

# G      Equation Chapter 1 Section 1

## Phase diagrams

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*By Atkins*



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## G.1 Introduction

*Phase diagrams for pure substances were introduced in Chapter 6. Now we shall 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.*

*The phase rule limits the appearance of phase diagrams by showing, for example, that a pure substance cannot be found in a state in which four phases coexist in equilibrium. With the rule established, we shall 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, first dealing with systems of two components and then introducing some features of three components. 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 construct and interpret phase diagrams. These diagrams let us judge whether two or three 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.

All phase diagrams can be discussed in terms of a relationship, the phase rule, derived by Gibbs. We shall derive this rule first, and then apply it to a wide variety of systems.

## G.2 PHASES, COMPONENTS, AND DEGREES OF FREEDOM **Equation Section (Next)**

The derivation and application of the phase rule requires a careful terms, so we shall begin by presenting a number of definitions.

### G.2.1 Definitions

The term **phase** was introduced at the start of Chapter 6, where we saw that it signifies a state of matter that is uniform throughout, not only chemical composition but also in physical state. (The words are Gibb's.) Thus we speak of the solid, liquid, and gas phases of a substance, 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. 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 ( $P = 2$ ) system 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  $A$  in solid  $B$  – 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 (Figure G.2.1). Such 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. It is the ability to control this microstructure resulting from phase equilibria that makes it possible to tailor the mechanical properties of the materials to a particular application.

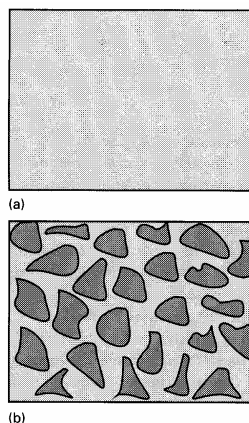
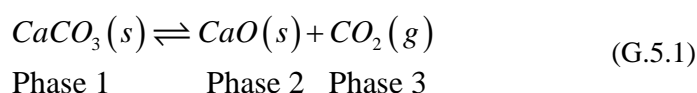


Figure G.2.1 The difference between (a) a single-phase solution, in which composition is uniform on a microscopic scale, and (b) a dispersion, in which regions of one component are embedded in a matrix of a second component

By a **constituent** of a system we shall mean a chemical species (an ion or a molecule) that is present. Thus, a mixture of ethanol and water has two constituents. 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, the number of components is equal to the number of constituents. Thus, pure water is a one-component system (because we need only the species  $\text{H}_2\text{O}$  to specify its composition). Similarly, a mixture of ethanol and water is a two-component system (we need the species  $\text{H}_2\text{O}$  and  $\text{C}_2\text{H}_5\text{OH}$  to specify its composition). 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, a system in which the equilibrium occurs.



To specify the composition of the gas we need the species  $\text{CO}_2$  and to specify the composition of phase 2 we need the species  $\text{CaO}$ . However, we do not need an additional species to specify phase 1 because its identity (' $\text{CaCO}_3$ ') can be expressed in terms of the other two constituents by making use of the reaction



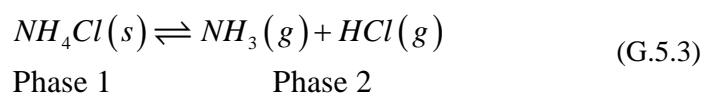
Hence, the system has two components ( $C = 2$ ).

#### Example 8.1 *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. However,  $\text{NH}_3$  and  $\text{HCl}$  can be prepared in the correct stoichiometric proportions by the reaction



Therefore, the compositions of both phase 1 and phase 2 can be expressed in terms of the single species  $\text{NH}_4\text{Cl}$ . Therefore, there is only one component in the system ( $C = 1$ ).

**Comment.** If additional  $\text{HCl}$  (or  $\text{NH}_3$ ) were supplied to the system, then the decomposition of  $\text{NH}_4\text{Cl}$  would not give the correct composition of the gas phase and  $\text{HCl}$  (or  $\text{NH}_3$ ) would have to be invoked as a second component. A system that consists of hydrogen, oxygen, and water at room temperature has *three* components, despite it being possible to form  $\text{H}_2\text{O}$  from  $\text{H}_2$  and  $\text{O}_2$ : under the conditions prevailing in the system, hydrogen and oxygen do not react to form water, so they are independent constituents.

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 ( $C = 1$ ), single-phase systems, 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), then to preserve that number of phases when the temperature is changed, the pressure must be adjusted to match the new vapour pressure. The variance of the system has fallen to 1 because only the pressure (or the temperature) can be changed independently.

### G.2.2 The phase rule

In one of the most elegant calculations in the whole of chemical thermodynamics, J. W. Gibbs<sup>1</sup> deduced the **phase rule**, which is a general relation between the variance  $F$ , the number of components  $C$ , and the number of phases  $P$  at equilibrium for a system of any composition:

$$F = C - P + 2 \quad (\text{G.5.5})$$

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#### JUSTIFICATION

<sup>1</sup> 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.



We begin by counting the total number of intensive variables (properties that do not depend on the size of the system). 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 (Chapter 6):

$$\mu_{J,\alpha} = \mu_{J,\beta} = \dots \text{for } P \text{ phases} \quad (\text{G.5.6})$$

That is, there are  $P-1$  equations 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 variance is

$$F = P(C-1) + 2 - C(P-1) = C - P + 2 \quad (\text{G.5.7})$$

which is **eqn 1**.

We shall now go on to see how the phase rule summarizes what we already know about one-component systems and then apply it to more complex cases.

### One-component systems

For a one-component system, such as pure water,

$$F = 3 - P \quad (\text{G.5.8})$$

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 which is characteristic of the substance and outside our control. The equilibrium of three phases is therefore represented by a point, the **triple point**, on the phase diagram. Four phases cannot be in equilibrium in a one-component system because  $F$  cannot be negative. These features are summarized in Figure G.2.2.

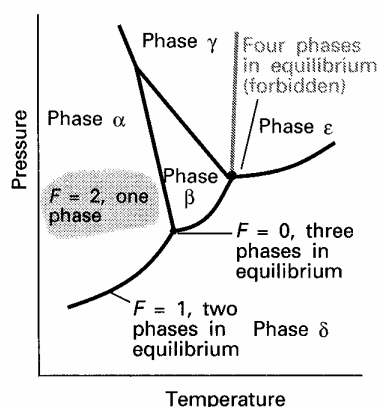


Figure G.2.2 The typical regions of a one-component phase diagram. The lines represent conditions under which the two adjoining phases are in equilibrium. A point represents the unique set of conditions under which three phases coexist in equilibrium. Four phases cannot mutually coexist in equilibrium.

The features summarized in the illustration can be identified in the experimentally determined phase diagram for water shown in Figure G.2.3. 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 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.

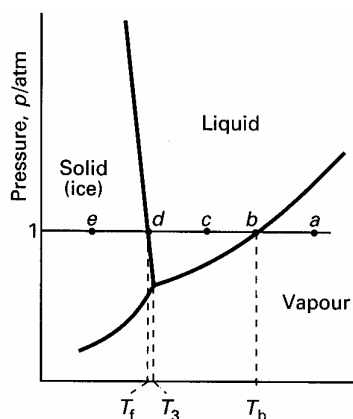


Figure G.2.3 The phase diagram for water, a simplified version of Fig. 6.5. The label  $T_3$  marks the temperature of the triple point,  $T_b$  the normal boiling point, and  $T_f$  the normal freezing point.

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.

### Experimental procedures

Detecting a phase change is not always as simple as seeing a kettle boil, so special techniques have been developed. One technique is **thermal analysis**, which takes advantage of the effect of the enthalpy change during a first-order transition (Section 6.5). In this method, 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 Figure G.2.3 therefore has the shape shown in Figure G.2.4. The transition temperature is obvious, and is used to mark point  $d$  on the phase diagram. This technique is useful for solid-solid transitions, where simple visual inspection of the sample may be inadequate.

