

6

Phase diagrams

Phases, components, and degrees of freedom

6.1 Definitions

6.2 The phase rule

Two-component systems

6.3 Vapour pressure diagrams

6.4 Temperature–composition diagrams

6.5 Liquid–liquid phase diagrams

6.6 Liquid–solid phase diagrams

16.1 Impact on materials science:
Liquid crystals

16.2 Impact on materials science:
Ultrapurity and controlled
impurity

Checklist of key ideas

Further reading

Discussion questions

Exercises

Problems

Phase diagrams for pure substances were introduced in Chapter 4. Now we develop their use systematically and show how they are rich summaries of empirical information about a wide range of systems. To set the stage, we introduce the famous phase rule of Gibbs, which shows the extent to which various parameters can be varied yet the equilibrium between phases preserved. With the rule established, we see how it can be used to discuss the phase diagrams that we met in the two preceding chapters. The chapter then introduces systems of gradually increasing complexity. In each case we shall see how the phase diagram for the system summarizes empirical observations on the conditions under which the various phases of the system are stable.

In this chapter we describe a systematic way of discussing the physical changes mixtures undergo when they are heated or cooled and when their compositions are changed. In particular, we see how to use phase diagrams to judge whether two substances are mutually miscible, whether an equilibrium can exist over a range of conditions, or whether the system must be brought to a definite pressure, temperature, and composition before equilibrium is established. Phase diagrams are of considerable commercial and industrial significance, particularly for semiconductors, ceramics, steels, and alloys. They are also the basis of separation procedures in the petroleum industry and of the formulation of foods and cosmetic preparations.

Phases, components, and degrees of freedom

All phase diagrams can be discussed in terms of a relationship, the phase rule, derived by J.W. Gibbs. We shall derive this rule first, and then apply it to a wide variety of systems. The phase rule requires a careful use of terms, so we begin by presenting a number of definitions.

6.1 Definitions

The term **phase** was introduced at the start of Chapter 4, where we saw that it signifies a state of matter that is uniform throughout, not only in chemical composition but also in physical state.¹ Thus we speak of the solid, liquid, and gas phases of a substance, and of its various solid phases (as for black phosphorus and white phosphorus). The number of phases in a system is denoted P . A gas, or a gaseous mixture, is a single phase, a crystal is a single phase, and two totally miscible liquids form a single phase.

¹ The words are Gibbs's.

A solution of sodium chloride in water is a single phase. Ice is a single phase ($P = 1$) even though it might be chipped into small fragments. A slurry of ice and water is a two-phase system ($P = 2$) even though it is difficult to map the boundaries between the phases. A system in which calcium carbonate undergoes thermal decomposition consists of two solid phases (one consisting of calcium carbonate and the other of calcium oxide) and one gaseous phase (consisting of carbon dioxide).

An alloy of two metals is a two-phase system ($P = 2$) if the metals are immiscible, but a single-phase system ($P = 1$) if they are miscible. This example shows that it is not always easy to decide whether a system consists of one phase or of two. A solution of solid B in solid A—a homogeneous mixture of the two substances—is uniform on a molecular scale. In a solution, atoms of A are surrounded by atoms of A and B, and any sample cut from the sample, however small, is representative of the composition of the whole.

A dispersion is uniform on a macroscopic scale but not on a microscopic scale, for it consists of grains or droplets of one substance in a matrix of the other. A small sample could come entirely from one of the minute grains of pure A and would not be representative of the whole (Fig. 6.1). Dispersions are important because, in many advanced materials (including steels), heat treatment cycles are used to achieve the precipitation of a fine dispersion of particles of one phase (such as a carbide phase) within a matrix formed by a saturated solid solution phase. The ability to control this microstructure resulting from phase equilibria makes it possible to tailor the mechanical properties of the materials to a particular application.

By a **constituent** of a system we mean a chemical species (an ion or a molecule) that is present. Thus, a mixture of ethanol and water has two constituents. A solution of sodium chloride has three constituents: water, Na^+ ions, and Cl^- ions. The term constituent should be carefully distinguished from ‘component’, which has a more technical meaning. A **component** is a *chemically independent* constituent of a system. The number of components, C , in a system is the minimum number of independent species necessary to define the composition of all the phases present in the system.

When no reaction takes place and there are no other constraints (such as charge balance), the number of components is equal to the number of constituents. Thus, pure water is a one-component system ($C = 1$), because we need only the species H_2O to specify its composition. Similarly, a mixture of ethanol and water is a two-component system ($C = 2$): we need the species H_2O and $\text{C}_2\text{H}_5\text{OH}$ to specify its composition. An aqueous solution of sodium chloride has two components because, by charge balance, the number of Na^+ ions must be the same as the number of Cl^- ions.

A system that consists of hydrogen, oxygen, and water at room temperature has three components ($C = 3$), despite it being possible to form H_2O from H_2 and O_2 : under the conditions prevailing in the system, hydrogen and oxygen do not react to form water, so they are independent constituents. When a reaction can occur under the conditions prevailing in the system, we need to decide the minimum number of species that, after allowing for reactions in which one species is synthesized from others, can be used to specify the composition of all the phases. Consider, for example, the equilibrium



Phase 1 Phase 2 Phase 3

in which there are three constituents and three phases. To specify the composition of the gas phase (Phase 3) we need the species CO_2 , and to specify the composition of Phase 2 we need the species CaO . However, we do not need an additional species to specify the composition of Phase 1 because its identity (CaCO_3) can be expressed in terms of the other two constituents by making use of the stoichiometry of the reaction. Hence, the system has only two components ($C = 2$).

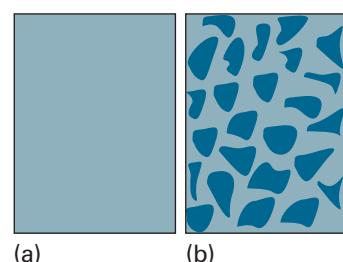


Fig. 6.1 The difference between (a) a single-phase solution, in which the composition is uniform on a microscopic scale, and (b) a dispersion, in which regions of one component are embedded in a matrix of a second component.

Example 6.1 Counting components

How many components are present in a system in which ammonium chloride undergoes thermal decomposition?

Method Begin by writing down the chemical equation for the reaction and identifying the constituents of the system (all the species present) and the phases. Then decide whether, under the conditions prevailing in the system, any of the constituents can be prepared from any of the other constituents. The removal of these constituents leaves the number of independent constituents. Finally, identify the minimum number of these independent constituents that are needed to specify the composition of all the phases.

Answer The chemical reaction is



There are three constituents and two phases (one solid, one gas). However, NH_3 and HCl are formed in fixed stoichiometric proportions by the reaction. Therefore, the compositions of both phases can be expressed in terms of the single species NH_4Cl . It follows that there is only one component in the system ($C = 1$). If additional HCl (or NH_3) were supplied to the system, the decomposition of NH_4Cl would not give the correct composition of the gas phase and HCl (or NH_3) would have to be invoked as a second component.

Self-test 6.1 Give the number of components in the following systems: (a) water, allowing for its autoprotolysis, (b) aqueous acetic acid, (c) magnesium carbonate in equilibrium with its decomposition products.
[(a) 1, (b) 2, (c) 2]

The **variance**, F , of a system is the number of intensive variables that can be changed independently without disturbing the number of phases in equilibrium. In a single-component, single-phase system ($C = 1, P = 1$), the pressure and temperature may be changed independently without changing the number of phases, so $F = 2$. We say that such a system is **bivariant**, or that it has two **degrees of freedom**. On the other hand, if two phases are in equilibrium (a liquid and its vapour, for instance) in a single-component system ($C = 1, P = 2$), the temperature (or the pressure) can be changed at will, but the change in temperature (or pressure) demands an accompanying change in pressure (or temperature) to preserve the number of phases in equilibrium. That is, the variance of the system has fallen to 1.

Comment 6.1

Josiah Willard Gibbs spent most of his working life at Yale, and may justly be regarded as the originator of chemical thermodynamics. He reflected for years before publishing his conclusions, and then did so in precisely expressed papers in an obscure journal (*The Transactions of the Connecticut Academy of Arts and Sciences*). He needed interpreters before the power of his work was recognized and before it could be applied to industrial processes. He is regarded by many as the first great American theoretical scientist.

6.2 The phase rule

In one of the most elegant calculations of the whole of chemical thermodynamics, J.W. Gibbs deduced the **phase rule**, which is a general relation between the variance, F , the number of components, C , and the number of phases at equilibrium, P , for a system of any composition:

$$F = C - P + 2 \tag{6.1}$$

Justification 6.1 The phase rule

Consider first the special case of a one-component system. For two phases in equilibrium, we can write $\mu_j(\alpha) = \mu_j(\beta)$. Each chemical potential is a function of the pressure and temperature, so

$$\mu_j(\alpha; p, T) = \mu_j(\beta; p, T)$$

This is an equation relating p and T , so only one of these variables is independent (just as the equation $x + y = 2$ is a relation for y in terms of x : $y = 2 - x$). That conclusion is consistent with $F = 1$. For three phases in mutual equilibrium,

$$\mu_j(\alpha; p, T) = \mu_j(\beta; p, T) = \mu_j(\gamma; p, T)$$

This relation is actually two equations for two unknowns ($\mu_j(\alpha; p, T) = \mu_j(\beta; p, T)$ and $\mu_j(\beta; p, T) = \mu_j(\gamma; p, T)$), and therefore has a solution only for a single value of p and T (just as the pair of equations $x + y = 2$ and $3x - y = 4$ has the single solution $x = \frac{3}{2}$ and $y = \frac{1}{2}$). That conclusion is consistent with $F = 0$. Four phases cannot be in mutual equilibrium in a one-component system because the three equalities

$$\mu_j(\alpha; p, T) = \mu_j(\beta; p, T) = \mu_j(\gamma; p, T) = \mu_j(\delta; p, T)$$

are three equations for two unknowns (p and T) and are not consistent (just as $x + y = 2$, $3x - y = 4$, and $x + 4y = 6$ have no solution).

Now consider the general case. We begin by counting the total number of intensive variables. The pressure, p , and temperature, T , count as 2. We can specify the composition of a phase by giving the mole fractions of $C - 1$ components. We need specify only $C - 1$ and not all C mole fractions because $x_1 + x_2 + \dots + x_C = 1$, and all mole fractions are known if all except one are specified. Because there are P phases, the total number of composition variables is $P(C - 1)$. At this stage, the total number of intensive variables is $P(C - 1) + 2$.

At equilibrium, the chemical potential of a component J must be the same in every phase (Section 4.4):

$$\mu_j(\alpha) = \mu_j(\beta) = \dots \quad \text{for } P \text{ phases}$$

That is, there are $P - 1$ equations of this kind to be satisfied for each component J. As there are C components, the total number of equations is $C(P - 1)$. Each equation reduces our freedom to vary one of the $P(C - 1) + 2$ intensive variables. It follows that the total number of degrees of freedom is

$$F = P(C - 1) + 2 - C(P - 1) = C - P + 2$$

which is eqn 6.1.

(a) One-component systems

For a one-component system, such as pure water, $F = 3 - P$. When only one phase is present, $F = 2$ and both p and T can be varied independently without changing the number of phases. In other words, a single phase is represented by an *area* on a phase diagram. When two phases are in equilibrium $F = 1$, which implies that pressure is not freely variable if the temperature is set; indeed, at a given temperature, a liquid has a characteristic vapour pressure. It follows that the equilibrium of two phases is represented by a *line* in the phase diagram. Instead of selecting the temperature, we could select the pressure, but having done so the two phases would be in equilibrium at a single definite temperature. Therefore, freezing (or any other phase transition) occurs at a definite temperature at a given pressure.

When three phases are in equilibrium, $F = 0$ and the system is invariant. This special condition can be established only at a definite temperature and pressure that is characteristic of the substance and outside our control. The equilibrium of three phases is therefore represented by a *point*, the triple point, on a phase diagram. Four phases cannot be in equilibrium in a one-component system because F cannot be negative. These features are summarized in Fig. 6.2.

We can identify the features in Fig. 6.2 in the experimentally determined phase diagram for water (Fig. 6.3). This diagram summarizes the changes that take place as a sample, such as that at a , is cooled at constant pressure. The sample remains entirely

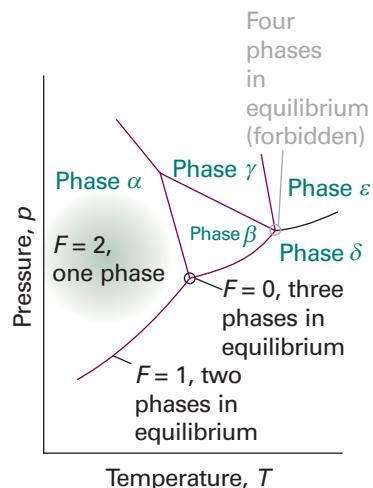


Fig. 6.2 The typical regions of a one-component phase diagram. The lines represent conditions under which the two adjoining phases are in equilibrium. A point represents the unique set of conditions under which three phases coexist in equilibrium. Four phases cannot mutually coexist in equilibrium.

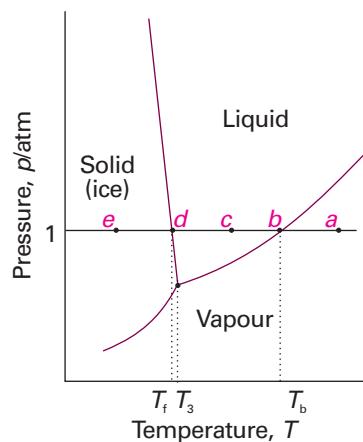


Fig. 6.3 The phase diagram for water, a simplified version of Fig. 4.5. The label T_3 marks the temperature of the triple point, T_b the normal boiling point, and T_f the normal freezing point.

gaseous until the temperature reaches b , when liquid appears. Two phases are now in equilibrium and $F = 1$. Because we have decided to specify the pressure, which uses up the single degree of freedom, the temperature at which this equilibrium occurs is not under our control. Lowering the temperature takes the system to c in the one-phase, liquid region. The temperature can now be varied around the point c at will, and only when ice appears at d does the variance become 1 again.

(b) Experimental procedures

Detecting a phase change is not always as simple as seeing water boil in a kettle, so special techniques have been developed. Two techniques are **thermal analysis**, which takes advantage of the effect of the enthalpy change during a first-order transition (Section 4.7), and differential scanning calorimetry (see *Impact 12.1*). They are useful for solid–solid transitions, where simple visual inspection of the sample may be inadequate. In thermal analysis, a sample is allowed to cool and its temperature is monitored. At a first-order transition, heat is evolved and the cooling stops until the transition is complete. The cooling curve along the isobar cde in Fig. 6.3 therefore has the shape shown in Fig. 6.4. The transition temperature is obvious, and is used to mark point d on the phase diagram.

