy and the entropy of mixing combine graphically to produce mixing free energy curves. The curves represent four values of C. In sequence (a), the interaction parameter Ω is negative, so C < 0 at any temperature. The curve on the right shows that the mixing free energy is negative at all compositions. This implies that the homogeneous solution is the stable (equilibrium) condition, and no phase separation occurs. Curve (b) for $\Omega = 0$ (hence C = 0) represents an ideal system, for which $g - g_{comp}$ is negative at all compositions and temperatures and the solution is the stable state. Note that stability is provided by the entropy of mixing.

The set of curves represented in (c) and (d) of Fig. 9.5 represent variations in C that are best regarded as due to changes in temperature while holding constant a positive value of Ω . In (c), the temperature is higher than the critical solution temperature so C is less than 2. The mixing free energy curve on the right is qualitatively the same as those in (a) and (b), and the homogeneous solution is stable at all compositions. As the temperature is reduced below T* in (d), the positive h^{ex} curve is sufficiently large to produce a bump in the center of the $g - g_{comp}$ curve when added to the s_{mix} curve. Instead of a minimum at $x_B = 0.5$, there is now a maximum. More importantly, two off-center minima appear at abcissa locations I and II. The interpretation of this graphical feature is that for any overall composition between the two minima, the lowest total free energy is



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Fig. 9.5 Graphical addition of excess enthalpy and entropy of mixing for various values of the dimensionless interaction parameter (regular solution theory)

achieved by dividing the system into two partially miscible phases with compositions at the off-center minima, namely x_{BI} and x_{BII} . The phase diagram of Fig. 9.4 can be constructed from a number of graphs like (d) in Fig. 9.5 for different temperatures lower than T* and transferring the compositions of the off-center minima to the phase diagram.

This is a cumbersome procedure for this particularly simple system, but as shown in the next section, graphical construction of phase diagrams from free energy Vs composition curves becomes the method of choice for complicated systems.

<u>Problem</u>: Show (analytically) that the compositions of the two phases at the off-center minima in Fig. 9.5(d) are identical to those obtained by the analytical method for the value of T^* corresponding to C = 3 applied to the graphical method.

<u>Analytical Method:</u> Eliminating Ω between Eqs (9.18) and (9.20) gives:

$$\frac{\mathrm{T}}{\mathrm{T}^*} = \frac{2}{\mathrm{C}} = \frac{2}{3}$$

Solving Eq (9.21) (numerically) for this value of the relative temperature gives $x_{BI} = 0.07$ and a second solution at $x_{BII} = 0.93$.

<u>Graphical Method:</u> The minima in the lower right hand graph of Fig. 9.5 satisfy the condition of minimum Gibbs free energy. From Eq (9.22) this is:

$$\frac{d}{dx_{B}}(g - g_{comp}) = \frac{d}{dx_{B}}(h^{ex} - Ts_{mix}) = 0$$

Using h^{ex} from Eq (9.15), s_{mix} from Eq(9.24), C from Eq (9.18) and dividing by RT yields:

$$\frac{d}{dx_B}(Cx_Ax_B) + \frac{d}{dx_B}(x_A\ln x_A + x_B\ln x_B) = 0$$

With $x_A = 1 - x_B$, taking the derivatives as indicated leads to Eq (9.19). For the specified value of C = 3, this equation yields the pair of solutions $x_{BI} = 0.07$, $x_{BII} = 0.93$. The exact correspondence of these phase compositions with those obtained by the analytical method is expected because Eq (9.21) was derived from Eq (9.19).

Problem 9.3 offers an additional exercise in analyzing phase separation in a binary regular solution.

Real Systems

The symmetry of the two-phase boundary in Fig. 9.4 arises from the use of regular solution theory to account for nonideality. Deviations from this model are common. Figure 9.6 shows the phase diagram of the binary liquid system consisting of n-hexane and nitrobenzene. The critical solution temperature of 295 K is achieved at a mole fraction of nitrobenzene of 0.6. The symmetry of the curve in Fig. 9.4 is lost because h^{ex} cannot be represented by the single-parameter regular solution formula given by Eq (9.15).

