Physical transformations of pure substances

4

The discussion of the phase transitions of pure substances is among the simplest applications of thermodynamics to chemistry. We shall see that a phase diagram is a map of the pressures and temperatures at which each phase of a substance is the most stable. First, we describe the interpretation of empirically determined phase diagrams for a selection of materials. Then we turn to a consideration of the factors that determine the positions and shapes of the boundaries between the regions on a phase diagram. The practical importance of the expressions we derive is that they show how the vapour pressure of a substance varies with temperature and how the melting point varies with pressure. We shall see that the transitions between phases can be classified by noting how various thermodynamic functions change when the transition occurs. This chapter also introduces the chemical potential, a property that is at the centre of discussions of phase transitions and chemical reactions.

Vaporization, melting, and the conversion of graphite to diamond are all examples of changes of phase without change of chemical composition. In this chapter we describe such processes thermodynamically, using as the guiding principle the tendency of systems at constant temperature and pressure to minimize their Gibbs energy.

Phase diagrams

One of the most succinct ways of presenting the physical changes of state that a substance can undergo is in terms of its phase diagram. We present the concept in this section.

4.1 The stabilities of phases

A **phase** of a substance is a form of matter that is uniform throughout in chemical composition and physical state. Thus, we speak of solid, liquid, and gas phases of a substance, and of its various solid phases, such as the white and black allotropes of phosphorus. A **phase transition**, the spontaneous conversion of one phase into another phase, occurs at a characteristic temperature for a given pressure. Thus, at 1 atm, ice is the stable phase of water below 0°C, but above 0°C liquid water is more stable. This difference indicates that below 0°C the Gibbs energy decreases as liquid water changes into ice and that above 0°C the Gibbs energy decreases as ice changes into liquid water. The **transition temperature**, T_{trs}, is the temperature at which the two phases are in equilibrium and the Gibbs energy is minimized at the prevailing pressure.
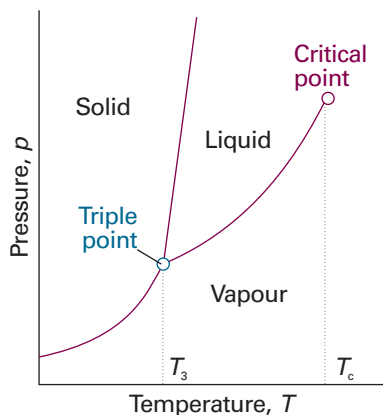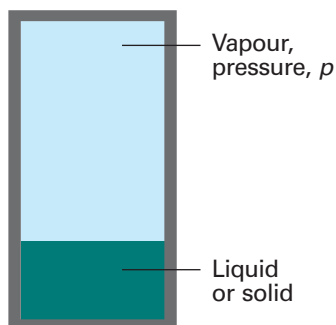
Fig. 4.1 The general regions of pressure and temperature where solid, liquid, or gas is stable (that is, has minimum molar Gibbs energy) are shown on this phase diagram. For example, the solid phase is the most stable phase at low temperatures and high pressures. In the following paragraphs we locate the precise boundaries between the regions.

Fig. 4.2 The vapour pressure of a liquid or solid is the pressure exerted by the vapour in equilibrium with the condensed phase.

Comment 4.1

The *NIST Chemistry WebBook* is a good source of links to online databases of data on phase transitions.

As we stressed at the beginning of Chapter 3, we must distinguish between the thermodynamic description of a phase transition and the rate at which the transition occurs. A transition that is predicted from thermodynamics to be spontaneous may occur too slowly to be significant in practice. For instance, at normal temperatures and pressures the molar Gibbs energy of graphite is lower than that of diamond, so there is a thermodynamic tendency for diamond to change into graphite. However, for this transition to take place, the C atoms must change their locations, which is an immeasurably slow process in a solid except at high temperatures. The discussion of the rate of attainment of equilibrium is a kinetic problem and is outside the range of thermodynamics. In gases and liquids the mobilities of the molecules allow phase transitions to occur rapidly, but in solids thermodynamic instability may be frozen in. Thermodynamically unstable phases that persist because the transition is kinetically hindered are called **metastable phases**. Diamond is a metastable phase of carbon under normal conditions.

4.2 Phase boundaries

The **phase diagram** of a substance shows the regions of pressure and temperature at which its various phases are thermodynamically stable (Fig. 4.1). The lines separating the regions, which are called **phase boundaries**, show the values of p and T at which two phases coexist in equilibrium.

Consider a liquid sample of a pure substance in a closed vessel. The pressure of a vapour in equilibrium with the liquid is called the **vapour pressure** of the substance (Fig. 4.2). Therefore, the liquid–vapour phase boundary in a phase diagram shows how the vapour pressure of the liquid varies with temperature. Similarly, the solid–vapour phase boundary shows the temperature variation of the **sublimation vapour pressure**, the vapour pressure of the solid phase. The vapour pressure of a substance increases with temperature because at higher temperatures more molecules have sufficient energy to escape from their neighbours.

(a) Critical points and boiling points

When a liquid is heated in an open vessel, the liquid vaporizes from its surface. At the temperature at which its vapour pressure would be equal to the external pressure, vaporization can occur throughout the bulk of the liquid and the vapour can expand freely into the surroundings. The condition of free vaporization throughout the liquid is called **boiling**. The temperature at which the vapour pressure of a liquid is equal to the external pressure is called the **boiling temperature** at that pressure. For the special case of an external pressure of 1 atm, the boiling temperature is called the **normal boiling point**, T_b. With the replacement of 1 atm by 1 bar as standard pressure, there is some advantage in using the **standard boiling point** instead: this is the temperature at which the vapour pressure reaches 1 bar. Because 1 bar is slightly less than 1 atm (1.00 bar = 0.987 atm), the standard boiling point of a liquid is slightly lower than its normal boiling point. The normal boiling point of water is 100.0°C; its standard boiling point is 99.6°C.

Boiling does not occur when a liquid is heated in a rigid, closed vessel. Instead, the vapour pressure, and hence the density of the vapour, rise as the temperature is raised (Fig. 4.3). At the same time, the density of the liquid decreases slightly as a result of its expansion. There comes a stage when the density of the vapour is equal to that of the remaining liquid and the surface between the two phases disappears. The temperature at which the surface disappears is the **critical temperature**, T_c, of the substance. We first encountered this property in Section 1.3d. The vapour pressure at the critical temperature is called the **critical pressure**, p_c. At and above the critical temperature, a single uniform phase called a **supercritical fluid** fills the container and an interface no

longer exists. That is, above the critical temperature, the liquid phase of the substance does not exist.