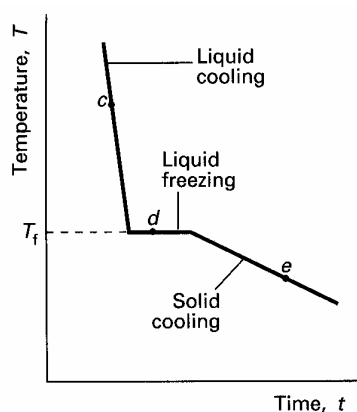


Figure G.2.4 The cooling curve for the isobar  $cde$  in Figure G.2.3. The halt marked  $d$  corresponds to the pause in the fall of temperature while the first-order exothermic transition (freezing) occurs. This pause enables  $T_f$  to be located even if the transition cannot be observed visually.

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 Figure G.2.5. 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 which 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, for instance, becomes metallic at around 200 kbar while remaining as  $I_2$ , but makes a transition to a monatomic metallic 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.

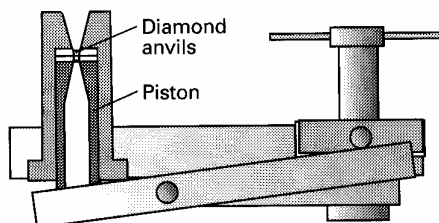


Figure G.2.5 Ultrahigh pressures (up to about 2 Mbar) can be achieved using a diamond anvil. The sample, together with a ruby for pressure measurement and a drop of liquid for pressure transmission, are placed between two gem-quality diamonds. The principle of its action is that of a nutcracker: the pressure is exerted by turning the screw by hand.

### G.3 TWO-COMPONENT SYSTEMS Equation Section (Next)

In this section we shall begin by showing how the general form of a phase diagram for a binary mixture of two volatile liquids can be constructed by drawing on the properties of ideal solutions introduced in Chapter 7, particularly Raoult's law (eqn 7.11). Then we shall see how deviations

from ideality distort the diagrams in a way that has important implications for distillations. Finally, we shall meet phase diagrams for systems consisting of a variety of liquids and solids and see how the phase rule can be used to guide our interpretation of them. 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. 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. We shall introduce both types of diagram.

#### G.3.1 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:

$$p_A = x_A p_A^* \quad p_B = x_B p_B^* \quad (\text{G.6.1})$$

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

$$p = p_A + p_B = x_A p_A^* + x_B p_B^* = p_B^* + (p_A^* - p_B^*) \cdot x_A \quad (\text{G.6.2})$$

This expression shows that the total vapour pressure (at same fixed temperature) changes linearly with the composition from  $p_B^*$  to  $p_A^*$  (Figure G.3.1).

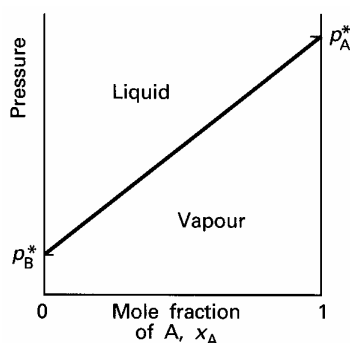


Figure G.3.1 The variation of the total vapour pressure of a binary mixture with the mole fraction of A in the liquid when Raoult's law is obeyed.

### The composition of the vapour

The compositions of the liquid and vapour that are in equilibrium are not necessarily the same, and 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 (G.6.1). It follows from Dalton's law that the mole fractions in the gas,  $y_A$  and  $y_B$ , are

$$y_A = \frac{p_A}{p} \quad y_B = \frac{p_B}{p} \quad (\text{G.6.3})$$

The partial pressures and the total pressure may be expressed in terms of the mole fractions in the liquid by using eqn (G.6.1) for  $p_j$  and eqn (G.6.2) for the total vapour pressure  $p$ , which gives

$$y_A = \frac{x_A p_A^*}{p_B^* + (p_A^* - p_B^*) \cdot x_A} \quad y_B = 1 - y_A \quad (\text{G.6.4})$$

We now have to show that, if A is the more volatile component, then its mole fraction in the vapour  $y_A$  is greater than its mole fraction in the liquid  $x_A$ . Figure G.3.2

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  $y_A > y_B$ , as we expect. 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 ( $y_B = 0$ ).

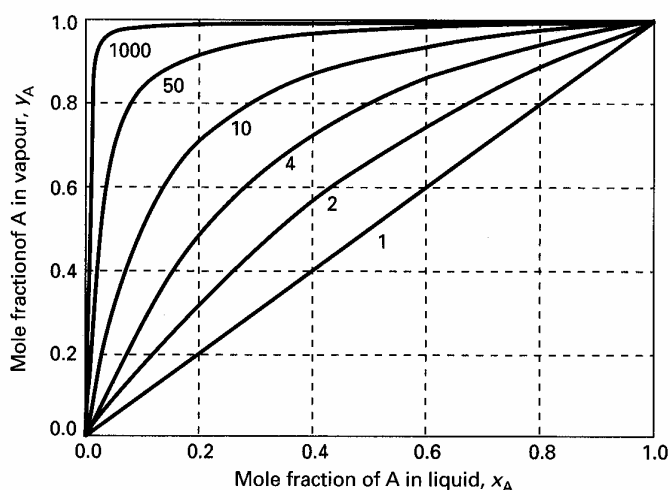


Figure G.3.2 The mole fraction of A in the vapour of a binary ideal solution expressed in terms of its mole fraction in the liquid, calculated using eqn (G.6.4) for various values of  $p_A^*/p_B^*$  (the label on each curve) with A more volatile than B. In all cases the vapour is richer than the liquid in A.

Equation (G.6.2) 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 (G.6.4), we can now also relate the total vapour pressure to the composition of the vapour:

$$p = \frac{p_A^* \cdot p_B^*}{p_A^* + (p_B^* - p_A^*) \cdot y_A} \quad (\text{G.6.5})$$

This expression is plotted in Figure G.3.3.

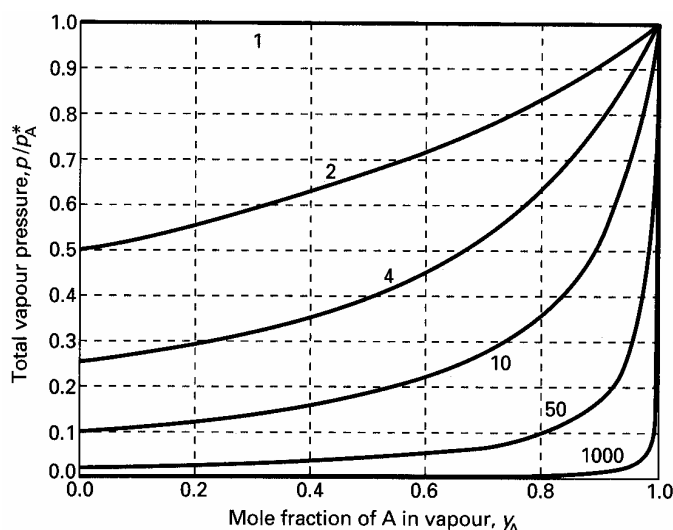


Figure G.3.3 The dependence of the vapour pressure of the same system as in Figure G.3.2, but expressed in terms of the mole fraction of A in the vapour by using eqn 6. Individual curves are labelled with the value of  $p_A^* / p_B^*$

### The interpretation of the diagrams

If we are interested in distillation, then both the vapour and the liquid compositions are of equal interest. It is then sensible to combine the two preceding diagrams into one. The result is summarized in Figure G.3.4. 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  $F' = 1$ . That is, if the composition is specified (so using up the only degree of freedom), the pressure at which the two phases are in equilibrium is fixed. Hence, the compositions and pressures at which the two phases are in equilibrium are represented by a line on the phase diagram.

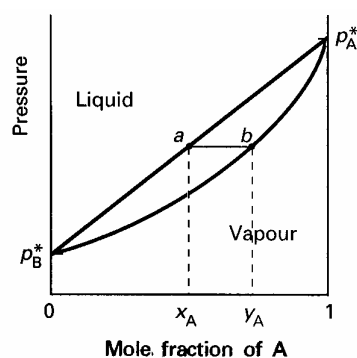


Figure G.3.4 The dependence of the vapour pressure of the same system as in Figure G.3.2, but expressed in terms of the mole fraction of A in the vapour by using eqn 6. Individual curves are labelled with the value of  $p_A^* / p_B^*$ .