Real systems may exhibit the characteristic features of ideal (or near-ideal) melting (Fig. 9.3) and phase separation (Fig. 9.4) in the same phase diagram. Figure 9.7 shows the phase diagram of the $ZrO_2 - ThO_2$ system. Although technically three-component systems, oxides can generally be represented as pseudo-binary systems consisting of the two very stable compounds.



Fig. 9.6 Phase diagram for nitrobenzene and n-hexane



Fig. 9.7 The ThO₂ - ZrO₂ Phase Diagram

9.7 Graphical Construction of Binary Phase Diagrams

The cases of melting of two-component ideal solutions and of phase separation in a regular solution described in the preceding sections were handily treated by purely analytical methods. The graphical method applied to the phase-separation system in Sect. 9.6 offered no improvement in translating thermodynamic properties to the phase diagram. However, as the nonideal behavior of the liquid and solid solutions become more complicated (i.e., do not follow regular solution theory), the analytical methods based on Eq (9.2) as the starting point quickly become sufficiently complex to preclude derivation of simple formulae such Eqs (9.12) and (9.21). The graphical method does not have this restriction. Provided only that the free energy Vs composition curves can be drawn for each phase, construction of the phase diagram is straightforward. Moreover, the graphical method provides a qualitative understanding of the process that would be lost in complex mathematical analysis.

Common tangent rule

The foundation of the graphical method is called the common tangent rule. This is a graphical construction applied to free energy curves that provides the link to the phase diagram. The common tangent rule states that the compositions of the two coexisting equilibrium phases lie at the points of common tangency of the free energy curves. The two phases may be both solids, both liquids, or one solid and one liquid. For generality, the two phases are labeled I and II. As usual, the components are A and B.

Applying Eq (8.32) to each phase and using $dx_A = -dx_B$ gives:

$$\left(\frac{\mathrm{d}g}{\mathrm{d}x_{\mathrm{B}}}\right)_{\mathrm{I}} = \mu_{\mathrm{BI}} - \mu_{\mathrm{AI}}$$
 and $\left(\frac{\mathrm{d}g}{\mathrm{d}x_{\mathrm{B}}}\right)_{\mathrm{II}} = \mu_{\mathrm{BII}} - \mu_{\mathrm{AII}}$

The equilibrium condition of Eq (9.2) requires that $\mu_{AI} = \mu_{AII}$ and $\mu_{BI} = \mu_{BII}$. When these equalities substituted into either of the above equations, the result is the common tangent condition:

$$\left(\frac{\mathrm{dg}}{\mathrm{dx}_{\mathrm{B}}}\right)_{\mathrm{I}} = \left(\frac{\mathrm{dg}}{\mathrm{dx}_{\mathrm{B}}}\right)_{\mathrm{II}} \tag{9.25}$$

This equation states that the equilibrium concentrations of two coexisting phases in a binary system are the points on the free energy curves touched by the same straight line. The common tangency rule was used (without proof) in assigning the compositions of the two coexisting phases in the lower right hand panel of Fig. 9.5 to those of the off-center minima.

Melting/solidification of a two-component ideal system

The melting characteristics of a binary system that is ideal in both liquid and solid states were derived analytically in Sect. 9.5. Here, the same analysis is performed graphically, and the results are shown to be identical to those obtained by the analytical method.

All graphical determinations of binary phase diagrams begin with the free energy Vs composition curves for all possible phases in the system. For ideal systems, these curves are given by Eqs (9.22) - (9.24) with $h^{ex} = 0$ in both solid and liquid phases:

$$g(L) = x_A g_A(L) + x_B g_B(L) + RT(x_A \ln x_A + x_B \ln x_B)$$
(9.26a)

$$g(S) = x_A g_A(S) + x_B g_B(S) + RT(x_A \ln x_A + x_B \ln x_B)$$
(9.26b)