Modern work on phase transitions often deals with systems at very high pressures, and more sophisticated detection procedures must be adopted. Some of the highest pressures currently attainable are produced in a **diamond-anvil cell** like that illustrated in Fig. 6.5. The sample is placed in a minute cavity between two gem-quality diamonds, and then pressure is exerted simply by turning the screw. The advance in design this represents is quite remarkable for, with a turn of the screw, pressures of up to about 1 Mbar can be reached that a few years ago could not be reached with equipment weighing tons.

The pressure is monitored spectroscopically by observing the shift of spectral lines in small pieces of ruby added to the sample, and the properties of the sample itself are observed optically through the diamond anvils. One application of the technique is to study the transition of covalent solids to metallic solids. Iodine, I_2 , for instance, becomes metallic at around 200 kbar and makes a transition to a monatomic metallic

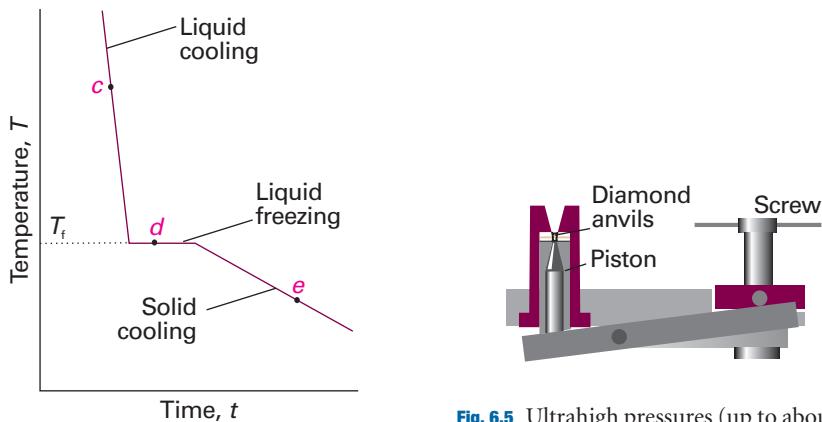


Fig. 6.4 The cooling curve for the isobar cde in Fig. 6.3. The halt marked d corresponds to the pause in the fall of temperature while the first-order exothermic transition (freezing) occurs. This pause enables T_f to be located even if the transition cannot be observed visually.

Fig. 6.5 Ultrahigh pressures (up to about 2 Mbar) can be achieved using a diamond anvil. The sample, together with a ruby for pressure measurement and a drop of liquid for pressure transmission, are placed between two gem-quality diamonds. The principle of its action is like that of a nutcracker: the pressure is exerted by turning the screw by hand.

solid at around 210 kbar. Studies such as these are relevant to the structure of material deep inside the Earth (at the centre of the Earth the pressure is around 5 Mbar) and in the interiors of the giant planets, where even hydrogen may be metallic.

Two-component systems

When two components are present in a system, $C=2$ and $F=4-P$. If the temperature is constant, the remaining variance is $F'=3-P$, which has a maximum value of 2. (The prime on F indicates that one of the degrees of freedom has been discarded, in this case the temperature.) One of these two remaining degrees of freedom is the pressure and the other is the composition (as expressed by the mole fraction of one component). Hence, one form of the phase diagram is a map of pressures and compositions at which each phase is stable. Alternatively, the pressure could be held constant and the phase diagram depicted in terms of temperature and composition.

6.3 Vapour pressure diagrams

The partial vapour pressures of the components of an ideal solution of two volatile liquids are related to the composition of the liquid mixture by Raoult's law (Section 5.3a)

$$p_A = x_A p_A^* \quad p_B = x_B p_B^* \quad (6.2)^{\circ}$$

where p_A^* is the vapour pressure of pure A and p_B^* that of pure B. The total vapour pressure p of the mixture is therefore

$$p = p_A + p_B = x_A p_A^* + x_B p_B^* = p_B^* + (p_A^* - p_B^*)x_A \quad (6.3)^{\circ}$$

This expression shows that the total vapour pressure (at some fixed temperature) changes linearly with the composition from p_B^* to p_A^* as x_A changes from 0 to 1 (Fig. 6.6).

(a) The composition of the vapour

The compositions of the liquid and vapour that are in mutual equilibrium are not necessarily the same. Common sense suggests that the vapour should be richer in the more volatile component. This expectation can be confirmed as follows. The partial pressures of the components are given by eqn 6.2. It follows from Dalton's law that the mole fractions in the gas, y_A and y_B , are

$$y_A = \frac{p_A}{p} \quad y_B = \frac{p_B}{p} \quad (6.4)$$

Provided the mixture is ideal, the partial pressures and the total pressure may be expressed in terms of the mole fractions in the liquid by using eqn 6.2 for p_j and eqn 6.3 for the total vapour pressure p , which gives

$$y_A = \frac{x_A p_A^*}{p_B^* + (p_A^* - p_B^*)x_A} \quad y_B = 1 - y_A \quad (6.5)^{\circ}$$

Figure 6.7 shows the composition of the vapour plotted against the composition of the liquid for various values of $p_A^*/p_B^* > 1$. We see that in all cases $y_A > x_A$, that is, the vapour is richer than the liquid in the more volatile component. Note that if B is non-volatile, so that $p_B^* = 0$ at the temperature of interest, then it makes no contribution to the vapour ($y_B = 0$).

Equation 6.3 shows how the total vapour pressure of the mixture varies with the composition of the liquid. Because we can relate the composition of the liquid to the composition of the vapour through eqn 6.5, we can now also relate the total vapour pressure to the composition of the vapour:

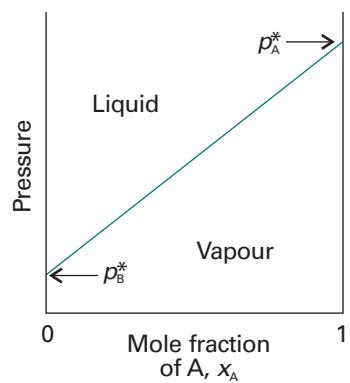


Fig. 6.6 The variation of the total vapour pressure of a binary mixture with the mole fraction of A in the liquid when Raoult's law is obeyed.

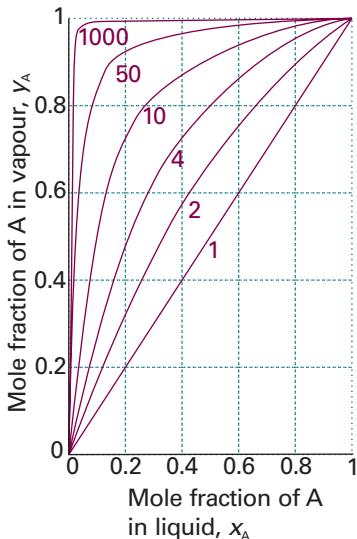


Fig. 6.7 The mole fraction of A in the vapour of a binary ideal solution expressed in terms of its mole fraction in the liquid, calculated using eqn 6.5 for various values of p_A^*/p_B^* (the label on each curve) with A more volatile than B. In all cases the vapour is richer than the liquid in A.

Exploration To reproduce the results of Fig. 6.7, first rearrange eqn 6.5 so that y_A is expressed as a function of x_A and the ratio p_A^*/p_B^* . Then plot y_A against x_A for several values of $p_A^*/p_B^* > 1$.

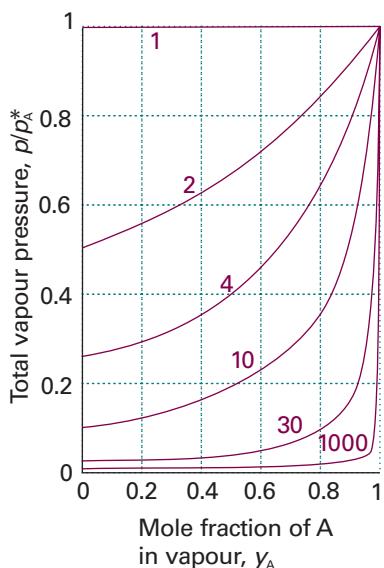


Fig. 6.8 The dependence of the vapour pressure of the same system as in Fig. 6.7, but expressed in terms of the mole fraction of A in the vapour by using eqn 6.6. Individual curves are labelled with the value of p_A^*/p_B^* .

Exploration To reproduce the results of Fig. 6.8, first rearrange eqn 6.6 so that the ratio p_A/p_A^* is expressed as a function of y_A and the ratio p_A^*/p_B^* . Then plot p_A/p_A^* against y_A for several values of $p_A^*/p_B^* > 1$.

$$p = \frac{p_A^* p_B^*}{p_A^* + (p_B^* - p_A^*) y_A} \quad (6.6)^o$$

This expression is plotted in Fig. 6.8.

(b) The interpretation of the diagrams

If we are interested in distillation, both the vapour and the liquid compositions are of equal interest. It is therefore sensible to combine Figs. 6.7 and 6.8 into one (Fig. 6.9). The point a indicates the vapour pressure of a mixture of composition x_A , and the point b indicates the composition of the vapour that is in equilibrium with the liquid at that pressure. Note that, when two phases are in equilibrium, $P = 2$ so $F' = 1$ (as usual, the prime indicating that one degree of freedom, the temperature, has already been discarded). That is, if the composition is specified (so using up the only remaining degree of freedom), the pressure at which the two phases are in equilibrium is fixed.

A richer interpretation of the phase diagram is obtained if we interpret the horizontal axis as showing the *overall* composition, z_A , of the system. If the horizontal axis of the vapour pressure diagram is labelled with z_A , then all the points down to the solid diagonal line in the graph correspond to a system that is under such high pressure that it contains only a liquid phase (the applied pressure is higher than the vapour pressure), so $z_A = x_A$, the composition of the liquid. On the other hand, all points below the lower curve correspond to a system that is under such low pressure that it contains only a vapour phase (the applied pressure is lower than the vapour pressure), so $z_A = y_A$.

Points that lie between the two lines correspond to a system in which there are two phases present, one a liquid and the other a vapour. To see this interpretation, consider the effect of lowering the pressure on a liquid mixture of overall composition a in Fig. 6.10. The lowering of pressure can be achieved by drawing out a piston (Fig. 6.11). This degree of freedom is permitted by the phase rule because $F' = 2$ when $P = 1$, and even if the composition is selected one degree of freedom remains. The changes to the system do not affect the overall composition, so the state of the system moves down the vertical line that passes through a . This vertical line is called an

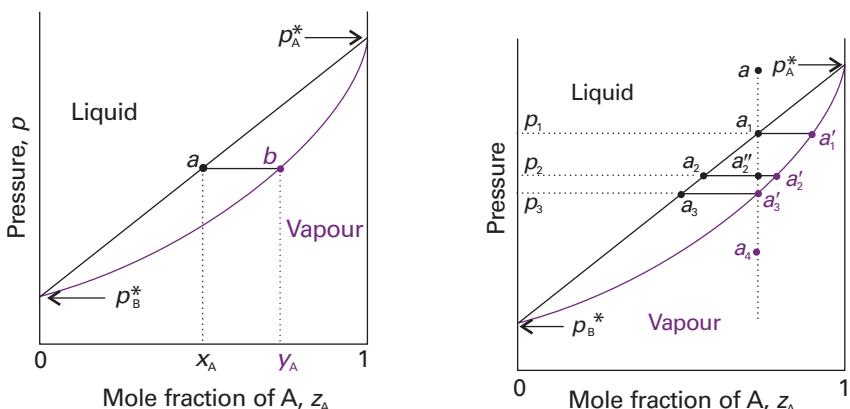


Fig. 6.9 The dependence of the total vapour pressure of an ideal solution on the mole fraction of A in the entire system. A point between the two lines corresponds to both liquid and vapour being present; outside that region there is only one phase present. The mole fraction of A is denoted z_A , as explained below.

Fig. 6.10 The points of the pressure-composition diagram discussed in the text. The vertical line through a is an *isopleth*, a line of constant composition of the entire system.

isopleth, from the Greek words for ‘equal abundance’. Until the point a_1 is reached (when the pressure has been reduced to p_1), the sample consists of a single liquid phase. At a_1 the liquid can exist in equilibrium with its vapour. As we have seen, the composition of the vapour phase is given by point a'_1 . A line joining two points representing phases in equilibrium is called a **tie line**. The composition of the liquid is the same as initially (a_1 lies on the isopleth through a), so we have to conclude that at this pressure there is virtually no vapour present; however, the tiny amount of vapour that is present has the composition a'_1 .

Now consider the effect of lowering the pressure to p_2 , so taking the system to a pressure and overall composition represented by the point a''_2 . This new pressure is below the vapour pressure of the original liquid, so it vaporizes until the vapour pressure of the remaining liquid falls to p_2 . Now we know that the composition of such a liquid must be a_2 . Moreover, the composition of the vapour in equilibrium with that liquid must be given by the point a'_2 at the other end of the tie line. Note that two phases are now in equilibrium, so $F' = 1$ for all points between the two lines; hence, for a given pressure (such as at p_2) the variance is zero, and the vapour and liquid phases have fixed compositions (Fig. 6.12). If the pressure is reduced to p_3 , a similar readjustment in composition takes place, and now the compositions of the liquid and vapour are represented by the points a_3 and a'_3 , respectively. The latter point corresponds to a system in which the composition of the vapour is the same as the overall composition, so we have to conclude that the amount of liquid present is now virtually zero, but the tiny amount of liquid present has the composition a_3 . A further decrease in pressure takes the system to the point a_4 ; at this stage, only vapour is present and its composition is the same as the initial overall composition of the system (the composition of the original liquid).