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, allowing for the different compositions and amounts of the liquid and vapour phases. 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 Figure G.3.4 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 grey 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 lowering the pressure on a liquid mixture of overall composition  $a$  in Figure G.3.5:

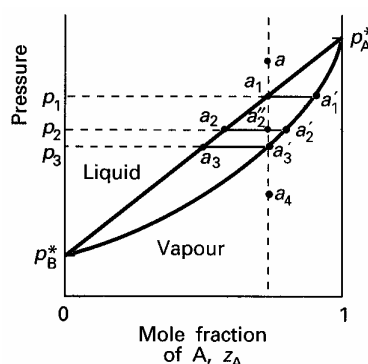


Figure G.3.5 The points of the pressure-composition diagram discussed in the text. The vertical line through  $a$  is an isopleth, a line of constant composition of the entire system.

the lowering of pressure can be achieved by drawing out a piston (Figure G.3.6); 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 **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  $a_1'$ . The horizontal line joining the two points 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  $a_1'$ .



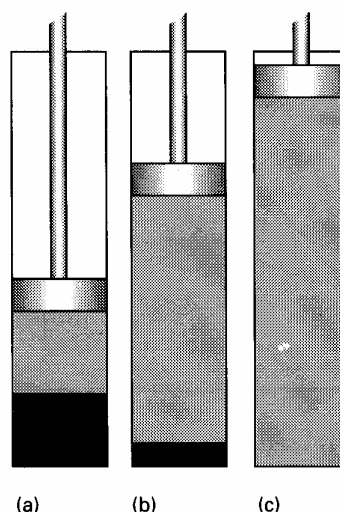


Figure G.3.6 (a) A liquid in a container exists in equilibrium with its vapour. (b) When the pressure is changed by drawing out a piston, the compositions of the phases adjust. (c) When the piston is pulled so far out that all the liquid has vaporized and only the vapour is present, the pressure falls as the piston is withdrawn.

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 (Figure G.3.7).

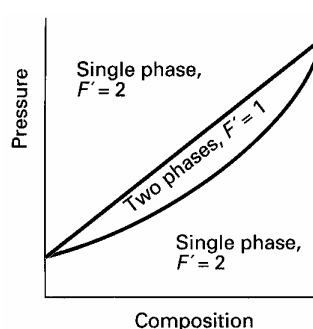


Figure G.3.7 The general scheme of interpretation of a pressure-composition diagram (a vapour pressure diagram).

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 that is 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).

### 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  $\alpha$  and  $\beta$  that are in equilibrium, we measure the distances  $l_\alpha$  and  $l_\beta$  along the horizontal tie line, and then use the **lever rule** (Figure G.3.8):

$$n_\alpha l_\alpha = n_\beta l_\beta \quad (\text{G.6.6})$$

where  $n_\alpha$  is the amount of phase  $\alpha$  and  $n_\beta$  the amount of phase  $\beta$ . In the case illustrated in Figure G.3.8, because  $l_\beta \approx 2l_\alpha$ , the amount of phase  $\alpha$  is about twice the amount of phase  $\beta$ .

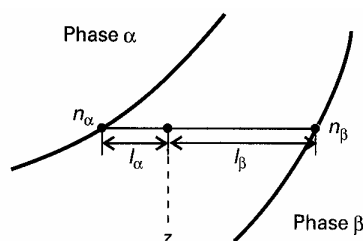


Figure G.3.8 The lever rule. The distances  $l_\alpha$  and  $l_\beta$  are used to find the proportions of the amounts of phases  $\alpha$  (such as vapour) and  $\beta$  (for example liquid) present at equilibrium. The lever rule is so called because a similar rule relates the masses at two ends of a lever to their distances from a pivot ( $m_\alpha l_\alpha = m_\beta l_\beta$  for balance).

### JUSTIFICATION

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:

$$nz_A = n_\alpha x_A + n_\beta y_A \quad (\text{G.6.7})$$

Since also

$$nz_A = n_\alpha z_A + n_\beta z_A \quad (\text{G.6.8})$$

by equating these two expressions it follows that

$$n_\alpha (z_A - x_A) = n_\beta (y_A - z_A) \quad (\text{G.6.9})$$

or

$$n_\alpha l_\alpha = n_\beta l_\beta \quad (\text{G.6.10})$$

as was to be proved.

To see in more detail how the lever rule is used, consider the changes in Figure G.3.5 again. At  $p_1$ , 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 0.7, so  $n_{\text{liq}}/n_{\text{vap}} \approx 0.7$  and the amount of liquid is about 0.7 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.

### G.3.2 Temperature-composition diagrams

Reducing the pressure at constant temperature is one way of doing distillation, but it is more common to distil at constant pressure by raising the temperature. To discuss distillation in this way 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 Figure G.3.9. Note that the liquid phase region now lies in the lower part of the diagram.

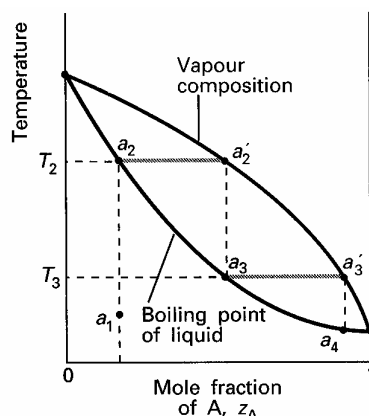


Figure G.3.9 The temperature-composition diagram corresponding to an ideal mixture with the component A more volatile than component B. Successive boilings and condensations of a liquid originally of composition  $a_1$ , lead to a condensate that is pure A. The separation technique is called fractional distillation.

### The distillation of mixtures

The interpretation of a temperature-composition diagram is similar to that of the pressure-composition diagram. The region between the lines is a two-phase region where  $F' = 1$  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 modifiable.

To understand the content of the phase diagram 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), as common sense leads us to expect. 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. If the vapour in this example is drawn off and completely condensed, then it gives a liquid of composition  $a_3$ , which is richer in the more volatile component than the original liquid. In **fractional distillation** the boiling and condensation cycle is repeated successively. We can follow the changes that occur by seeing what happens when the condensate of composition on the vertical line through  $a_3$  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 it condenses to a liquid of composition  $a_4$ . The cycle can then be repeated until in due course almost pure A is obtained.

In chemical engineering applications, the efficiency of a fractionating column is expressed in terms of the number of **theoretical plates**, the number of effective vaporization

zation 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 Figure G.3.10a, the fractionating column must correspond to three theoretical plates, whereas to achieve the same separation for the system shown in Figure G.3.10b the fractionating column must be designed to correspond to five theoretical plates.

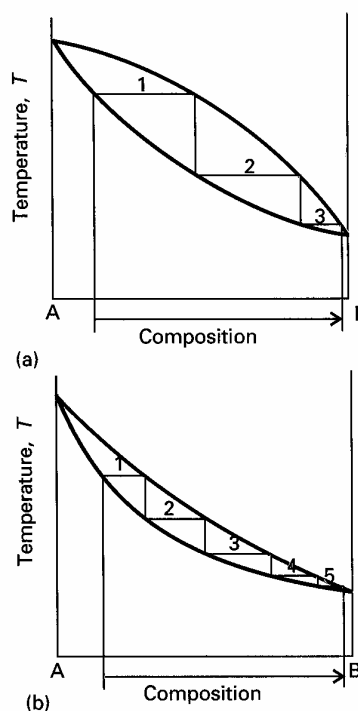


Figure G.3.10 The number of theoretical plates is the number of steps needed to bring about a specified degree of separation of two components in a mixture. The two systems shown correspond to (a) three and (b) five theoretical plates.