In order to construct the free energy – composition curves using these equations, the four pure-component molar free energies must be specified. Equation (9.13) relates the molar free energies of the pure liquids and pure solids:

$$g_{A}(L) = g_{A}(S) + \left(1 - \frac{T}{T_{MA}}\right) \Delta h_{MA}; \qquad g_{B}(L) = g_{B}(S) + \left(1 - \frac{T}{T_{MB}}\right) \Delta h_{MB}$$
(9.27)

As discussed in Sect. 1.6, the Gibbs free energy (in common with u, h, and h) has no absolute value. Therefore, two molar free energies, say $g_A(S)$ and $g_B(S)$, can be specified arbitrarily. Of course, this choice affects the shapes and positions of the free energy curves, but the compositions at the common tangency points are unaffected. This can be proved by substituting Eqs (9.27) into (9.26) and then into Eq (9.25). The resulting common-tangent equation does not contain $g_A(S)$ and $g_B(S)$.

For convenience, we choose $g_A(S) = 0$ and $g_B(S) = 0$. The melting properties of the two components are those of uranium (component A) and zirconium (component B) and are given in Table 9.1.

 Table 9.1 Melting properties of Uranium and Zirconium

Component	Element	T _M , K	$\Delta h_{\rm M}$, kJ/mole
А	uranium	1406	15.5
В	zirconium	2130	23.0

To illustrate the common tangent construction, a temperature between the melting points of the two pure components is required. We choose 1500 K. Equation (9.27) gives $g_A(L) = -1.04 \text{ kJ/mole}$. The minus sign simply indicates that liquid U is more stable than the solid at a temperature above the melting point. For Zr, Eq (9.27) yields $g_B(L) = 6.80 \text{ kJ/mole}$.

Plots of Eqs (9.26a) and (9.26b) are shown in Fig. 9.8. The common tangent is the dotted line that by visual approximation is tangent to the liquid free-energy curve at $x_{BL} = 0.09$ and to the solid curve at $x_{BS} = 0.16$. For $x_B < x_{BL}$ the free energy of the liquid is lower than that of the solid, so the system is a single phase liquid. Similarly for $x_B > x_{BS}$, g(L) > g(S) and the system is a solid solution. At this temperature, the two-phase region occupies the overall composition interval $x_{BL} < x_B < x_{BS}$.

The melting behavior deduced from the graphical method corresponds to the phase diagram shown in Fig. 9.3 and the liquid and solid compositions calculated by this technique should be the same as those obtained by the analytical method. At T = 1500 K, Eq (9.14) gives $\alpha = -0.083$ and $\beta = 0.546$. Equations (9.12) yield $x_{BL} = 0.099$ and $x_{BS} = 0.17$. The discrepancy between these values and those obtained from the graphical method is due to the difficulty in pinpointing visually the tangency points in Fig. 9.8.



Fig. 9.8 Free energy curves for ideal solid and liquid solutions

Problems 9.11 and 9.17 use free energy plots and the common-tangent rule to deduce a more complex type of phase diagram than the ideal systems treated above. The following section shows how this method generates a particularly common phase diagram, called a *eutectic* phase diagram.

9.8 Eutectic Phase Diagram

The binary systems treated in the preceding sections were either ideal (meltingsolidification, Sects 9.5 and 9.7) or deviated positively from ideality according to regular solution theory (phase separation, Sect. 9.6). These simple types of behavior are rarely found in real binary systems. First, there may be more than one solid phase each with a distinct crystal structure, just as there are in pure substances (see Sect. 6.8). Second, the liquid phase and the solid phase(s) are generally nonideal. The extent of deviation from ideality is usually different in each phase, and may not be adequately represented by regular solution theory. For very negative deviations from ideal solution behavior, indicative of strong A-B interaction, often leads to the formation of distinct compounds that appear in the phase diagram (e.g., AB₂, A₂B, AB). The increased physical complexity of such systems renders analytic calculation of the phase diagram infeasible, although computer codes have been developed for this purpose.