(c) The lever rule

A point in the two-phase region of a phase diagram indicates not only qualitatively that both liquid and vapour are present, but represents quantitatively the relative amounts of each. To find the relative amounts of two phases α and β that are in equilibrium, we measure the distances l_α and l_β along the horizontal tie line, and then use the **lever rule** (Fig. 6.13):

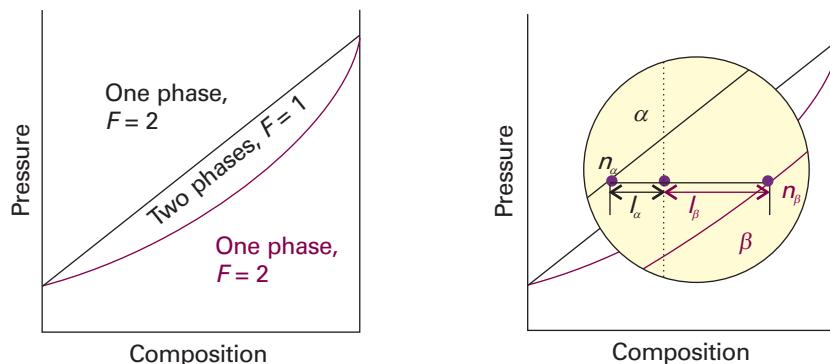


Fig. 6.12 The general scheme of interpretation of a pressure–composition diagram (a vapour pressure diagram).

Fig. 6.13 The lever rule. The distances l_α and l_β are used to find the proportions of the amounts of phases α (such as vapour) and β (for example, liquid) present at equilibrium. The lever rule is so called because a similar rule relates the masses at two ends of a lever to their distances from a pivot ($m_\alpha l_\alpha = m_\beta l_\beta$ for balance).

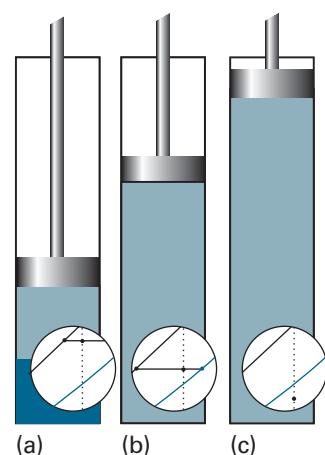


Fig. 6.11 (a) A liquid in a container exists in equilibrium with its vapour. The superimposed fragment of the phase diagram shows the compositions of the two phases and their abundances (by the lever rule). (b) When the pressure is changed by drawing out a piston, the compositions of the phases adjust as shown by the tie line in the phase diagram. (c) When the piston is pulled so far out that all the liquid has vaporized and only the vapour is present, the pressure falls as the piston is withdrawn and the point on the phase diagram moves into the one-phase region.

$$n_\alpha l_\alpha = n_\beta l_\beta \quad (6.7)$$

Here n_α is the amount of phase α and n_β the amount of phase β . In the case illustrated in Fig. 6.13, because $l_\beta \approx 2l_\alpha$, the amount of phase α is about twice the amount of phase β .

Justification 6.2 The lever rule

To prove the lever rule we write $n = n_\alpha + n_\beta$ and the overall amount of A as nz_A . The overall amount of A is also the sum of its amounts in the two phases:

$$nz_A = n_\alpha x_A + n_\beta y_A$$

Since also

$$nz_A = n_\alpha z_A + n_\beta z_A$$

by equating these two expressions it follows that

$$n_\alpha(x_A - z_A) = n_\beta(z_A - y_A)$$

which corresponds to eqn 6.7.

Illustration 6.1 Using the lever rule

At p_1 in Fig. 6.10, the ratio $l_{\text{vap}}/l_{\text{liq}}$ is almost infinite for this tie line, so $n_{\text{liq}}/n_{\text{vap}}$ is also almost infinite, and there is only a trace of vapour present. When the pressure is reduced to p_2 , the value of $l_{\text{vap}}/l_{\text{liq}}$ is about 0.3, so $n_{\text{liq}}/n_{\text{vap}} \approx 0.3$ and the amount of liquid is about 0.3 times the amount of vapour. When the pressure has been reduced to p_3 , the sample is almost completely gaseous and because $l_{\text{vap}}/l_{\text{liq}} \approx 0$ we conclude that there is only a trace of liquid present.

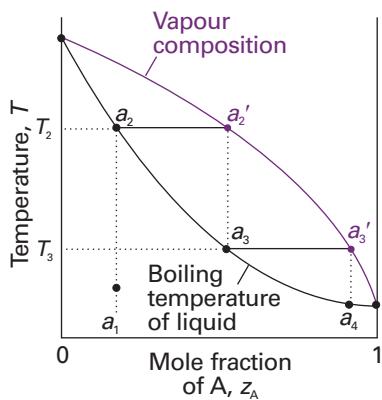


Fig. 6.14 The temperature–composition diagram corresponding to an ideal mixture with the component A more volatile than component B. Successive boilings and condensations of a liquid originally of composition a_1 lead to a condensate that is pure A. The separation technique is called fractional distillation.

Comment 6.2

The textbook's web site contains links to online databases of phase diagrams.

6.4 Temperature–composition diagrams

To discuss distillation we need a **temperature–composition diagram**, a phase diagram in which the boundaries show the composition of the phases that are in equilibrium at various temperatures (and a given pressure, typically 1 atm). An example is shown in Fig. 6.14. Note that the liquid phase now lies in the lower part of the diagram.

(a) The distillation of mixtures

The region between the lines in Fig. 6.14 is a two-phase region where $F' = 1$. As usual, the prime indicates that one degree of freedom has been discarded; in this case, the pressure is being kept fixed, and hence at a given temperature the compositions of the phases in equilibrium are fixed. The regions outside the phase lines correspond to a single phase, so $F' = 2$, and the temperature and composition are both independently variable.

Consider what happens when a liquid of composition a_1 is heated. It boils when the temperature reaches T_2 . Then the liquid has composition a_2 (the same as a_1) and the vapour (which is present only as a trace) has composition a'_2 . The vapour is richer in the more volatile component A (the component with the lower boiling point). From the location of a_2 , we can state the vapour's composition at the boiling point, and from the location of the tie line joining a_2 and a'_2 we can read off the boiling temperature (T_2) of the original liquid mixture.

In a **simple distillation**, the vapour is withdrawn and condensed. This technique is used to separate a volatile liquid from a non-volatile solute or solid. In **fractional distillation**, the boiling and condensation cycle is repeated successively. This technique is used to separate volatile liquids. We can follow the changes that occur by seeing what happens when the first condensate of composition a_3 is reheated. The phase diagram shows that this mixture boils at T_3 and yields a vapour of composition a'_3 , which is even richer in the more volatile component. That vapour is drawn off, and the first drop condenses to a liquid of composition a_4 . The cycle can then be repeated until in due course almost pure A is obtained.

The efficiency of a fractionating column is expressed in terms of the number of **theoretical plates**, the number of effective vaporization and condensation steps that are required to achieve a condensate of given composition from a given distillate. Thus, to achieve the degree of separation shown in Fig. 6.15a, the fractionating column must correspond to three theoretical plates. To achieve the same separation for the system shown in Fig. 6.15b, in which the components have more similar partial pressures, the fractionating column must be designed to correspond to five theoretical plates.

(b) Azeotropes

Although many liquids have temperature–composition phase diagrams resembling the ideal version in Fig. 6.14, in a number of important cases there are marked deviations. A maximum in the phase diagram (Fig. 6.16) may occur when the favourable interactions between A and B molecules reduce the vapour pressure of the mixture below the ideal value: in effect, the A–B interactions stabilize the liquid. In such cases the excess Gibbs energy, G^E (Section 5.4), is negative (more favourable to mixing than ideal). Examples of this behaviour include trichloromethane/propanone and nitric acid/water mixtures. Phase diagrams showing a minimum (Fig. 6.17) indicate that the mixture is destabilized relative to the ideal solution, the A–B interactions then being unfavourable. For such mixtures G^E is positive (less favourable to mixing than ideal), and there may be contributions from both enthalpy and entropy effects. Examples include dioxane/water and ethanol/water mixtures.

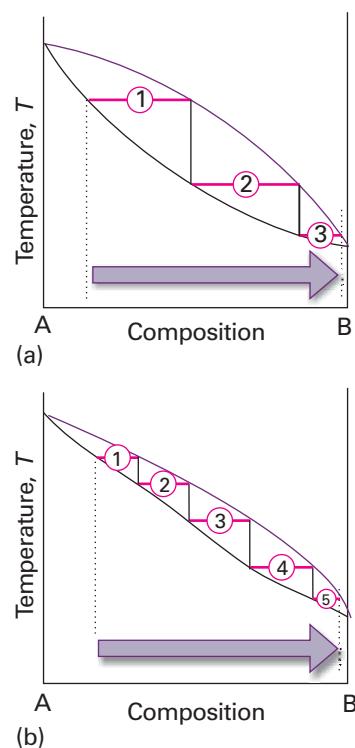


Fig. 6.15 The number of theoretical plates is the number of steps needed to bring about a specified degree of separation of two components in a mixture. The two systems shown correspond to (a) 3, (b) 5 theoretical plates.

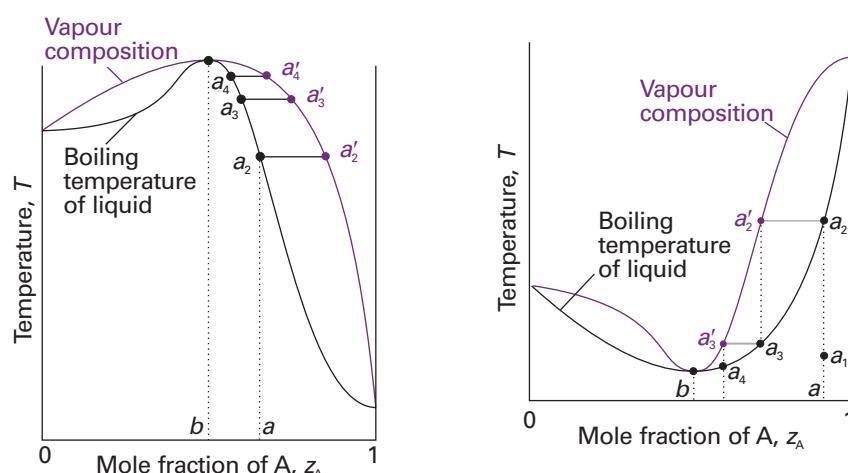


Fig. 6.16 A high-boiling azeotrope. When the liquid of composition a is distilled, the composition of the remaining liquid changes towards b but no further.

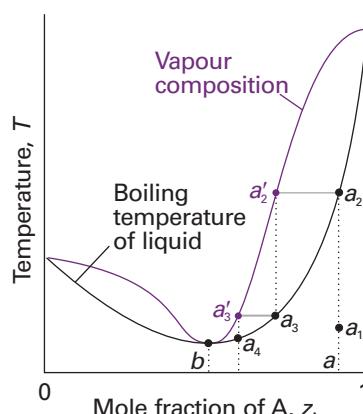


Fig. 6.17 A low-boiling azeotrope. When the mixture at a is fractionally distilled, the vapour in equilibrium in the fractionating column moves towards b and then remains unchanged.

Deviations from ideality are not always so strong as to lead to a maximum or minimum in the phase diagram, but when they do there are important consequences for distillation. Consider a liquid of composition a on the right of the maximum in Fig. 6.16. The vapour (at a'_2) of the boiling mixture (at a_2) is richer in A. If that vapour is removed (and condensed elsewhere), then the remaining liquid will move to a composition that is richer in B, such as that represented by a_3 , and the vapour in equilibrium with this mixture will have composition a'_3 . As that vapour is removed, the composition of the boiling liquid shifts to a point such as a_4 , and the composition of the vapour shifts to a'_4 . Hence, as evaporation proceeds, the composition of the remaining liquid shifts towards B as A is drawn off. The boiling point of the liquid rises, and the vapour becomes richer in B. When so much A has been evaporated that the liquid has reached the composition b , the vapour has the same composition as the liquid. Evaporation then occurs without change of composition. The mixture is said to form an **azeotrope**.² When the azeotropic composition has been reached, distillation cannot separate the two liquids because the condensate has the same composition as the azeotropic liquid. One example of azeotropic formation is hydrochloric acid/water, which is azeotropic at 80 per cent by mass of water and boils unchanged at 108.6°C.

The system shown in Fig. 6.17 is also azeotropic, but shows its azeotropy in a different way. Suppose we start with a mixture of composition a_1 , and follow the changes in the composition of the vapour that rises through a fractionating column (essentially a vertical glass tube packed with glass rings to give a large surface area). The mixture boils at a_2 to give a vapour of composition a'_2 . This vapour condenses in the column to a liquid of the same composition (now marked a_3). That liquid reaches equilibrium with its vapour at a'_3 , which condenses higher up the tube to give a liquid of the same composition, which we now call a_4 . The fractionation therefore shifts the vapour towards the azeotropic composition at b , but not beyond, and the azeotropic vapour emerges from the top of the column. An example is ethanol/water, which boils unchanged when the water content is 4 per cent by mass and the temperature is 78°C.

(c) Immiscible liquids

Finally we consider the distillation of two immiscible liquids, such as octane and water. At equilibrium, there is a tiny amount of A dissolved in B, and similarly a tiny amount of B dissolved in A: both liquids are saturated with the other component (Fig. 6.18a). As a result, the total vapour pressure of the mixture is close to $p = p_A^* + p_B^*$. If the temperature is raised to the value at which this total vapour pressure is equal to the atmospheric pressure, boiling commences and the dissolved substances are purged from their solution. However, this boiling results in a vigorous agitation of the mixture, so each component is kept saturated in the other component, and the purging continues as the very dilute solutions are replenished. This intimate contact is essential: two immiscible liquids heated in a container like that shown in Fig. 6.18b would not boil at the same temperature. The presence of the saturated solutions means that the ‘mixture’ boils at a lower temperature than either component would alone because boiling begins when the total vapour pressure reaches 1 atm, not when either vapour pressure reaches 1 atm. This distinction is the basis of **steam distillation**, which enables some heat-sensitive, water-insoluble organic compounds to be distilled at a lower temperature than their normal boiling point. The only snag is that the composition of the condensate is in proportion to the vapour pressures of the components, so oils of low volatility distil in low abundance.

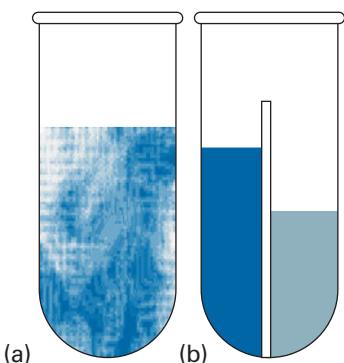


Fig. 6.18 The distillation of (a) two immiscible liquids can be regarded as (b) the joint distillation of the separated components, and boiling occurs when the sum of the partial pressures equals the external pressure.

² The name comes from the Greek words for ‘boiling without changing’.

