CHAPTER 13

THE PHASE RULE AND PHASE DIAGRAMS

We encountered the Gibbs phase rule and phase diagrams in Chap. 8 in connection with single-substance systems. The present chapter derives the full version of the Gibbs phase rule for multicomponent systems. It then discusses phase diagrams for some representative types of multicomponent systems, and shows how they are related to the phase rule and to equilibrium concepts developed in Chaps. 11 and 12.

13.1 THE GIBBS PHASE RULE FOR MULTICOMPONENT SYSTEMS

In Sec. 8.1.7, the Gibbs phase rule for a pure substance was written $F = 3 - P$. We now consider a system of more than one substance and more than one phase in an equilibrium state. The phase rule assumes the system is at thermal and mechanical equilibrium. We shall assume furthermore that in addition to the temperature and pressure, the only other state functions needed to describe the state are the amounts of the species in each phase; this means for instance that surface effects are ignored.

The derivations to follow will show that the phase rule may be written either in the form

$$F = 2 + C - P \tag{13.1.1}$$

or

$$F = 2 + s - r - P \tag{13.1.2}$$

where the symbols have the following meanings:

F = the number of degrees of freedom (or variance)

 = the maximum number of intensive variables that can be varied independently while the system remains in an equilibrium state;

C = the number of components

 = the minimum number of substances (or fixed-composition mixtures of substances) that could be used to prepare each phase individually;

P = the number of different phases;

s = the number of different species;

r = the number of independent relations among intensive variables of individual phases other than relations needed for thermal, mechanical, and transfer equilibrium.

If we subdivide a phase, that does not change the number of phases P. That is, we treat noncontiguous regions of the system that have identical intensive properties as parts of the same phase.

13.1.1 Degrees of freedom

Consider a system in an equilibrium state. In this state, the system has one or more phases; each phase contains one or more species; and intensive properties such as T, p, and the mole fraction of a species in a phase have definite values. Starting with the system in this state, we can make changes that place the system in a new equilibrium state having the same kinds of phases and the same species, but different values of some of the intensive properties. The number of different independent intensive variables that we may change in this way is the **number of degrees of freedom** or **variance**, F, of the system.

Clearly, the system remains in equilibrium if we change the *amount* of a phase without changing its temperature, pressure, or composition. This, however, is the change of an extensive variable and is not counted as a degree of freedom.

The phase rule, in the form to be derived, applies to a system that continues to have complete thermal, mechanical, and transfer equilibrium as intensive variables change. This means different phases are not separated by adiabatic or rigid partitions, or by semipermeable or impermeable membranes. Furthermore, every conceivable reaction among the species is either at reaction equilibrium or else is frozen at a fixed advancement during the time period we observe the system.

The number of degrees of freedom is the maximum number of intensive properties of the equilibrium system we may independently vary, or fix at arbitrary values, without causing a change in the number and kinds of phases and species. We cannot, of course, change one of these properties to just any value whatever. We are able to vary the value only within a certain finite (sometimes quite narrow) range before a phase disappears or a new one appears.

The number of degrees of freedom is also the number of independent intensive variables needed to specify the equilibrium state in all necessary completeness, aside from the amount of each phase. In other words, when we specify values of F different independent intensive variables, then the values of all other intensive variables of the equilibrium state have definite values determined by the physical nature of the system.

Just as for a one-component system, we can use the terms *bivariant*, *univariant*, and *invariant* depending on the value of F (Sec. 8.1.7).

13.1.2 Species approach to the phase rule

This section derives an expression for the number of degrees of freedom, F, based on *species*. Section 13.1.3 derives an expression based on *components*. Both approaches yield equivalent versions of the phase rule.

Recall that a *species* is an entity, uncharged or charged, distinguished from other species by its chemical formula (Sec. 9.1.1). Thus, CO_2 and $CO_3{}^{2-}$ are different species, but $CO_2(aq)$ and $CO_2(g)$ is the same species in different phases.

Consider an equilibrium system of P phases, each of which contains the same set of species. Let the number of different species be s. If we could make changes while the

system remains in thermal and mechanical equilibrium, but not necessarily in transfer equilibrium, we could independently vary the temperature and pressure of the system as a whole and the amount of each species in each phase; there would then be $2 + Ps$ independent variables.

The equilibrium system is, however, in transfer equilibrium, which requires each species to have the same chemical potential in each phase: $\mu_i^\beta = \mu_i^\alpha$, $\mu_i^\gamma = \mu_i^\alpha$, and so on. There are $P-1$ independent relations like this for each species, and a total of $s(P-1)$ independent relations for all species. Each such independent relation introduces a constraint and reduces the number of independent variables by one. Accordingly, taking transfer equilibrium into account, the number of independent variables is $2 + Ps - s(P - 1) = 2 + s$.

We obtain the same result if a species present in one phase is totally excluded from another. For example, solvent molecules of a solution are not found in a pure perfectly-ordered crystal of the solute, undissociated molecules of a volatile strong acid such as HCl can exist in a gas phase but not in aqueous solution, and ions of an electrolyte solute are usually not found in a gas phase. For each such species absent from a phase, there is one fewer amount variable and also one fewer relation for transfer equilibrium; on balance, the number of independent variables is still $2 + s$.

Next, we consider the possibility that further independent relations exist among intensive variables in addition to the relations needed for thermal, mechanical, and transfer equilibrium.[1] If there are r of these additional relations, the total number of independent variables is reduced to $2 + s - r$. These relations may come from

1. reaction equilibria,
2. the requirement of electroneutrality in a phase containing ions, and
3. initial conditions determined by the way the system is prepared.

In the case of a reaction equilibrium, the relation is $\Delta_r G = \sum_i \nu_i \mu_i = 0$, or the equivalent relation $K = \prod_i (a_i)^{\nu_i}$ for the thermodynamic equilibrium constant. Thus, r is the sum of the number of independent reaction equilibria, the number of phases containing ions, and the number of independent initial conditions. Several examples will be given in Sec. 13.1.4.

There is an infinite variety of possible choices of the independent variables (both extensive and intensive) for the equilibrium system, but the total *number* of independent variables is fixed at $2 + s - r$. Keeping intensive properties fixed, we can always vary how much of each phase is present (e.g., its volume, mass, or amount) without destroying the equilibrium. Thus, at least P of the independent variables, one for each phase, must be extensive. It follows that the maximum number of independent *intensive* variables is the difference $(2 + s - r) - P$.

> It may be that initial conditions establish relations among the amounts of phases, as will be illustrated in example 2 on page 423. If present, these are relations among *extensive* variables that are not counted in r. Each such independent relation decreases the total number of independent variables without changing the number of independent intensive variables calculated from $(2 + s - r) - P$.

Since the maximum number of independent intensive variables is the number of degrees

---

[1] Relations such as $\sum_i p_i = p$ for a gas phase or $\sum_i x_i = 1$ for a phase in general have already been accounted for in the derivation by the specification of p and the amount of each species.

of freedom, our expression for F based on species is

$$F = 2 + s - r - P \tag{13.1.3}$$

13.1.3   Components approach to the phase rule

The derivation of the phase rule in this section uses the concept of **components**. The number of components, C, is the minimum number of substances or mixtures of fixed composition from which we could in principle prepare each individual phase of an equilibrium state of the system, using methods that may be hypothetical. These methods include the addition or removal of one or more of the substances or fixed-composition mixtures, and the conversion of some of the substances into others by means of a reaction that is at equilibrium in the actual system.

It is not always easy to decide on the number of components of an equilibrium system. The number of components may be less than the number of substances present, on account of the existence of reaction equilibria that produce some substances from others. When we use a reaction to prepare a phase, nothing must remain unused. For instance, consider a system consisting of solid phases of $CaCO_3$ and CaO and a gas phase of CO_2. Assume the reaction $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$ is at equilibrium. We could prepare the $CaCO_3$ phase from CaO and CO_2 by the reverse of this reaction, but we can only prepare the CaO and CO_2 phases from the individual substances. We could not use $CaCO_3$ to prepare either the CaO phase or the CO_2 phase, because CO_2 or CaO would be left over. Thus this system has three substances but only two components, namely CaO and CO_2.

In deriving the phase rule by the components approach, it is convenient to consider only intensive variables. Suppose we have a system of P phases in which each substance present is a component (i.e., there are no reactions) and each of the C components is present in each phase. If we make changes to the system while it remains in thermal and mechanical equilibrium, but not necessarily in transfer equilibrium, we can independently vary the temperature and pressure of the whole system, and for each phase we can independently vary the mole fraction of all but one of the substances (the value of the omitted mole fraction comes from the relation $\sum_i x_i = 1$). This is a total of $2 + P(C - 1)$ independent intensive variables.

When there also exist transfer and reaction equilibria, not all of these variables are independent. Each substance in the system is either a component, or else can be formed from components by a reaction that is in reaction equilibrium in the system. Transfer equilibria establish $P - 1$ independent relations for each component ($\mu_i^\beta = \mu_i^\alpha$, $\mu_i^\gamma = \mu_i^\alpha$, etc.) and a total of $C(P - 1)$ relations for all components. Since these are relations among chemical potentials, which are intensive properties, each relation reduces the number of independent intensive variables by one. The resulting number of independent intensive variables is

$$F = [2 + P(C - 1)] - C(P - 1) = 2 + C - P \tag{13.1.4}$$

If the equilibrium system lacks a particular component in one phase, there is one fewer mole fraction variable and one fewer relation for transfer equilibrium. These changes cancel in the calculation of F, which is still equal to $2 + C - P$. If a phase contains a substance that is formed from components by a reaction, there is an additional mole fraction variable and also the additional relation $\sum_i \nu_i \mu_i = 0$ for the reaction; again the changes cancel.

We may need to *remove* a component from a phase to achieve the final composition. Note that it is not necessary to consider additional relations for electroneutrality or initial conditions; they are implicit in the definitions of the components. For instance, since each component is a substance of zero electric charge, the electrical neutrality of the phase is assured.

We conclude that, regardless of the kind of system, the expression for F based on components is given by $F = 2 + C - P$. By comparing this expression and $F = 2 + s - r - P$, we see that the number of components is related to the number of species by

$$C = s - r \tag{13.1.5}$$

13.1.4   Examples

The five examples below illustrate various aspects of using the phase rule.

Example 1: liquid water

For a single phase of pure water, P equals 1. If we treat the water as the single species H_2O, s is 1 and r is 0. The phase rule then predicts two degrees of freedom:

$$\begin{aligned} F &= 2 + s - r - P \\ &= 2 + 1 - 0 - 1 = 2 \end{aligned} \tag{13.1.6}$$

Since F is the number of intensive variables that can be varied independently, we could for instance vary T and p independently, or T and ρ, or any other pair of independent intensive variables.

Next let us take into account the proton transfer equilibrium

$$2\,H_2O(l) \;\rightleftharpoons\; H_3O^+(aq) + OH^-(aq)$$
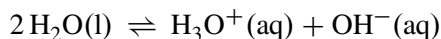
and consider the system to contain the three species H_2O, H_3O^+, and OH^-. Then for the species approach to the phase rule, we have $s = 3$. We can write two independent relations:

1. for reaction equilibrium, $-2\mu_{H_2O} + \mu_{H_3O^+} + \mu_{OH^-} = 0$;

2. for electroneutrality, $m_{H_3O^+} = m_{OH^-}$.

Thus, we have two relations involving intensive variables only. Now s is 3, r is 2, P is 1, and the number of degrees of freedom is given by

$$F = 2 + s - r - P = 2 \tag{13.1.7}$$

which is the same value of F as before.

If we consider water to contain additional cation species (e.g., $H_5O_2^+$), each such species would add 1 to s and 1 to r, but F would remain equal to 2. Thus, no matter how complicated are the equilibria that actually exist in liquid water, the number of degrees of freedom remains 2.

Applying the components approach to water is simple. All species that may exist in pure water are formed, in whatever proportions actually exist, from the single substance H_2O. Thus, there is only one component: $C = 1$. The component version of the phase rule, $F = 2 + C - P$, gives the same result as the species version: $F = 2$.

Example 2: carbon, oxygen, and carbon oxides

Consider a system containing solid carbon (graphite) and a gaseous mixture of O_2, CO, and CO_2. There are four species and two phases. If reaction equilibrium is absent, as might be the case at low temperature in the absence of a catalyst, we have $r = 0$ and $C = s - r = 4$. The four components are the four substances. The phase rule tells us the system has four degrees of freedom. We could, for instance, arbitrarily vary T, p, y_{O_2}, and y_{CO}.

Now suppose we raise the temperature or introduce an appropriate catalyst to allow the following reaction equilibria to exist:

1. $2\,C(s) + O_2(g) \rightleftharpoons 2\,CO(g)$
2. $C(s) + O_2(g) \rightleftharpoons CO_2(g)$

These equilibria introduce two new independent relations among chemical potentials and among activities. We could also consider the equilibrium $2\,CO(g) + O_2(g) \rightleftharpoons 2\,CO_2(g)$, but it does not contribute an additional independent relation because it depends on the other two equilibria: the reaction equation is obtained by subtracting the reaction equation for equilibrium 1 from twice the reaction equation for equilibrium 2. By the species approach, we have $s = 4$, $r = 2$, and $P = 2$; the number of degrees of freedom from these values is

$$F = 2 + s - r - P = 2 \tag{13.1.8}$$

If we wish to calculate F by the components approach, we must decide on the minimum number of substances we could use to prepare each phase separately. (This does not refer to how we actually prepare the two-phase system, but to a hypothetical preparation of each phase with any of the compositions that can actually exist in the equilibrium system.) Assume equilibria 1 and 2 are present. We prepare the solid phase with carbon, and we can prepare any possible equilibrium composition of the gas phase from carbon and O_2 by using the reactions of both equilibria. Thus, there are two components (C and O_2) giving the same result of two degrees of freedom.