## Azeotropes

Although many liquids have temperature-composition phase diagrams resembling the ideal version in Figure G.3.9, in a number of important cases there are marked deviations. A maximum in the phase diagram (Figure G.3.11) 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 7.4), is negative (more favourable to mixing than ideal). Examples of this behaviour include chloroform/acetone and nitric acid/water mixtures. Phase diagrams showing a minimum (Figure G.3.12) 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 mixtures of dioxane and water and of ethanol and water.

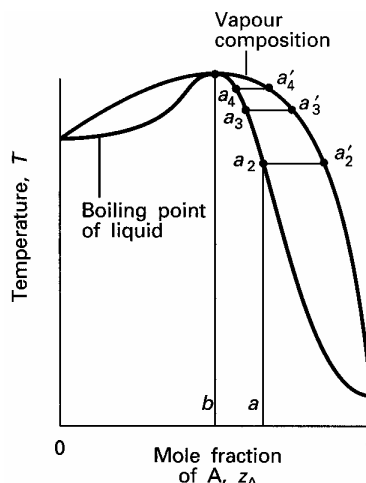


Figure G.3.11 A high-boiling azeotrope. When the liquid of composition  $a$  is distilled, the composition of the remaining liquid changes towards  $b$  but no further.

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 Figure G.3.11. 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  $a'_3$ . If that vapour is removed, then 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** (which comes from the Greek words for 'boiling without changing'). 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 azeotrope 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 Figure G.3.12 is also azeotropic, but shows it 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, 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 and the temperature is 78°C.

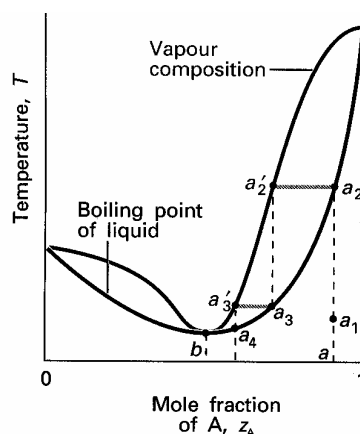


Figure G.3.12 A low-boiling azeotrope. When the mixture at *a* is fractionally distilled, the vapour in equilibrium in the fractionating column moves towards *b* and then remains unchanged.

### Immiscible liquids

Finally we consider the distillation of two immiscible liquids, such as octane and water. As they are immiscible we can regard their 'mixture' as unscrambled with each component in a separate vessel (Figure G.3.13). If the vapour pressures of the two pure components are  $p_A$  and  $p_B$ , then the total vapour pressure is  $p = p_A^* + p_B^*$  and the mixture boils (in an open container) when  $p = 1$  atm. The presence of the second component means that the agitated 'mixture' boils at a lower temperature than either would alone because boiling begins when the total pressure reaches 1 atm, not when either vapour pressure reaches 1 atm. This is the basis of steam distillation, which enables same 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.

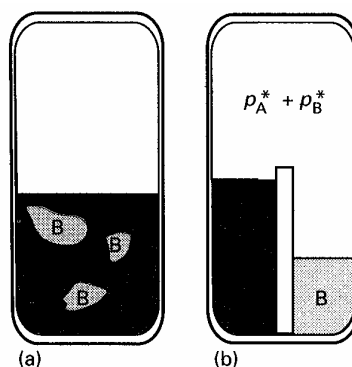


Figure G.3.13 The distillation of two immiscible liquids can be regarded as the joint distillation of the separated components, and boiling occurs when the sum of the partial pressures equals the external pressure.

### G.3.3 Liquid-liquid phase diagrams

Now we consider temperature-composition phase diagrams for binary 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  $P = 2$ ,  $F' = 1$ , and the selection of a temperature implies that the composition 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.

#### 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 more abundant one consisting of  $A$  saturated with  $B$ , the minor one of a trace of  $B$  saturated with  $A$ . In the temperature-composition diagram drawn in Figure G.3.14, the composition of the former is represented by the point  $a'$  that of the latter by the point  $a''$ . The relative abundances of the two phases are given by the lever rule.

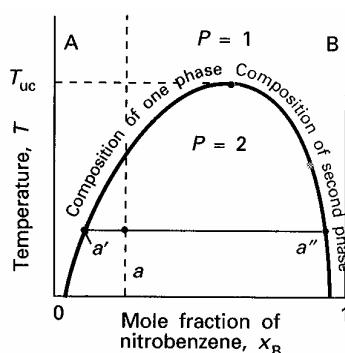


Figure G.3.14 The temperature-composition diagram for hexane and nitrobenzene at 1 atm. The region below the curve corresponds to the compositions and temperatures at which the liquids are partially miscible. The upper critical temperature  $T_{uc}$  is the temperature above which the two liquids are miscible in all proportions. For this system it lies at 293K.

When more  $A$  is added,  $A$  dissolves in it slightly. The compositions of the two phases in equilibrium remain  $a'$  and  $a''$  (because  $P = 2$  implies that  $F'' = 0$ , where the double prime indicates that two intensive variables, the temperature and the pressure, are held constant, and hence that the compositions of the phases are invariant at a fixed temperature and pressure), but the amount of the second phase increases at the expense of the first. 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  $A$ . The entire phase diagram can be constructed by repeating the observations at different temperatures and drawing the envelope of the two-phase region. This is usually done at fixed compositions by lowering the temperature to determine the envelope.

### Example 8.2 Interpreting a liquid-liquid phase diagram

A mixture of 50 g (0,59 mol) of hexane and 50 g (0,41 mol) of nitrobenzene 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 through the point representing the temperature and overall composition of the system intersect the phase boundary. Their proportions are given by the lever rule (eqn (G.6.6)). 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.

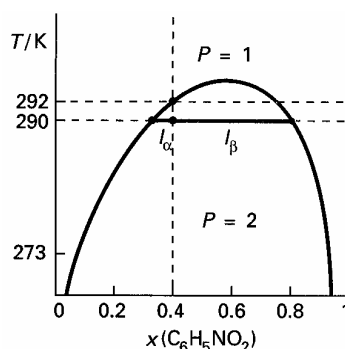


Figure G.3.15 The temperature-composition diagram for hexane and nitrobenzene at 1 atm again, with the points and lengths discussed in the text.

**Answer.** We denote hexane by H and nitrobenzene by N; refer to Figure G.3.15, which is a slightly simplified version of Figure G.3.14. 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 boundary at  $x_N = 0.35$  and  $x_N = 0.83$ , so those are the compositions of the two phases. The ratio of amounts of each phase is equal to the ratio of distances  $l_\alpha$  and  $l_\beta$ :

$$\frac{l_\beta}{l_\alpha} = \frac{0,83 - 0,41}{0,41 - 0,35} = \frac{0,42}{0,06} = 7 \quad (\text{G.6.11})$$

Heating the sample to 292 K takes it into the single-phase region.

**Comment.** Because the phase diagram has been constructed experimentally, these conclusions are exact. They would be modified if the system were subjected to a different pressure.

### Critical temperatures

The **upper critical temperature**  $T_{uc}$  is the highest temperature at which phase separation occurs (Figure G.3.16a). Above the upper critical temperature the two components are fully miscible. This temperature exists because the greater thermal motion overcomes any potential energy advantage for molecules of one type being close together.

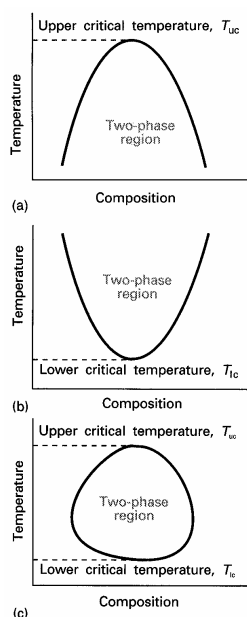


Figure G.3.16 The three types of critical-solution behaviour shown by liquids. (a) A system with an upper critical temperature, (b) a system with a lower critical temperature, (c) a system with both upper and lower critical temperatures.

One example is the nitrobenzene-hexane system shown in Figure G.3.14; another is the palladium-hydrogen system, which shows two phases, one a solid solution of  $H_2$  in palladium and the other a palladium hydride, up to 300°C, but forms a single phase at higher temperatures (Figure G.3.17).