(b) Melting points and triple points

The temperature at which, under a specified pressure, the liquid and solid phases of a substance coexist in equilibrium is called the **melting temperature**. Because a substance melts at exactly the same temperature as it freezes, the melting temperature of a substance is the same as its **freezing temperature**. The freezing temperature when the pressure is 1 atm is called the **normal freezing point**, T_f, and its freezing point when the pressure is 1 bar is called the **standard freezing point**. The normal and standard freezing points are negligibly different for most purposes. The normal freezing point is also called the **normal melting point**.

There is a set of conditions under which three different phases of a substance (typically solid, liquid, and vapour) all simultaneously coexist in equilibrium. These conditions are represented by the **triple point**, a point at which the three phase boundaries meet. The temperature at the triple point is denoted T_3. The triple point of a pure substance is outside our control: it occurs at a single definite pressure and temperature characteristic of the substance. The triple point of water lies at 273.16 K and 611 Pa (6.11 mbar, 4.58 Torr), and the three phases of water (ice, liquid water, and water vapour) coexist in equilibrium at no other combination of pressure and temperature. This invariance of the triple point is the basis of its use in the definition of the thermodynamic temperature scale (Section 3.2c).

As we can see from Fig. 4.1, the triple point marks the lowest pressure at which a liquid phase of a substance can exist. If (as is common) the slope of the solid–liquid phase boundary is as shown in the diagram, then the triple point also marks the lowest temperature at which the liquid can exist; the critical temperature is the upper limit.
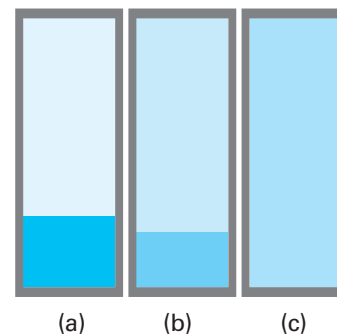
Fig. 4.3 (a) A liquid in equilibrium with its vapour. (b) When a liquid is heated in a sealed container, the density of the vapour phase increases and that of the liquid decreases slightly. There comes a stage, (c), at which the two densities are equal and the interface between the fluids disappears. This disappearance occurs at the critical temperature. The container needs to be strong: the critical temperature of water is 374°C and the vapour pressure is then 218 atm.

IMPACT ON CHEMICAL ENGINEERING AND TECHNOLOGY
I4.1 Supercritical fluids

Supercritical carbon dioxide, $scCO_2$, is the centre of attention for an increasing number of solvent-based processes. The critical temperature of CO_2, 304.2 K (31.0°C) and its critical pressure, 72.9 atm, are readily accessible, it is cheap, and it can readily be recycled. The density of $scCO_2$ at its critical point is 0.45 g cm^{-3}. However, the transport properties of any supercritical fluid depend strongly on its density, which in turn is sensitive to the pressure and temperature. For instance, densities may be adjusted from a gas-like 0.1 g cm^{-3} to a liquid-like 1.2 g cm^{-3}. A useful rule of thumb is that the solubility of a solute is an exponential function of the density of the supercritical fluid, so small increases in pressure, particularly close to the critical point, can have very large effects on solubility.

A great advantage of $scCO_2$ is that there are no noxious residues once the solvent has been allowed to evaporate, so, coupled with its low critical temperature, $scCO_2$ is ideally suited to food processing and the production of pharmaceuticals. It is used, for instance, to remove caffeine from coffee. The supercritical fluid is also increasingly being used for dry cleaning, which avoids the use of carcinogenic and environmentally deleterious chlorinated hydrocarbons.

Supercritical CO_2 has been used since the 1960s as a mobile phase in *supercritical fluid chromatography* (SFC), but it fell out of favour when the more convenient technique of high-performance liquid chromatography (HPLC) was introduced. However, interest in SFC has returned, and there are separations possible in SFC that cannot easily be achieved by HPLC, such as the separation of lipids and of phospholipids. Samples as small as 1 pg can be analysed. The essential advantage of SFC is that diffusion coefficients in supercritical fluids are an order of magnitude greater than in

liquids, so there is less resistance to the transfer of solutes through the column, with the result that separations may be effected rapidly or with high resolution.

The principal problem with $scCO_2$, though, is that the fluid is not a very good solvent and surfactants are needed to induce many potentially interesting solutes to dissolve. Indeed, $scCO_2$-based dry cleaning depends on the availability of cheap surfactants; so too does the use of $scCO_2$ as a solvent for homogeneous catalysts, such as metal complexes. There appear to be two principal approaches to solving the solubilization problem. One solution is to use fluorinated and siloxane-based polymeric stabilizers, which allow polymerization reactions to proceed in $scCO_2$. The disadvantage of these stabilizers for commercial use is their great expense. An alternative and much cheaper approach is poly(ether-carbonate) copolymers. The copolymers can be made more soluble in $scCO_2$ by adjusting the ratio of ether and carbonate groups.

The critical temperature of water is 374°C and its pressure is 218 atm. The conditions for using scH_2O are therefore much more demanding than for $scCO_2$ and the properties of the fluid are highly sensitive to pressure. Thus, as the density of scH_2O decreases, the characteristics of a solution change from those of an aqueous solution through those of a non-aqueous solution and eventually to those of a gaseous solution. One consequence is that reaction mechanisms may change from those involving ions to those involving radicals.

4.3 Three typical phase diagrams

We shall now see how these general features appear in the phase diagrams of pure substances.

(a) Carbon dioxide

The phase diagram for carbon dioxide is shown in Fig. 4.4. The features to notice include the positive slope of the solid–liquid boundary (the direction of this line is characteristic of most substances), which indicates that the melting temperature of solid carbon dioxide rises as the pressure is increased. Notice also that, as the triple point lies above 1 atm, the liquid cannot exist at normal atmospheric pressures whatever the temperature, and the solid sublimes when left in the open (hence the name 'dry ice'). To obtain the liquid, it is necessary to exert a pressure of at least 5.11 atm. Cylinders of carbon dioxide generally contain the liquid or compressed gas; at 25°C that implies a vapour pressure of 67 atm if both gas and liquid are present in equilibrium. When the gas squirts through the throttle it cools by the Joule–Thomson effect, so when it emerges into a region where the pressure is only 1 atm, it condenses into a finely divided snow-like solid.