What is the significance of there being two degrees of freedom when the reaction equilibria are present? There are two ways of viewing the situation:

1. We can arbitrarily vary the two intensive variables T and p. When we do, the mole fractions of the three substances in the gas phase change in a way determined by equilibria 1 and 2.

2. If we specify arbitrary values of T and p, each of the mole fractions has only one possible value that will allow the two phases and four substances to be in equilibrium.

Now to introduce an additional complexity: Suppose we prepare the system by placing a certain amount of O_2 and twice this amount of carbon in an evacuated container, and wait for the reactions to come to equilibrium. This method of preparation imposes an initial condition on the system, and we must decide whether the number of degrees of freedom is affected. Equating the total amount of carbon atoms to the total amount of oxygen atoms in the equilibrated system gives the relation

$$n_C + n_{CO} + n_{CO_2} = 2n_{O_2} + n_{CO} + 2n_{CO_2} \qquad \text{or} \qquad n_C = 2n_{O_2} + n_{CO_2} \tag{13.1.9}$$

Either equation is a relation among extensive variables of the two phases. From them, we are unable to obtain any relation among *intensive* variables of the phases. Therefore, this particular initial condition does not change the value of r, and F remains equal to 2.

Example 3: a solid salt and saturated aqueous solution

In this example, the equilibrium system consists of crystalline $PbCl_2$ and an aqueous phase containing the species H_2O, $Pb^{2+}(aq)$, and $Cl^-(aq)$.

Applying the components approach to this system is straightforward. The solid phase is prepared from $PbCl_2$ and the aqueous phase could be prepared by dissolving solid $PbCl_2$ in H_2O. Thus, there are two components and two phases:

$$F = 2 + C - P = 2 \tag{13.1.10}$$

For the species approach, we note that there are four species ($PbCl_2$, Pb^{2+}, Cl^-, and H_2O) and two independent relations among intensive variables:

1. equilibrium for the dissolution process, $-\mu_{PbCl_2} + \mu_{Pb^{2+}} + 2\mu_{Cl^-} = 0$;

2. electroneutrality of the aqueous phase, $2m_{Pb^{2+}} = m_{Cl^-}$.

We have $s = 4$, $r = 2$, and $P = 2$, giving the same result as the components approach:

$$F = 2 + s - r - P = 2 \tag{13.1.11}$$

Example 4: liquid water and water-saturated air

For simplicity, let "air" be a gaseous mixture of N_2 and O_2. The equilibrium system in this example has two phases: liquid water saturated with the dissolved constituents of air, and air saturated with gaseous H_2O.

If there is no special relation among the total amounts of N_2 and O_2, there are three components and the phase rule gives

$$F = 2 + C - P = 3 \tag{13.1.12}$$

Since there are three degrees of freedom, we could, for instance, specify arbitrary values[2] of T, p, and y_{N_2}; then the values of other intensive variables such as the mole fractions y_{H_2O} and x_{N_2} would have definite values.

Now suppose we impose an initial condition by preparing the system with water and dry air of a *fixed* composition. The mole ratio of N_2 and O_2 in the aqueous solution is not necessarily the same as in the equilibrated gas phase; consequently, the air does not behave like a single substance. The number of components is still three: H_2O, N_2, and O_2 are all required to prepare each phase individually, just as when there was no initial condition, giving $F = 3$ as before.[3]

We can reach the same conclusion with the species approach. The initial condition can be expressed by an equation such as

$$\frac{(n_{N_2}^l + n_{N_2}^g)}{(n_{O_2}^l + n_{O_2}^g)} = a \tag{13.1.13}$$

---

[2]Arbitrary, that is, within the limits that would allow the two phases to coexist.
[3]The fact that the compositions of both phases depend on the relative amounts of the phases is illustrated in Prob. 9.5.

where a is a constant equal to the mole ratio of N_2 and O_2 in the dry air. This equation cannot be changed to a relation between intensive variables such as x_{N_2} and x_{O_2}, so that r is zero and there are still three degrees of freedom.

Finally, let us assume that we prepare the system with dry air of fixed composition, as before, but consider the solubilities of N_2 and O_2 in water to be negligible. Then $n_{N_2}^l$ and $n_{O_2}^l$ are zero and Eq. 13.1.13 becomes $n_{N_2}^g / n_{O_2}^g = a$, or $y_{N_2} = a y_{O_2}$, which is a relation between intensive variables. In this case, r is 1 and the phase rule becomes

$$F = 2 + s - r - P = 2 \qquad (13.1.14)$$

The reduction in the value of F from 3 to 2 is a consequence of our inability to detect any dissolved N_2 or O_2. According to the components approach, we may prepare the liquid phase with H_2O and the gas phase with H_2O and air of fixed composition that behaves as a single substance; thus, there are only two components.

Example 5: equilibrium between two solid phases and a gas phase

Consider the following reaction equilibrium:

$$3\,CuO(s) + 2\,NH_3(g) \;\rightleftharpoons\; 3\,Cu(s) + 3\,H_2O(g) + N_2(g)$$
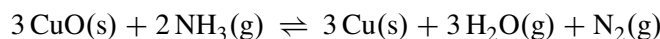
According to the species approach, there are five species, one relation (for reaction equilibrium), and three phases. The phase rule gives

$$F = 2 + s - r - P = 3 \qquad (13.1.15)$$

It is more difficult to apply the components approach to this example. As components, we might choose CuO and Cu (from which we could prepare the solid phases) and also NH_3 and H_2O. Then to obtain the N_2 needed to prepare the gas phase, we could use CuO and NH_3 as reactants in the reaction $3\,CuO + 2\,NH_3 \rightarrow 3\,Cu + 3\,H_2O + N_2$ and remove the products Cu and H_2O. In the components approach, we are allowed to remove substances from the system provided they are counted as components.

13.2 PHASE DIAGRAMS: BINARY SYSTEMS

As explained in Sec. 8.2, a phase diagram is a kind of two-dimensional map that shows which phase or phases are stable under a given set of conditions. This section discusses some common kinds of binary systems, and Sec. 13.3 will describe some interesting ternary systems.

13.2.1 Generalities

A binary system has two components; C equals 2, and the number of degrees of freedom is $F = 4 - P$. There must be at least one phase, so the maximum possible value of F is 3. Since F cannot be negative, the equilibrium system can have no more than four phases.

We can independently vary the temperature, pressure, and composition of the system as a whole. Instead of using these variables as the coordinates of a three-dimensional phase

diagram, we usually draw a two-dimensional phase diagram that is either a temperature–composition diagram at a fixed pressure or a pressure–composition diagram at a fixed temperature. The position of the system point on one of these diagrams then corresponds to a definite temperature, pressure, and overall composition. The composition variable usually varies along the horizontal axis and can be the mole fraction, mass fraction, or mass percent of one of the components, as will presently be illustrated by various examples.

The way in which we interpret a two-dimensional phase diagram to obtain the compositions of individual phases depends on the number of phases present in the system.

- If the system point falls within a *one-phase* area of the phase diagram, the composition variable is the composition of that single phase. There are three degrees of freedom. On the phase diagram, the value of either T or p has been fixed, so there are two other independent intensive variables. For example, on a temperature–composition phase diagram, the pressure is fixed and the temperature and composition can be changed independently within the boundaries of the one-phase area of the diagram.

- If the system point is in a *two-phase* area of the phase diagram, we draw a horizontal *tie line* of constant temperature (on a temperature–composition phase diagram) or constant pressure (on a pressure–composition phase diagram). The lever rule applies. The position of the point at each end of the tie line, at the boundary of the two-phase area, gives the value of the composition variable of one of the phases and also the physical state of this phase: either the state of an adjacent one-phase area, or the state of a phase of fixed composition when the boundary is a vertical line. Thus, a boundary that separates a two-phase area for phases α and β from a one-phase area for phase α is a curve that describes the composition of phase α as a function of T or p when it is in equilibrium with phase β. The curve is called a *solidus*, *liquidus*, or *vaporus* depending on whether phase α is a solid, liquid, or gas.

- A binary system with *three* phases has only one degree of freedom and cannot be represented by an area on a two-dimensional phase diagram. Instead, there is a horizontal boundary line between areas, with a special point along the line at the junction of several areas. The compositions of the three phases are given by the positions of this point and the points at the two ends of the line. The position of the system point on this line does not uniquely specify the relative amounts in the three phases.

The examples that follow show some of the simpler kinds of phase diagrams known for binary systems.

13.2.2   Solid–liquid systems

Figure 13.1 on the next page is a temperature–composition phase diagram at a fixed pressure. The composition variable z_B is the mole fraction of component B in the system as a whole. The phases shown are a binary liquid mixture of A and B, pure solid A, and pure solid B.

The one-phase liquid area is bounded by two curves, which we can think of either as freezing-point curves for the liquid or as solubility curves for the solids. These curves comprise the liquidus. As the mole fraction of either component in the liquid phase decreases from unity, the freezing point decreases. The curves meet at point a, which is a **eutectic**
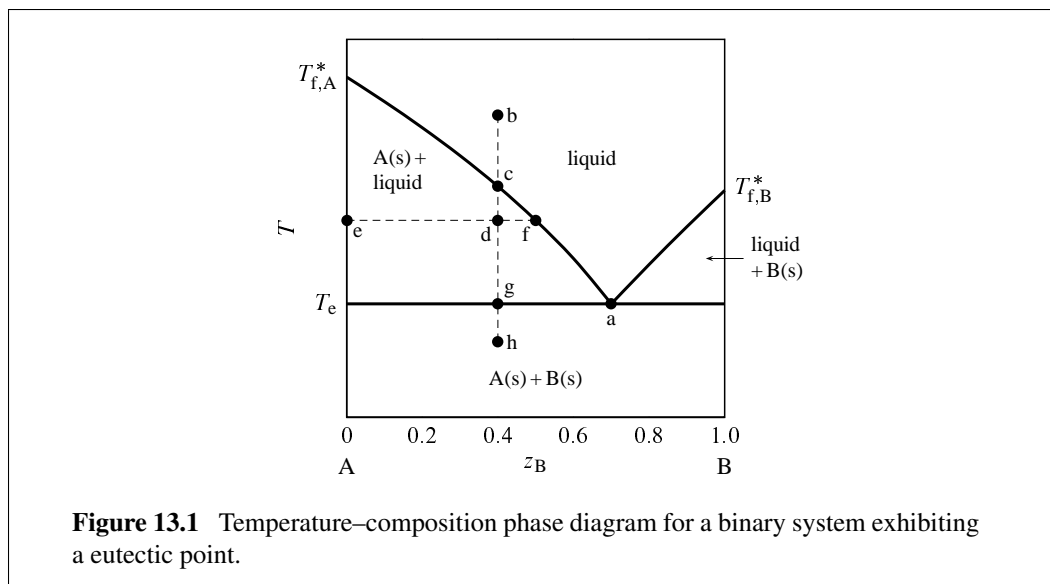
Figure 13.1 Temperature–composition phase diagram for a binary system exhibiting a eutectic point.

point. At this point, both solid A and solid B can coexist in equilibrium with a binary liquid mixture. The composition at this point is the *eutectic composition*, and the temperature here (denoted T_e) is the *eutectic temperature*. T_e is the lowest temperature for the given pressure at which the liquid phase is stable.[4]

Suppose we combine 0.60 mol A and 0.40 mol B ($z_B = 0.40$) and adjust the temperature so as to put the system point at b. This point is in the one-phase liquid area, so the equilibrium system at this temperature has a single liquid phase. If we now place the system in thermal contact with a cold reservoir, heat is transferred out of the system and the system point moves down along the *isopleth* (path of constant overall composition) b–h. The cooling rate depends on the temperature gradient at the system boundary and the system's heat capacity.
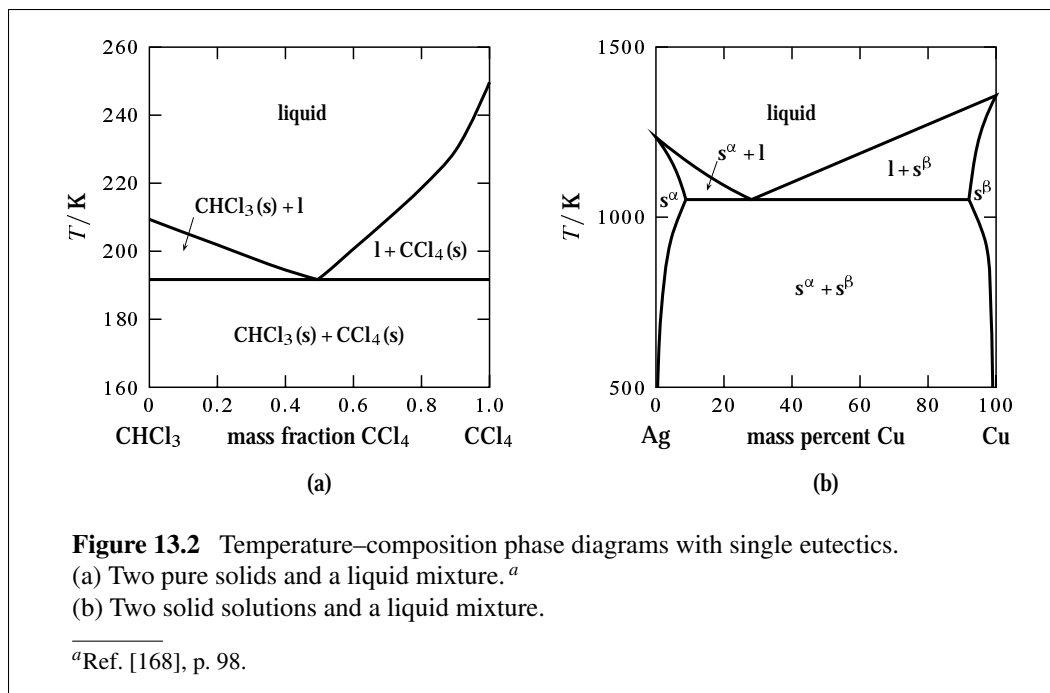
At point c on the isopleth, the system point reaches the boundary of the one-phase area and is about to enter the two-phase area labeled A(s) + liquid. At this point in the cooling process, the liquid is saturated with respect to solid A, and solid A is about to freeze out from the liquid. There is an abrupt decrease (break) in the cooling rate at this point, because the freezing process involves an extra enthalpy decrease.