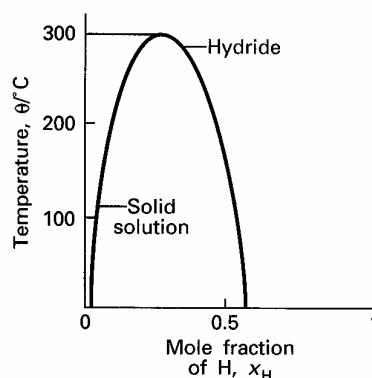


Figure G.3.17 The phase diagram for palladium and palladium hydride, which has an upper critical temperature at 300°C.

Some systems show a **lower critical temperature**  $T_{lc}$ , below which they mix in all proportions and above which they form two phases (Figure G.3.16b). An example is water and triethylamine (Figure G.3.18). 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.

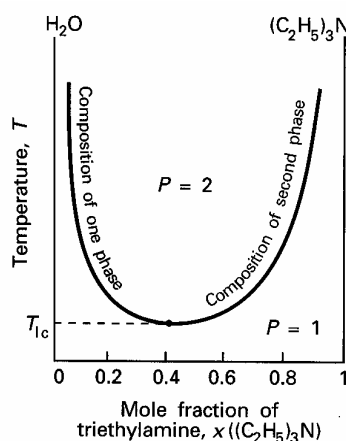


Figure G.3.18 The temperature-composition diagram for water and triethylamine. This system shows a lower critical temperature at 292 K. The labels indicate the interpretation of the boundaries.

Some systems have both upper and lower critical temperatures (Figure G.3.16c). 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 that of nicotine and water, which are partially miscible between 61°C and 210°C (Figure G.3.19).

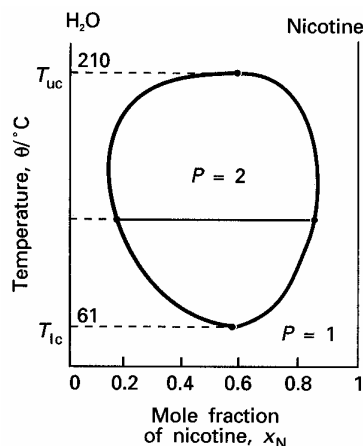


Figure G.3.19 The temperature-composition diagram for water and nicotine which has both upper and lower critical temperatures. Note the high temperatures for the liquid (especially the water): the diagram corresponds to a sample under pressure.

### The distillation of partially miscible liquids

We now consider what happens when the conditions are such that a vapour may be present too. We shall consider a pair of liquids that are partially miscible and form a low-boiling azeotrope. This combination of properties 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 G.3.20 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  $a_1$ .

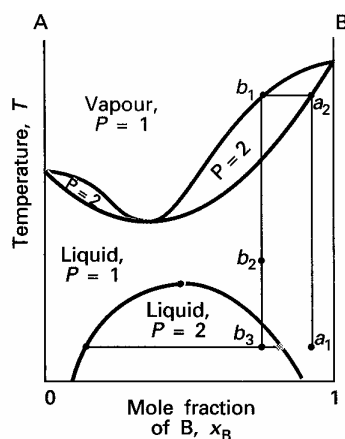


Figure G.3.20 The temperature-composition diagram for a binary system in which the upper critical temperature is less than the boiling point at all compositions. The mixture forms a low-boiling azeotrope.

Figure G.3.21 shows the second possibility, in which there is no upper critical 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  $b''_3$ .

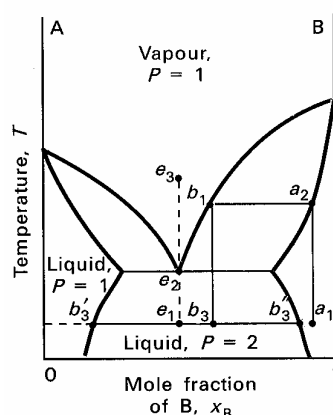


Figure G.3.21 The temperature-composition diagram for a binary system in which boiling occurs before the two liquids are fully miscible.

The behaviour of a system of composition represented by the isopleth  $e$  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 composition as the liquid (the liquid is an azeotrope). Similarly, condensing a vapour of composition  $e_3$  gives a liquid of the same composition. At a fixed temperature, the mixture vaporizes and condenses like a single substance.

### Example 8.3 Interpreting a phase diagram

State the changes that occur when a mixture of composition  $x_B = 0.95$  ( $a_1$  in Figure G.3.22) is boiled and the vapour condensed.

**Method.** The area occupied by the point 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 (G.6.6)).

**Answer.** The initial point is in the one-phase region. When heated it boils at 370 K ( $a_2$  in Figure G.3.22) giving a vapour of composition  $x_B = 0.66$  ( $b_1$  in Figure G.3.22). The liquid gets richer in  $B$  and the last drop (of pure  $B$ ) evaporates at 392 K. The boiling range of the liquid is therefore 370 to 392 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  $x_B = 0.66$  iso-

pleth. At 350 K, for instance, the liquid phase has composition  $x_B = 0.87$ , the vapour  $x_B = 0.49$ , in relative proportions 1: 1.3. At 340 K the sample consists of three phases, the vapour, and two liquids, one of composition  $x_B = 0.30$ , the other of composition  $x_B = 0.80$  in the ratio 0.62: 1. Further cooling moves the system into the two-phase liquid 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.

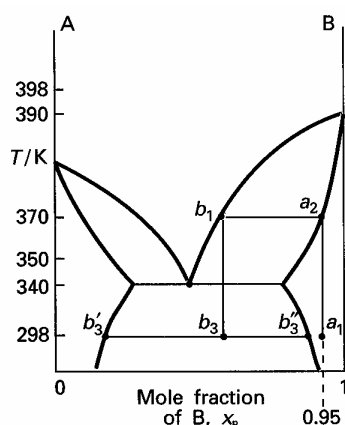


Figure G.3.22 The points of the phase diagram in Figure G.3.21 that are discussed in Example 8.3.

### G.3.4 Liquid-solid phase diagrams

Solid and liquid phases may both be present in a system at temperatures below the boiling point. An example is a pair of metals that are almost completely immiscible right up to their melting points (such as antimony and bismuth). The phase diagram is shown in Figure G.3.23; note how closely it resembles Figure G.3.21, but instead of liquid and vapour phases the system has solid and liquid phases.

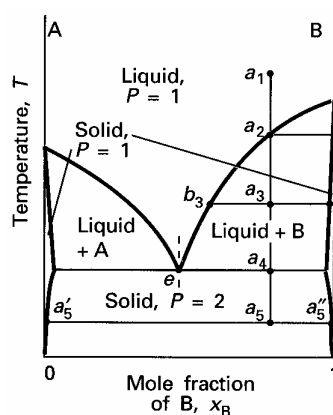


Figure G.3.23 The temperature-composition phase diagram for two almost immiscible solids and their completely miscible liquids. Note the similarity to Figure G.3.21. The isopleth through  $e$  corresponds to the eutectic composition, the mixture with lowest melting point.

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

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

$a_1 \rightarrow a_3$ . 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  $a_3$  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, at  $a_4$ , 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 almost pure  $B$  and almost pure  $A$ . At  $a_5$ , for example, the compositions of the two phases are  $a'_5$  and  $a''_5$ .

### Eutectics

The isopleth at  $e$  in Figure G.3.23 corresponds to the **eutectic** composition the name coming from the Greek words for 'easily melted'. 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 67 per cent tin and 33 per cent lead and melts at  $183^\circ\text{C}$ . The eutectic formed by 23 per cent NaCl and 77 per cent  $\text{H}_2\text{O}$  melts at  $-21.1^\circ\text{C}$ . 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  $-21.1^\circ\text{C}$  (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.

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 Figure G.3.23. The liquid cools steadily (Figure G.3.24) until it reaches  $a_2$ , when  $B$  begins to be deposited. 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, then the liquid cools steadily down to the freezing temperature of the eutectic, when there is a long eutectic halt as the entire sample solidifies (like the freezing of a pure liquid).

