Fig. 5.51 The temperature–composition phase diagram for two almost immiscible solids and their completely miscible liquids. Note the similarity to Fig. 5.49. The isopleth through e corresponds to the eutectic composition, the mixture with lowest melting point.
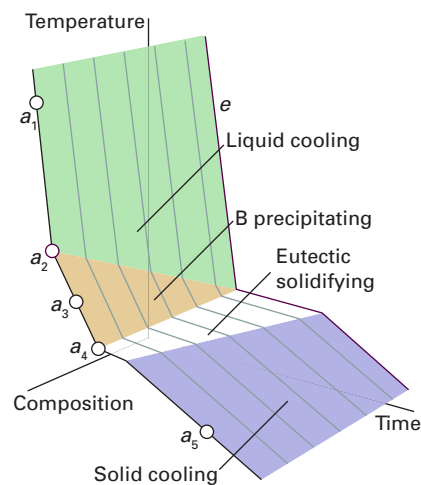
(a) Eutectics

Consider the two-component liquid of composition a_1 in Fig. 5.51. The changes that occur as the system is cooled may be expressed as follows.

1. $a_1 \rightarrow a_2$. 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.

2. $a_2 \rightarrow a_3$. More of the solid B 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.

3. $a_3 \rightarrow a_4$. At the end of this step, there is less liquid than at a_3, and its composition is given by e_2. This liquid now freezes to give a two-phase system of pure B and pure A.

The isopleth at e_2 in Fig. 5.51 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_2 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 without gradually unloading one or other of the components from the liquid.

One technologically important eutectic is solder, which in one form 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 H_2O 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 19).

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. 5.51. The liquid cools steadily until it reaches a_2, when B begins to be deposited (Fig. 5.52). 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 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, 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.

Fig. 5.52 The cooling curves for the system shown in Fig. 5.51. 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.

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[3] The name comes from the Greek words for 'easily melted'.

(b) Reacting systems

Many binary mixtures react to produce compounds, and technologically important examples of this behaviour include the Group 13/15 (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 $Ga + As \rightleftharpoons GaAs$. 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. 5.53).

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. 5.51 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. 5.53) and pure B. The interpretation of the information in the diagram is obtained in the same way as for Fig. 5.51. 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. 5.54). Consider what happens as a liquid at a_1 is cooled:

1. $a_1 \rightarrow a_2$. A solid solution rich in 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 a solid solution rich in Na and solid Na_2K.

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 a solid solution rich in Na begins to deposit.

2. $b_2 \rightarrow b_3$. A solid solution rich in 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 a solid solution rich in Na. The horizontal line representing this three-phase equilibrium is called a **peritectic line**.
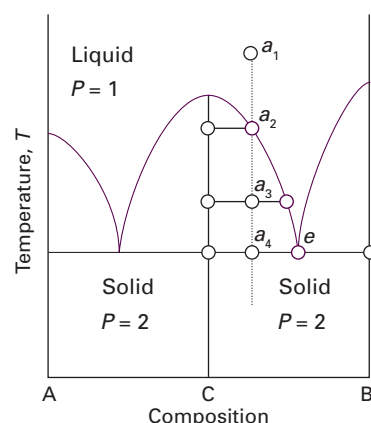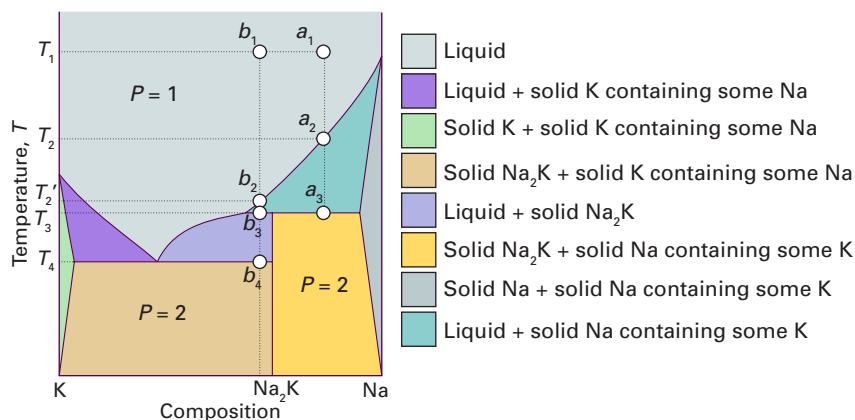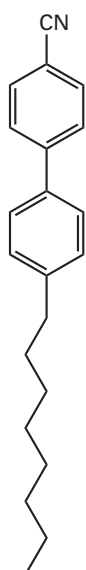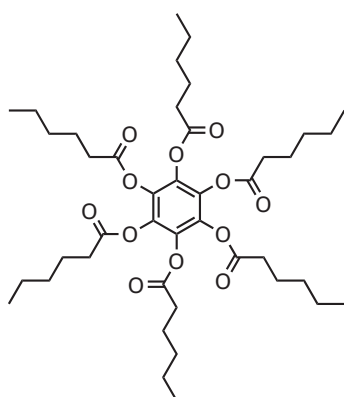
Fig. 5.53 The phase diagram for a system in which A and B react to form a compound C = AB. This resembles two versions of Fig. 5.51 in each half of the diagram. The constituent C is a true compound, not just an equimolar mixture.

Fig. 5.54 The phase diagram for an actual system (sodium and potassium) like that shown in Fig. 5.53, 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.

Legend for Fig. 5.54:
- Liquid
- Liquid + solid K containing some Na
- Solid K + solid K containing some Na
- Solid Na_2K + solid K containing some Na
- Liquid + solid Na_2K
- Solid Na_2K + solid Na containing some K
- Solid Na + solid Na containing some K
- Liquid + solid Na containing some K

CN

1

2

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 a solid solution rich in 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.

IMPACT ON MATERIALS SCIENCE
I5.2 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 disc-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 disc-like molecules. A *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 (Fig. 5.55). 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
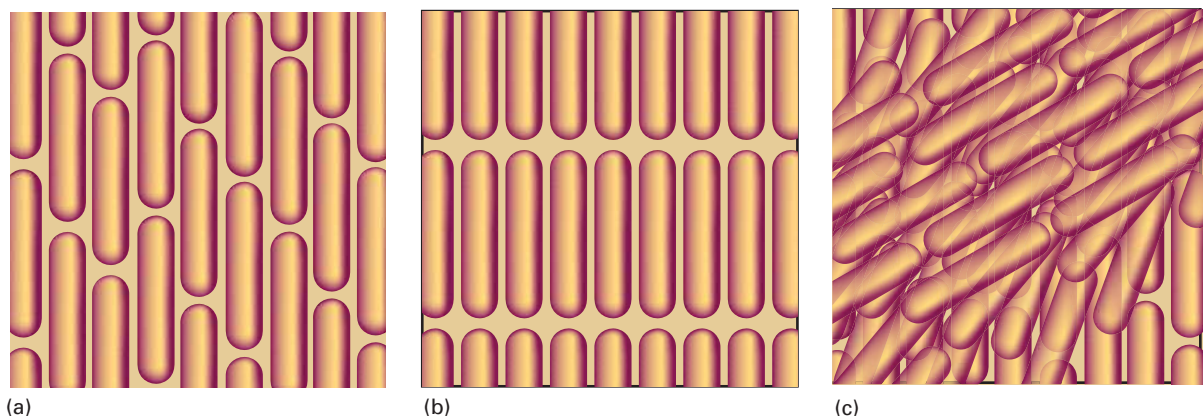
(a) (b) (c)

Fig. 5.55 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.