Irrespective of the complexity of the nonideal behavior of the phases involved, the phase diagram can always be constructed if the free energy Vs composition curves for each phase can be drawn. The link between the two graphical representations is the common-tangent rule. Because of the wide variations in the shapes of free-energy curves, the types of phase diagrams deduced from them reaches zoological proportions. In this section, a common variety called the *eutectic phase diagram* is developed by the graphical method.

The prototypical eutectic system consists of one liquid and two solid phases, labeled α and β . The α phase has the crystal structure of pure solid A and the β phase that of pure B. The two structures are usually different, as opposed to the phase-separation system, in which solids A and B have the same structure (see Figs. 9.6 and 9.7).

The free energy curves are plots of Eq (9.22) for each phase. Deviation from ideality is expressed by the excess enthalpy term in Eq (9.22). For solutions that do not obey regular solution theory, h^{ex} is replaced by the more general nonideality term g^{ex} , the excess Gibbs free energy. Figure 9.9 shows plots of g Vs x_B for the three phases at six temperatures, with T₆ the highest and T₁ the lowest. In the six graphs, the curves for each phase keep approximately the same shape but shift relative to each other. Examination of the six plots shows that the liquid phase curve shifts upward as the temperature is reduced more rapidly than do the curves for the two solid phases. This feature arises from the thermodynamic relation of Eq (7.16):

$$\left(\frac{\partial g}{\partial T}\right)_{p} = -s$$

Since the entropy of a liquid is always larger than that of the corresponding solid phases, the relative movement of the g Vs x_B curves for the liquid and solid phases in Fig. 9.9 is understandable.

The free energies of the solid phases at first decrease from the pure-component value then increase rapidly as the other component is added. The initial decreases are due



Fig. 9.9 Free energy – composition curves for an A-B binary system with two solid phases (**a** and **b**) and a liquid phase

chiefly to stabilization of the dilute solutions by the entropy of mixing. The shape of the curve is also affected by the composition-dependence of the nonideality term, h^{ex} or g^{ex} . The subsequent rise in free energy is due for the most part to crystal structure effects. Thus, the intercept of the α curve with the left-hand axis (e.g., point *a* in the T₆ plot)

represents the free energy of pure A in the crystal structure α . If the α phase curve were extended to intersect the right-hand axis, the free energy here would represent that of pure B in the α crystal structure. That this intercept is higher than the intercept of the β curve with the right-hand axis simply reflects that fact that pure B is more stable in the β crystal structure than it is in the structure of the α phase.

The phase diagram deduced from the free energy plots in Fig. 9.9 is shown in Fig. 9.10. The mapping of the former to the latter is explained below at each temperature, which is reduced in steps from T_6 to T_1 .



Fig. 9.10 Eutectic phase diagram derived from Fig. 9.9

Temperature T_6 is the melting point of pure A, and is the first temperature at which a solid phase appears from the liquid. At this point, the free energy-composition plot shows that $g_L = g_{\alpha}$. For the entire composition range thereafter, the liquid is the stable phase because its free energy is lower than that of either of the two solid phases. Transferring this information from the T_6 plot in Fig. 9.9 to the T_6 isotherm in the phase diagram of Fig. 9.10 shows a liquid-to-solid α transition at point *a* but only liquid over the composition range $0 < x_B \le 1$.

At temperature T₅, point *b* is the melting temperature of pure B in the β crystal structure. In addition, the α and L(for liquid) curves are joined by a common tangent at points *c* and *d*. At all compositions to the left of *c*, solid solutions of B in A with the α crystal structure exist. Between *c* and *d*, the system's lowest free energy lies along the common tangent. In this interval, liquid of composition at point *d* and solid α of

composition *c* coexist. For compositions larger than that at *d*, liquid is the lowest free energy phase. Translating points *b*, *c*, and *d* to the T_5 isotherm in the phase diagram shows the phases indicated by the common-tangent interpretation of the free energy curves.

At temperature T₄, the liquid free energy curve has risen relative to the solid curves to the extent that two common tangents can be drawn, one to the α curve and the other to the β curve. This implies that both α +L and β +L two phase zones are present in the phase diagram at this temperature.