6.5 Liquid–liquid phase diagrams

Now we consider temperature–composition diagrams for systems that consist of pairs of **partially miscible** liquids, which are liquids that do not mix in all proportions at all temperatures. An example is hexane and nitrobenzene. The same principles of interpretation apply as to liquid–vapour diagrams. When $P = 2$, $F' = 1$ (the prime denoting the adoption of constant pressure), and the selection of a temperature implies that the compositions of the immiscible liquid phases are fixed. When $P = 1$ (corresponding to a system in which the two liquids are fully mixed), both the temperature and the composition may be adjusted.

(a) Phase separation

Suppose a small amount of a liquid B is added to a sample of another liquid A at a temperature T' . It dissolves completely, and the binary system remains a single phase. As more B is added, a stage comes at which no more dissolves. The sample now consists of two phases in equilibrium with each other ($P = 2$), the most abundant one consisting of A saturated with B, the minor one a trace of B saturated with A. In the temperature–composition diagram drawn in Fig. 6.19, the composition of the former is represented by the point a' and that of the latter by the point a'' . The relative abundances of the two phases are given by the lever rule.

When more B is added, A dissolves in it slightly. The compositions of the two phases in equilibrium remain a' and a'' because $P = 2$ implies that $F' = 0$, and hence that the compositions of the phases are invariant at a fixed temperature and pressure. However, the amount of one phase increases at the expense of the other. A stage is reached when so much B is present that it can dissolve all the A, and the system reverts to a single phase. The addition of more B now simply dilutes the solution, and from then on it remains a single phase.

The composition of the two phases at equilibrium varies with the temperature. For hexane and nitrobenzene, raising the temperature increases their miscibility. The two-phase system therefore becomes less extensive, because each phase in equilibrium is richer in its minor component: the A-rich phase is richer in B and the B-rich phase is richer in A. We can construct the entire phase diagram by repeating the observations at different temperatures and drawing the envelope of the two-phase region.

Example 6.2 Interpreting a liquid–liquid phase diagram

A mixture of 50 g of hexane ($0.59 \text{ mol } \text{C}_6\text{H}_{14}$) and 50 g of nitrobenzene ($0.41 \text{ mol } \text{C}_6\text{H}_5\text{NO}_2$) was prepared at 290 K. What are the compositions of the phases, and in what proportions do they occur? To what temperature must the sample be heated in order to obtain a single phase?

Method The compositions of phases in equilibrium are given by the points where the tie-line representing the temperature intersects the phase boundary. Their proportions are given by the lever rule (eqn 6.7). The temperature at which the components are completely miscible is found by following the isopleth upwards and noting the temperature at which it enters the one-phase region of the phase diagram.

Answer We denote hexane by H and nitrobenzene by N; refer to Fig. 6.20, which is a simplified version of Fig. 6.19. The point $x_N = 0.41$, $T = 290 \text{ K}$ occurs in the two-phase region of the phase diagram. The horizontal tie line cuts the phase

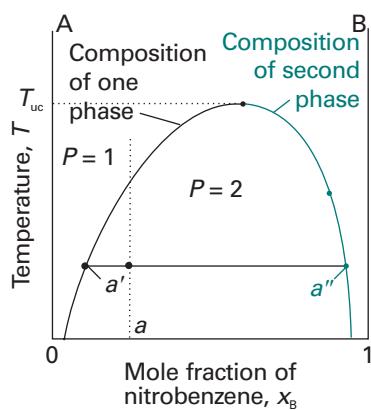


Fig. 6.19 The temperature–composition diagram for hexane and nitrobenzene at 1 atm. The region below the curve corresponds to the compositions and temperatures at which the liquids are partially miscible. The upper critical temperature, T_{uc} , is the temperature above which the two liquids are miscible in all proportions.

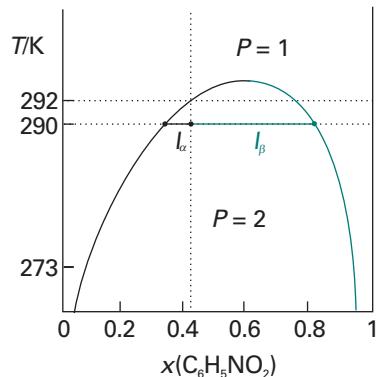


Fig. 6.20 The temperature–composition diagram for hexane and nitrobenzene at 1 atm again, with the points and lengths discussed in the text.

boundary at $x_N = 0.35$ and $x_N = 0.83$, so those are the compositions of the two phases. According to the lever rule, the ratio of amounts of each phase is equal to the ratio of the distances l_α and l_β :

$$\frac{n_\alpha}{n_\beta} = \frac{l_\beta}{l_\alpha} = \frac{0.83 - 0.41}{0.41 - 0.35} = \frac{0.42}{0.06} = 7$$

That is, there is about 7 times more hexane-rich phase than nitrobenzene-rich phase. Heating the sample to 292 K takes it into the single-phase region.

Because the phase diagram has been constructed experimentally, these conclusions are not based on any assumptions about ideality. They would be modified if the system were subjected to a different pressure.

Self-test 6.2 Repeat the problem for 50 g of hexane and 100 g of nitrobenzene at 273 K.
[$x_N = 0.09$ and 0.95 in ratio 1:1.3; 294 K]

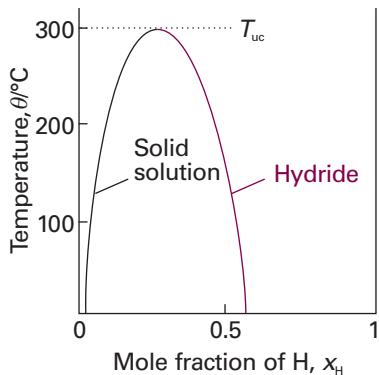


Fig. 6.21 The phase diagram for palladium and palladium hydride, which has an upper critical temperature at 300°C.

Comment 6.3

This expression is an example of a *transcendental equation*, an equation that does not have a solution that can be expressed in a closed form. The solutions can be found numerically by using mathematical software or by plotting the first term against the second and identifying the points of intersection as β is changed.

Comment 6.4

The upper critical solution temperature and the lower critical solution temperature are also called the ‘upper consolute temperature’ and ‘lower consolute temperature’, respectively.

(b) Critical solution temperatures

The **upper critical solution temperature**, T_{uc} , is the highest temperature at which phase separation occurs. Above the upper critical temperature the two components are fully miscible. This temperature exists because the greater thermal motion overcomes any potential energy advantage in molecules of one type being close together. One example is the nitrobenzene/hexane system shown in Fig. 6.19. An example of a solid solution is the palladium/hydrogen system, which shows two phases, one a solid solution of hydrogen in palladium and the other a palladium hydride, up to 300°C but forms a single phase at higher temperatures (Fig. 6.21).

The thermodynamic interpretation of the upper critical solution temperature focuses on the Gibbs energy of mixing and its variation with temperature. We saw in Section 5.4 that a simple model of a real solution results in a Gibbs energy of mixing that behaves as shown in Fig. 5.20. Provided the parameter β that was introduced in eqn 5.30 is greater than 2, the Gibbs energy of mixing has a double minimum (Fig. 6.22). As a result, for $\beta > 2$ we can expect phase separation to occur. The same model shows that the compositions corresponding to the minima are obtained by looking for the conditions at which $\partial\Delta_{\text{mix}}G/\partial x = 0$, and a simple manipulation of eqn 5.31 shows that we have to solve

$$\ln \frac{x}{1-x} + \beta(1-2x) = 0$$

The solutions are plotted in Fig. 6.23. We see that, as β decreases, which can be interpreted as an increase in temperature provided the intermolecular forces remain constant, then the two minima move together and merge when $\beta=2$.

Some systems show a **lower critical solution temperature**, T_{lc} , below which they mix in all proportions and above which they form two phases. An example is water and triethylamine (Fig. 6.24). In this case, at low temperatures the two components are more miscible because they form a weak complex; at higher temperatures the complexes break up and the two components are less miscible.

Some systems have both upper and lower critical solution temperatures. They occur because, after the weak complexes have been disrupted, leading to partial miscibility, the thermal motion at higher temperatures homogenizes the mixture again, just as in the case of ordinary partially miscible liquids. The most famous example is nicotine and water, which are partially miscible between 61°C and 210°C (Fig. 6.25).

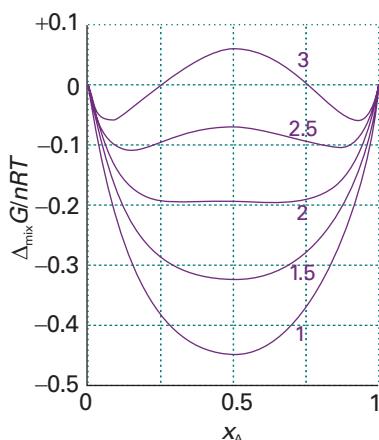


Fig. 6.22 The temperature variation of the Gibbs energy of mixing of a system that is partially miscible at low temperatures. A system of composition in the region $P = 2$ forms two phases with compositions corresponding to the two local minima of the curve. This illustration is a duplicate of Fig. 5.20.

 **Exploration** Working from eqn 5.31, write an expression for T_{\min} , the temperature at which $\Delta_{\text{mix}}G$ has a minimum, as a function of β and x_A . Then, plot T_{\min} against x_A for several values of β . Provide a physical interpretation for any maxima or minima that you observe in these plots.

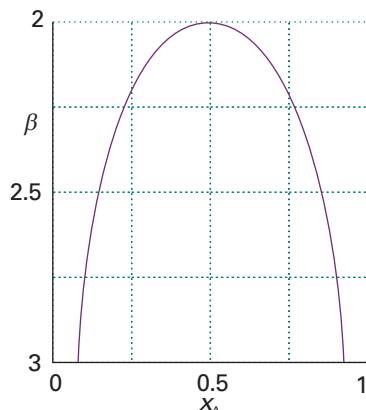


Fig. 6.23 The location of the phase boundary as computed on the basis of the β -parameter model introduced in Section 5.4.

 **Exploration** Using mathematical software or an electronic spreadsheet, generate the plot of β against x_A by one of two methods: (a) solve the transcendental equation $\ln \{(x/(1-x)\} + \beta(1-2x) = 0$ numerically, or (b) plot the first term of the transcendental equation against the second and identify the points of intersection as β is changed.

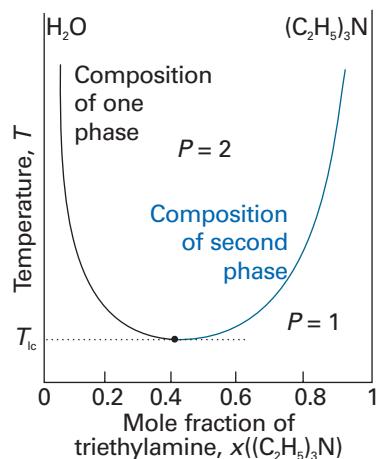


Fig. 6.24 The temperature–composition diagram for water and triethylamine. This system shows a lower critical temperature at 292 K. The labels indicate the interpretation of the boundaries.

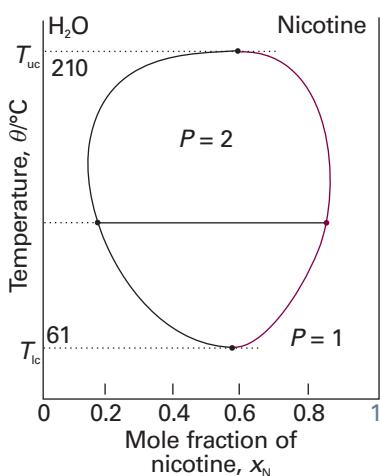


Fig. 6.25 The temperature–composition diagram for water and nicotine, which has both upper and lower critical temperatures. Note the high temperatures for the liquid (especially the water): the diagram corresponds to a sample under pressure.

(c) The distillation of partially miscible liquids

Consider a pair of liquids that are partially miscible and form a low-boiling azeotrope. This combination is quite common because both properties reflect the tendency of the two kinds of molecule to avoid each other. There are two possibilities: one in which the liquids become fully miscible before they boil; the other in which boiling occurs before mixing is complete.

Figure 6.26 shows the phase diagram for two components that become fully miscible before they boil. Distillation of a mixture of composition a_1 leads to a vapour of composition b_1 , which condenses to the completely miscible single-phase solution at b_2 . Phase separation occurs only when this distillate is cooled to a point in the two-phase liquid region, such as b_3 . This description applies only to the first drop of distillate. If distillation continues, the composition of the remaining liquid changes. In the end, when the whole sample has evaporated and condensed, the composition is back to a_1 .

Figure 6.27 shows the second possibility, in which there is no upper critical solution temperature. The distillate obtained from a liquid initially of composition a_1 has composition b_3 and is a two-phase mixture. One phase has composition b'_3 and the other has composition b''_3 .

The behaviour of a system of composition represented by the isopleth e in Fig. 6.27 is interesting. A system at e_1 forms two phases, which persist (but with changing proportions) up to the boiling point at e_2 . The vapour of this mixture has the same

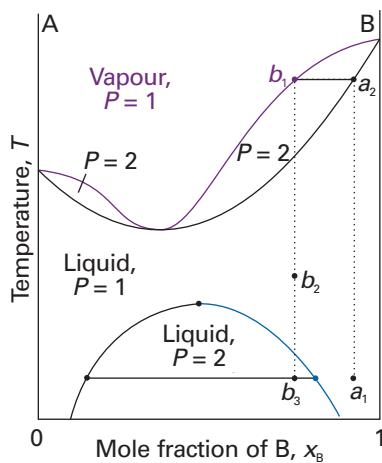


Fig. 6.26 The temperature–composition diagram for a binary system in which the upper critical temperature is less than the boiling point at all compositions. The mixture forms a low-boiling azeotrope.

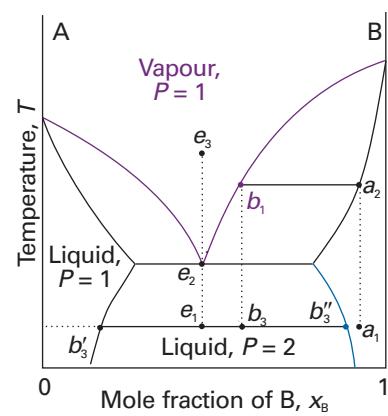


Fig. 6.27 The temperature–composition diagram for a binary system in which boiling occurs before the two liquids are fully miscible.

composition as the liquid (the liquid is an azeotrope). Similarly, condensing a vapour of composition e_3 gives a two-phase liquid of the same overall composition. At a fixed temperature, the mixture vaporizes and condenses like a single substance.