At the still lower temperature at point d, the system point is within the two-phase solid–liquid area. The tie line through this point is line e–f. The compositions of the two phases are given by the values of z_B at the ends of the tie line: $x_B^s = 0$ for the solid and $x_B^l = 0.50$ for the liquid. From the general lever rule (Eq. 8.2.8 on page 209), the ratio of the amounts in these phases is

$$\frac{n^l}{n^s} = \frac{z_B - x_B^s}{x_B^l - z_B} = \frac{0.40 - 0}{0.50 - 0.40} = 4.0 \tag{13.2.1}$$

Since the total amount is $n^s + n^l = 1.00$ mol, the amounts of the two phases must be $n^s = 0.20$ mol and $n^l = 0.80$ mol.

---

[4]"Eutectic" comes from the Greek for *easy melting*.

Figure 13.2 Temperature–composition phase diagrams with single eutectics.
(a) Two pure solids and a liquid mixture. [a]
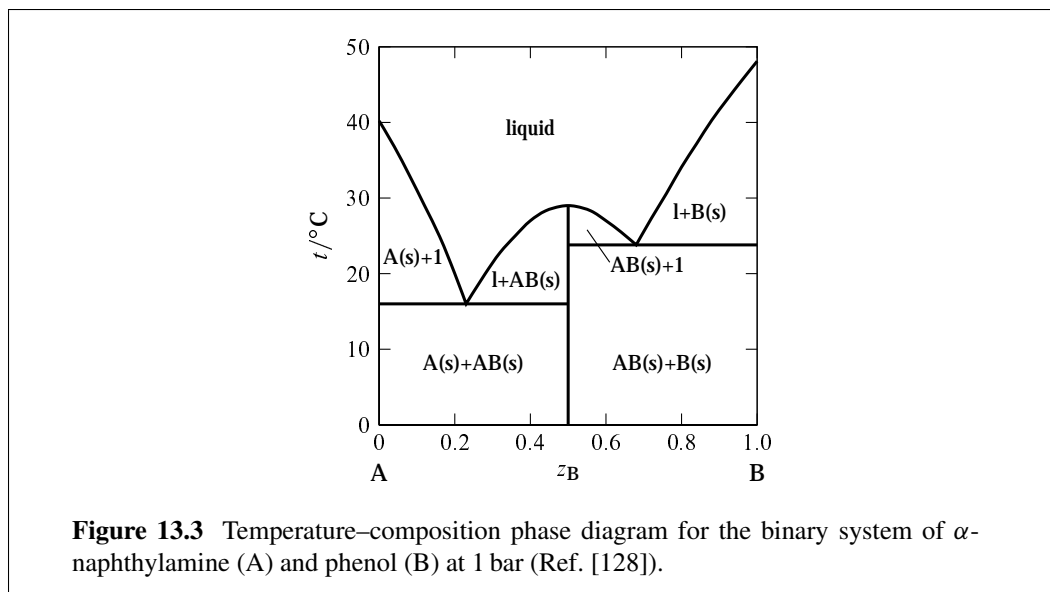(b) Two solid solutions and a liquid mixture.

———————
[a]Ref. [168], p. 98.

When the system point reaches the eutectic temperature at point g, cooling halts until all of the liquid freezes. Solid B freezes out as well as solid A. During this *eutectic halt*, there are at first three phases: liquid with the eutectic composition, solid A, and solid B. As heat continues to be withdrawn from the system, the amount of liquid decreases and the amounts of the solids increase until finally only 0.60 mol of solid A and 0.40 mol of solid B are present. The temperature then begins to decrease again and the system point enters the two-phase area for solid A and solid B; tie lines in this area extend from $z_B = 0$ to $z_B = 1$.

Temperature–composition phase diagrams such as this are often mapped out experimentally by observing the cooling curve (temperature as a function of time) along isopleths of various compositions. This procedure is *thermal analysis*. A break in the slope of a cooling curve at a particular temperature indicates the system point has moved from a one-phase liquid area to a two-phase area of liquid and solid. A temperature halt indicates the temperature is either the freezing point of the liquid to form a solid of the same composition, or else a eutectic temperature.

Figure 13.2 shows two temperature–composition phase diagrams with single eutectic points. The left-hand diagram is for the binary system of chloroform and carbon tetrachloride, two liquids that form nearly ideal mixtures. The solid phases are pure crystals, as in Fig. 13.1. The right-hand diagram is for the silver–copper system and involves solid phases that are solid solutions (substitutional alloys of variable composition). The area labeled s^α is a solid solution that is mostly silver, and s^β is a solid solution that is mostly copper. Tie lines in the two-phase areas do not end at a vertical line for a pure solid component as they do in the system shown in the left-hand diagram. The three phases that can coexist at the eutectic temperature of 1,052 K are the melt of the eutectic composition and the two solid solutions.

Section 12.5.4 discussed the possibility of the appearance of a *solid compound* when a

Figure 13.3 Temperature–composition phase diagram for the binary system of α-naphthylamine (A) and phenol (B) at 1 bar (Ref. [128]).
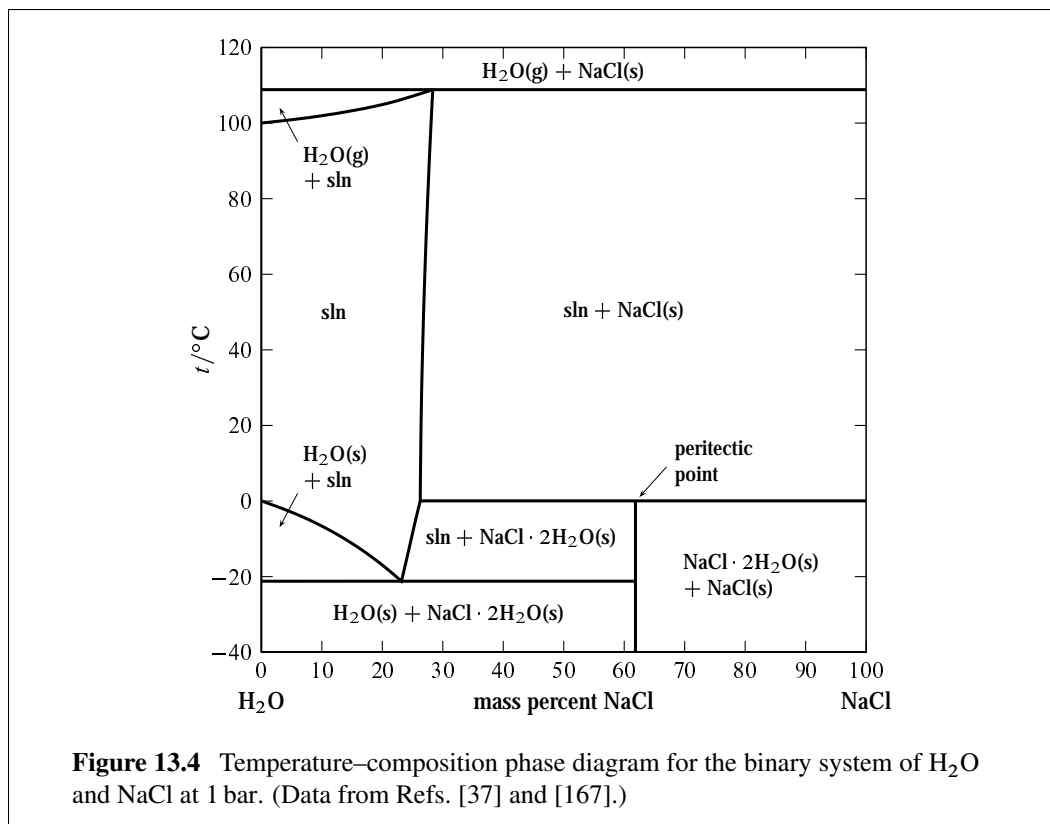
binary liquid mixture is cooled. An example of this behavior is shown in Fig. 13.3, in which the solid compound contains equal amounts of the two components α-naphthylamine and phenol. The possible solid phases are pure A, pure B, and the solid compound AB. Only one or two of these solids can be present simultaneously in an equilibrium state. The vertical line in the figure at $z_B = 0.5$ represents the solid compound. The temperature at the upper end of this line is the melting point of the solid compound, 29 °C. The solid melts *congruently* to give a liquid of the same composition. A melting process with this behavior is called a *dystectic reaction*. The cooling curve for liquid of this composition would display a halt at the melting point.

The phase diagram in Fig. 13.3 has two eutectic points. It resembles two simple phase diagrams like Fig. 13.1 placed side by side. There is one important difference: the slope of the freezing-point curve (liquidus curve) is nonzero at the composition of a pure component, but is zero at the composition of a solid compound that is completely dissociated in the liquid (as derived theoretically on page 388). Thus, the curve in Fig. 13.3 has a relative maximum at the composition of the solid compound ($z_B = 0.5$) and is rounded there, instead of having a cusp—like a Romanesque arch rather than a Gothic arch.

An example of a solid compound that does not melt congruently is shown in Fig. 13.4 on the next page. The solid hydrate $NaCl \cdot 2H_2O$ is 61.9% NaCl by mass. It decomposes at 0 °C to form an aqueous solution of composition 26.3% NaCl by mass and a solid phase of anhydrous NaCl. These three phases can coexist at equilibrium at 0 °C. A phase transition like this, in which a solid compound changes into a liquid and a different solid, is called *incongruent* or *peritectic* melting, and the point on the phase diagram at this temperature at the composition of the liquid is a *peritectic point*.

Figure 13.4 shows there are two other temperatures at which three phases can be present simultaneously: -21 °C, where the phases are ice, the solution at its eutectic point, and the solid hydrate; and 109 °C, where the phases are gaseous H_2O, a solution of composition 28.3% NaCl by mass, and solid NaCl. Note that both segments of the right-hand boundary of the one-phase solution area have positive slopes, meaning that the solubilities of the solid
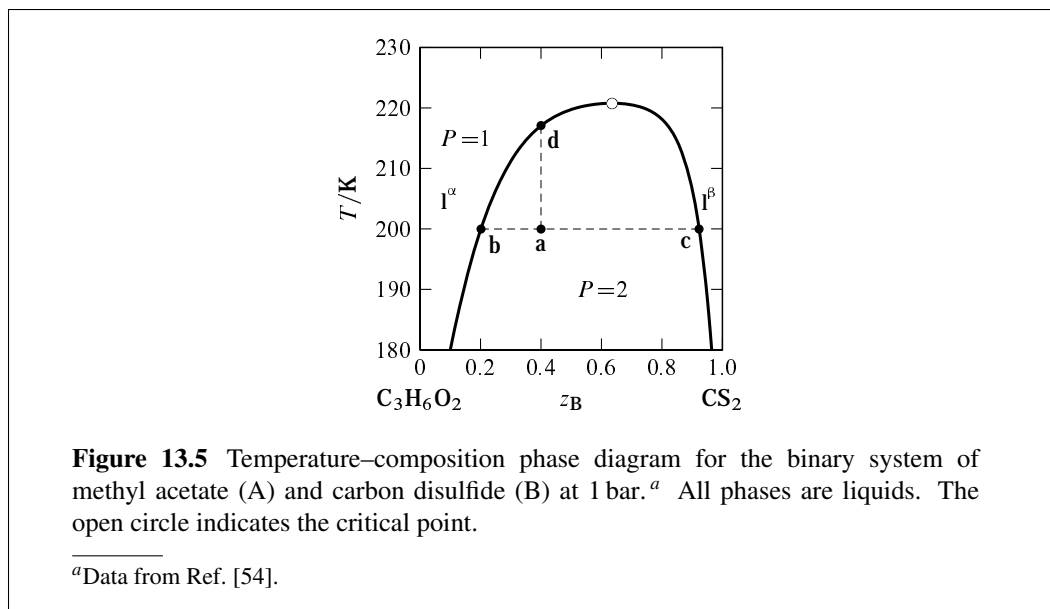
Figure 13.4   Temperature–composition phase diagram for the binary system of H_2O and NaCl at 1 bar. (Data from Refs. [37] and [167].)

hydrate and the anhydrous salt both increase with increasing temperature.

13.2.3   Partially-miscible liquids

When two liquids that are partially miscible are combined in certain proportions, phase separation occurs (Sec. 11.1.6). Two liquid phases in equilibrium with one another are called *conjugate phases*. Obviously the two phases must have different compositions or they would be identical; the difference is called a *miscibility gap*. A binary system with two phases has two degrees of freedom, so that at a given temperature and pressure each conjugate phase has a fixed composition.