 T_3 is a unique temperature because a single common tangent links the three free energy curves in Fig. 9.9. When transferred to the phase diagram, the isotherm at T_3 shows that three phases coexist at equilibrium: α and β solid solutions with compositions at points *j* and *l*, respectively, and a liquid with composition at point *k*. This point is called the *eutectic point*, meaning that it corresponds to the lowest-temperature point in the phase diagram at which the system is all liquid.

At the two temperatures T_2 and T_1 below the eutectic temperature, common tangents join the two solid phases. In Fig. 9.10, A-rich solid solutions with crystal structure α are stable up to mole fractions of B corresponding to points *m* and *o*. Further addition of B to the system results in precipitation of a B-rich β phase at the corresponding compositions *n* and *p*. The two-branch curve *omj/acej* is called the *terminal solubility* of B in α -A. Similarly, the counterpart on the B-rich side of the phase diagram is the terminal solubility of A in β -B.

The solid-to-liquid transformation in the eutectic system is more complex than the melting process in the ideal-solution phase diagram discussed in connection with Fig. 9.3. In Fig. 9.10, suppose the system starts at temperature T_1 with a mole fraction B a bit greater than the terminal solubility at o. The initial state is in the $\alpha+\beta$ two-phase region. Upon increasing the temperature holding the overall composition constant, the β phase disappears when the terminal solubility curve is reached at, say, point m. Further temperature increase moves the system through the single-phase α region without phase changes until point e is reached. Here the first liquid with composition at point f appears. Additional heating occurs in the two-phase $\alpha+L$ region, with the composition of the α phase decreasing from e to c and the liquid phase composition moving from f to d. Complete liquefaction occurs when the liquidus *adfk* is reached. The changes in the relative proportions of the phases in the two-phase zones are determined by the lever rule (see following section). For a two-phase mixture with overall B mole fraction complete melting at the eutectic temperature T_3 .

A degenerate form of the eutectic phase diagram is characterized by negligible solubility of A in B and of B in A. The single-phase α and β regions in Fig. 9.10 disappear and points *j* and *l* are displaced to their respective temperature axes. Fig. 9.11 shows the gold-silicon phase diagram, which is a prototypical degenerate eutectic system.

<u>Problem:</u> Calculate the activity coefficients of the two components in the liquid phase along the two liquidus curves in Fig. 9.11. Is regular solution theory obeyed? The melting temperatures of gold and silicon are 1063°C and 1404°C, respectively, and the enthalpies of fusion are 12.8 and 50.6 kJ/mole, respectively.



Fig. 9.11 The gold-silicon phase diagram

In the Au+L two-phase region, pure solid gold is in equilibrium with a liquid phase with compositions along the Au-rich liquidus. Equating the chemical potentials of these two phases as expressed by Eq (9.3) gives:

$$g_{Au,S} = g_{Au,L} + RT \ln(\gamma_{Au,L} x_{Au,L})$$
(9.28)

where $x_{Au,L}$ is the mole fraction of gold along the Au-rich liquidus. Solving for $\gamma_{Au,L}$ using the terminology of Eqs(9.13) and (9.14) yields:

$$\gamma_{\mathrm{Au},\mathrm{L}} = \mathrm{e}^{-\alpha} / \mathrm{x}_{\mathrm{Au},\mathrm{L}} \tag{9.29}$$

where

$$\alpha = \left(1 - \frac{T}{T_{M,Au}}\right) \frac{\Delta h_{M,Au}}{RT} = \left(1 - \frac{T}{1336}\right) \frac{1540}{T}$$
(9.30)

Similarly, the activity coefficient of silicon in the Si-rich liquidus is:

$$\gamma_{\mathrm{Si,L}} = \mathrm{e}^{-\beta} / \mathrm{x}_{\mathrm{Si,L}} \tag{9.31}$$

where

$$\beta = \left(1 - \frac{T}{T_{M,Si}}\right) \frac{\Delta h_{M,Si}}{RT} = \left(1 - \frac{T}{1677}\right) \frac{6110}{T}$$
(9.32)

Tables 9.2a and 9.2b list the activity coefficients along the two liquidus curves calculated from the above equations. The activity coefficients approach unity as the mole fraction of the component approaches unity, which is expected behavior. At lower concentrations, the activity coefficients are less than unity, indicating attractive Au-Si molecular interactions in the liquid phase. This behavior contrasts with the strong repulsive Au-Si interactions in the solid phase, as indicated by the complete immiscibility of the two components.