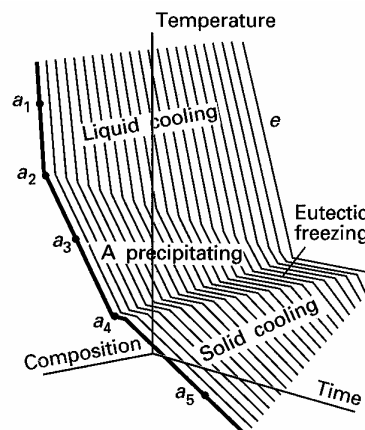


Figure G.3.24 The cooling curves for the system shown in Figure G.3.23. For isopleth  $a$ , the rate of cooling slows at  $a_2$  because solid  $B$  deposits from solution. There is a complete halt at  $a_4$  while the eutectic solidifies. This halt is longest for the eutectic isopleth  $e$ . The eutectic halt shortens again for compositions beyond  $e$  (richer in  $A$ ). Cooling curves are used to construct the phase diagram.

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.

### Reacting systems

Many binary mixtures react to produce compounds, and technologically important examples of this behaviour include the III/V semiconductors, such as gallium arsenide, which forms the compound  $\text{GaAs}$ . Although three constituents are present, there are only two components because  $\text{GaAs}$  is formed from the reaction  $\text{Ga} + \text{As} \rightarrow \text{GaAs}$ . 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  $B$ .

A system prepared by mixing an excess of  $B$  with  $A$  consists of  $C$  and unreacted  $B$ . This is a binary  $C, B$  system, which we suppose forms a eutectic. The principal change from the eutectic phase diagram in Figure G.3.23 is that the whole of the diagram is squeezed into the range of compositions lying between equal amounts of  $A$  and  $B$  ( $x_B = 0.5$ , marked  $C$  in Figure G.3.25) and pure  $B$ . The interpretation of the information in the diagram is obtained in the same way as for Figure G.3.23: the solid deposited on cooling along the isopleth at  $a_1$  in Figure G.3.25 is the compound  $C$  slightly contaminated with  $B$ , and the two-phase solid that exists when the temperature is below  $e$  consists of  $C$  and  $B$  (each one slightly contaminated by the other).



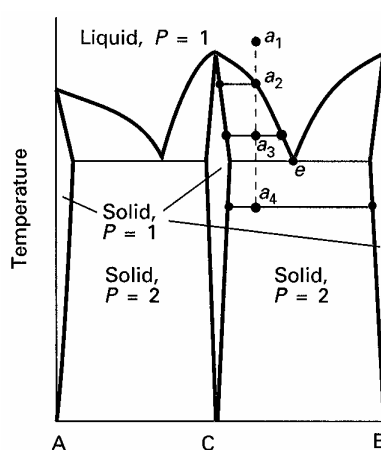


Figure G.3.25 The phase diagram for a system in which A and B react to form a compound  $C = AB$ . This diagram resembles two versions of Figure G.3.21 in each half of the diagram. The constituent C is a true compound, not just an equimolar mixture.

### Incongruent melting

In some cases the compound C is not stable as a liquid. An example is the alloy  $\text{Na}_2\text{K}$ , which survives only as a solid (Figure G.3.26).

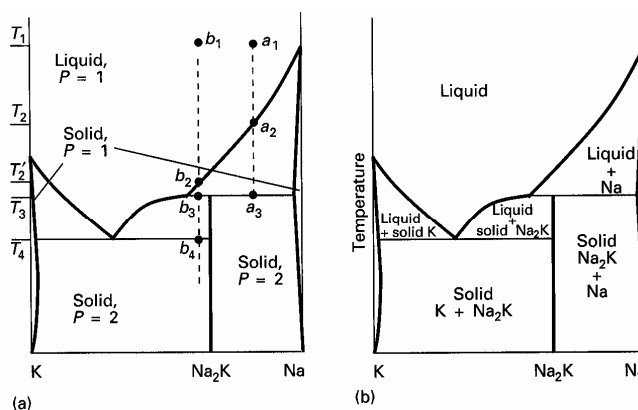


Figure G.3.26 (a) The phase diagram for an actual system (sodium and potassium) like that shown in Figure G.3.25, but with two differences. One is that the compound is  $\text{Na}_2\text{K}$ , corresponding to  $\text{A}_2\text{B}$  and not  $\text{AB}$  as in that illustration. The second is that the compound exists only as a solid, not as a liquid. The transformation of the compound at its melting point is an example of incongruent melting. (b) The species present in each region of the phase diagram.

Consider what happens as a liquid at  $a_1$  is cooled:

$a_1 \rightarrow a_2$ . Some solid Na (slightly contaminated with K) is deposited, and the remaining liquid is richer in K.

$a_2 \rightarrow$  just below  $a_3$ . The sample is now entirely solid, and consists of solid Na and solid  $\text{Na}_2\text{K}$  (each slightly contaminated by the other).

Now consider the isopleth at  $b_1$ :

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

$b_2 \rightarrow b_3$ . Solid Na deposits, but at  $b_3$  a reaction occurs to form  $\text{Na}_2\text{K}$ : this compound is formed by the K atoms diffusing into the solid Na.

At this stage the liquid Na/K mixture is in equilibrium with a little solid  $\text{Na}_2\text{K}$ , but there is still no liquid compound.

$b_3 \rightarrow b_4$ . 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  $\text{Na}_2\text{K}$ .

If the solid is reheated, the sequence of events is reversed. No liquid  $\text{Na}_2\text{K}$  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.

### G.3.5 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 in  $10^9$  (which corresponds to about one grain of salt in 5 tons of sugar).

Consider a liquid of composition on the isopleth through  $a$  in Figure G.3.27: it is mainly  $A$  with some  $B$  impurity. On cooling to  $a_1$ , a solid of composition  $b_1$  appears. Removing that solid gives a slightly purer material than the original, but not much of it (by the lever rule). That solid could be used as the starting substance for a second stage of this **fractional crystallization** process. In each stage, the composition is shifted towards pure  $A$ , in the manner of fractional distillation, but the procedure is slow and wasteful.

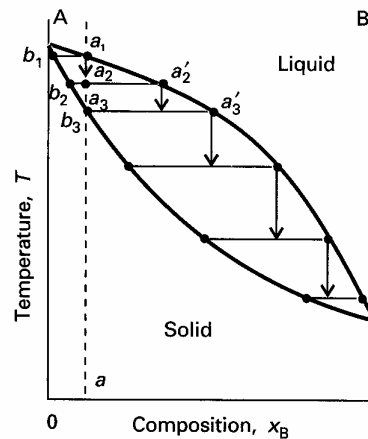


Figure G.3.27 A binary temperature-composition diagram can be used to discuss zone refining, as explained in the text.

We should recognize, however, that Figure G.3.27 applies when the freezing is so slow that the composition of the solid is uniform and has its equilibrium composition. In a real system equilibrium is not achieved because *B* does not have time to disperse throughout the whole solid sample. The technique of **zone refining** 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.

Consider a liquid (this represents the molten zone) on the isopleth through *a*, 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, so when that freezes it occludes the air in a mist of tiny bubbles.

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 that 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 (Figure G.3.28). 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.

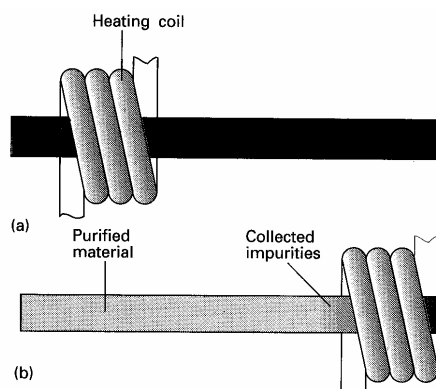


Figure G.3.28 The procedure for zone refining. (a) Initially, impurities are distributed uniformly along the sample. (b) After a molten zone is passed along the rod, the impurities are more concentrated at the right. In practice, a series of molten zones are passed along the rod from left to right.

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.