The typical dependence of a miscibility gap on temperature is shown in Fig. 13.5 on the next page. The miscibility gap (the difference in compositions at the left and right boundaries of the two-phase area) decreases as the temperature increases until at the *upper consolute temperature*, also called the *upper critical solution temperature*, the gap vanishes. The point at the maximum of the boundary curve of the two-phase area, where the temperature is the upper consolute temperature, is the *consolute point* or *critical point*. At this point, the two liquid phases become identical, just as the liquid and gas phases become identical at the critical point of a pure substance. Critical opalescence (page 205) is observed in the vicinity of this point, caused by large local composition fluctuations. At temperatures at and above the critical point, the system is a single binary liquid mixture.

Suppose we combine 6.0 mol of component A (methyl acetate) and 4.0 mol of component B (carbon disulfide) in a cylindrical vessel and adjust the temperature to 200 K. The

Figure 13.5 Temperature–composition phase diagram for the binary system of methyl acetate (A) and carbon disulfide (B) at 1 bar.[a] All phases are liquids. The open circle indicates the critical point.

———
[a]Data from Ref. [54].

overall mole fraction of B is $z_B = 0.40$. The system point is at point a in the two-phase region. From the positions of points b and c at the ends of the tie line through point a, we find the two liquid layers have compositions $x_B^\alpha = 0.20$ and $x_B^\beta = 0.92$. Since carbon disulfide is the more dense of the two pure liquids, the bottom layer is phase β, the layer that is richer in carbon disulfide. According to the lever rule, the ratio of the amounts in the two phases is given by

$$\frac{n^\beta}{n^\alpha} = \frac{z_B - x_B^\alpha}{x_B^\beta - z_B} = \frac{0.40 - 0.20}{0.92 - 0.40} = 0.38 \tag{13.2.2}$$
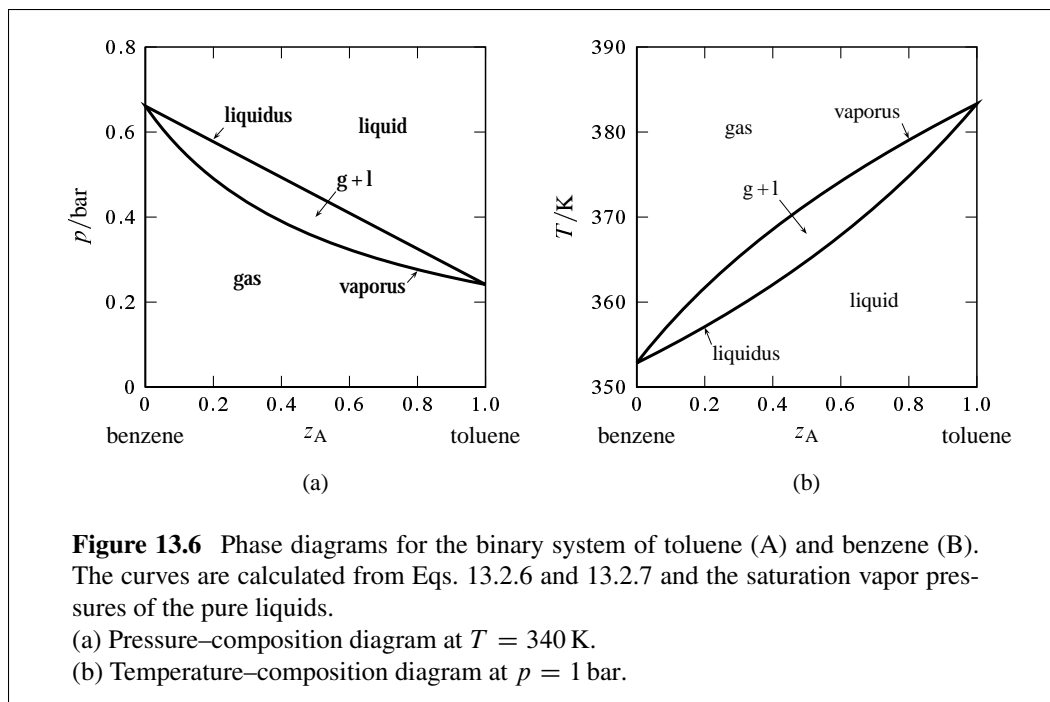
Combining this value with $n^\alpha + n^\beta = 10.0\,\text{mol}$ gives us $n^\alpha = 7.2\,\text{mol}$ and $n^\beta = 2.8\,\text{mol}$.

If we gradually add more carbon disulfide to the vessel while gently stirring and keeping the temperature constant, the system point moves to the right along the tie line. Since the ends of this tie line have fixed positions, neither phase changes its composition, but the amount of phase β increases at the expense of phase α. The liquid–liquid interface moves up in the vessel toward the top of the liquid column until, at overall composition $z_B = 0.92$ (point c), there is only one liquid phase.

Now suppose the system point is back at point a and we raise the temperature while keeping the overall composition constant at $z_B = 0.40$. The system point moves up the isopleth a–d. The phase diagram shows that the ratio $(z_B - x_B^\alpha)/(x_B^\beta - z_B)$ decreases during this change. As a result, the amount of phase α increases, the amount of phase β decreases, and the liquid–liquid interface moves down toward the bottom of the vessel until at 217 K (point d) there again is only one liquid phase.

13.2.4 Liquid–gas systems with ideal liquid mixtures

Toluene and benzene form liquid mixtures that are practically ideal and closely obey Raoult's law for partial pressure. For the binary system of these components, we can use the vapor

Figure 13.6 Phase diagrams for the binary system of toluene (A) and benzene (B). The curves are calculated from Eqs. 13.2.6 and 13.2.7 and the saturation vapor pressures of the pure liquids.
(a) Pressure–composition diagram at $T = 340\,\mathrm{K}$.
(b) Temperature–composition diagram at $p = 1\,\mathrm{bar}$.

pressures of the pure liquids to generate the liquidus and vaporus curves of the pressure–composition and temperature–composition phase diagram. The results are shown in Fig. 13.6. The composition variable z_A is the overall mole fraction of component A (toluene).

The equations needed to generate the curves can be derived as follows. Consider a binary liquid mixture of components A and B and mole fraction composition x_A that obeys Raoult's law for partial pressure (Eq. 9.4.2):

$$p_A = x_A p_A^* \qquad p_B = (1 - x_A) p_B^* \qquad\qquad (13.2.3)$$

Strictly speaking, Raoult's law applies to a liquid–gas system maintained at a constant pressure by means of a third gaseous component, and p_A^* and p_B^* are the vapor pressures of the pure liquid components at this pressure and the temperature of the system. However, when a liquid phase is equilibrated with a gas phase, the partial pressure of a constituent of the liquid is practically independent of the total pressure (Sec. 12.8.1), so that it is a good approximation to apply the equations to a *binary* liquid–gas system and treat p_A^* and p_B^* as functions only of T.

When the binary system contains a liquid phase and a gas phase in equilibrium, the pressure is the sum of p_A and p_B, which from Eq. 13.2.3 is given by

$$\begin{aligned} p &= x_A p_A^* + (1 - x_A) p_B^* \\ &= p_B^* + (p_A^* - p_B^*) x_A \end{aligned} \qquad\qquad (13.2.4)$$
$$(C = 2,\ \text{ideal liquid mixture})$$

where x_A is the mole fraction of A in the liquid phase. Equation 13.2.4 shows that in the two-phase system, p has a value between p_A^* and p_B^*, and that if T is constant, p is a linear

function of x_A. The mole fraction composition of the gas in the two-phase system is given by

$$y_A = \frac{p_A}{p} = \frac{x_A p_A^*}{p_B^* + (p_A^* - p_B^*)x_A} \tag{13.2.5}$$

A binary two-phase system has two degrees of freedom. At a given T and p, each phase must have a fixed composition. We can calculate the liquid composition by rearranging Eq. 13.2.4:

$$x_A = \frac{p - p_B^*}{p_A^* - p_B^*} \tag{13.2.6}$$

$$(C=2, \text{ideal liquid mixture})$$

The gas composition is then given by

$$y_A = \frac{p_A}{p} = \frac{x_A p_A^*}{p}$$

$$= \left(\frac{p - p_B^*}{p_A^* - p_B^*} \right) \frac{p_A^*}{p} \tag{13.2.7}$$

$$(C=2, \text{ideal liquid mixture})$$

If we know p_A^* and p_B^* as functions of T, we can use Eqs. 13.2.6 and 13.2.7 to calculate the compositions for any combination of T and p at which the liquid and gas phases can coexist, and thus construct a pressure–composition or temperature–composition phase diagram.

In Fig. 13.6(a), the liquidus curve shows the relation between p and x_A for equilibrated liquid and gas phases at constant T, and the vaporus curve shows the relation between p and y_A under these conditions. We see that p is a linear function of x_A but not of y_A.

In a similar fashion, the liquidus curve in Fig. 13.6(b) shows the relation between T and x_A, and the vaporus curve shows the relation between T and y_A, for equilibrated liquid and gas phases at constant p. Neither curve is linear.

A liquidus curve is also called a *bubble-point* curve or a *boiling-point* curve. Other names for a vaporus curve are *dew-point* curve and *condensation* curve. These curves are actually cross-sections of liquidus and vaporus *surfaces* in a three-dimensional $T–p–z_A$ phase diagram, as shown in Fig. 13.7 on the next page. In this figure, the liquidus surface is in view at the front and the vaporus surface is hidden behind it.

13.2.5 Liquid–gas systems with nonideal liquid mixtures

Most binary liquid mixtures do not behave ideally. The most common situation is *positive* deviations from Raoult's law.[5] Some mixtures, however, have specific A–B interactions, such as solvation or molecular association, that prevent random mixing of the molecules of A and B, and the result is then *negative* deviations from Raoult's law. If the deviations from Raoult's law, either positive or negative, are large enough, the constant-temperature liquidus curve exhibits a maximum or minimum and *azeotropic* behavior results.

Figure 13.8 on page 435 shows the azeotropic behavior of the binary methanol-benzene system at constant temperature. In Fig. 13.8(a), the experimental partial pressures in a

---

[5]In the molecular model of Sec. 11.1.5, positive deviations correspond to a less negative value of k_{AB} than the average of k_{AA} and k_{BB}.
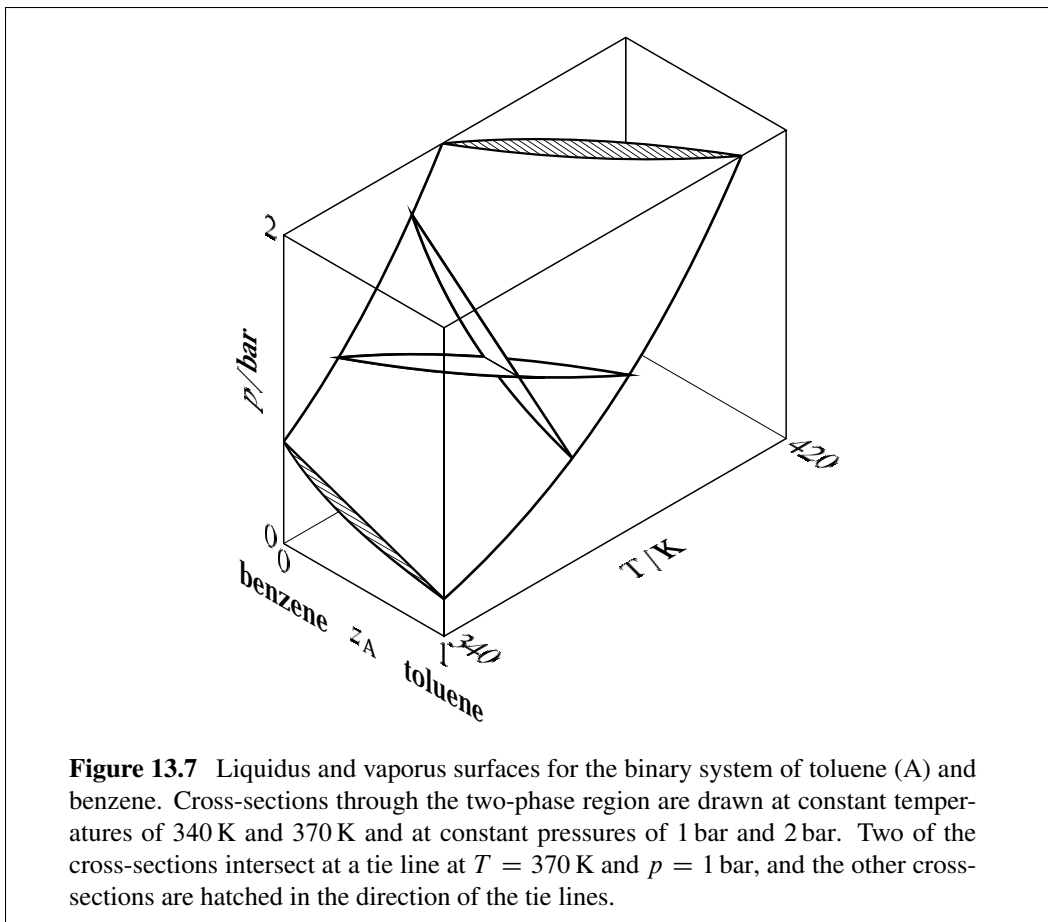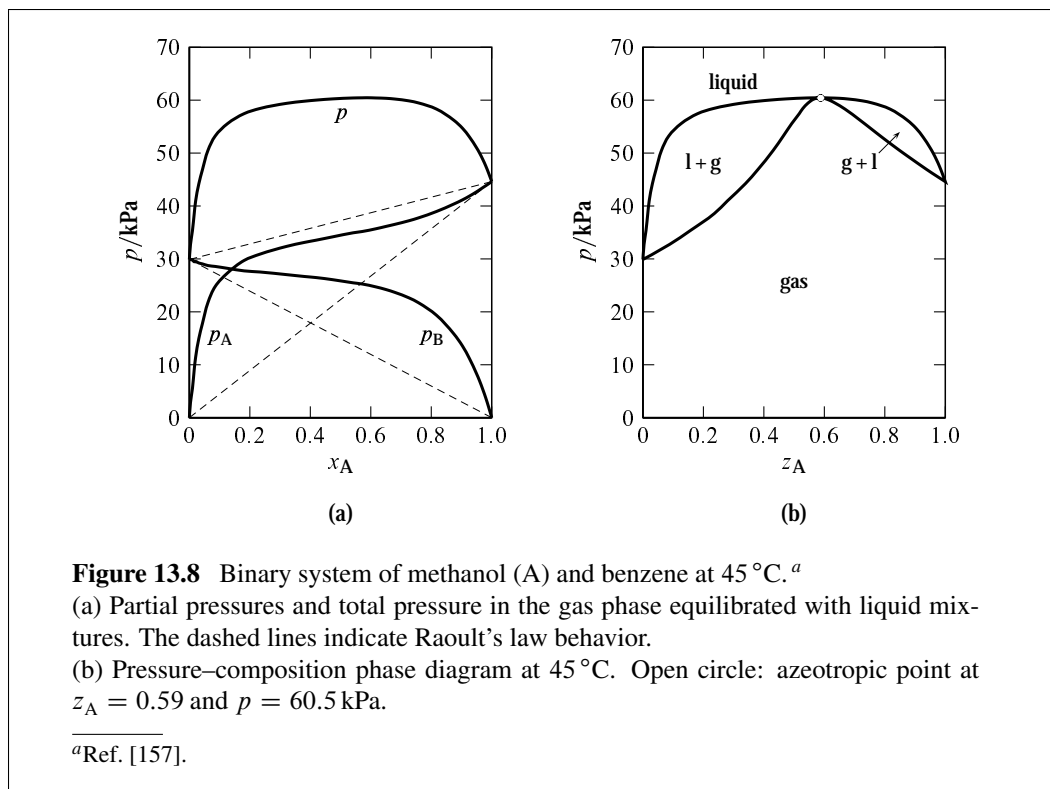
Figure 13.7 Liquidus and vaporus surfaces for the binary system of toluene (A) and benzene. Cross-sections through the two-phase region are drawn at constant temperatures of 340 K and 370 K and at constant pressures of 1 bar and 2 bar. Two of the cross-sections intersect at a tie line at $T = 370$ K and $p = 1$ bar, and the other cross-sections are hatched in the direction of the tie lines.