The last column in the tables constitutes a test of whether the system obeys regular solution theory. If it did, according to Eq (8.44), the combination of variables in the last column should be a constant. However, the data show substantial variation of this group of parameters, indicating that nonideality in liquid solutions of gold and silicon cannot be described by regular solution theory.

T, ⁰C	a	X _{Au,L}	g u,L	$Tln g_{u,L}/(1 - x_{Au,L})$
1000	0.057	0.93	1.00	-
800	0.283	0.78	0.97	-700
600	0.611	0.73	0.74	-3600
370*	1.242	0.69	0.42	-5800

Table 9.2a Activity coefficients of gold along the Au-rich liquidus in the Au-Si System

Table 9.2b	Activity	coefficients (of silicon	along	the S	Si-rich	liquidus	in the <i>A</i>	Au-Si S	ystem
									,	

T, ⁰C	b	X _{Si,L}	g i,L	$Tln g_{i,L}/(1 - x_{Si,L})$
1300	0.241	0.83	0.95	-2800
1200	0.505	0.70	0.86	-2500
1000	1.156	0.54	0.58	-3300
800	2.051	0.44	0.30	-4100
600	3.355	0.37	0.094	-5200
370*	5.859	0.31	0.009	-6300

* Eutectic temperature

The tables give the activity coefficients of only one of the components along each liquidus curve. In order to compute the other component's activity coefficient (e.g., $\gamma_{Si,L}$ along the Au-rich liquidus), the Gibbs-Duhem equation, Eq (8.36b), would have to be utilized. Only at the eutectic point are both activity coefficients available for both components in the same solution. Table 9.2b shows a very low activity coefficient of Si in the eutectic liquid. According to Eq (9.6) with B = Si(L), the pressure of gaseous Si in equilibrium with the eutectic liquid is less than 1% of what an ideal solution would generate. Yet, the eutectic liquid is in equilibrium with the same vapor. The consequence of this is that along the entire Si-rich liquidus:

$$p_{Si} = \gamma_{Si,L} x_{Si,L} p_{sat,Si(L)}$$
(9.33)

It can be shown that the ratio of the vapor pressures of pure solid and pure liquid is $e^{-\beta}$, so that Eq (9.33) is identical to Eq (9.31).

The Ag-Pb binary system exhibits features similar to those shown in Fig. 9.11. This system is the subject of problem 9.5.

Eutectic features often appear in parts of more complex phase diagrams, as shown in the iron-uranium diagram of Fig. 9.12. The Fe-rich portion of this diagram resembles Fig. 9.11 with two added features. The first is the number of phases of the pure components. The left hand ordinate of Fig. 9.12 makes provision for three crystallographic modifications of iron: The α phase (designated as α Fe) is stable up to 912°C; γ Fe exists in the range 912 $\leq T \leq 1394$ °C; the δ Fe phase is the equilibrium form from 1394°C to the melting point. The α Fe/ γ Fe and the γ Fe/ δ Fe transitions are indicated by horizontal lines at 912 and 1394°C. Note that uranium is completely insoluble in all three crystal forms of iron. The eutectic point is at 17 mole percent uranium and 1080°C.

The other feature that distinguishes the Fe-rich portion of the Fe-U phase diagram from the gold-silicon diagram of Fig. 9.11 is the right hand border. In the Au-Si system, the eutectic is bounded on the right by pure Si. The eutectic portion of the Fe-U diagram, on the other hand, has an intermetallic compound, Fe_2U , as the right hand border. Intermetallic compounds form when integer atom ratios of the two components form a crystallographic structure of high stability. These compounds often have high melting points, as does Fe_2U , thus enabling it to serve as the second "wall" of the eutectic field. The Fe-rich portion of the Fe-U phase diagram consists solely of two-phase regions (except for the liquid). The two-phase regions contain various combinations of the three phases of pure iron and the liquid or Fe_2U .