(b) Water

Figure 4.5 is the phase diagram for water. The liquid–vapour boundary in the phase diagram summarizes how the vapour pressure of liquid water varies with temperature. It also summarizes how the boiling temperature varies with pressure: we simply read off the temperature at which the vapour pressure is equal to the prevailing atmospheric pressure. The solid–liquid boundary shows how the melting temperature varies with the pressure. Its very steep slope indicates that enormous pressures are needed to bring about significant changes. Notice that the line has a negative slope up to 2 kbar, which means that the melting temperature falls as the pressure is raised. The reason for this almost unique behaviour can be traced to the decrease in volume that occurs on melting, and hence it being more favourable for the solid to transform into the liquid as the pressure is raised. The decrease in volume is a result of the very
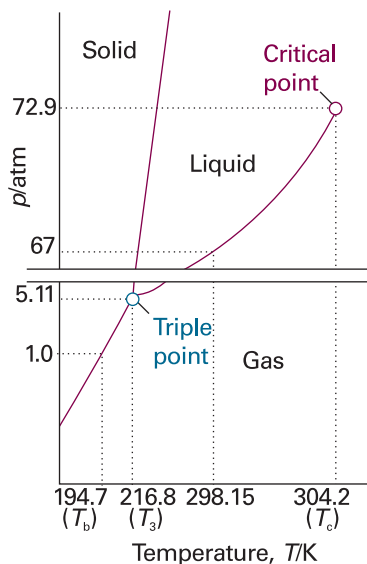
Fig. 4.4 The experimental phase diagram for carbon dioxide. Note that, as the triple point lies at pressures well above atmospheric, liquid carbon dioxide does not exist under normal conditions (a pressure of at least 5.11 atm must be applied).
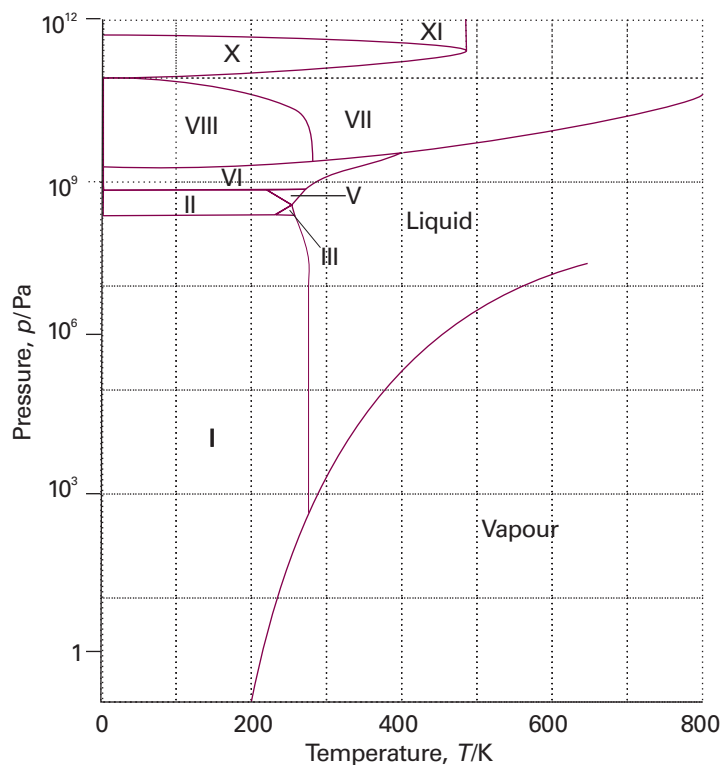
Fig. 4.5 The experimental phase diagram for water showing the different solid phases.

Fig. 4.6 A fragment of the structure of ice (ice-I). Each O atom is linked by two covalent bonds to H atoms and by two hydrogen bonds to a neighbouring O atom, in a tetrahedral array.

Fig. 4.7 The phase diagram for helium (^{4}He). The λ-line marks the conditions under which the two liquid phases are in equilibrium. Helium-II is the superfluid phase. Note that a pressure of over 20 bar must be exerted before solid helium can be obtained. The labels hcp and bcc denote different solid phases in which the atoms pack together differently: hcp denotes hexagonal closed packing and bcc denotes body-centred cubic (see Section 20.1 for a description of these structures).

open molecular structure of ice: as shown in Fig 4.6, the water molecules are held apart, as well as together, by the hydrogen bonds between them but the structure partially collapses on melting and the liquid is denser than the solid.

Figure 4.5 shows that water has one liquid phase but many different solid phases other than ordinary ice ('ice I', shown in Fig. 4.5). Some of these phases melt at high temperatures. Ice VII, for instance, melts at 100°C but exists only above 25 kbar. Note that five more triple points occur in the diagram other than the one where vapour, liquid, and ice I coexist. Each one occurs at a definite pressure and temperature that cannot be changed. The solid phases of ice differ in the arrangement of the water molecules: under the influence of very high pressures, hydrogen bonds buckle and the H_2O molecules adopt different arrangements. These **polymorphs**, or different solid phases, of ice may be responsible for the advance of glaciers, for ice at the bottom of glaciers experiences very high pressures where it rests on jagged rocks.

(c) Helium

Figure 4.7 shows the phase diagram of helium. Helium behaves unusually at low temperatures. For instance, the solid and gas phases of helium are never in equilibrium however low the temperature: the atoms are so light that they vibrate with a large-amplitude motion even at very low temperatures and the solid simply shakes itself apart. Solid helium can be obtained, but only by holding the atoms together by applying pressure.

When considering helium at low temperatures it is necessary to distinguish between the isotopes ^{3}He and ^{4}He. Pure helium-4 has two liquid phases. The phase marked He-I in the diagram behaves like a normal liquid; the other phase, He-II, is a **superfluid**;
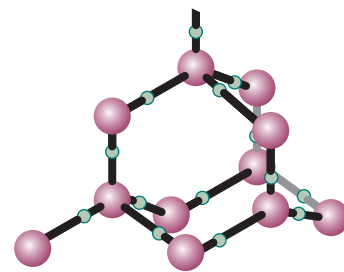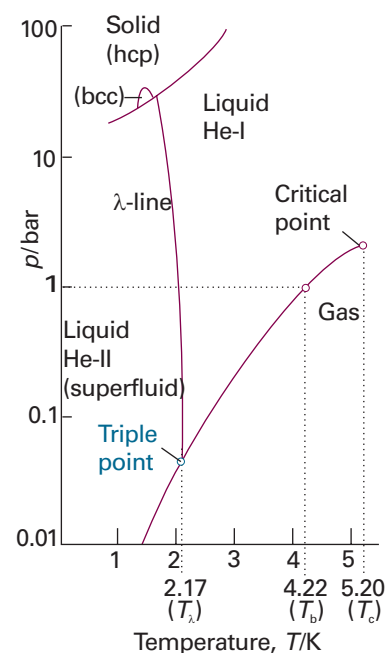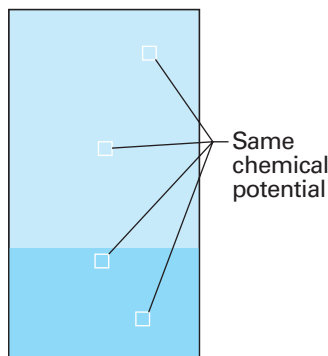
Fig. 4.8 When two or more phases are in equilibrium, the chemical potential of a substance (and, in a mixture, a component) is the same in each phase and is the same at all points in each phase.

it is so called because it flows without viscosity.[1] Provided we discount the liquid crystalline substances discussed in Section 6.6, helium is the only known substance with a liquid–liquid boundary, shown as the **λ-line** (lambda line) in Fig. 4.7. The phase diagram of helium-3 differs from the phase diagram of helium-4, but it also possesses a superfluid phase. Helium-3 is unusual in that the entropy of the liquid is lower than that of the solid, and melting is exothermic.