Example 6.3 Interpreting a phase diagram

State the changes that occur when a mixture of composition $x_B = 0.95$ (a_1) in Fig. 6.28 is boiled and the vapour condensed.

Method The area in which the point lies gives the number of phases; the compositions of the phases are given by the points at the intersections of the horizontal tie line with the phase boundaries; the relative abundances are given by the lever rule (eqn 6.7).

Answer The initial point is in the one-phase region. When heated it boils at 350 K (a_2) giving a vapour of composition $x_B = 0.66$ (b_1). The liquid gets richer in B, and the last drop (of pure B) evaporates at 390 K. The boiling range of the liquid is therefore 350 to 390 K. If the initial vapour is drawn off, it has a composition $x_B = 0.66$. This composition would be maintained if the sample were very large, but for a finite sample it shifts to higher values and ultimately to $x_B = 0.95$. Cooling the distillate corresponds to moving down the $x_B = 0.66$ isopleth. At 330 K, for instance, the liquid phase has composition $x_B = 0.87$, the vapour $x_B = 0.49$; their relative proportions are 1:3. At 320 K the sample consists of three phases: the vapour and two liquids. One liquid phase has composition $x_B = 0.30$; the other has composition $x_B = 0.80$ in the ratio 0.62:1. Further cooling moves the system into the two-phase region, and at 298 K the compositions are 0.20 and 0.90 in the ratio 0.82:1. As further distillate boils over, the overall composition of the distillate becomes richer in B. When the last drop has been condensed the phase composition is the same as at the beginning.

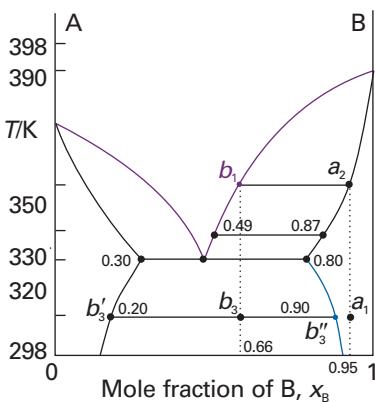


Fig. 6.28 The points of the phase diagram in Fig. 6.27 that are discussed in Example 6.3.

Self-test 6.3 Repeat the discussion, beginning at the point $x_B = 0.4$, $T = 298$ K.

6.6 Liquid–solid phase diagrams

Knowledge of the temperature–composition diagrams for solid mixtures guides the design of important industrial processes, such as the manufacture of liquid crystal displays and semiconductors. In this section, we shall consider systems where solid and liquid phases may both be present at temperatures below the boiling point.

Consider the two-component liquid of composition a_1 in Fig. 6.29. The changes that occur may be expressed as follows.

- $a_1 \rightarrow a_2$. The system enters the two-phase region labelled ‘Liquid + B’. Pure solid B begins to come out of solution and the remaining liquid becomes richer in A.

- $a_2 \rightarrow a_3$. More of the solid forms, and the relative amounts of the solid and liquid (which are in equilibrium) are given by the lever rule. At this stage there are roughly equal amounts of each. The liquid phase is richer in A than before (its composition is given by b_3) because some B has been deposited.

- $a_3 \rightarrow a_4$. At the end of this step, there is less liquid than at a_3 , and its composition is given by e . This liquid now freezes to give a two-phase system of pure B and pure A.

(a) Eutectics

The isopleth at e in Fig. 6.29 corresponds to the **eutectic** composition, the mixture with the lowest melting point.³ A liquid with the eutectic composition freezes at a single temperature, without previously depositing solid A or B. A solid with the eutectic composition melts, without change of composition, at the lowest temperature of any mixture. Solutions of composition to the right of e deposit B as they cool, and solutions to the left deposit A: only the eutectic mixture (apart from pure A or pure B) solidifies at a single definite temperature ($F' = 0$ when $C = 2$ and $P = 3$) without gradually unloading one or other of the components from the liquid.

One technologically important eutectic is solder, which has mass composition of about 67 per cent tin and 33 per cent lead and melts at 183°C. The eutectic formed by 23 per cent NaCl and 77 per cent H₂O by mass melts at –21.1°C. When salt is added to ice under isothermal conditions (for example, when spread on an icy road) the mixture melts if the temperature is above –21.1°C (and the eutectic composition has been achieved). When salt is added to ice under adiabatic conditions (for example, when added to ice in a vacuum flask) the ice melts, but in doing so it absorbs heat from the rest of the mixture. The temperature of the system falls and, if enough salt is added, cooling continues down to the eutectic temperature. Eutectic formation occurs in the great majority of binary alloy systems, and is of great importance for the microstructure of solid materials. Although a eutectic solid is a two-phase system, it crystallizes out in a nearly homogeneous mixture of microcrystals. The two microcrystalline phases can be distinguished by microscopy and structural techniques such as X-ray diffraction (Chapter 20).

Thermal analysis is a very useful practical way of detecting eutectics. We can see how it is used by considering the rate of cooling down the isopleth through a_1 in Fig. 6.29. The liquid cools steadily until it reaches a_2 , when B begins to be deposited (Fig. 6.30). Cooling is now slower because the solidification of B is exothermic and retards the cooling. When the remaining liquid reaches the eutectic composition, the temperature remains constant ($F' = 0$) until the whole sample has solidified: this region of constant temperature is the eutectic halt. If the liquid has the eutectic composition e initially, the liquid cools steadily down to the freezing temperature of the eutectic,

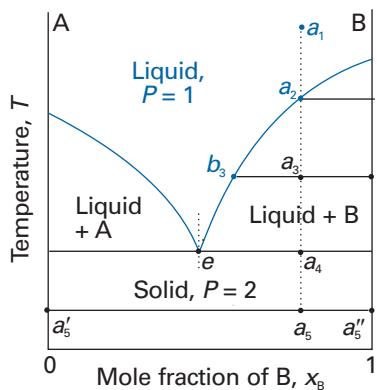


Fig. 6.29 The temperature–composition phase diagram for two almost immiscible solids and their completely miscible liquids. Note the similarity to Fig. 6.27. The isopleth through e corresponds to the eutectic composition, the mixture with lowest melting point.

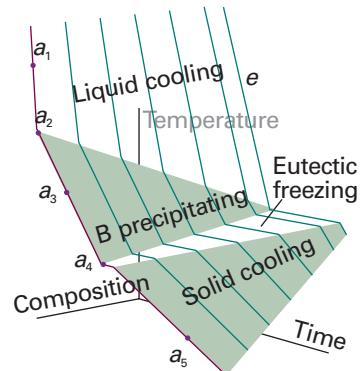


Fig. 6.30 The cooling curves for the system shown in Fig. 6.29. For isopleth a , the rate of cooling slows at a_2 because solid B deposits from solution. There is a complete halt at a_4 while the eutectic solidifies. This halt is longest for the eutectic isopleth, e . The eutectic halt shortens again for compositions beyond e (richer in A). Cooling curves are used to construct the phase diagram.

³ The name comes from the Greek words for ‘easily melted’.

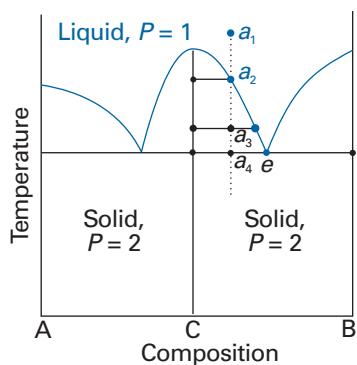


Fig. 6.31 The phase diagram for a system in which A and B react to form a compound $C = AB$. This resembles two versions of Fig. 6.29 in each half of the diagram. The constituent C is a true compound, not just an equimolar mixture.

when there is a long **eutectic halt** as the entire sample solidifies (like the freezing of a pure liquid).

Monitoring the cooling curves at different overall compositions gives a clear indication of the structure of the phase diagram. The solid–liquid boundary is given by the points at which the rate of cooling changes. The longest eutectic halt gives the location of the eutectic composition and its melting temperature.

(b) Reacting systems

Many binary mixtures react to produce compounds, and technologically important examples of this behaviour include the III/V semiconductors, such as the gallium arsenide system, which forms the compound GaAs. Although three constituents are present, there are only two components because GaAs is formed from the reaction $\text{Ga} + \text{As} \rightleftharpoons \text{GaAs}$. We shall illustrate some of the principles involved with a system that forms a compound C that also forms eutectic mixtures with the species A and B (Fig. 6.31).

A system prepared by mixing an excess of B with A consists of C and unreacted B. This is a binary B, C system, which we suppose forms a eutectic. The principal change from the eutectic phase diagram in Fig. 6.29 is that the whole of the phase diagram is squeezed into the range of compositions lying between equal amounts of A and B ($x_B = 0.5$, marked C in Fig. 6.31) and pure B. The interpretation of the information in the diagram is obtained in the same way as for Fig. 6.32. The solid deposited on cooling along the isopleth a is the compound C. At temperatures below a_4 there are two solid phases, one consisting of C and the other of B. The pure compound C melts **congruently**, that is, the composition of the liquid it forms is the same as that of the solid compound.

(c) Incongruent melting

In some cases the compound C is not stable as a liquid. An example is the alloy Na_2K , which survives only as a solid (Fig. 6.32). Consider what happens as a liquid at a_1 is cooled:

1. $a_1 \rightarrow a_2$. Some solid Na is deposited, and the remaining liquid is richer in K.
2. $a_2 \rightarrow$ just below a_3 . The sample is now entirely solid, and consists of solid Na and solid Na_2K .

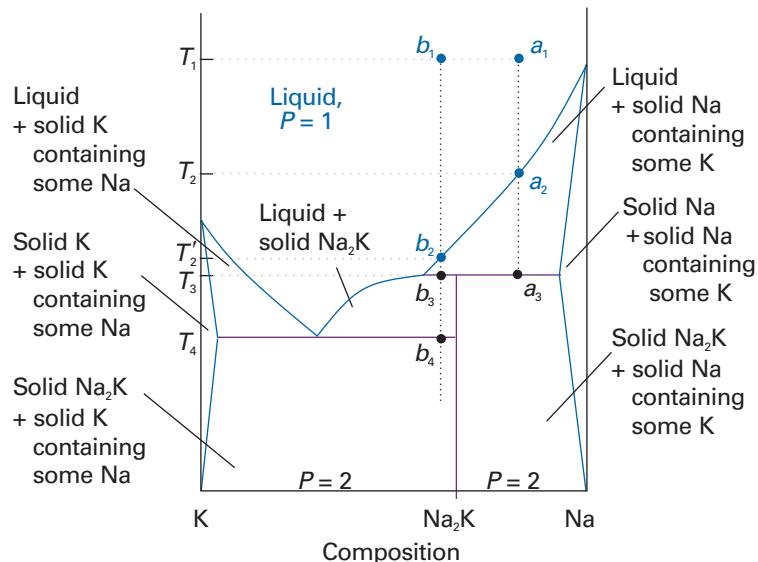


Fig. 6.32 The phase diagram for an actual system (sodium and potassium) like that shown in Fig. 6.35, but with two differences. One is that the compound is Na_2K , corresponding to A_2B and not AB as in that illustration. The second is that the compound exists only as the solid, not as the liquid. The transformation of the compound at its melting point is an example of incongruent melting.

Now consider the isopleth through b_1 :

1. $b_1 \rightarrow b_2$. No obvious change occurs until the phase boundary is reached at b_2 when solid Na begins to deposit.

2. $b_2 \rightarrow b_3$. Solid Na deposits, but at b_3 a reaction occurs to form Na_2K : this compound is formed by the K atoms diffusing into the solid Na.

3. b_3 . At b_3 , three phases are in mutual equilibrium: the liquid, the compound Na_2K , and solid Na. The horizontal line representing this three-phase equilibrium is called a **peritectic line**.

At this stage the liquid Na/K mixture is in equilibrium with a little solid Na_2K , but there is still no liquid compound.

4. $b_3 \rightarrow b_4$. As cooling continues, the amount of solid compound increases until at b_4 the liquid reaches its eutectic composition. It then solidifies to give a two-phase solid consisting of solid K and solid Na_2K .

If the solid is reheated, the sequence of events is reversed. No liquid Na_2K forms at any stage because it is too unstable to exist as a liquid. This behaviour is an example of **incongruent melting**, in which a compound melts into its components and does not itself form a liquid phase.

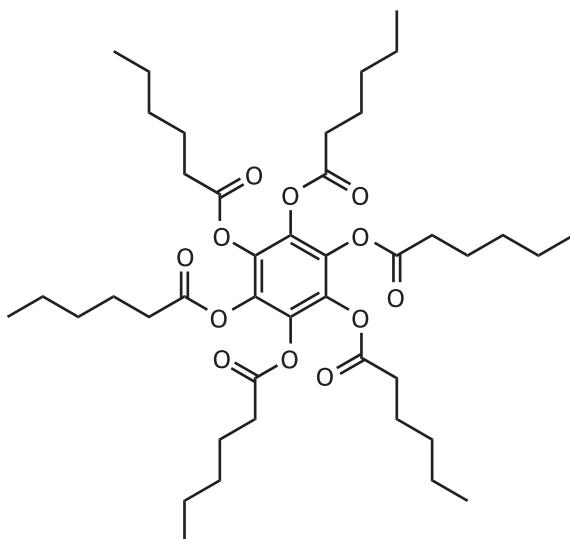


1

IMPACT ON MATERIALS SCIENCE

16.1 Liquid crystals

A *mesophase* is a phase intermediate between solid and liquid. Mesophases are of great importance in biology, for they occur as lipid bilayers and in vesicular systems. A mesophase may arise when molecules have highly non-spherical shapes, such as being long and thin (1), or disk-like (2). When the solid melts, some aspects of the long-range order characteristic of the solid may be retained, and the new phase may be a *liquid crystal*, a substance having liquid-like imperfect long-range order in at least one direction in space but positional or orientational order in at least one other direction. *Calamitic liquid crystals* (from the Greek word for reed) are made from long and thin molecules, whereas *discotic liquid crystals* are made from disk-like molecules. A



2

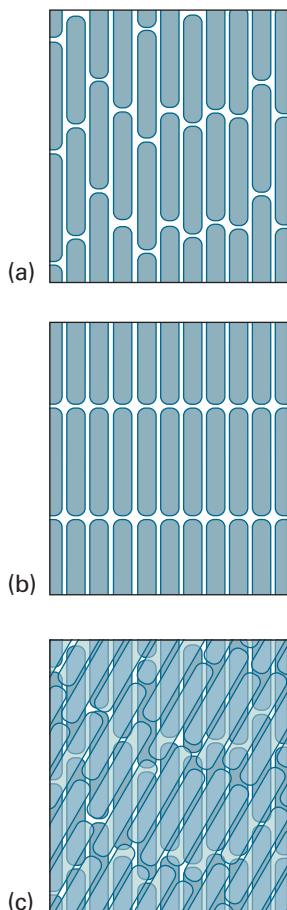


Fig. 6.33 The arrangement of molecules in (a) the nematic phase, (b) the smectic phase, and (c) the cholesteric phase of liquid crystals. In the cholesteric phase, the stacking of layers continues to give a helical arrangement of molecules.

thermotropic liquid crystal displays a transition to the liquid crystalline phase as the temperature is changed. A *lyotropic* liquid crystal is a solution that undergoes a transition to the liquid crystalline phase as the composition is changed.