gas phase equilibrated with the nonideal liquid mixture are plotted as a function of the liquid composition. The partial pressures of both components exhibit positive deviations from Raoult's law,[6] and the total pressure (equal to the sum of the partial pressures) has a maximum value greater than the vapor pressure of either pure component. The curve of p versus x_A becomes the liquidus curve of the pressure–composition phase diagram shown in Fig. 13.8(b). Points on the vaporus curve are calculated from $p = p_A/y_A$.

> In practice, the data needed to generate the liquidus and vaporus curves of a nonideal binary system are usually obtained by allowing liquid mixtures of various compositions to boil in an equilibrium still at a fixed temperature or pressure. When the liquid and gas phases have become equilibrated, samples of each are withdrawn for analysis. The partial pressures shown in Fig. 13.8(a) were calculated from the experimental gas-phase compositions with the relations $p_A = y_A p$ and $p_B = p - p_A$.

If the constant-temperature liquidus curve has a maximum pressure at a liquid composition not corresponding to one of the pure components, which is the case for the methanol–

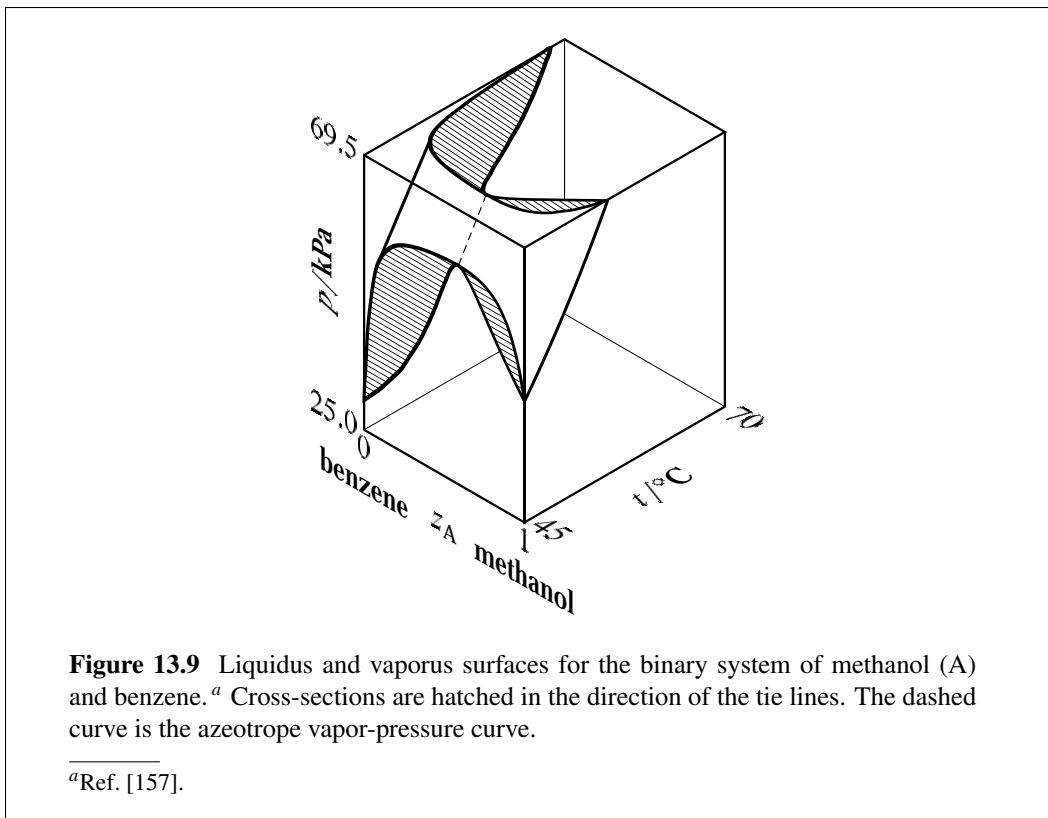[6]This behavior is consistent with the statement in Sec. 12.8.2 that if one constituent of a binary liquid mixture exhibits positive deviations from Raoult's law, with only one inflection point in the curve of fugacity versus mole fraction, the other constituent also has positive deviations from Raoult's law.

Figure 13.8 Binary system of methanol (A) and benzene at 45 °C. [a]
(a) Partial pressures and total pressure in the gas phase equilibrated with liquid mixtures. The dashed lines indicate Raoult's law behavior.
(b) Pressure–composition phase diagram at 45 °C. Open circle: azeotropic point at $z_A = 0.59$ and $p = 60.5$ kPa.

---

[a]Ref. [157].

benzene system, then the liquid and gas phases are mixtures of identical compositions at this pressure. This behavior was deduced on page 405 at the end of Sec. 12.8.3. On the pressure–composition phase diagram, the liquidus and vaporus curves both have maxima at this pressure, and the two curves coincide at an *azeotropic point*. A binary system with negative deviations from Raoult's law can have an isothermal liquidus curve with a *minimum* pressure at a particular mixture composition, in which case the liquidus and vaporus curves coincide at an azeotropic point at this minimum. The general phenomenon in which equilibrated liquid and gas mixtures have identical compositions is called *azeotropy*, and the liquid with this composition is an azeotropic mixture or **azeotrope** (Greek: *boils unchanged*). An azeotropic mixture vaporizes as if it were a pure substance, undergoing an equilibrium phase transition to a gas of the same composition.

If the liquidus and vaporus curves exhibit a *maximum* on a pressure–composition phase diagram, then they exhibit a *minimum* on a temperature–composition phase diagram. This relation is explained for the methanol–benzene system by the three-dimensional liquidus and vaporus surfaces drawn in Fig. 13.9 on the next page. In this diagram, the vaporus surface is hidden behind the liquidus surface. The hatched cross-section at the front of the figure is the same as the pressure–composition diagram of Fig. 13.8(b), and the hatched cross-section at the top of the figure is a temperature–composition phase diagram in which the system exhibits a *minimum-boiling azeotrope*.

A binary system containing an azeotropic mixture in equilibrium with its vapor has two species, two phases, and one relation among intensive variables: $x_A = y_A$. The number of degrees of freedom is then $F = 2 + s - r - P = 2 + 2 - 1 - 2 = 1$; the system is

---

Figure 13.9 Liquidus and vaporus surfaces for the binary system of methanol (A) and benzene.[a] Cross-sections are hatched in the direction of the tie lines. The dashed curve is the azeotrope vapor-pressure curve.

[a]Ref. [157].

univariant. At a given temperature, the azeotrope can exist at only one pressure and have only one composition. As T changes, so do p and z_A along an *azeotrope vapor-pressure curve* as illustrated by the dashed curve in Fig. 13.9.
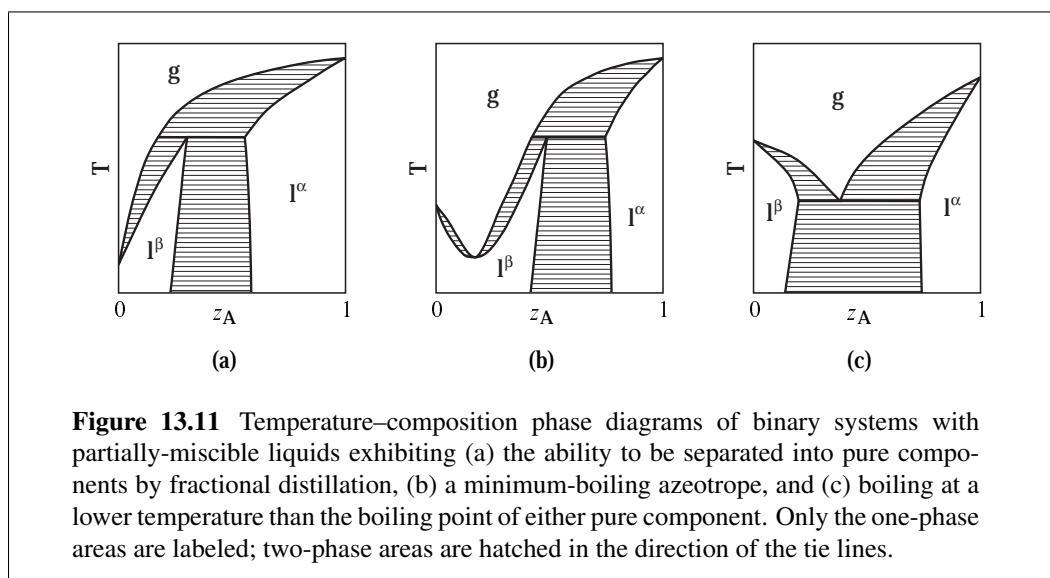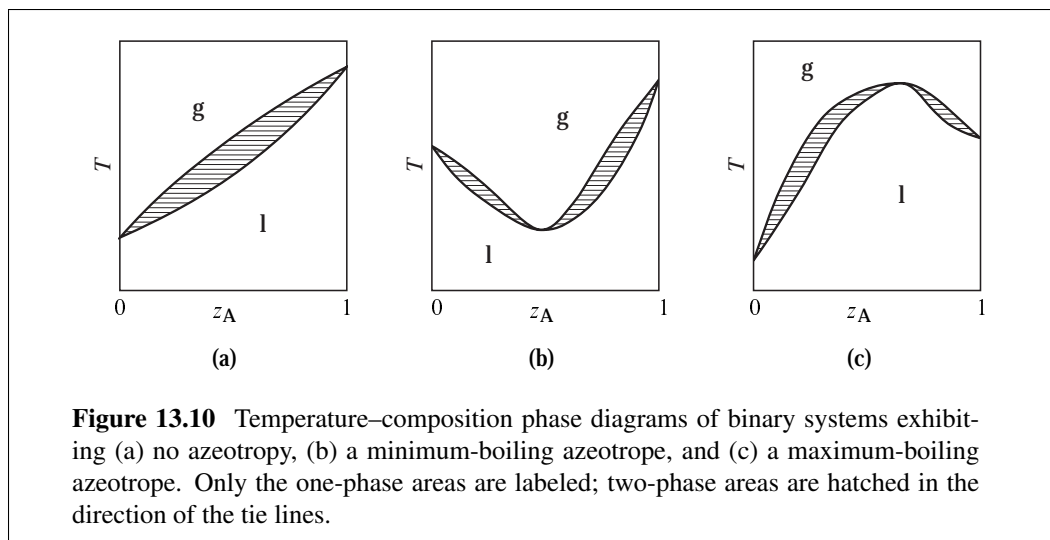
Figure 13.10 on the next page summarizes the general appearance of some relatively simple temperature–composition phase diagrams of binary systems. If the system does not form an azeotrope (*zeotropic* behavior), the equilibrated gas phase is richer in one component than the liquid phase at all liquid compositions, and the liquid mixture can be separated into its two components by fractional distillation. The gas in equilibrium with an azeotropic mixture, however, is not enriched in either component. Fractional distillation of a system with an azeotrope leads to separation into one pure component and the azeotropic mixture.

More complicated behavior is shown in the phase diagrams of Fig. 13.11. These are binary systems with partially-miscible liquids in which the boiling point is reached before an upper consolute temperature can be observed.