Phase stability and phase transitions

We shall now see how thermodynamic considerations can account for the features of the phase diagrams we have just described. All our considerations will be based on the Gibbs energy of a substance, and in particular on its molar Gibbs energy, G_m. In fact, this quantity will play such an important role in this chapter and the rest of the text that we give it a special name and symbol, the **chemical potential**, μ (mu). For a one-component system, 'molar Gibbs energy' and 'chemical potential' are synonyms, so $\mu = G_m$, but in Chapter 5 we shall see that chemical potential has a broader significance and a more general definition. The name 'chemical potential' is also instructive: as we develop the concept, we shall see that μ is a measure of the potential that a substance has for undergoing change in a system. In this chapter, it reflects the potential of a substance to undergo physical change. In Chapter 7 we shall see that μ is the potential of a substance to undergo chemical change.

4.4 The thermodynamic criterion of equilibrium

We base our discussion on the following consequence of the Second Law: *at equilibrium, the chemical potential of a substance is the same throughout a sample, regardless of how many phases are present.* When the liquid and solid phases of a substance are in equilibrium, the chemical potential of the substance is the same throughout the system (Fig. 4.8).

To see the validity of this remark, consider a system in which the chemical potential of a substance is μ_1 at one location and μ_2 at another location. The locations may be in the same or in different phases. When an amount dn of the substance is transferred from one location to the other, the Gibbs energy of the system changes by $-\mu_1 dn$ when material is removed from location 1, and it changes by $+\mu_2 dn$ when that material is added to location 2. The overall change is therefore $dG = (\mu_2 - \mu_1)dn$. If the chemical potential at location 1 is higher than that at location 2, the transfer is accompanied by a decrease in G, and so has a spontaneous tendency to occur. Only if $\mu_1 = \mu_2$ is there no change in G, and only then is the system at equilibrium. We conclude that the transition temperature, T_{trs}, is the temperature at which the chemical potentials of two phases are equal.

4.5 The dependence of stability on the conditions

At low temperatures and provided the pressure is not too low, the solid phase of a substance has the lowest chemical potential and is therefore the most stable phase. However, the chemical potentials of different phases change with temperature in different ways, and above a certain temperature the chemical potential of another phase (perhaps another solid phase, a liquid, or a gas) may turn out to be the lowest. When that happens, a transition to the second phase is spontaneous and occurs if it is kinetically feasible to do so.

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[1] Recent work has suggested that water may also have a superfluid liquid phase.

(a) The temperature dependence of phase stability

The temperature dependence of the Gibbs energy is expressed in terms of the entropy of the system by eqn 3.50 ($(\partial G/\partial T)_p = -S$). Because the chemical potential of a pure substance is just another name for its molar Gibbs energy, it follows that

$$\left(\frac{\partial \mu}{\partial T}\right)_p = -S_m \tag{4.1}$$

This relation shows that, as the temperature is raised, the chemical potential of a pure substance decreases: $S_m > 0$ for all substances, so the slope of a plot of μ against T is negative.

Equation 4.1 implies that the slope of a plot of μ against temperature is steeper for gases than for liquids, because $S_m(g) > S_m(l)$. The slope is also steeper for a liquid than the corresponding solid, because $S_m(l) > S_m(s)$ almost always. These features are illustrated in Fig. 4.9. The steep negative slope of $\mu(l)$ results in its falling below $\mu(s)$ when the temperature is high enough, and then the liquid becomes the stable phase: the solid melts. The chemical potential of the gas phase plunges steeply downwards as the temperature is raised (because the molar entropy of the vapour is so high), and there comes a temperature at which it lies lowest. Then the gas is the stable phase and vaporization is spontaneous.

(b) The response of melting to applied pressure

Most substances melt at a higher temperature when subjected to pressure. It is as though the pressure is preventing the formation of the less dense liquid phase. Exceptions to this behaviour include water, for which the liquid is denser than the solid. Application of pressure to water encourages the formation of the liquid phase. That is, water freezes at a lower temperature when it is under pressure.

We can rationalize the response of melting temperatures to pressure as follows. The variation of the chemical potential with pressure is expressed (from the second of eqn 3.50) by

$$\left(\frac{\partial \mu}{\partial p}\right)_T = V_m \tag{4.2}$$

This equation shows that the slope of a plot of chemical potential against pressure is equal to the molar volume of the substance. An increase in pressure raises the chemical potential of any pure substance (because $V_m > 0$). In most cases, $V_m(l) > V_m(s)$ and the equation predicts that an increase in pressure increases the chemical potential of the liquid more than that of the solid. As shown in Fig. 4.10a, the effect of pressure in such
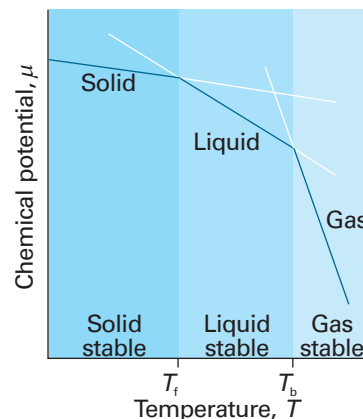
Fig. 4.9 The schematic temperature dependence of the chemical potential of the solid, liquid, and gas phases of a substance (in practice, the lines are curved). The phase with the lowest chemical potential at a specified temperature is the most stable one at that temperature. The transition temperatures, the melting and boiling temperatures (T_f and T_b, respectively), are the temperatures at which the chemical potentials of the two phases are equal.
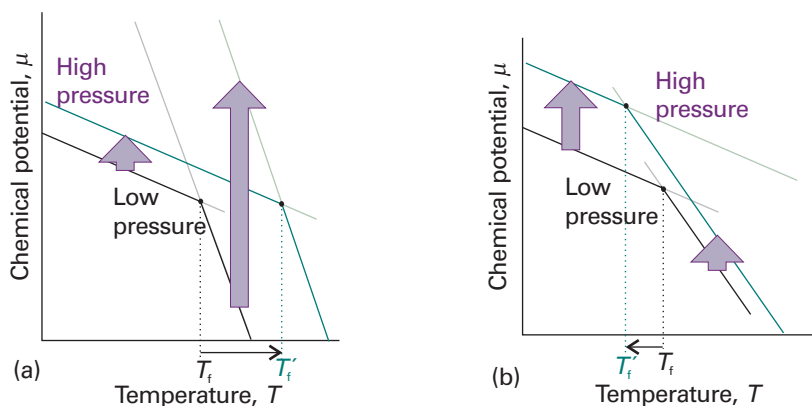
Fig. 4.10 The pressure dependence of the chemical potential of a substance depends on the molar volume of the phase. The lines show schematically the effect of increasing pressure on the chemical potential of the solid and liquid phases (in practice, the lines are curved), and the corresponding effects on the freezing temperatures. (a) In this case the molar volume of the solid is smaller than that of the liquid and $\mu(s)$ increases less than $\mu(l)$. As a result, the freezing temperature rises. (b) Here the molar volume is greater for the solid than the liquid (as for water), $\mu(s)$ increases more strongly than $\mu(l)$, and the freezing temperature is lowered.

a case is to raise the melting temperature slightly. For water, however, $V_m(l) < V_m(s)$, and an increase in pressure increases the chemical potential of the solid more than that of the liquid. In this case, the melting temperature is lowered slightly (Fig. 4.10b).