One type of retained long-range order gives rise to a *smectic phase* (from the Greek word for soapy), in which the molecules align themselves in layers (see Fig. 6.33). Other materials, and some smectic liquid crystals at higher temperatures, lack the layered structure but retain a parallel alignment; this mesophase is called a *nematic phase* (from the Greek for thread, which refers to the observed defect structure of the phase). In the *cholesteric phase* (from the Greek for bile solid) the molecules lie in sheets at angles that change slightly between each sheet. That is, they form helical structures with a pitch that depends on the temperature. As a result, cholesteric liquid crystals diffract light and have colours that depend on the temperature. Disk-like molecules such as (2) can form nematic and *columnar* mesophases. In the latter, the aromatic rings stack one on top of the other and are separated by very small distances (less than 0.5 nm).

The optical properties of nematic liquid crystals are anisotropic, meaning that they depend on the relative orientation of the molecular assemblies with respect to the polarization of the incident beam of light. Nematic liquid crystals also respond in special ways to electric fields. Together, these unique optical and electrical properties form the basis of operation of liquid crystal displays (LCDs). In a ‘twisted nematic’ LCD, the liquid crystal is held between two flat plates about 10 µm apart. The inner surface of each plate is coated with a transparent conducting material, such as indium–tin oxide. The plates also have a surface that causes the liquid crystal to adopt a particular orientation at its interface and are typically set at 90° to each other but 270° in a ‘supertwist’ arrangement. The entire assembly is set between two polarizers, optical filters that allow light of one specific plane of polarization to pass. The incident light passes through the outer polarizer, then its plane of polarization is rotated as it passes through the twisted nematic and, depending on the setting of the second polarizer, will pass through (if that is how the second polarizer is arranged). When a potential difference is applied across the cell, the helical arrangement is lost and the plane of the light is no longer rotated and will be blocked by the second polarizer.

Although there are many liquid crystalline materials, some difficulty is often experienced in achieving a technologically useful temperature range for the existence of the mesophase. To overcome this difficulty, mixtures can be used. An example of the type of phase diagram that is then obtained is shown in Fig. 6.34. As can be seen, the mesophase exists over a wider range of temperatures than either liquid crystalline material alone.

IMPACT ON MATERIALS SCIENCE

16.2 Ultrapurity and controlled impurity

Advances in technology have called for materials of extreme purity. For example, semiconductor devices consist of almost perfectly pure silicon or germanium doped to a precisely controlled extent. For these materials to operate successfully, the impurity level must be kept down to less than 1 ppb (1 part in 10^9 , which corresponds to 1 mg of impurity in 1 t of material, about a small grain of salt in 5 t of sugar).⁴

In the technique of *zone refining* the sample is in the form of a narrow cylinder. This cylinder is heated in a thin disk-like zone which is swept from one end of the sample to the other. The advancing liquid zone accumulates the impurities as it passes. In practice, a train of hot and cold zones are swept repeatedly from one end to the other

⁴ 1 t = 10^3 kg.

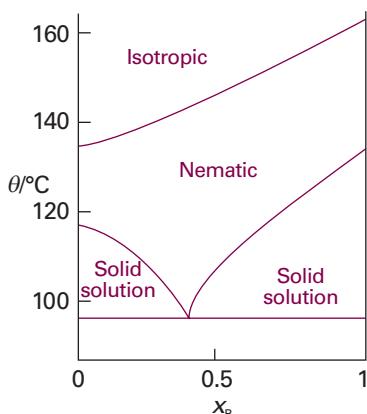


Fig. 6.34 The phase diagram at 1 atm for a binary system of two liquid crystalline materials, 4,4'-dimethoxyazobenzene (A) and 4,4'-diethoxyazobenzene (B).

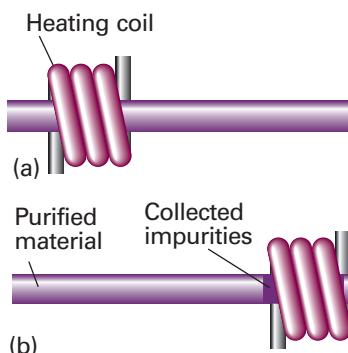


Fig. 6.35 The procedure for zone refining. (a) Initially, impurities are distributed uniformly along the sample. (b) After a molten zone is passed along the rod, the impurities are more concentrated at the right. In practice, a series of molten zones are passed along the rod from left to right.

as shown in Fig. 6.35. The zone at the end of the sample is the impurity dump: when the heater has gone by, it cools to a dirty solid which can be discarded.

The technique makes use of the non-equilibrium properties of the system. It relies on the impurities being more soluble in the molten sample than in the solid, and sweeps them up by passing a molten zone repeatedly from one end to the other along a sample. The phase diagram in Fig. 6.36 gives some insight into the process. Consider a liquid (this represents the molten zone) on the isopleth through a_1 , and let it cool without the entire sample coming to overall equilibrium. If the temperature falls to a_2 a solid of composition b_2 is deposited and the remaining liquid (the zone where the heater has moved on) is at a'_2 . Cooling that liquid down an isopleth passing through a'_2 deposits solid of composition b_3 and leaves liquid at a'_3 . The process continues until the last drop of liquid to solidify is heavily contaminated with B. There is plenty of everyday evidence that impure liquids freeze in this way. For example, an ice cube is clear near the surface but misty in the core: the water used to make ice normally contains dissolved air; freezing proceeds from the outside, and air is accumulated in the retreating liquid phase. It cannot escape from the interior of the cube, and so when that freezes it occludes the air in a mist of tiny bubbles.

A modification of zone refining is *zone levelling*. It is used to introduce controlled amounts of impurity (for example, of indium into germanium). A sample rich in the required dopant is put at the head of the main sample, and made molten. The zone is then dragged repeatedly in alternate directions through the sample, where it deposits a uniform distribution of the impurity.

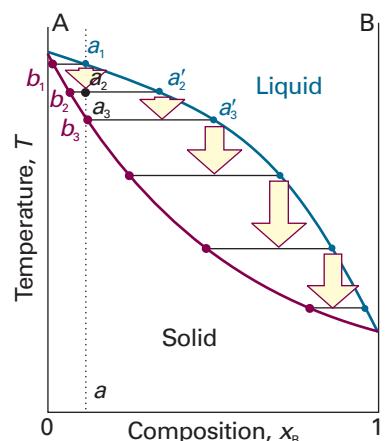


Fig. 6.36 A binary temperature–composition diagram can be used to discuss zone refining, as explained in the text.

Checklist of key ideas

- 1. A phase is a state of matter that is uniform throughout, not only in chemical composition but also in physical state.
- 2. A constituent is a chemical species (an ion or a molecule). A component is a chemically independent constituent of a system.
- 3. The variance F , or degree of freedom, is the number of intensive variables that can be changed independently without disturbing the number of phases in equilibrium.
- 4. The phase rule states that $F = C - P + 2$.

- 5. Thermal analysis is a technique for detecting phase transitions that takes advantage of the effect of the enthalpy change during a first-order transition.
- 6. The vapour pressure of an ideal solution is given by $p = p_B^* + (p_A^* - p_B^*)x_A$. The composition of the vapour, $y_A = x_A p_A^*/(p_A^* + (p_B^* - p_A^*)x_A)$, $y_B = 1 - y_A$.
- 7. The total vapour pressure of a mixture is given by $p = p_A^* p_B^*/\{p_A^* + (p_B^* - p_A^*)y_A\}$.
- 8. An isopleth is a line of constant composition in a phase diagram. A tie line is a line joining two points representing phases in equilibrium.
- 9. The lever rule allows for the calculation of the relative amounts of two phases in equilibrium: $n_\alpha l_\alpha = n_\beta l_\beta$.
- 10. A temperature–composition diagram is a phase diagram in which the boundaries show the composition of the phases that are in equilibrium at various temperatures.
- 11. An azeotrope is a mixture that boils without change of composition.
- 12. Partially miscible liquids are liquids that do not mix in all proportions at all temperatures.
- 13. The upper critical solution temperature is the highest temperature at which phase separation occurs in a binary liquid mixture. The lower critical solution temperature is the temperature below which the components of a binary mixture mix in all proportions and above which they form two phases.
- 14. A eutectic is the mixture with the lowest melting point; a liquid with the eutectic composition freezes at a single temperature. A eutectic halt is a delay in cooling while the eutectic freezes.
- 15. Incongruent melting occurs when a compound melts into its components and does not itself form a liquid phase.

Further reading

Articles and texts

- J.S. Alper, The Gibbs phase rule revisited: interrelationships between components and phases. *J. Chem. Educ.* **76**, 1567 (1999).
- W.D. Callister, Jr., *Materials science and engineering, an introduction*. Wiley, New York (2000).
- P.J. Collings and M. Hird, *Introduction to liquid crystals: chemistry and physics*. Taylor & Francis, London (1997).
- M. Hillert, *Phase equilibria, phase diagrams and phase transformations: a thermodynamic basis*. Cambridge University Press (1998).
- H.-G. Lee, *Chemical thermodynamics for metals and materials*. Imperial College Press, London (1999).

R.J. Stead and K. Stead, Phase diagrams for ternary liquid systems. *J. Chem. Educ.* **67**, 385 (1990).

S.I. Sandler, *Chemical and engineering thermodynamics*. Wiley, New York (1998).

Sources of data and information

- A. Alper, *Phase diagrams*, Vols. 1, 2, and 3. Academic Press, New York (1970).
- J. Wisniak, *Phase diagrams: a literature source book*. Elsevier, Amsterdam (1981–86).

Discussion questions

- 6.1** Define the following terms: phase, constituent, component, and degree of freedom.
- 6.2** What factors determine the number of theoretical plates required to achieve a desired degree of separation in fractional distillation?
- 6.3** Draw phase diagrams for the following types of systems. Label the regions and intersections of the diagrams, stating what materials (possibly compounds or azeotropes) are present and whether they are solid liquid or gas. (a) One-component, pressure–temperature diagram, liquid density greater than that of solid. (b) Two-component, temperature–composition, solid–liquid diagram, one compound AB formed that melts congruently, negligible solid–solid solubility.
- 6.4** Draw phase diagrams for the following types of systems. Label the regions and intersections of the diagrams, stating what materials (possibly

compounds or azeotropes) are present and whether they are solid liquid or gas. (a) Two-component, temperature–composition, solid–liquid diagram, one compound of formula AB_2 that melts incongruently, negligible solid–solid solubility; (b) two-component, constant temperature–composition, liquid–vapour diagram, formation of an azeotrope at $x_B = 0.333$, complete miscibility.

6.5 Label the regions of the phase diagram in Fig. 6.37. State what substances (if compounds give their formulas) exist in each region. Label each substance in each region as solid, liquid, or gas.

6.6 Label the regions of the phase diagram in Fig. 6.38. State what substances (if compounds give their formulas) exist in each region. Label each substance in each region as solid, liquid, or gas.

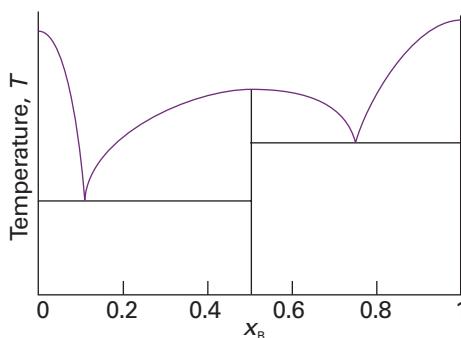


Fig. 6.37

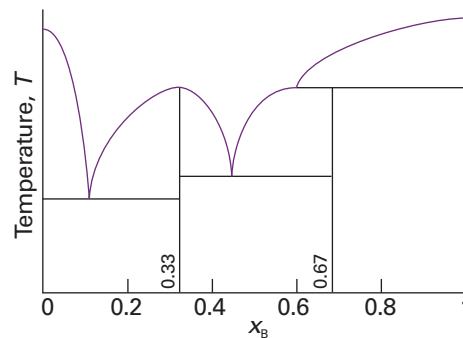


Fig. 6.38

Exercises

6.1(a) At 90°C, the vapour pressure of methylbenzene is 53.3 kPa and that of 1,2-dimethylbenzene is 20.0 kPa. What is the composition of a liquid mixture that boils at 90°C when the pressure is 0.50 atm? What is the composition of the vapour produced?

6.1(b) At 90°C, the vapour pressure of 1,2-dimethylbenzene is 20 kPa and that of 1,3-dimethylbenzene is 18 kPa. What is the composition of a liquid mixture that boils at 90°C when the pressure is 19 kPa? What is the composition of the vapour produced?

6.2(a) The vapour pressure of pure liquid A at 300 K is 76.7 kPa and that of pure liquid B is 52.0 kPa. These two compounds form ideal liquid and gaseous mixtures. Consider the equilibrium composition of a mixture in which the mole fraction of A in the vapour is 0.350. Calculate the total pressure of the vapour and the composition of the liquid mixture.

6.2(b) The vapour pressure of pure liquid A at 293 K is 68.8 kPa and that of pure liquid B is 82.1 kPa. These two compounds form ideal liquid and gaseous mixtures. Consider the equilibrium composition of a mixture in which the mole fraction of A in the vapour is 0.612. Calculate the total pressure of the vapour and the composition of the liquid mixture.

6.3(a) It is found that the boiling point of a binary solution of A and B with $x_A = 0.6589$ is 88°C. At this temperature the vapour pressures of pure A and B are 127.6 kPa and 50.60 kPa, respectively. (a) Is this solution ideal? (b) What is the initial composition of the vapour above the solution?

6.3(b) It is found that the boiling point of a binary solution of A and B with $x_A = 0.4217$ is 96°C. At this temperature the vapour pressures of pure A and B are 110.1 kPa and 76.5 kPa, respectively. (a) Is this solution ideal? (b) What is the initial composition of the vapour above the solution?