The diagram of Fig. 9.12 contains another eutectic point at 66 mole percent U and 725°C. This eutectic region is bounded by Fe_2U and another intermetallic compound, FeU_6 .

Pure uranium exhibits three crystal forms: αU stable up to 660°C, βU from 660°C to 776°C, and γU from 776°C to the melting point. Contrary to the total insolubility of U in solid Fe, solid uranium dissolves small amounts of iron in each of the three crystal

structures. The three zones labeled αU , βU and γU in Fig. 9.12 are single-phase zones resembling the β region in Fig. 9.10. The three U-rich solutions appear in adjacent two-phase regions along with the liquid or with FeU₆. These regions are analogous to the two-phase zones in the Fe-rich portion of the diagram.



Fig. 9.12 The iron-uranium phase diagram

Additional practice in identifying the species and phases present in regions of phase diagrams is provided in problems 9.7, 9.12, 9.13, 9.14 and 9.20. Problem 9.21 shows how to describe the change in the relative amounts and the compositions of phases that appear as a binary system is cooled from the liquid state.

9.9 The Lever Rule

In addition to indicating the phases present at each combination of temperature and composition, the curves in binary phase diagrams provide the bounding compositions of single-phase regions that enclose a two-phase zone. If intermetallic compounds are present, two-phase regions may be bounded by other two-phase zones, as in the low-temperature portion of the Fe-U diagram in Fig. 9.12. When the adjacent phases are single solutions, the curve on the left of the two-phase zone is called the *upper phase boundary* of the left-hand single-phase region. Similarly, the right-hand curve is the *lower phase boundary* of the single-phase solution on the right of the two-phase region. These bounding curves are often given other names. For example, the upper phase boundary of the liquid in Fig. 9.3 is the liquidus, and the lower phase boundary of the solid phase is the solidus. The upper phase boundary of the α phase in Fig. 9.10 is the terminal solubility of component B in α A. The lower phase boundary of the β region is the terminal solubility of A in β B.

Along these phase boundaries, and anywhere within a single-phase region, the abcissa of the phase diagram is the actual composition of the solution represented by the temperature-composition point. In two-phase regions, on the other hand, the abcissa gives the overall composition of the two coexisting solutions. Figure 9.13 shows a two-phase region (shaded area) bounded on the left by single phase I and on the right by single phase II. This diagram represents any of the two-phase regions with single-phase neighbors in the phase diagrams depicted in this chapter. At point P in the two-phase region of Fig. 9.13, the overall composition is x_B . The compositions of the two phases present are located at the intersections of the



Fig. 9.13 Application of the lever rule to a point P in a two phase region surrounded by two single phases.

horizontal line through P with the upper and lower phase boundaries of the adjacent single phases – that is, at points *a* and *b*. The lengths of the line segments *a*-*P* and *P*-*b* give the relative quantities (in moles) of phases I and II in the mixture. This can be shown by material balances. If the mixture contains n_I moles of phase I of composition x_{BI} and n_{II} moles of phase II of composition x_{BII} , the total number of moles is:

$$N = n_I + n_{II}$$

and the total moles of component B in the mixture is:

$$\mathbf{x}_{\mathrm{B}}\mathbf{N} = \mathbf{x}_{\mathrm{BI}}\mathbf{n}_{\mathrm{I}} + \mathbf{x}_{\mathrm{BII}}\mathbf{n}_{\mathrm{II}}$$

These two equations are solved for the fraction of phase I in the mixture:

fraction phase I =
$$\frac{n_{I}}{N} = \frac{x_{BII} - x_{B}}{x_{BII} - x_{BI}} = \frac{P\overline{b}}{\overline{a}\overline{b}}$$
 (9.34)

This formula is known as the *lever rule*. It applies to any two-phase region in a phase diagram but has no meaning if applied to a single-phase zone.