Example 4.1 *Assessing the effect of pressure on the chemical potential*

Calculate the effect on the chemical potentials of ice and water of increasing the pressure from 1.00 bar to 2.00 bar at 0°C. The density of ice is 0.917 g cm^{-3} and that of liquid water is 0.999 g cm^{-3} under these conditions.

Method From eqn 4.2, we know that the change in chemical potential of an incompressible substance when the pressure is changed by Δp is $\Delta\mu = V_m\Delta p$. Therefore, to answer the question, we need to know the molar volumes of the two phases of water. These values are obtained from the mass density, ρ, and the molar mass, M, by using $V_m = M/\rho$. We therefore use the expression $\Delta\mu = M\Delta p/\rho$.

**Answer** The molar mass of water is 18.02 g mol^{-1} (1.802×10^{-2} kg mol^{-1}); therefore,

$$\Delta\mu(\text{ice}) = \frac{(1.802 \times 10^{-2}\text{ kg mol}^{-1}) \times (1.00 \times 10^5\text{ Pa})}{917\text{ kg m}^{-3}} = +1.97\text{ J mol}^{-1}$$

$$\Delta\mu(\text{water}) = \frac{(1.802 \times 10^{-2}\text{ kg mol}^{-1}) \times (1.00 \times 10^5\text{ Pa})}{999\text{ kg m}^{-3}} = +1.80\text{ J mol}^{-1}$$

We interpret the numerical results as follows: the chemical potential of ice rises more sharply than that of water, so if they are initially in equilibrium at 1 bar, then there will be a tendency for the ice to melt at 2 bar.

Self-test 4.1 Calculate the effect of an increase in pressure of 1.00 bar on the liquid and solid phases of carbon dioxide (of molar mass 44.0 g mol^{-1}) in equilibrium with densities 2.35 g cm^{-3} and 2.50 g cm^{-3}, respectively.

[$\Delta\mu(l) = +1.87$ J mol^{-1}, $\Delta\mu(s) = +1.76$ J mol^{-1}; solid forms]
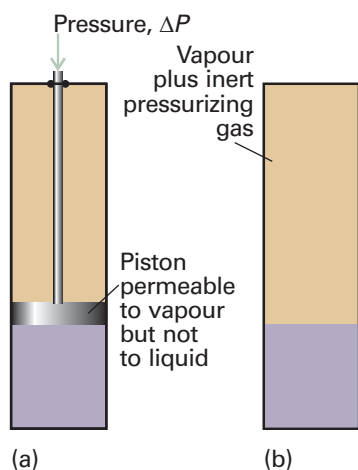
Fig. 4.11 Pressure may be applied to a condensed phases either (a) by compressing the condensed phase or (b) by subjecting it to an inert pressurizing gas. When pressure is applied, the vapour pressure of the condensed phase increases.

(c) The effect of applied pressure on vapour pressure

When pressure is applied to a condensed phase, its vapour pressure rises: in effect, molecules are squeezed out of the phase and escape as a gas. Pressure can be exerted on the condensed phases mechanically or by subjecting it to the applied pressure of an inert gas (Fig. 4.11); in the latter case, the vapour pressure is the partial pressure of the vapour in equilibrium with the condensed phase, and we speak of the **partial vapour pressure** of the substance. One complication (which we ignore here) is that, if the condensed phase is a liquid, then the pressurizing gas might dissolve and change the properties of the liquid. Another complication is that the gas phase molecules might attract molecules out of the liquid by the process of **gas solvation**, the attachment of molecules to gas phase species.

As shown in the following *Justification*, the quantitative relation between the vapour pressure, p, when a pressure ΔP is applied and the vapour pressure, $p^\star$, of the liquid in the absence of an additional pressure is

$$p = p^\star e^{V_m(l)\Delta P/RT} \tag{4.3}$$

This equation shows how the vapour pressure increases when the pressure acting on the condensed phase is increased.

Justification 4.1 *The vapour pressure of a pressurized liquid*

We calculate the vapour pressure of a pressurized liquid by using the fact that at equilibrium the chemical potentials of the liquid and its vapour are equal: $\mu(l) = \mu(g)$. It follows that, for any change that preserves equilibrium, the resulting change in $\mu(l)$ must be equal to the change in $\mu(g)$; therefore, we can write $d\mu(g) = d\mu(l)$. When the pressure P on the liquid is increased by dP, the chemical potential of the liquid changes by $d\mu(l) = V_m(l)dP$. The chemical potential of the vapour changes by $d\mu(g) = V_m(g)dp$ where dp is the change in the vapour pressure we are trying to find. If we treat the vapour as a perfect gas, the molar volume can be replaced by $V_m(g) = RT/p$, and we obtain

$$d\mu(g) = \frac{RTdp}{p}$$

Next, we equate the changes in chemical potentials of the vapour and the liquid:

$$\frac{RTdp}{p} = V_m(l)dP$$

We can integrate this expression once we know the limits of integration.

When there is no additional pressure acting on the liquid, P (the pressure experienced by the liquid) is equal to the normal vapour pressure p^*, so when $P = p^*$, $p = p^*$ too. When there is an additional pressure ΔP on the liquid, with the result that $P = p + \Delta P$, the vapour pressure is p (the value we want to find). Provided the effect of pressure on the vapour pressure is small (as will turn out to be the case) a good approximation is to replace the p in $p + \Delta P$ by p^* itself, and to set the upper limit of the integral to $p^* + \Delta P$. The integrations required are therefore as follows:

$$RT \int_{p^*}^{p} \frac{dp}{p} = \int_{p^*}^{p^* + \Delta P} V_m(l)dP$$

We now divide both sides by RT and assume that the molar volume of the liquid is the same throughout the small range of pressures involved:

$$\int_{p^*}^{p} \frac{dp}{p} = \frac{V_m(l)}{RT} \int_{p^*}^{p^* + \Delta P} dP$$

Then both integrations are straightforward, and lead to

$$\ln \frac{p}{p^*} = \frac{V_m(l)}{RT} \Delta P$$

which rearranges to eqn 4.3 because $e^{\ln x} = x$.