6.4(a) Dibromoethene (DE, $p_{DE}^* = 22.9$ kPa at 358 K) and dibromopropene (DP, $p_{DP}^* = 17.1$ kPa at 358 K) form a nearly ideal solution. If $z_{DE} = 0.60$, what is (a) p_{total} when the system is all liquid, (b) the composition of the vapour when the system is still almost all liquid?

6.4(b) Benzene and toluene form nearly ideal solutions. Consider an equimolar solution of benzene and toluene. At 20°C the vapour pressures of pure benzene and toluene are 9.9 kPa and 2.9 kPa, respectively. The solution is boiled by reducing the external pressure below the vapour pressure. Calculate (a) the pressure when boiling begins, (b) the composition of each component in the vapour, and (c) the vapour pressure when only a few drops of liquid remain. Assume that the rate of vaporization is low enough for the temperature to remain constant at 20°C.

6.5(a) The following temperature/composition data were obtained for a mixture of octane (O) and methylbenzene (M) at 1.00 atm, where x is the

mole fraction in the liquid and y the mole fraction in the vapour at equilibrium.

θ/C	110.9	112.0	114.0	115.8	117.3	119.0	121.1	123.0
x_M	0.908	0.795	0.615	0.527	0.408	0.300	0.203	0.097
y_M	0.923	0.836	0.698	0.624	0.527	0.410	0.297	0.164

The boiling points are 110.6°C and 125.6°C for M and O, respectively. Plot the temperature/composition diagram for the mixture. What is the composition of the vapour in equilibrium with the liquid of composition (a) $x_M = 0.250$ and (b) $x_O = 0.250$?

6.5(b) The following temperature/composition data were obtained for a mixture of two liquids A and B at 1.00 atm, where x is the mole fraction in the liquid and y the mole fraction in the vapour at equilibrium.

θ/C	125	130	135	140	145	150
x_A	0.91	0.65	0.45	0.30	0.18	0.098
y_A	0.99	0.91	0.77	0.61	0.45	0.25

The boiling points are 124°C for A and 155°C for B. Plot the temperature-composition diagram for the mixture. What is the composition of the vapour in equilibrium with the liquid of composition (a) $x_A = 0.50$ and (b) $x_B = 0.33$?

6.6(a) State the number of components in the following systems.

- (a) NaH_2PO_4 in water at equilibrium with water vapour but disregarding the fact that the salt is ionized.
- (b) The same, but taking into account the ionization of the salt.

6.6(b) State the number of components for a system in which AlCl_3 is dissolved in water, noting that hydrolysis and precipitation of $\text{Al}(\text{OH})_3$ occur.

6.7(a) Blue $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ crystals release their water of hydration when heated. How many phases and components are present in an otherwise empty heated container?

6.7(b) Ammonium chloride, NH_4Cl , decomposes when it is heated.

- (a) How many components and phases are present when the salt is heated in an otherwise empty container?
- (b) Now suppose that additional ammonia is also present. How many components and phases are present?

6.8(a) A saturated solution of Na_2SO_4 , with excess of the solid, is present at equilibrium with its vapour in a closed vessel. (a) How many phases and components are present. (b) What is the variance (the number of degrees of freedom) of the system? Identify the independent variables.

6.8(b) Suppose that the solution referred to in Exercise 6.8a is not saturated.

- (a) How many phases and components are present.
- (b) What is the variance (the number of degrees of freedom) of the system? Identify the independent variables.

6.9(a) Methylethyl ether (A) and diborane, B_2H_6 (B), form a compound that melts congruently at 133 K. The system exhibits two eutectics, one at 25 mol per cent B and 123 K and a second at 90 mol per cent B and 104 K. The melting points of pure A and B are 131 K and 110 K, respectively. Sketch the phase diagram for this system. Assume negligible solid–solid solubility.

6.9(b) Sketch the phase diagram of the system NH_3/N_2H_4 given that the two substances do not form a compound with each other, that NH_3 freezes at $-78^\circ C$ and N_2H_4 freezes at $+2^\circ C$, and that a eutectic is formed when the mole fraction of N_2H_4 is 0.07 and that the eutectic melts at $-80^\circ C$.

6.10(a) Figure 6.39 shows the phase diagram for two partially miscible liquids, which can be taken to be that for water (A) and 2-methyl-1-propanol (B). Describe what will be observed when a mixture of composition $x_B = 0.8$ is heated, at each stage giving the number, composition, and relative amounts of the phases present.

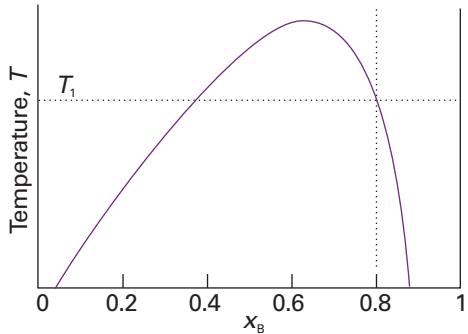


Fig. 6.39

6.10(b) Figure 6.40 is the phase diagram for silver and tin. Label the regions, and describe what will be observed when liquids of compositions *a* and *b* are cooled to 200 K.

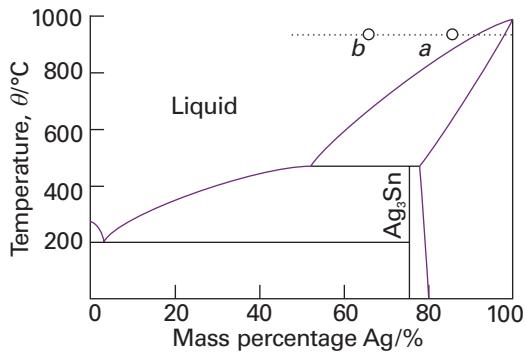


Fig. 6.40

6.11(a) Indicate on the phase diagram in Fig. 6.41 the feature that denotes incongruent melting. What is the composition of the eutectic mixture and at what temperature does it melt?

6.11(b) Indicate on the phase diagram in Fig. 6.42 the feature that denotes incongruent melting. What is the composition of the eutectic mixture and at what temperature does it melt?

6.12(a) Sketch the cooling curves for the isopleths *a* and *b* in Fig. 6.41.

6.12(b) Sketch the cooling curves for the isopleths *a* and *b* in Fig. 6.42.

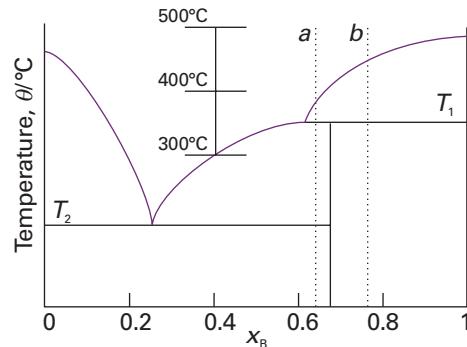


Fig. 6.41

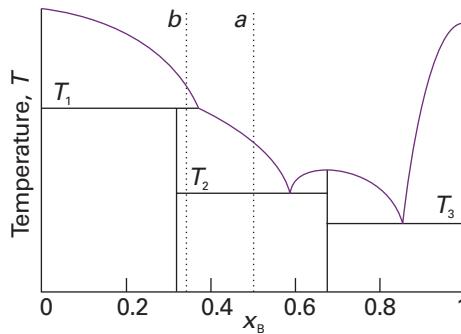


Fig. 6.42

6.13(a) Use the phase diagram in Fig. 6.40 to state (a) the solubility of Ag in Sn at $800^\circ C$ and (b) the solubility of Ag_3Sn in Ag at $460^\circ C$, (c) the solubility of Ag_3Sn in Ag at $300^\circ C$.

6.13(b) Use the phase diagram in Fig. 6.41 to state (a) the solubility of B in A at $500^\circ C$ and (b) the solubility of AB_2 in A at $390^\circ C$, (c) the solubility of AB_2 in B at $300^\circ C$.

6.14(a) Figure 6.43 shows the experimentally determined phase diagrams for the nearly ideal solution of hexane and heptane. (a) Label the regions of the diagrams as to which phases are present. (b) For a solution containing 1 mol each of hexane and heptane, estimate the vapour pressure at $70^\circ C$ when vaporization on reduction of the external pressure just begins. (c) What is the vapour pressure of the solution at $70^\circ C$ when just one drop of liquid remains. (d) Estimate from the figures the mole fraction of hexane in the liquid and vapour phases for the conditions of part b. (e) What are the mole fractions for the conditions of part c? (f) At $85^\circ C$ and 760 Torr, what are the amounts of substance in the liquid and vapour phases when $z_{\text{heptane}} = 0.40$?

6.14(b) Uranium tetrafluoride and zirconium tetrafluoride melt at $1035^\circ C$ and $912^\circ C$, respectively. They form a continuous series of solid solutions with a minimum melting temperature of $765^\circ C$ and composition $x(\text{ZrF}_4) = 0.77$. At $900^\circ C$, the liquid solution of composition $x(\text{ZrF}_4) = 0.28$ is in equilibrium with a solid solution of composition $x(\text{ZrF}_4) = 0.14$. At $850^\circ C$ the two compositions are 0.87 and 0.90, respectively. Sketch the phase diagram for this system and state what is observed when a liquid of composition $x(\text{ZrF}_4) = 0.40$ is cooled slowly from $900^\circ C$ to $500^\circ C$.

6.15(a) Methane (melting point 91 K) and tetrafluoromethane (melting point 89 K) do not form solid solutions with each other, and as liquids they are only partially miscible. The upper critical temperature of the liquid mixture is 94 K at $x(\text{CF}_4) = 0.43$ and the eutectic temperature is 84 K at $x(\text{CF}_4) = 0.88$. At 86 K, the phase in equilibrium with the tetrafluoromethane-rich

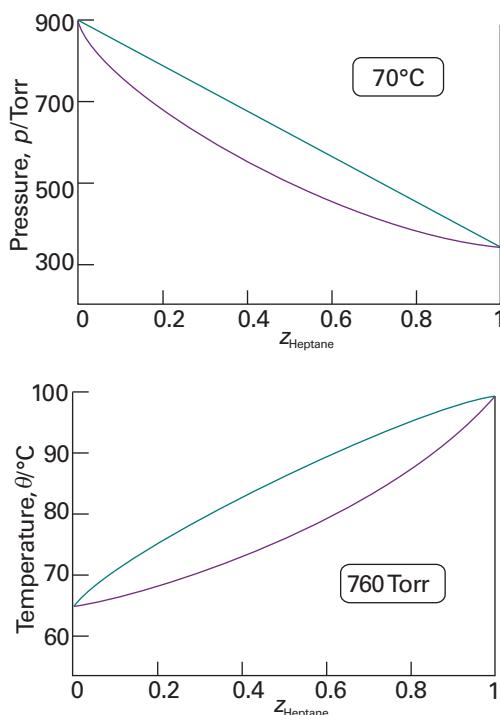


Fig. 6.43

Problems*

Numerical problems

6.1‡ 1-Butanol and chlorobenzene form a minimum-boiling azeotropic system. The mole fraction of 1-butanol in the liquid (x) and vapour (y) phases at 1.000 atm is given below for a variety of boiling temperatures (H. Artigas, C. Lafuente, P. Cea, F.M. Royo, and J.S. Urieta, *J. Chem. Eng. Data* **42**, 132 (1997)).

T/K	396.57	393.94	391.60	390.15	389.03	388.66	388.57
x	0.1065	0.1700	0.2646	0.3687	0.5017	0.6091	0.7171
y	0.2859	0.3691	0.4505	0.5138	0.5840	0.6409	0.7070

Pure chlorobenzene boils at 404.86 K. (a) Construct the chlorobenzene-rich portion of the phase diagram from the data. (b) Estimate the temperature at which a solution whose mole fraction of 1-butanol is 0.300 begins to boil. (c) State the compositions and relative proportions of the two phases present after a solution initially 0.300 1-butanol is heated to 393.94 K.

6.2‡ An *et al.* investigated the liquid–liquid coexistence curve of *N,N*-dimethylacetamide and heptane (X. An, H. Zhao, F. Fuguo, and W. Shen, *J. Chem. Thermodynamics* **28**, 1221 (1996)). Mole fractions of *N,N*-dimethylacetamide in the upper (x_1) and lower (x_2) phases of a two-phase region are given below as a function of temperature:

T/K	309.820	309.422	309.031	308.006	306.686
x_1	0.473	0.400	0.371	0.326	0.293
x_2	0.529	0.601	0.625	0.657	0.690
T/K	304.553	301.803	299.097	296.000	294.534
x_1	0.255	0.218	0.193	0.168	0.157
x_2	0.724	0.758	0.783	0.804	0.814

solution changes from solid methane to a methane-rich liquid. At that temperature, the two liquid solutions that are in mutual equilibrium have the compositions $x(\text{CF}_4) = 0.10$ and $x(\text{CF}_4) = 0.80$. Sketch the phase diagram.

6.15(b) Describe the phase changes that take place when a liquid mixture of 4.0 mol B_2H_6 (melting point 131 K) and 1.0 mol CH_3OCH_3 (melting point 135 K) is cooled from 140 K to 90 K. These substances form a compound $(\text{CH}_3)_2\text{OB}_2\text{H}_6$ that melts congruently at 133 K. The system exhibits one eutectic at $x(\text{B}_2\text{H}_6) = 0.25$ and 123 K and another at $x(\text{B}_2\text{H}_6) = 0.90$ and 104 K.

6.16(a) Refer to the information in Exercise 6.15(b) and sketch the cooling curves for liquid mixtures in which $x(\text{B}_2\text{H}_6)$ is (a) 0.10, (b) 0.30, (c) 0.50, (d) 0.80, and (e) 0.95.

6.16(b) Refer to the information in Exercise 6.15(a) and sketch the cooling curves for liquid mixtures in which $x(\text{CF}_4)$ is (a) 0.10, (b) 0.30, (c) 0.50, (d) 0.80, and (e) 0.95.

6.17(a) Hexane and perfluorohexane show partial miscibility below 22.70°C. The critical concentration at the upper critical temperature is $x = 0.355$, where x is the mole fraction of C_6F_{14} . At 22.0°C the two solutions in equilibrium have $x = 0.24$ and $x = 0.48$, respectively, and at 21.5°C the mole fractions are 0.22 and 0.51. Sketch the phase diagram. Describe the phase changes that occur when perfluorohexane is added to a fixed amount of hexane at (a) 23°C, (b) 22°C.