## G.4 THREE-COMPONENT SYSTEMS Equation Section (Next)

For a three-component system,  $F = 5 - P$ , so the variance may reach 4. Holding the temperature and pressure constant leaves two degrees of freedom (the mole fractions of two of the components). One of the best ways of showing how phase equilibria vary with the composition of the system is to use a triangular phase diagram. This section explains how these diagrams are constructed and interpreted and gives two simple examples.

### G.4.1 Triangular phase diagrams

The mole fractions of the three components of a ternary system ( $C = 3$ ) satisfy

$$x_A + x_B + x_C = 1 \quad (\text{G.7.1})$$

A phase diagram drawn as an equilateral triangle ensures that this property is satisfied automatically because the sum of the distances to a point inside an equilateral triangle measured parallel to the edges is equal to the length of the side of the triangle (Figure G.4.1), and that side may be taken to have unit length.

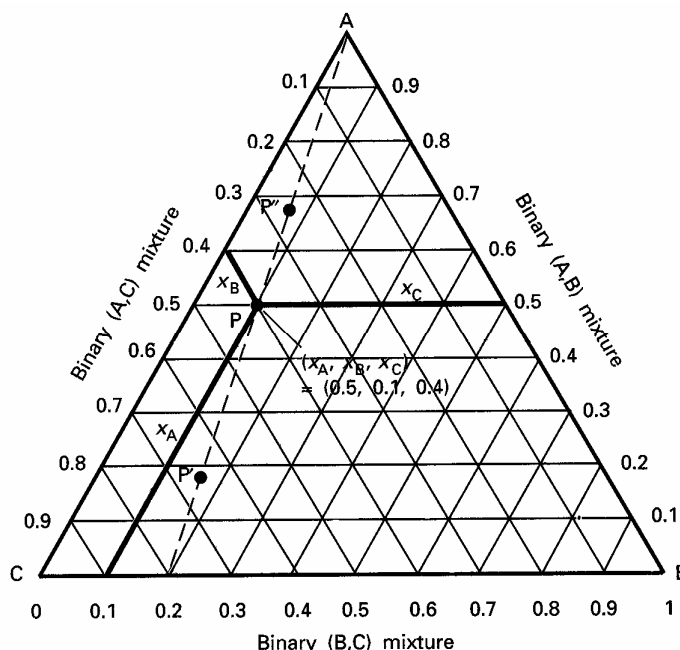


Figure G.4.1 The triangular coordinates used for the discussion of three-component systems. The edges correspond to binary systems. All points along the broken line correspond to mole fractions of C and B in the same ratio.

Figure G.4.1 shows how this approach works in practice. The edge  $AB$  corresponds to  $x_C = 0$ , and likewise for the other two edges. Hence, each of the three edges corresponds to one of the three binary systems  $(A,B)$ ,  $(B,C)$ , and  $(C,A)$ . An interior point corresponds to a system in which all three substances are present. The point  $P$ , for instance, represents  $x_A = 0.50$ ,  $x_B = 0.10$ , and  $x_C = 0.40$ .

Any point on a straight line joining an apex to a point on the opposite edge (the broken line in Figure G.4.1) represents a composition that is progressively richer in  $A$  the closer the point is to the  $A$  apex but which has the same proportions of  $B$  and  $C$ . Therefore, if we wish to represent the changing composition of a system as  $A$  is added, we draw a line from the  $A$  apex to the point on  $BC$  representing the initial binary system. Any ternary system formed by adding  $A$  then lies at some point on this line.

#### Example 8.4 Marking points on a ternary phase diagram

Mark the following points on a triangular composition diagram:

- (a)  $x_A = 0.20, x_B = 0.80, x_C = 0$
- (b)  $x_A = 0.42, x_B = 0.26, x_C = 0.32$

(c)  $x_A = 0.80, x_B = 0.10, x_C = 0.10$

(d)  $x_A = 0.10, x_B = 0.20, x_C = 0.70$

(e)  $x_A = 0.20, x_B = 0.40, x_C = 0.40$

(f)  $x_A = 0.30, x_B = 0.60, x_C = 0.10$

**Method.** The mole fraction  $x_A$  is measured along either edge leading to apex  $A$ ; likewise for  $x_B$  and  $B$ ;  $x_C$  takes care of itself (but it is sensible to check).

**Answer.** The points are plotted in Figure G.4.2.

**Comment.** Note that the points (d), (e), and (f) have  $x_A/x_B = 0.50$ , and fall on a straight line, as stated in the text.

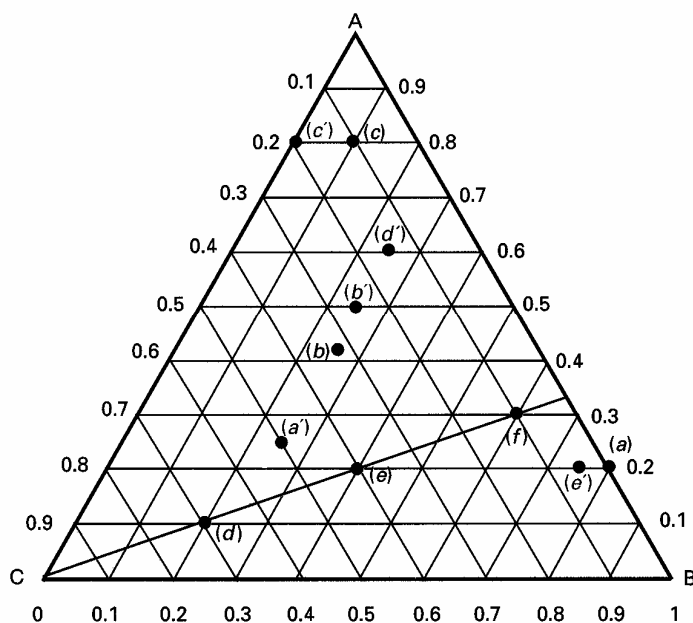


Figure G.4.2 The points referred to in Example 8.4 (black).

### G.4.2 Partially miscible liquids

Water and acetic acid are fully miscible, as are chloroform and acetic acid. Water and chloroform are only partially miscible. What happens when all three are present together?

The phase diagram for this ternary system at room temperature and pressure is shown in Figure G.4.3.

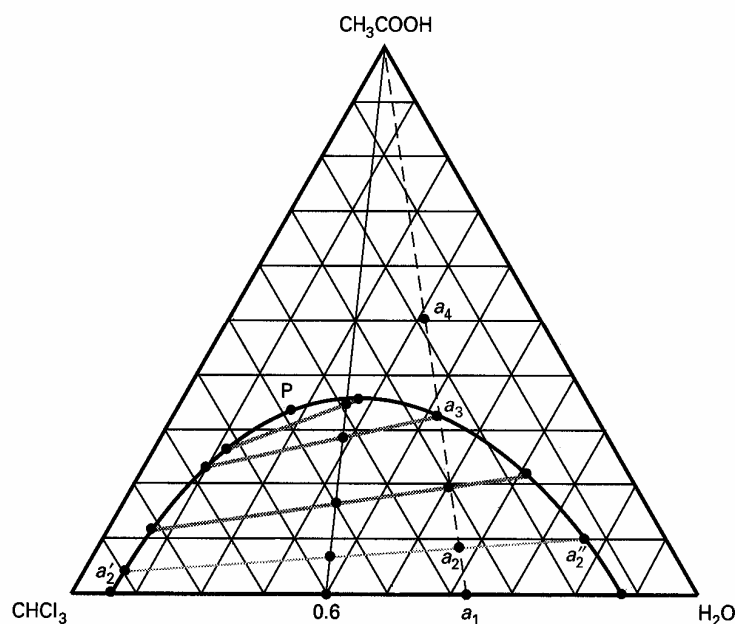


Figure G.4.3 The phase diagram, at fixed temperature and pressure, of the three-component system acetic acid, chloroform, and water. Only some of the tie lines have been drawn in the two-phase region. All points along the line  $a$  correspond to chloroform and water present in the same ratio.

It shows that the two fully miscible pairs form single-phase regions and that the water/chloroform system (along the base of the triangle) has a two-phase region. The base of the triangle corresponds to one of the horizontal lines in a two-component phase diagram. The tie lines in the two-phase regions are constructed experimentally by determining the compositions of the two phases that are in equilibrium, marking them on the diagram, and then joining them with a straight line.