Illustration 4.1 *The effect of applied pressure on the vapour pressure of liquid water*

For water, which has density 0.997 g cm^{-3} at 25°C and therefore molar volume 18.1 cm^3 mol^{-1}, when the pressure is increased by 10 bar (that is, $\Delta P = 1.0 \times 10^5$ Pa)

$$\frac{V_m(l)\Delta P}{RT} = \frac{(1.81 \times 10^{-5}\ m^3\ mol^{-1}) \times (1.0 \times 10^6\ Pa)}{(8.3145\ J\ K^{-1}\ mol^{-1}) \times (298\ K)} = \frac{1.81 \times 1.0 \times 10}{8.3145 \times 298}$$

where we have used 1 J = 1 Pa m^3. It follows that $p = 1.0073p^*$, an increase of 0.73 per cent.

Self-test 4.2 Calculate the effect of an increase in pressure of 100 bar on the vapour pressure of benzene at 25°C, which has density 0.879 g cm^{-3}.   [43 per cent]
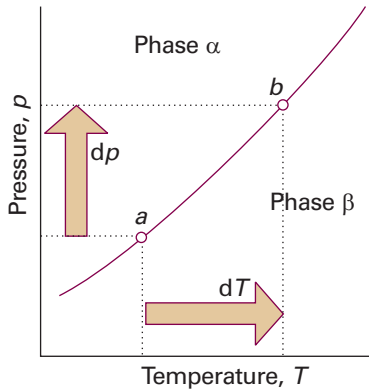
Fig. 4.12 When pressure is applied to a system in which two phases are in equilibrium (at a), the equilibrium is disturbed. It can be restored by changing the temperature, so moving the state of the system to b. It follows that there is a relation between dp and dT that ensures that the system remains in equilibrium as either variable is changed.
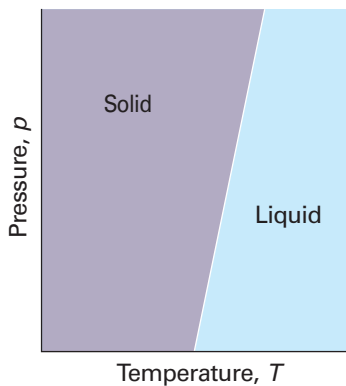
4.6 The location of phase boundaries

We can find the precise locations of the phase boundaries—the pressures and temperatures at which two phases can coexist—by making use of the fact that, when two phases are in equilibrium, their chemical potentials must be equal. Therefore, where the phases α and β are in equilibrium,

$$\mu_\alpha(p,T) = \mu_\beta(p,T) \tag{4.4}$$

By solving this equation for p in terms of T, we get an equation for the phase boundary.

(a) The slopes of the phase boundaries

It turns out to be simplest to discuss the phase boundaries in terms of their slopes, dp/dT. Let p and T be changed infinitesimally, but in such a way that the two phases α and β remain in equilibrium. The chemical potentials of the phases are initially equal (the two phases are in equilibrium). They remain equal when the conditions are changed to another point on the phase boundary, where the two phases continue to be in equilibrium (Fig. 4.12). Therefore, the changes in the chemical potentials of the two phases must be equal and we can write $d\mu_\alpha = d\mu_\beta$. Because, from eqn 3.49 ($dG = Vdp - SdT$), we know that $d\mu = -S_m dT + V_m dp$ for each phase, it follows that

$$-S_{\alpha,m}dT + V_{\alpha,m}dp = -S_{\beta,m}dT + V_{\beta,m}dp$$

where $S_{\alpha,m}$ and $S_{\beta,m}$ are the molar entropies of the phases and $V_{\alpha,m}$ and $V_{\beta,m}$ are their molar volumes. Hence

$$(V_{\beta,m} - V_{\alpha,m})dp = (S_{\beta,m} - S_{\alpha,m})dT \tag{4.5}$$

which rearranges into the **Clapeyron equation**:

$$\frac{dp}{dT} = \frac{\Delta_{trs}S}{\Delta_{trs}V} \tag{4.6}$$

In this expression $\Delta_{trs}S = S_{\beta,m} - S_{\alpha,m}$ and $\Delta_{trs}V = V_{\beta,m} - V_{\alpha,m}$ are the entropy and volume of transition, respectively. The Clapeyron equation is an exact expression for the slope of the phase boundary and applies to any phase equilibrium of any pure substance. It implies that we can use thermodynamic data to predict the appearance of phase diagrams and to understand their form. A more practical application is to the prediction of the response of freezing and boiling points to the application of pressure.

(b) The solid–liquid boundary

Melting (fusion) is accompanied by a molar enthalpy change $\Delta_{fus}H$ and occurs at a temperature T. The molar entropy of melting at T is therefore $\Delta_{fus}H/T$ (Section 3.3), and the Clapeyron equation becomes

$$\frac{dp}{dT} = \frac{\Delta_{fus}H}{T\Delta_{fus}V} \tag{4.7}$$

where $\Delta_{fus}V$ is the change in molar volume that occurs on melting. The enthalpy of melting is positive (the only exception is helium-3) and the volume change is usually positive and always small. Consequently, the slope dp/dT is steep and usually positive (Fig. 4.13).

We can obtain the formula for the phase boundary by integrating dp/dT, assuming that $\Delta_{fus}H$ and $\Delta_{fus}V$ change so little with temperature and pressure that they can be treated as constant. If the melting temperature is T^* when the pressure is p^*, and T when the pressure is p, the integration required is

Fig. 4.13 A typical solid–liquid phase boundary slopes steeply upwards. This slope implies that, as the pressure is raised, the melting temperature rises. Most substances behave in this way.

$$\int_{p^*}^{p} dp = \frac{\Delta_{fus}H}{\Delta_{fus}V} \int_{T^*}^{T} \frac{dT}{T}$$

Therefore, the approximate equation of the solid–liquid boundary is

$$p \approx p^* + \frac{\Delta_{fus}H}{\Delta_{fus}V} \ln \frac{T}{T^*} \qquad (4.8)$$

This equation was originally obtained by yet another Thomson—James, the brother of William, Lord Kelvin. When T is close to T^*, the logarithm can be approximated by using

$$\ln \frac{T}{T^*} = \ln\left(1 + \frac{T - T^*}{T^*}\right) \approx \frac{T - T^*}{T^*}$$

therefore,

$$p \approx p^* + \frac{\Delta_{fus}H}{T^*\Delta_{fus}V}(T - T^*) \qquad (4.9)$$

This expression is the equation of a steep straight line when p is plotted against T (as in Fig. 4.13).