13.2.6 Solid–gas systems

As an example of a two-component system with equilibrated solid and gas phases, consider the components $CuSO_4$ and H_2O, denoted A and B respectively. In the pressure–composition phase diagram shown in Fig. 13.12 on page 438, the composition variable z_B is as usual the mole fraction of component B in the system as a whole.

The anhydrous salt and its hydrates (solid compounds) form the series of solids $CuSO_4$, $CuSO_4 \cdot H_2O$, $CuSO_4 \cdot 3H_2O$, and $CuSO_4 \cdot 5H_2O$. In the phase diagram these formulas are

Figure 13.10 Temperature–composition phase diagrams of binary systems exhibiting (a) no azeotropy, (b) a minimum-boiling azeotrope, and (c) a maximu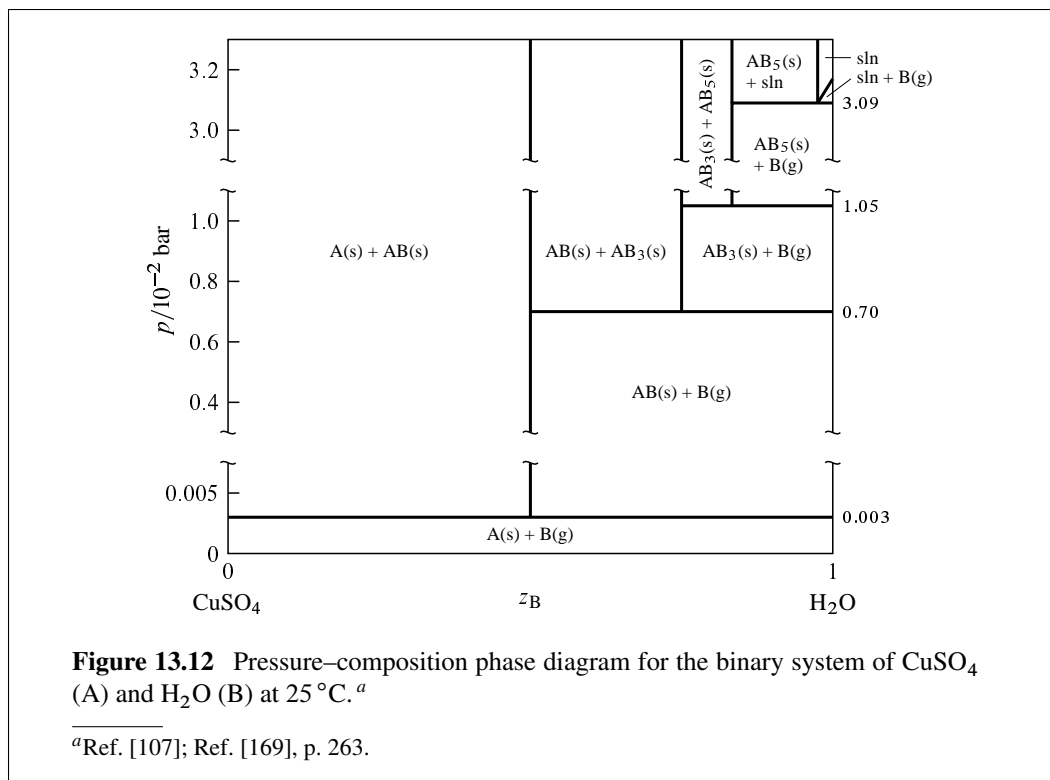m-boiling azeotrope. Only the one-phase areas are labeled; two-phase areas are hatched in the direction of the tie lines.

Figure 13.11 Temperature–composition phase diagrams of binary systems with partially-miscible liquids exhibiting (a) the ability to be separated into pure components by fractional distillation, (b) a minimum-boiling azeotrope, and (c) boiling at a lower temperature than the boiling point of either pure component. Only the one-phase areas are labeled; two-phase areas are hatched in the direction of the tie lines.

abbreviated A, AB, AB_3, and AB_5. The following dissociation equilibria (dehydration equilibria) are possible:

$$CuSO_4 \cdot H_2O(s) \; \rightleftharpoons \; CuSO_4(s) + H_2O(g)$$
$$\tfrac{1}{2}CuSO_4 \cdot 3H_2O(s) \; \rightleftharpoons \; \tfrac{1}{2}CuSO_4 \cdot H_2O(s) + H_2O(g)$$
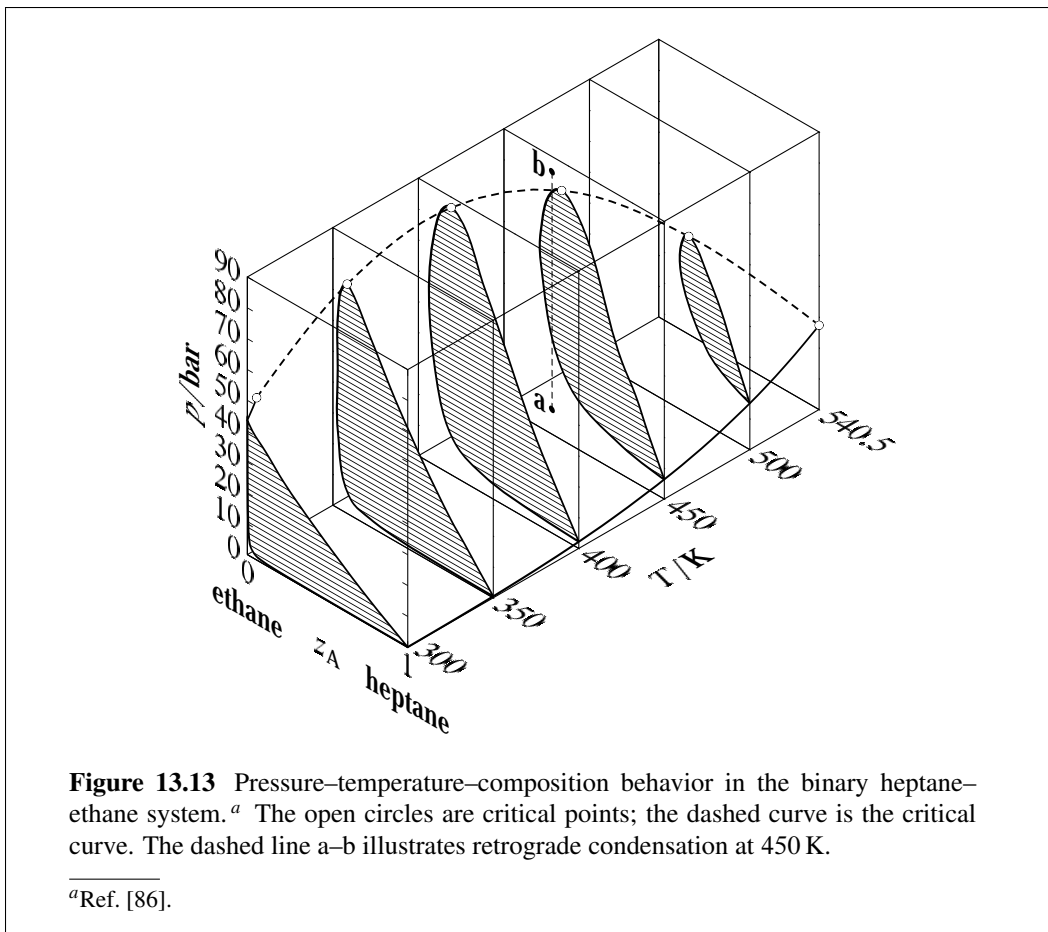$$\tfrac{1}{2}CuSO_4 \cdot 5H_2O(s) \; \rightleftharpoons \; \tfrac{1}{2}CuSO_4 \cdot 3H_2O(s) + H_2O(g)$$
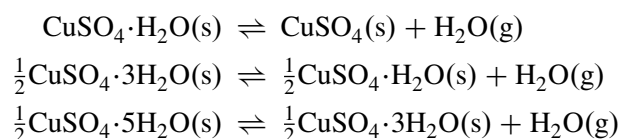
The equilibria are written above with coefficients that make the coefficient of $H_2O(g)$ unity. When one of these equilibria is established in the system, there are two components and three phases; the phase rule then tells us the system is univariant and the pressure has only one possible value at a given temperature. This pressure is called the *dissociation pressure* of the higher hydrate.

Figure 13.12 Pressure–composition phase diagram for the binary system of $CuSO_4$ (A) and H_2O (B) at 25 °C. [a]

[a]Ref. [107]; Ref. [169], p. 263.

The dissociation pressures of the three hydrates are indicated by horizontal lines in Fig. 13.12. For instance, the dissociation pressure of $CuSO_4 \cdot 5H_2O$ is 1.05×10^{-2} bar. At the pressure of each horizontal line, the equilibrium system can have one, two, or three phases, with compositions given by the intersections of the line with vertical lines. A fourth three-phase equilibrium is shown at $p = 3.09 \times 10^{-2}$ bar; this is the equilibrium between solid $CuSO_4 \cdot 5H_2O$, the saturated aqueous solution of this hydrate, and water vapor.

Consider the thermodynamic equilibrium constant of one of the dissociation reactions. At the low pressures shown in the phase diagram, the activities of the solids are practically unity and the fugacity of the water vapor is practically the same as the pressure, so the equilibrium constant is almost exactly equal to $p_d/p°$, where p_d is the dissociation pressure of the higher hydrate in the reaction. Thus, a hydrate cannot exist in equilibrium with water vapor at a pressure below the dissociation pressure of the hydrate because dissociation would be spontaneous under these conditions. Conversely, the salt formed by the dissociation of a hydrate cannot exist in equilibrium with water vapor at a pressure above the dissociation pressure because hydration would be spontaneous.

> If the system contains dry air as an additional gaseous component and one of the dissociation equilibria is established, the partial pressure p_{H_2O} of H_2O is equal (approximately) to the dissociation pressure p_d of the higher hydrate. The prior statements regarding dissociation and hydration now depend on the value of p_{H_2O}. If a hydrate is placed in air in which p_{H_2O} is less than p_d, dehydration is spontaneous; this phenomenon is called **efflorescence** (Latin: *blossoming*). If p_{H_2O} is greater than the vapor pressure of the saturated solution of the highest hydrate that can form in the system,

Figure 13.13 Pressure–temperature–composition behavior in the binary heptane–ethane system. [a] The open circles are critical points; the dashed curve is the critical curve. The dashed line a–b illustrates retrograde condensation at 450 K.
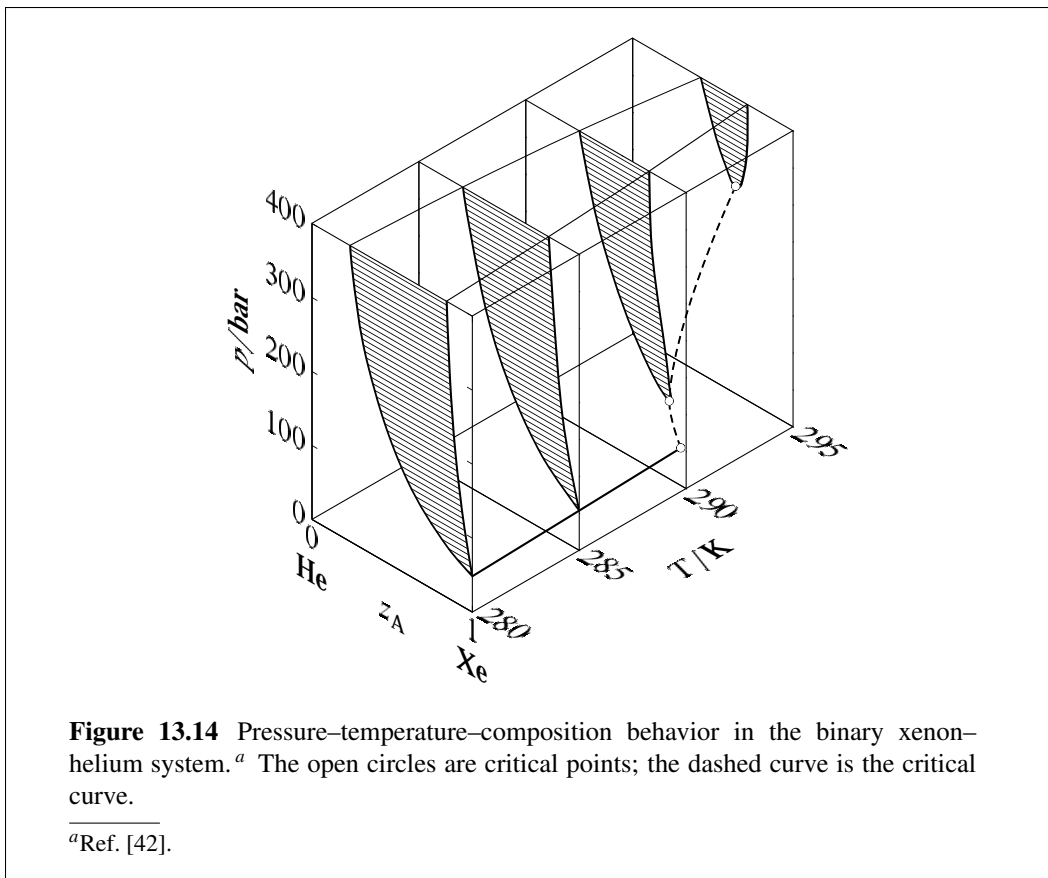
---

[a]Ref. [86].

the anhydrous salt and any of its hydrates will spontaneously absorb water and form the saturated solution; this is **deliquescence** (Latin: *becoming fluid*).