6.17(b) Two liquids, A and B, show partial miscibility below 52.4°C. The critical concentration at the upper critical temperature is $x = 0.459$, where x is the mole fraction of A. At 40.0°C the two solutions in equilibrium have $x = 0.22$ and $x = 0.60$, respectively, and at 42.5°C the mole fractions are 0.24 and 0.48. Sketch the phase diagram. Describe the phase changes that occur when B is added to a fixed amount of A at (a) 48°C, (b) 52.4°C.

(a) Plot the phase diagram. (b) State the proportions and compositions of the two phases that form from mixing 0.750 mol of *N,N*-dimethylacetamide with 0.250 mol of heptane at 296.0 K. To what temperature must the mixture be heated to form a single-phase mixture?

6.3‡ The following data have been obtained for the liquid–vapour equilibrium compositions of mixtures of nitrogen and oxygen at 100 kPa.

T/K	77.3	78	80	82	84	86	88	90.2
$x(\text{O}_2)$	0	10	34	54	70	82	92	100
$y(\text{O}_2)$	0	2	11	22	35	52	73	100
$p^*(\text{O}_2)/\text{Torr}$	154	171	225	294	377	479	601	760

Plot the data on a temperature–composition diagram and determine the extent to which it fits the predictions for an ideal solution by calculating the activity coefficients of O_2 at each composition.

6.4 Phosphorus and sulfur form a series of binary compounds. The best characterized are P_4S_3 , P_4S_7 , and P_4S_{10} , all of which melt congruently. Assuming that only these three binary compounds of the two elements exist, (a) draw schematically only the P/S phase diagram. Label each region of the diagram with the substance that exists in that region and indicate its phase. Label the horizontal axis as x_{S} and give the numerical values of x_{S} that correspond to the compounds. The melting point of pure phosphorus is 44°C and that of pure sulfur is 119°C. (b) Draw, schematically, the cooling curve for a mixture of composition $x_{\text{S}} = 0.28$. Assume that a eutectic occurs at $x_{\text{S}} = 0.2$ and negligible solid–solid solubility.

6.5 The table below gives the break and halt temperatures found in the cooling curves of two metals A and B. Construct a phase diagram consistent

* Problems denoted with the symbol ‡ were supplied by Charles Trapp, Carmen Giunta, and Marshall Cady.

with the data of these curves. Label the regions of the diagram, stating what phases and substances are present. Give the probable formulas of any compounds that form.

$100x_B$	$\theta_{\text{break}}/^\circ\text{C}$	$\theta_{\text{halt},1}/^\circ\text{C}$	$\theta_{\text{halt},2}/^\circ\text{C}$
0		1100	
10.0	1060	700	
20.0	1000	700	
30.0	940	700	400
40.0	850	700	400
50.0	750	700	400
60.0	670	400	
70.0	550	400	
80.0		400	
90.0	450	400	
100.0		500	

6.6 Consider the phase diagram in Fig. 6.44, which represents a solid–liquid equilibrium. Label all regions of the diagram according to the chemical species that exist in that region and their phases. Indicate the number of species and phases present at the points labelled *b*, *d*, *e*, *f*, *g*, and *k*. Sketch cooling curves for compositions $x_B = 0.16$, 0.23 , 0.57 , 0.67 , and 0.84 .

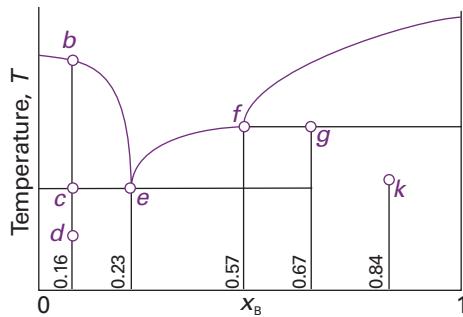


Fig. 6.44

6.7 Sketch the phase diagram for the Mg/Cu system using the following information: $\theta_f(\text{Mg}) = 648^\circ\text{C}$, $\theta_f(\text{Cu}) = 1085^\circ\text{C}$; two intermetallic compounds are formed with $\theta_f(\text{MgCu}_2) = 800^\circ\text{C}$ and $\theta_f(\text{Mg}_2\text{Cu}) = 580^\circ\text{C}$; eutectics of mass percentage Mg composition and melting points 10 per cent (690°C), 33 per cent (560°C), and 65 per cent (380°C). A sample of Mg/Cu alloy containing 25 per cent Mg by mass was prepared in a crucible heated to 800°C in an inert atmosphere. Describe what will be observed if the melt is cooled slowly to room temperature. Specify the composition and relative abundances of the phases and sketch the cooling curve.

6.8‡ Figure 6.45 shows $\Delta_{\text{mix}}G(x_{\text{pb}}, T)$ for a mixture of copper and lead. (a) What does the graph reveal about the miscibility of copper and lead and the spontaneity of solution formation? What is the variance (F) at (i) 1500 K , (ii) 1100 K ? (b) Suppose that at 1500 K a mixture of composition (i) $x_{\text{pb}} = 0.1$, (ii) $x_{\text{pb}} = 0.7$, is slowly cooled to 1100 K . What is the equilibrium composition of the final mixture? Include an estimate of the relative amounts of each phase. (c) What is the solubility of (i) lead in copper, (ii) copper in lead at 1100 K ?

6.9‡ The temperature–composition diagram for the Ca/Si binary system is shown in Fig. 6.46. (a) Identify eutectics, congruent melting compounds, and incongruent melting compounds. (b) If a 20 per cent by atom composition melt of silicon at 1500°C is cooled to 1000°C , what phases (and phase composition) would be at equilibrium? Estimate the relative amounts of each phase. (c) Describe the equilibrium phases observed when an 80 per cent by

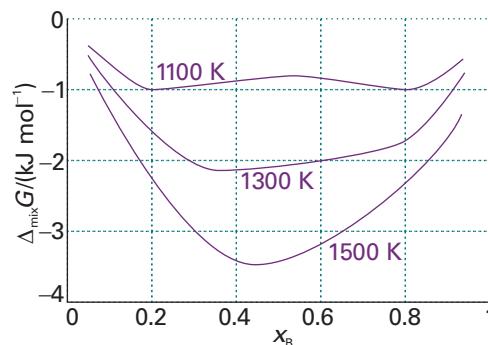


Fig. 6.45

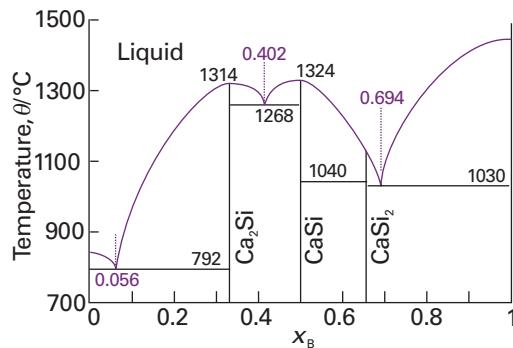


Fig. 6.46

atom composition Si melt is cooled to 1030°C . What phases, and relative amounts, would be at equilibrium at a temperature (i) slightly higher than 1030°C , (ii) slightly lower than 1030°C ? Draw a graph of the mole percentages of both $\text{Si}(\text{s})$ and $\text{CaSi}_2(\text{s})$ as a function of mole percentage of melt that is freezing at 1030°C .

6.10 Iron(II) chloride (melting point 677°C) and potassium chloride (melting point 776°C) form the compounds KFeCl_3 and K_2FeCl_4 at elevated temperatures. KFeCl_3 melts congruently at 380°C and K_2FeCl_4 melts incongruently at 399°C . Eutectics are formed with compositions $x = 0.38$ (melting point 351°C) and $x = 0.54$ (melting point 393°C), where x is the mole fraction of FeCl_2 . The KCl solubility curve intersects the K_2FeCl_4 curve at $x = 0.34$. Sketch the phase diagram. State the phases that are in equilibrium when a mixture of composition $x = 0.36$ is cooled from 400°C to 300°C .

Theoretical problems

6.11 Show that two phases are in thermal equilibrium only if their temperatures are the same.

6.12 Show that two phases are in mechanical equilibrium only if their pressures are equal.

Applications: to biology, materials science, and chemical engineering

6.13 The unfolding, or *denaturation*, of a biological macromolecule may be brought about by treatment with substances, called *denaturants*, that disrupt the intermolecular interactions responsible for the native three-dimensional conformation of the polymer. For example, urea, $\text{CO}(\text{NH}_2)_2$, competes for NH and CO groups and interferes with hydrogen bonding in a polypeptide.

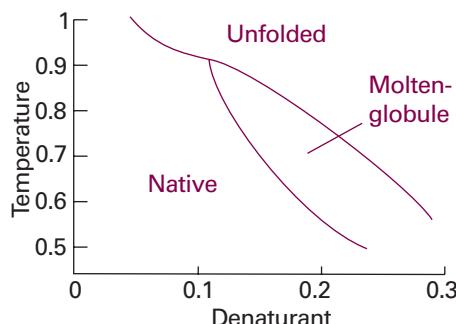


Fig. 6.47

In a theoretical study of a protein, the temperature–composition diagram shown in Fig. 6.47 was obtained. It shows three structural regions: the native form, the unfolded form, and a ‘molten globule’ form, a partially unfolded but still compact form of the protein. (i) Is the molten globule form ever stable when the denaturant concentration is below 0.1? (ii) Describe what happens to the polymer as the native form is heated in the presence of denaturant at concentration 0.15.

6.14 The basic structural element of a membrane is a phospholipid, such as phosphatidyl choline, which contains long hydrocarbon chains (typically in the range C₁₄–C₂₄) and a variety of polar groups, such as –CH₂CH₂N(CH₃)₃⁺. The hydrophobic chains stack together to form an extensive bilayer about 5 nm across, leaving the polar groups exposed to the aqueous environment on either side of the membrane (see Chapter 19 for details). All lipid bilayers undergo a transition from a state of low chain mobility (the *gel* form) to high chain mobility (the *liquid crystal* form) at a temperature that depends on the structure of the lipid. Biological cell membranes exist as liquid crystals at physiological temperatures. In an experimental study of membrane-like assemblies, a phase diagram like that shown in Fig. 6.48 was obtained. The two components are dielaidoylphosphatidylcholine (DEL) and dipalmitoylphosphatidylcholine (DPL). Explain what happens as a liquid mixture of composition $x_{\text{DEL}} = 0.5$ is cooled from 45°C.

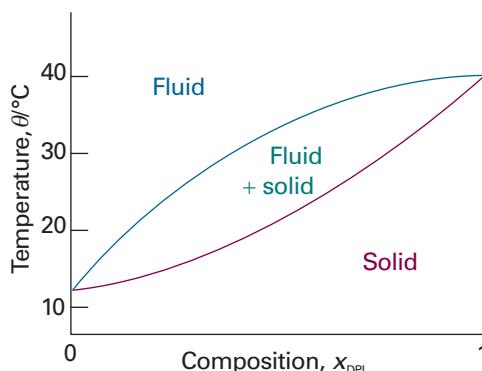
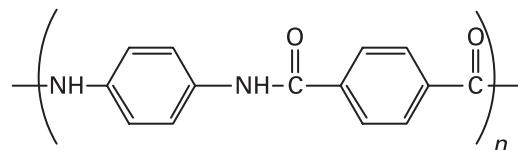


Fig. 6.48

6.15 The compound *p*-azoxyanisole forms a liquid crystal. 5.0 g of the solid was placed in a tube, which was then evacuated and sealed. Use the phase rule to prove that the solid will melt at a definite temperature and that the liquid

crystal phase will make a transition to a normal liquid phase at a definite temperature.

6.16 Some polymers can form liquid crystal mesophases with unusual physical properties. For example, liquid crystalline Kevlar (3) is strong enough to be the material of choice for bulletproof vests and is stable at temperatures up to 600 K. What molecular interactions contribute to the formation, thermal stability, and mechanical strength of liquid crystal mesophases in Kevlar?

**3**

6.17 Use a phase diagram like that shown in Fig. 6.36 to indicate how zone levelling may be described.

6.18 The technique of *float zoning*, which is similar to zone refining (*Impact I6.2*), has produced very pure samples of silicon for use in the semiconductor industry. Consult a textbook of materials science or metallurgy and prepare a discussion of the principles, advantages, and disadvantages of float zoning.

6.19 Magnesium oxide and nickel oxide withstand high temperatures. However, they do melt when the temperature is high enough and the behaviour of mixtures of the two is of considerable interest to the ceramics industry. Draw the temperature–composition diagram for the system using the data below, where x is the mole fraction of MgO in the solid and y its mole fraction in the liquid.

$\theta/^\circ\text{C}$	1960	2200	2400	2600	2800
x	0	0.35	0.60	0.83	1.00
y	0	0.18	0.38	0.65	1.00

State (a) the melting point of a mixture with $x = 0.30$, (b) the composition and proportion of the phases present when a solid of composition $x = 0.30$ is heated to 2200°C, (c) the temperature at which a liquid of composition $y = 0.70$ will begin to solidify.

6.20 The bismuth–cadmium phase diagram is of interest in metallurgy, and its general form can be estimated from expressions for the depression of freezing point. Construct the diagram using the following data: $T_f(\text{Bi}) = 544.5 \text{ K}$, $T_f(\text{Cd}) = 594 \text{ K}$, $\Delta_{\text{fus}}H(\text{Bi}) = 10.88 \text{ kJ mol}^{-1}$, $\Delta_{\text{fus}}H(\text{Cd}) = 6.07 \text{ kJ mol}^{-1}$. The metals are mutually insoluble as solids. Use the phase diagram to state what would be observed when a liquid of composition $x(\text{Bi}) = 0.70$ is cooled slowly from 550 K. What are the relative abundances of the liquid and solid at (a) 460 K and (b) 350 K? Sketch the cooling curve for the mixture.

6.21‡ Carbon dioxide at high pressure is used to separate various compounds in citrus oil. The mole fraction of CO₂ in the liquid (x) and vapour (y) at 323.2 K is given below for a variety of pressures (Y. Iwai, T. Morotomi, K. Sakamoto, Y. Koga, and Y. Arai, *J. Chem. Eng. Data* **41**, 951 (1996)).

p/MPa	3.94	6.02	7.97	8.94	9.27
x	0.2873	0.4541	0.6650	0.7744	0.8338
y	0.9982	0.9980	0.9973	0.9958	0.9922

(a) Plot the portion of the phase diagram represented by these data. (b) State the compositions and relative proportions of the two phases present after an equimolar gas mixture is compressed to 6.02 MPa at 323.2 K.