A single-phase system is formed when enough acetic acid is added to the binary water-chloroform mixture. This effect is shown by following the line  $a_1$ ,  $a_4$  in Figure G.4.3.

At  $a_1$ . The system consists of two phases and the relative amounts of the two phases can be read off in the usual way (by using the lever rule).

(2)  $a_1 \rightarrow a_2$ . The addition of acetic acid takes the system along the line joining  $a_1$  to the acetic acid apex. At  $a_2$  the solution still has two phases, but there is more water in the chloroform phase ( $a_2'$ ) and more chloroform in the water ( $a_2''$ ) because the acid helps both to dissolve. The phase diagram shows that there is more acetic acid in the water-rich phase than in the orner ( $a_2''$  is closer than  $a_2'$  to the acetic acid apex).

$a_2 \rightarrow a_3$ . At  $a_3$  two phases are present, but the chloroform-rich layer is present only as a trace.

$a_3 \rightarrow a_4$ . Further addition of acid takes the system towards  $a_4$ , and only a single phase is present.

**Example 8.5** *Interpreting a ternary phase diagram (1)*

A mixture is prepared consisting of chloroform ( $x_c = 0.60$ ) and water ( $x_w = 0.40$ ). Describe the changes that occur when acetic acid is added to the mixture.

**Method.** We base the answer on Figure G.4.3. The relative proportions of chloroform and water remain constant, and so the addition of acetic acid ( $A$ ) corresponds to motion along the line from the point  $x_c = 0.60$  on the base line opposite the  $A$  apex to the apex itself. The tie lines give the compositions of the phases at their intersections with the boundaries; the lever rule gives their proportions. We shall denote compositions in the order  $(x_c, x_w, x_A)$ .

**Answer.** The initial composition is  $(0.60, 0.40, 0)$ . This point lies in the two-phase region, the phase compositions being  $(0.95, 0.05, 0)$  and  $(0.12, 0.88, 0)$  with relative proportions 1.3: . Addition of acetic acid takes the system along the straight line to  $A$ . When sufficient acid has been added to raise its mole fraction to 0.18 the overall composition is  $(0.49, 0.33, 0.18)$  and the system consists of two phases of compositions  $(0.82, 0.06, 0.12)$  and  $(0.17, 0.60, 0.23)$  in almost equal abundance.

When enough acid has been added to raise its mole fraction to 0.37 the system consists of a trace of a phase of composition  $(0.64, 0.11, 0.25)$  and a dominating phase of composition  $(0.35, 0.28, 0.37)$ . Further addition of acid takes the system into the single-phase region, where it remains right up to the point corresponding to pure acid.

### G.4.3 The role of added salts

The presence of one solute may affect the solubility of another. The **salting-out effect** is the reduction of the solubility of a gas (or other non-electrolyte) in water when a salt is added. A **salting-in effect** may also occur, in which the ternary system is more concentrated (in the sense of having less water) than in the binary system. A salt may also affect the solubility of another electrolyte, as we can see by examining the ternary system consisting of ammonium chloride, ammonium sulfate, and water (Figure G.4.4).



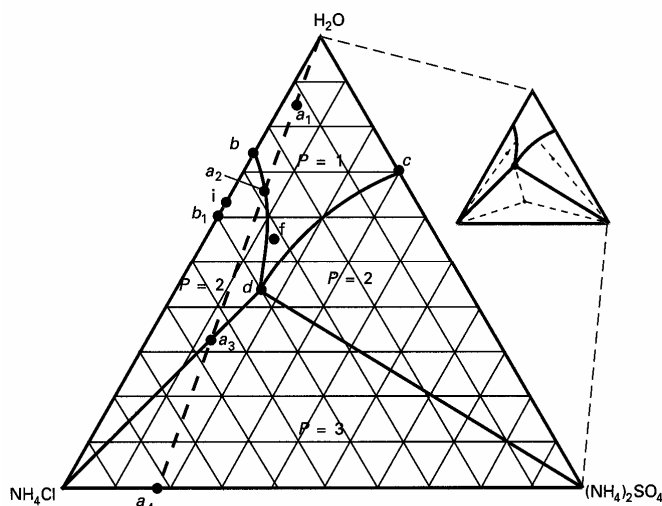


Figure G.4.4 The phase diagram, at constant temperature and pressure, for the ternary system  $\text{NH}_4\text{Cl}/(\text{NH}_4)_2\text{SO}_4/\text{H}_2\text{O}$ . The points  $i$  and  $f$  are the ones mentioned in Example 8.6. All tie lines in the two-phase regions terminate at an apex, and all tie lines in the three-phase region terminate at the three corners of the triangular area, as shown in the insert.

The phase diagram has the following interpretation.

$b$ . This point indicates the solubility of the chloride in water, and a mixture of composition  $b_1$  consists of the undissolved chloride and a saturated solution of composition  $b$ .

$c$ . This point similarly indicates the solubility of the sulfate.

$a_1$ . This point corresponds to a single phase; as water is evaporated, the composition moves along the line  $a_1$  to  $a_2$ .

$a_1 \rightarrow a_2$ . At  $a_2$  the system enters the two-phase region, and some solid chloride crystallizes (all the tie lines ending on that boundary also end at the pure chloride apex). The liquid becomes richer in sulfate, and its composition moves towards  $d$ .

$a_2 \rightarrow a_3$ . When enough water has been removed to bring the overall composition to  $a_3$  the liquid composition is  $d$ . At this point (which is joined to the chloride apex and to the sulfate apex), the system consists of saturated solution in equilibrium with the two solids.

Note that this point, which corresponds to the joint solubility of the two solids, corresponds to a smaller mole fraction of water than in either of the binary systems  $b$  and  $c$ . This means that the two salts form a more concentrated solution overall than either does alone.

$a_3 \rightarrow a_4$ . If more water is removed after the system has arrived at  $d$ , the amount of solution decreases, but its composition remains constant (at  $d$ , the saturated solution).

Both solids are precipitated, and the system has three phases: each point in the three-phase region is tied to  $d$  and the two solid apexes.

$a_4$ . All the water has been evaporated; the system is now binary and consists of a mixture of the two solids.

**Example 8.6** *Interpreting a ternary phase diagram (2)*

A solution of 50 g of ammonium chloride in 30 g of water is prepared at room temperature, and then 45 g of ammonium sulfate is added. Describe the initial and final states.

**Method.** We use Figure G.4.4 after converting compositions to mole fractions. We shall write compositions in the order  $(x_W, x_C, x_S)$  for water (W), chloride (C), and sulfate (S) and use the lever rule for proportions of each phase.

**Answer.** Molar masses are as follows:  $\text{H}_2\text{O}$ , 18.02;  $\text{NH}_4\text{Cl}$ , 53.49;  $(\text{NH}_4)_2\text{SO}_4$ , 132.1  $\text{g mol}^{-1}$ . The initial amounts are  $n_W = 1.66$  mol and  $n_C = 0.93$  mol, so the initial composition (point  $i$  in Figure G.4.4) is (0.64, 0.36, 0). In the final state the amounts of W and S are the same but  $n_S = 0.34$  mol. Therefore the final composition (point  $f$  in Figure G.4.4) is (0.57, 0.31, 0.12). From Figure G.4.4 we see that (0.64, 0.36, 0) corresponds to a two-phase system consisting of solid  $C$  with saturated solution of composition (0.74, 0.26, 0) in relative proportions 0.16:1. After addition of S there is only one phase.

Although phase diagrams might look complicated, they convey simple, experimentally established information. To interpret them it is helpful to think operationally. That is, definite processes should be imagined, and the diagram should be considered bearing in mind how it was constructed originally: phases come and go, systems boil and freeze, and relative amounts of different phases change. It is also wise to concentrate on the lines rather than the areas. The points at the ends of the tie lines give the compositions of the phases in equilibrium with each other. The distances of the points from the isopleth give (through the lever rule) their relative abundances.