If the two-component equilibrium system contains only two phases, it is bivariant corresponding to one of the areas in Fig. 13.12. Here both the temperature and the pressure can be varied. In the case of areas labeled with two *solid* phases, the pressure has to be applied to the solids by a fluid (other than H_2O) that is not considered part of the system.

13.2.7 Systems at high pressure

Binary phase diagrams begin to look different when the pressure is greater than the critical pressure of either of the pure components. Various types of behavior have been observed in this region. One common type, that found in the binary system of heptane and ethane, is shown in Fig. 13.13. This figure shows sections of a three-dimensional phase diagram at five temperatures. Each section is a pressure–composition phase diagram at constant T. The two-phase areas are hatched in the direction of the tie lines. At the left end of each tie line (at low z_A) is a vaporus curve, and at the right end is a liquidus curve. The vapor pressure curve of pure ethane ($z_A = 0$) ends at the critical point of ethane at 305.4 K; between this point and the critical point of heptane at 540.5 K, there is a continuous *critical curve*,

Figure 13.14 Pressure–temperature–composition behavior in the binary xenon–helium system.[a] The open circles are critical points; the dashed curve is the critical curve.
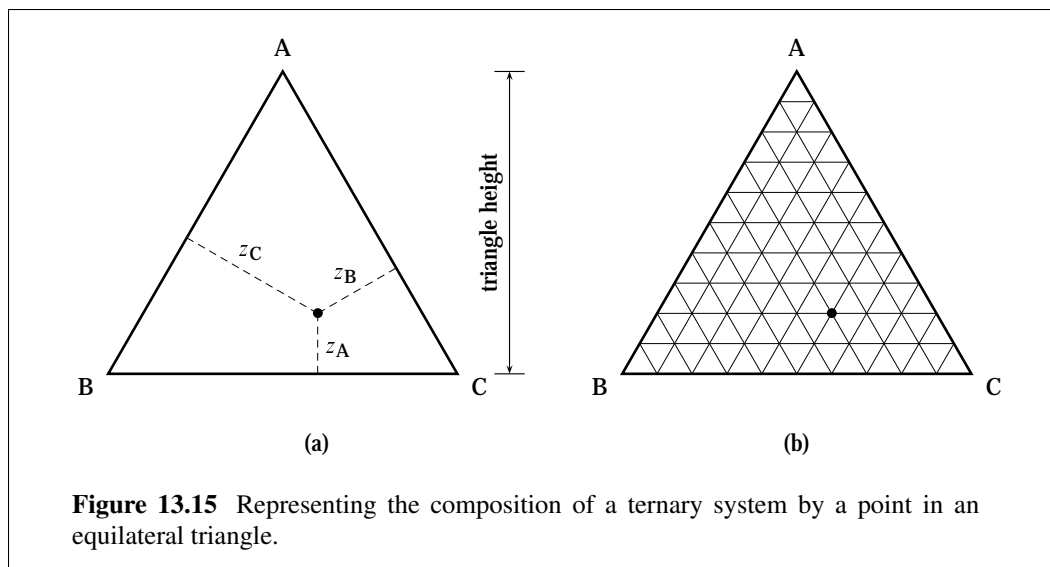
[a]Ref. [42].

which is the locus of critical points at which gas and liquid mixtures become identical in composition and density.

Consider what happens when the system point is at point a in Fig. 13.13 and the pressure is then increased by isothermal compression along line a–b. The system point moves from the area for a gas phase into the two-phase gas–liquid area and then out into the gas-phase area again. This curious phenomenon, condensation followed by vaporization, is called *retrograde condensation*.

Under some conditions, an isobaric increase of T can result in vaporization followed by condensation; this is *retrograde vaporization*.

A different type of high-pressure behavior, that found in the xenon–helium system, is shown in Fig. 13.14. Here, the critical curve begins at the critical point of the less volatile component (xenon) and continues to *higher* temperatures and pressures than the critical temperature and pressure of either pure component. The two-phase region at pressures above this critical curve is sometimes said to represent *gas–gas equilibrium*, or *gas–gas immiscibility*, because we would not usually consider a liquid to exist beyond the critical points of the pure components. Of course, the coexisting phases in this two-phase region are not gases in the ordinary sense of being tenuous fluids, but are instead high-pressure fluids of liquid-like densities. If we want to call both phases gases, then we have to say that pure gaseous substances at high pressure do not necessarily mix spontaneously in all proportions as they do at ordinary pressures.

Figure 13.15 Representing the composition of a ternary system by a point in an equilateral triangle.

If the pressure of a system is increased isothermally, eventually solid phases will appear; these are not shown in Figs. 13.13 and Fig. 13.14.
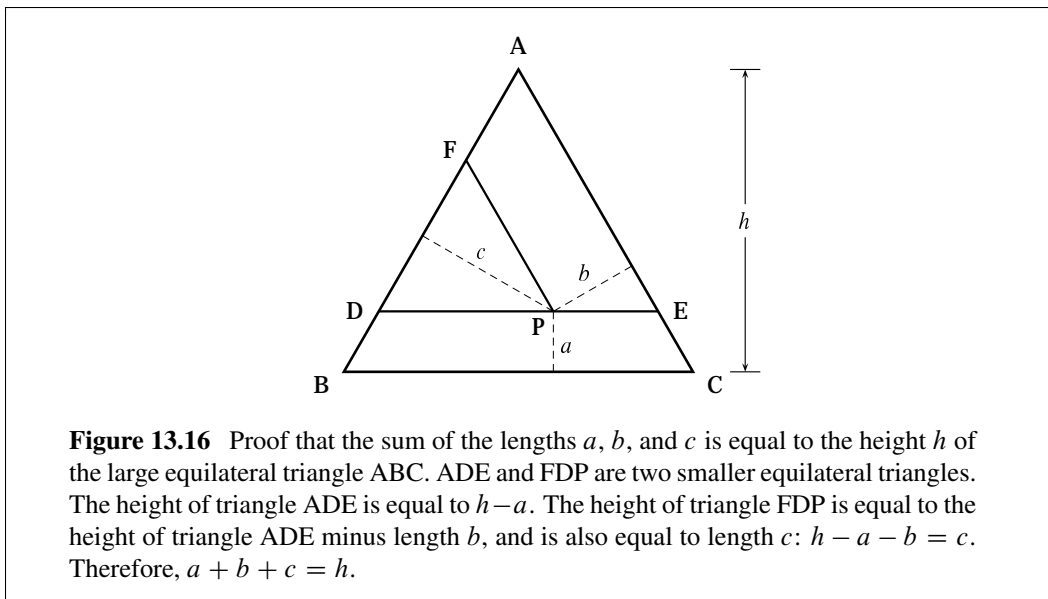
13.3 PHASE DIAGRAMS: TERNARY SYSTEMS

A ternary system is one with three components. We can independently vary the temperature, the pressure, and two independent composition variables for the system as a whole. A two-dimensional phase diagram for a ternary system is usually drawn for conditions of constant T and p.

Although we could draw a two-dimensional phase diagram with Cartesian coordinates to express the mole fractions of two of the components, there are advantages in using instead the triangular coordinates shown in Fig. 13.15. Each vertex of the equilateral triangle represents one of the pure components A, B, or C. A point on the side of the triangle opposite a vertex represents a binary system of the other two components, and a point within the triangle represents a ternary system with all three components.

To determine the mole fraction z_A of component A in the system as a whole represented by a point within the triangle, we measure the distance to the point from the side of the triangle that is opposite the vertex for pure A, then express this distance as a fraction of the height of the triangle. We follow the same procedure to determine z_B and z_C. The concept is shown in Fig. 13.15(a).

As an aid for the conversion between the position of a point and the overall composition, we can draw equally-spaced lines within the triangle parallel to the sides as shown in Fig. 13.15(b). One of these lines, being at a constant distance from one side of the triangle, represents a constant mole fraction of one component. In the figure, the lines divide the distance from each side to the opposite vertex into ten equal parts; thus, adjacent parallel lines represent a difference of 0.1 in the mole fraction of a component, starting with 0 at the side of the triangle and ending with 1 at the vertex. Using the lines, we see that the filled circle in the figure represents the overall composition $z_A = 0.20$, $z_B = 0.30$, and

Figure 13.16 Proof that the sum of the lengths a, b, and c is equal to the height h of the large equilateral triangle ABC. ADE and FDP are two smaller equilateral triangles. The height of triangle ADE is equal to $h-a$. The height of triangle FDP is equal to the height of triangle ADE minus length b, and is also equal to length c: $h - a - b = c$. Therefore, $a + b + c = h$.

$z_C = 0.50$.

The sum of z_A, z_B, and z_C must be 1. The method of representing composition with a point in an equilateral triangle works because the sum of the lines drawn from the point to the three sides, perpendicular to the sides, equals the height of the triangle. The proof is shown in Fig. 13.16.

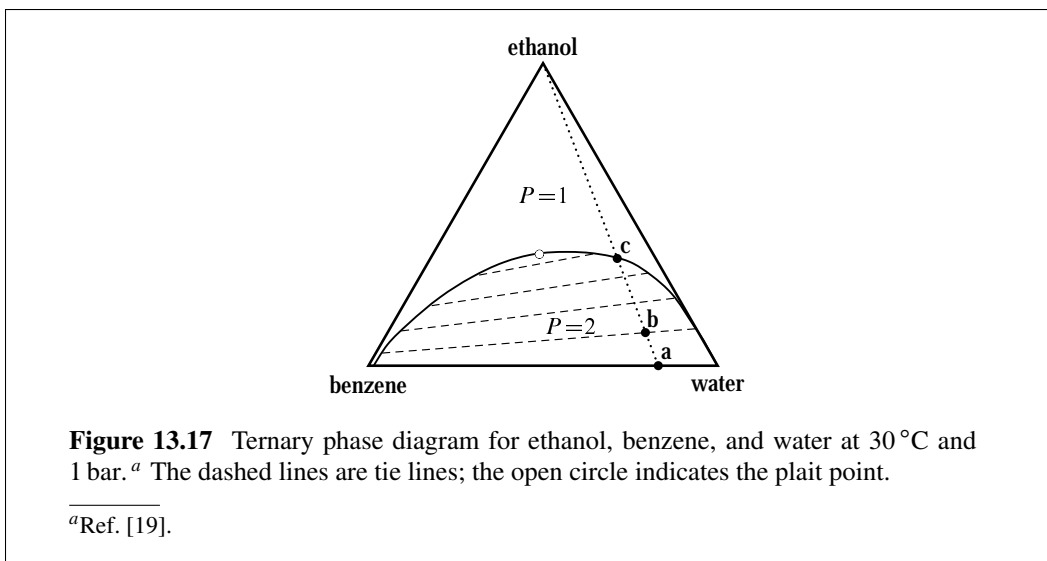Two useful properties of this way of representing a ternary composition are as follows:

1. Points on a line parallel to a side of the triangle represent systems in which one of the mole fractions remains constant.
2. Points on a line passing through a vertex represent systems in which the ratio of two of the mole fractions remains constant.

13.3.1 Three liquids

Figure 13.17 on the next page is the ternary phase diagram of a system of ethanol, benzene, and water at a temperature and pressure at which the phases are liquids. When the system point is in the area labeled $P{=}1$, there is a single liquid phase whose composition is described by the position of the point. The one-phase area extends to the side of the triangle representing binary mixtures of ethanol and benzene, and to the side representing binary mixtures of ethanol and water. In other words, ethanol and benzene mix in all proportions, and so also do ethanol and water.

When the overall composition is such that the system point falls in the area labeled $P{=}2$, two liquid phases are present. The compositions of these phases are given by the positions of the ends of a tie line through the system point. Four representative tie lines are included in the diagram, and these must be determined experimentally. The relative amounts of the two phases can be determined from the lever rule.[7] In the limit of zero mole

---

[7] The lever rule works, according to the general derivation in Sec. 8.2.4, because the ratio n_A/n, which is equal to z_A, varies linearly with the position of the system point along a tie line on the triangular phase diagram.

Figure 13.17 Ternary phase diagram for ethanol, benzene, and water at 30 °C and
1 bar. [a] The dashed lines are tie lines; the open circle indicates the plait point.
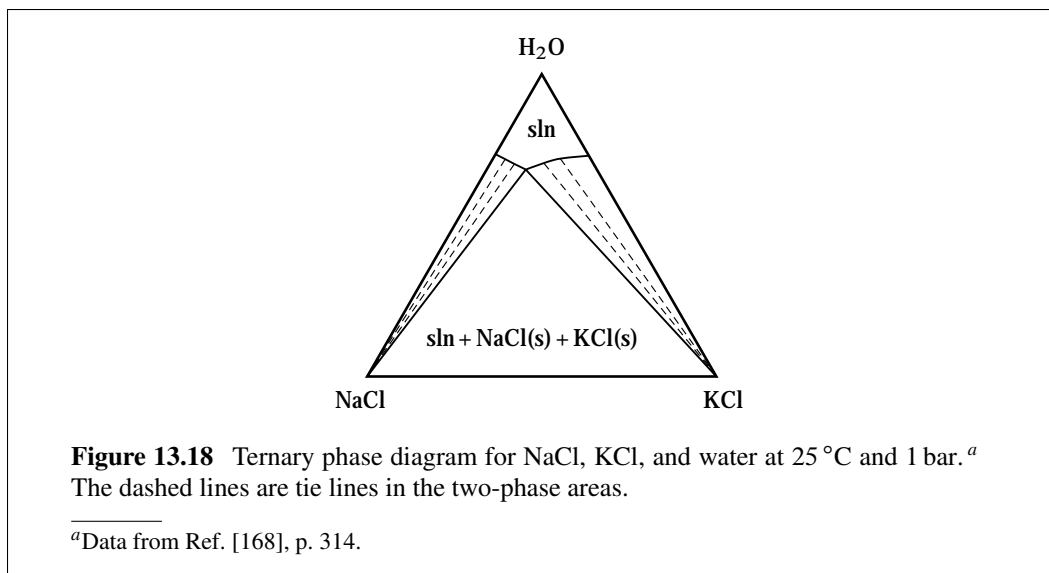
[a]Ref. [19].

fraction of ethanol, the tie line falls along the horizontal base of the triangle and displays a
miscibility gap for the binary system of benzene and water. (The conjugate phases are very
nearly pure benzene and pure water).