(c) The liquid–vapour boundary

The entropy of vaporization at a temperature T is equal to $\Delta_{vap}H/T$; the Clapeyron equation for the liquid–vapour boundary is therefore

$$\frac{dp}{dT} = \frac{\Delta_{vap}H}{T\Delta_{vap}V} \qquad (4.10)$$

The enthalpy of vaporization is positive; $\Delta_{vap}V$ is large and positive. Therefore, dp/dT is positive, but it is much smaller than for the solid–liquid boundary. It follows that dT/dp is large, and hence that the boiling temperature is more responsive to pressure than the freezing temperature.

Example 4.2 *Estimating the effect of pressure on the boiling temperature*

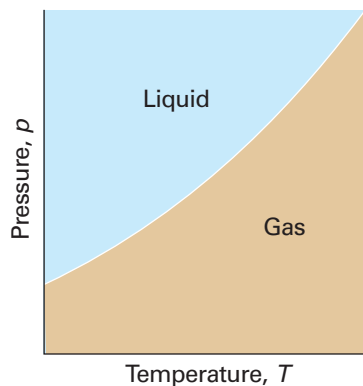Estimate the typical size of the effect of increasing pressure on the boiling point of a liquid.

Method To use eqn 4.10 we need to estimate the right-hand side. At the boiling point, the term $\Delta_{vap}H/T$ is Trouton's constant (Section 3.3b). Because the molar volume of a gas is so much greater than the molar volume of a liquid, we can write

$$\Delta_{vap}V = V_m(g) - V_m(l) \approx V_m(g)$$

and take for $V_m(g)$ the molar volume of a perfect gas (at low pressures, at least).

Answer Trouton's constant has the value 85 J K^{-1} mol^{-1}. The molar volume of a perfect gas is about 25 dm^3 mol^{-1} at 1 atm and near but above room temperature. Therefore,

$$\frac{dp}{dT} \approx \frac{85 \text{ J K}^{-1} \text{ mol}^{-1}}{2.5 \times 10^{-2} \text{ m}^3 \text{ mol}^{-1}} = 3.4 \times 10^3 \text{ Pa K}^{-1}$$

Comment 4.2

Calculations involving natural logarithms often become simpler if we note that, provided $-1 < x < 1$, $\ln(1+x) = x - \frac{1}{2}x^2 + \frac{1}{3}x^3 \cdots$. If $x \ll 1$, a good approximation is $\ln(1+x) \approx x$.

Fig. 4.14 A typical liquid–vapour phase boundary. The boundary can be regarded as a plot of the vapour pressure against the temperature. Note that, in some depictions of phase diagrams in which a logarithmic pressure scale is used, the phase boundary has the opposite curvature (see Fig. 4.7). This phase boundary terminates at the critical point (not shown).

We have used $1\,J = 1\,Pa\,m^3$. This value corresponds to 0.034 atm K^{-1}, and hence to $dT/dp = 29$ K atm^{-1}. Therefore, a change of pressure of +0.1 atm can be expected to change a boiling temperature by about +3 K.

Self-test 4.3 Estimate dT/dp for water at its normal boiling point using the information in Table 3.2 and $V_m(g) = RT/p$.   [28 K atm^{-1}]

Because the molar volume of a gas is so much greater than the molar volume of a liquid, we can write $\Delta_{vap}V \approx V_m(g)$ (as in *Example 4.2*). Moreover, if the gas behaves perfectly, $V_m(g) = RT/p$. These two approximations turn the exact Clapeyron equation into

$$\frac{dp}{dT} = \frac{\Delta_{vap}H}{T(RT/p)}$$

which rearranges into the **Clausius–Clapeyron equation** for the variation of vapour pressure with temperature:

$$\frac{d\ln p}{dT} = \frac{\Delta_{vap}H}{RT^2} \qquad (4.11)°$$

(We have used $dx/x = d\ln x$.) Like the Clapeyron equation, the Clausius–Clapeyron equation is important for understanding the appearance of phase diagrams, particularly the location and shape of the liquid–vapour and solid–vapour phase boundaries. It lets us predict how the vapour pressure varies with temperature and how the boiling temperature varies with pressure. For instance, if we also assume that the enthalpy of vaporization is independent of temperature, this equation can be integrated as follows:

$$\int_{\ln p^\star}^{\ln p} d\ln p = \frac{\Delta_{vap}H}{R}\int_{T^\star}^{T}\frac{dT}{T^2} = -\frac{\Delta_{vap}H}{R}\left(\frac{1}{T} - \frac{1}{T^\star}\right)$$

where $p^\star$ is the vapour pressure when the temperature is $T^\star$ and p the vapour pressure when the temperature is T. Therefore, because the integral on the left evaluates to $\ln(p/p^\star)$, the two vapour pressures are related by

$$p = p^\star e^{-\chi} \qquad \chi = \frac{\Delta_{vap}H}{R}\left(\frac{1}{T} - \frac{1}{T^\star}\right) \qquad (4.12)°$$

Equation 4.12 is plotted as the liquid–vapour boundary in Fig. 4.14. The line does not extend beyond the critical temperature T_c, because above this temperature the liquid does not exist.

Illustration 4.2 *The effect of temperature on the vapour pressure of a liquid*

Equation 4.12 can be used to estimate the vapour pressure of a liquid at any temperature from its normal boiling point, the temperature at which the vapour pressure is 1.00 atm (101 kPa). Thus, because the normal boiling point of benzene is 80°C (353 K) and (from Table 2.3), $\Delta_{vap}H^\ominus = 30.8$ kJ mol^{-1}, to calculate the vapour pressure at 20°C (293 K), we write

$$\chi = \frac{3.08 \times 10^4\,J\,mol^{-1}}{8.3145\,J\,K^{-1}\,mol^{-1}}\left(\frac{1}{293\,K} - \frac{1}{353\,K}\right) = \frac{3.08 \times 10^4}{8.3145}\left(\frac{1}{293} - \frac{1}{353}\right)$$

and substitute this value into eqn 4.12 with $p^* = 101$ kPa. The result is 12 kPa. The experimental value is 10 kPa.

A note on good practice Because exponential functions are so sensitive, it is good practice to carry out numerical calculations like this without evaluating the intermediate steps and using rounded values.

(d) The solid–vapour boundary

The only difference between this case and the last is the replacement of the enthalpy of vaporization by the enthalpy of sublimation, $\Delta_{sub}H$. Because the enthalpy of sublimation is greater than the enthalpy of vaporization ($\Delta_{sub}H = \Delta_{fus}H + \Delta_{vap}H$), the equation predicts a steeper slope for the sublimation curve than for the vaporization curve at similar temperatures, which is near where they meet at the triple point (Fig. 4.15).

4.7 The Ehrenfest classification of phase transitions

There are many different types of phase transition, including the familiar examples of fusion and vaporization and the less familiar examples of solid–solid, conducting–superconducting, and fluid–superfluid transitions. We shall now see that it is possible to use thermodynamic properties of substances, and in particular the behaviour of the chemical potential, to classify phase transitions into different types. The classification scheme was originally proposed by Paul Ehrenfest, and is known as the **Ehrenfest classification**.