The *plait point* shown as an open circle in the figure is also called a *critical solution
point*. As the system point approaches the plait point from within the two-phase area, the
length of the tie line through the system point approaches zero, the miscibility gap disap-
pears, and the compositions of the two conjugate liquid phases become identical.

Suppose we have the binary system of benzene and water represented by point a. Two
liquid phases are present: one is wet benzene and the other is water containing a very small
mole fraction of benzene. If we gradually stir ethanol into this system, the system point
moves along the dotted line from point a toward the vertex for pure ethanol, but can never
quite reach the vertex. At point b, there are still two phases, and we can consider the ethanol
to have distributed itself between two partially-miscible solvents, benzene and water (Sec.
12.6.3). From the position of point b relative to the ends of the tie line passing through
point b, we see that the mole fraction of ethanol is greater in the water-rich phase. As we
continue to add ethanol, the amount of the water-rich phase increases and the amount of the
benzene-rich phase decreases, until at point c the benzene-rich phase completely disappears.
The added ethanol has increased the mutual solubilities of benzene and water and resulted
in a single liquid phase.

13.3.2 Two solids and a solvent

The phase diagram in Fig. 13.18 on the next page is for a ternary system of water and two
salts with an ion in common. There is a one-phase area for solution, labeled sln; a pair
of two-phase areas in which the phases are a single solid salt and the saturated solution;
and a triangular three-phase area. The upper vertex of the three-phase area, the *eutonic
point*, represents the composition of solution saturated with respect to both salts. Some
representative tie lines are drawn in the two-phase areas.

Figure 13.18 Ternary phase diagram for NaCl, KCl, and water at 25 °C and 1 bar.[a]
The dashed lines are tie lines in the two-phase areas.

---

[a]Data from Ref. [168], p. 314.

A system of three components and three phases has two degrees of freedom; at fixed
values of T and p, each phase must have a fixed composition. The fixed compositions
of the phases that are present when the system point falls in the three-phase area are the
compositions at the three vertices of the inner triangle: solid NaCl, solid KCl, and solution
of the eutonic composition $x_{NaCl} = 0.20$ and $x_{KCl} = 0.11$.

From the position of the curved boundary that separates the one-phase solution area
from the two-phase area for solution and solid KCl, we can see that adding NaCl to the
saturated solution of KCl decreases the mole fraction of KCl in the saturated solution. Al-
though it is not obvious in the phase diagram, adding KCl to a saturated solution of NaCl
decreases the mole fraction of NaCl. These decreases in solubility when a common ion is
added are examples of the *common ion effect* mentioned in Sec. 12.5.5.

PROBLEMS

An underlined problem number or problem-part letter indicates that the numerical answer appears in Appendix I.

13.1 Consider a single-phase system that is a gaseous mixture of N_2, H_2, and NH_3. For each of the following cases, find the number of degrees of freedom and give an example of the independent intensive variables that could be used to specify the equilibrium state, apart from the total amount of gas.

  (a) There is no reaction.

  (b) The reaction $N_2(g) + 3\,H_2(g) \;\rightarrow\; 2\,NH_3(g)$ is at equilibrium.

  (c) The reaction is at equilibrium and the system is prepared from NH_3 only.

13.2 How many components has a mixture of water and deuterium oxide in which the equilibrium $H_2O + D_2O \;\rightleftharpoons\; 2\,HDO$ exists?

13.3 Consider a system containing only $NH_4Cl(s)$, $NH_3(g)$, and $HCl(g)$. Assume that the equilibrium $NH_4Cl(s) \;\rightleftharpoons\; NH_3(g) + HCl(g)$ exists.

  (a) Suppose you prepare the system by placing solid NH_4Cl in an evacuated flask and heating to 400 K. Use the phase rule to decide whether you can vary the pressure while both phases remain in equilibrium at 400 K.

  (b) According to the phase rule, if the system is not prepared as described in part (a) could you vary the pressure while both phases remain in equilibrium at 400 K? Explain.

  (c) Rationalize your conclusions for these two cases on the basis of the thermodynamic equilibrium constant. Assume that the gas phase is an ideal gas mixture and use the approximate expression $K = p_{NH_3}\,p_{HCl}/(p^\circ)^2$.

13.4 Consider the lime-kiln process $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$. Find the number of intensive variables that can be varied independently in the equilibrium system under the following conditions:

  (a) The system is prepared by placing calcium carbonate, calcium oxide, and carbon dioxide in a container.

  (b) The system is prepared from calcium carbonate only.

  (c) The temperature is fixed at 1000 K.

13.5 What are the values of C and F in systems consisting of solid AgCl in equilibrium with an aqueous phase containing H_2O, $Ag^+(aq)$, $Cl^-(aq)$, $Na^+(aq)$, and $NO_3^-(aq)$ prepared in the following ways? Give examples of intensive variables that could be varied independently.

  (a) The system is prepared by equilibrating excess solid AgCl with an aqueous solution of $NaNO_3$.

  (b) The system is prepared by mixing aqueous solutions of $AgNO_3$ and NaCl in arbitrary proportions; some solid AgCl forms by precipitation.

13.6 How many degrees of freedom has a system consisting of solid NaCl in equilibrium with an aqueous phase containing H_2O, $Na^+(aq)$, $Cl^-(aq)$, $H^+(aq)$, and $OH^-(aq)$? Would it be possible to independently vary T, p, and m_{OH^-}? If so, explain how you could do this.

13.7 Consult the phase diagram shown in Fig. 13.4 on page 430. Suppose the system contains 36.0 g (2.00 mol) H_2O and 58.4 g (1.00 mol) NaCl at 25 °C and 1 bar.

(a) Describe the phases present in the equilibrium system and their masses.

(b) Describe the changes that occur at constant pressure if the system is placed in thermal contact with a heat reservoir at $-30\,°C$.

(c) Describe the changes that occur if the temperature is raised from $25\,°C$ to $120\,°C$ at constant pressure.

(d) Describe the system after $200\,g\ H_2O$ is added at $25\,°C$.

Table 13.1 Aqueous solubilities of sodium sulfate decahydrate and anhydrous sodium sulfate[a]

$Na_2SO_4 \cdot 10H_2O$		Na_2SO_4	
$t/°C$	x_B	$t/°C$	x_B
10	0.011	40	0.058
15	0.016	50	0.056
20	0.024		
25	0.034		
30	0.048		

[a]Ref. [55], p. 179–180.

13.8 Use the following information to draw a temperature–composition phase diagram for the binary system of H_2O (A) and Na_2SO_4 (B) at $p = 1\,bar$, confining t to the range -20 to $50\,°C$ and z_B to the range 0–0.2. The solid decahydrate, $Na_2SO_4 \cdot 10H_2O$, is stable below $32.4\,°C$. The anhydrous salt, Na_2SO_4, is stable above this temperature. There is a peritectic point for these two solids and the solution at $x_B = 0.059$ and $t = 32.4\,°C$. There is a eutectic point for ice, $Na_2SO_4 \cdot 10H_2O$, and the solution at $x_B = 0.006$ and $t = -1.3\,°C$. Table 13.1 gives the temperature dependence of the solubilities of the ionic solids.

13.9 Iron(III) chloride forms various solid hydrates, all of which melt congruently. Table 13.2 on the next page lists the temperatures t of aqueous solutions of various compositions that are saturated with respect to a solid phase.

(a) Use these data to construct a t–z_B phase diagram for the binary system of $FeCl_3$ (A) and H_2O (B). Identify the formula and melting point of each hydrate. Hint: derive a formula for the mole ratio n_B/n_A as a function of x_A in a binary mixture.

(b) For the following conditions, determine the phase or phases present at equilibrium and the composition of each.
  1. $t = -70.0°C$ and $z_A = 0.100$
  2. $t = 50.0°C$ and $z_A = 0.275$

13.10 Figure 13.19 on the next page is a temperature–composition phase diagram for the binary system of water (A) and phenol (B) at 1 bar. These liquids are partially miscible below $67\,°C$. Phenol is more dense than water, so the layer with the higher mole fraction of phenol is the bottom layer. Suppose you place $4.0\,mol$ of H_2O and $1.0\,mol$ of phenol in a beaker at $30\,°C$ and gently stir to allow the layers to equilibrate.

(a) What are the compositions of the equilibrated top and bottom layers?

(b) Find the amount of each component in the bottom layer.

Table 13.2 Data for Problem 13.9. Temperatures of saturated solutions of aqueous iron(III) chloride at $p = 1$ bar (A = $FeCl_3$, B = H_2O)[a]

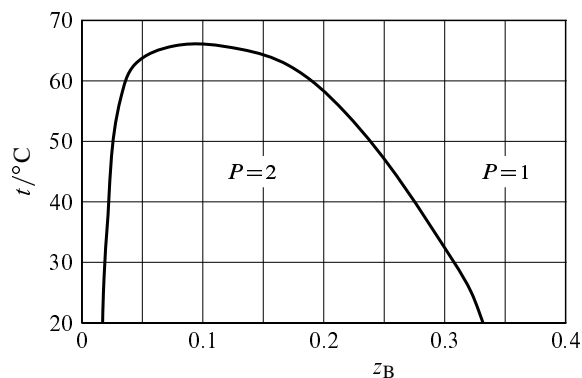| x_A	$t/°C$	x_A	$t/°C$	x_A	$t/°C$
0.000	0.0	0.119	35.0	0.286	56.0
0.020	−10.0	0.143	37.0	0.289	55.0
0.032	−20.5	0.157	36.0	0.293	60.0
0.037	−27.5	0.173	33.0	0.301	69.0
0.045	−40.0	0.183	30.0	0.318	72.5
0.052	−55.0	0.195	27.4	0.333	73.5
0.053	−41.0	0.213	32.0	0.343	72.5
0.056	−27.0	0.222	32.5	0.358	70.0
0.076	0.0	0.232	30.0	0.369	66.0
0.083	10.0	0.238	35.0	0.369	80.0
0.093	20.0	0.259	50.0	0.373	100.0
0.106	30.0	0.277	55.0		

[a]Data from Ref. [55], page 193.

Figure 13.19 Temperature–composition phase diagram for the binary system of water (A) and phenol (B) at 1 bar.[a] Only liquid phases are present.

[a]Ref. [55], p. 95.

(c) As you gradually stir more phenol into the beaker, maintaining the temperature at 30 °C, what changes occur in the volumes and compositions of the two layers? Assuming that one layer eventually disappears, what additional amount of phenol is needed to cause this to happen?

13.11 The standard boiling point of propane is −41.8 °C and that of *n*-butane is −0.2 °C. Table 13.3 on the next page lists vapor pressure data for the pure liquids. Assume that the liquid mixtures obey Raoult's law.

(a) Calculate the compositions, x_A, of the liquid mixtures with boiling points of −10.0 °C, −20.0 °C, and −30.0 °C at a pressure of 1 bar.

(b) Calculate the compositions, y_A, of the equilibrium vapor at these three temperatures.

Table 13.3   Saturation vapor pressures
of propane (A) and n-butane (B)

$t/°C$	p_A^*/bar	p_B^*/bar
−10.0	3.360	0.678
−20.0	2.380	0.441
−30.0	1.633	0.275

(c) Plot the temperature–composition phase diagram at $p = 1$ bar using these data, and label
the areas appropriately.

(d) Suppose a system containing 10.0 mol propane and 10.0 mol n-butane is brought to a
pressure of 1 bar and a temperature of −25 °C. From your phase diagram, estimate the
compositions and amounts of both phases.

Table 13.4   Liquid and gas compositions in the two-phase
system of 2-propanol (A) and benzene at 45 °C [a]

x_A	y_A	p/kPa	x_A	y_A	p/kPa
0	0	29.89	0.5504	0.3692	35.32
0.0472	0.1467	33.66	0.6198	0.3951	34.58
0.0980	0.2066	35.21	0.7096	0.4378	33.02
0.2047	0.2663	36.27	0.8073	0.5107	30.28
0.2960	0.2953	36.45	0.9120	0.6658	25.24
0.3862	0.3211	36.29	0.9655	0.8252	21.30
0.4753	0.3463	35.93	1.0000	1.0000	18.14

[a]Ref. [24].

13.12 Use the data in Table 13.4 to draw a pressure–composition phase diagram for the 2-propanol–
benzene system at 45 °C. Label the axes and each area.

Table 13.5   Liquid and gas compositions in the two-
phase system of acetone (A) and chloroform at 35.2 °C
[a]

x_A	y_A	p/kPa	x_A	y_A	p/kPa
0	0	39.08	0.634	0.727	36.29
0.083	0.046	37.34	0.703	0.806	38.09
0.200	0.143	34.92	0.815	0.896	40.97
0.337	0.317	33.22	0.877	0.936	42.62
0.413	0.437	33.12	0.941	0.972	44.32
0.486	0.534	33.70	1.000	1.000	45.93
0.577	0.662	35.09			

[a]Ref. [167], p. 286.

13.13 Use the data in Table 13.5 to draw a pressure–composition phase diagram for the acetone–
chloroform system at 35.2 °C. Label the axes and each area.