Many familiar phase transitions, like fusion and vaporization, are accompanied by changes of enthalpy and volume. These changes have implications for the slopes of the chemical potentials of the phases at either side of the phase transition. Thus, at the transition from a phase α to another phase β,

$$\left(\frac{\partial \mu_\beta}{\partial p}\right)_T - \left(\frac{\partial \mu_\alpha}{\partial p}\right)_T = V_{\beta,m} - V_{\alpha,m} = \Delta_{trs}V$$

$$\left(\frac{\partial \mu_\beta}{\partial T}\right)_p - \left(\frac{\partial \mu_\alpha}{\partial T}\right)_p = -S_{\beta,m} + S_{\alpha,m} = \Delta_{trs}S = \frac{\Delta_{trs}H}{T_{trs}}$$

(4.13)

Because $\Delta_{trs}V$ and $\Delta_{trs}H$ are non-zero for melting and vaporization, it follows that for such transitions the slopes of the chemical potential plotted against either pressure or temperature are different on either side of the transition (Fig. 4.16a). In other words, the first derivatives of the chemical potentials with respect to pressure and temperature are discontinuous at the transition.

A transition for which the first derivative of the chemical potential with respect to temperature is discontinuous is classified as a **first-order phase transition**. The constant-pressure heat capacity, C_p, of a substance is the slope of a plot of the enthalpy with respect to temperature. At a first-order phase transition, H changes by a finite amount for an infinitesimal change of temperature. Therefore, at the transition the heat capacity is infinite. The physical reason is that heating drives the transition rather than raising the temperature. For example, boiling water stays at the same temperature even though heat is being supplied.
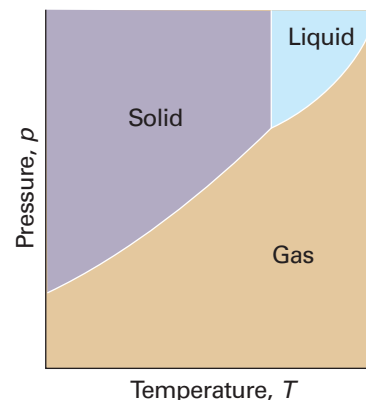

Fig. 4.15 Near the point where they coincide (at the triple point), the solid–gas boundary has a steeper slope than the liquid–gas boundary because the enthalpy of sublimation is greater than the enthalpy of vaporization and the temperatures that occur in the Clausius–Clapeyron equation for the slope have similar values.
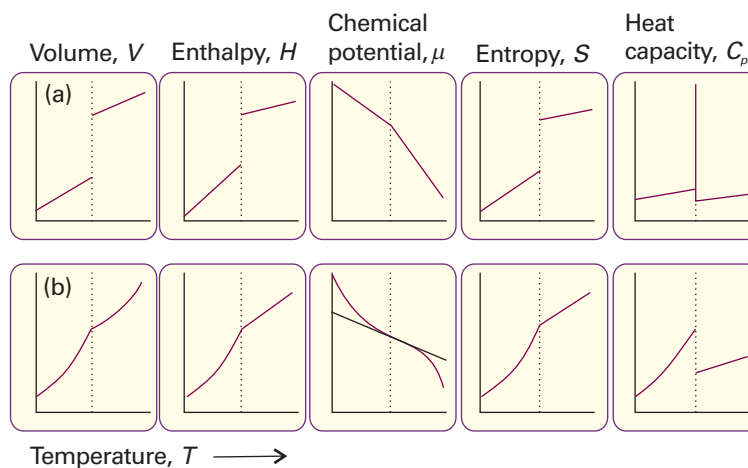
Fig. 4.16 The changes in thermodynamic properties accompanying (a) first-order and (b) second-order phase transitions.

A **second-order phase transition** in the Ehrenfest sense is one in which the first derivative of μ with respect to temperature is continuous but its second derivative is discontinuous. A continuous slope of μ (a graph with the same slope on either side of the transition) implies that the volume and entropy (and hence the enthalpy) do not change at the transition (Fig. 4.16b). The heat capacity is discontinuous at the transition but does not become infinite there. An example of a second-order transition is the conducting–superconducting transition in metals at low temperatures.[2]

The term **λ-transition** is applied to a phase transition that is not first-order yet the heat capacity becomes infinite at the transition temperature. Typically, the heat capacity of a system that shows such a transition begins to increase well before the transition (Fig. 4.17), and the shape of the heat capacity curve resembles the Greek letter lambda. This type of transition includes order–disorder transitions in alloys, the onset of ferromagnetism, and the fluid–superfluid transition of liquid helium.
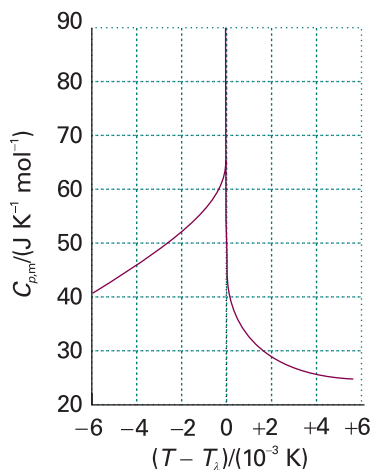

Fig. 4.17 The λ-curve for helium, where the heat capacity rises to infinity. The shape of this curve is the origin of the name λ-transition.

Molecular interpretation 4.1 *Second-order phase transitions and λ-transitions*

One type of second-order transition is associated with a change in symmetry of the crystal structure of a solid. Thus, suppose the arrangement of atoms in a solid is like that represented in Fig. 4.18a, with one dimension (technically, of the unit cell) longer than the other two, which are equal. Such a crystal structure is classified as tetragonal (see Section 20.1). Moreover, suppose the two shorter dimensions increase more than the long dimension when the temperature is raised. There may come a stage when the three dimensions become equal. At that point the crystal has cubic symmetry (Fig. 4.18b), and at higher temperatures it will expand equally in all three directions (because there is no longer any distinction between them). The tetragonal → cubic phase transition has occurred, but as it has not involved a discontinuity in the interaction energy between the atoms or the volume they occupy, the transition is not first-order.
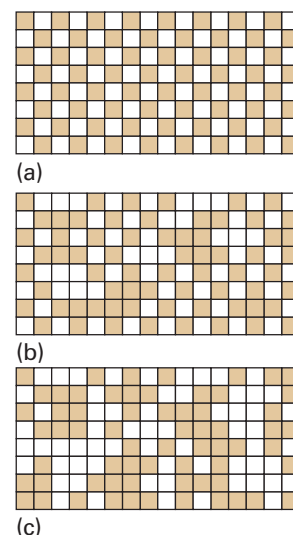
[2] A metallic conductor is a substance with an electrical conductivity that decreases as the temperature increases. A superconductor is a solid that conducts electricity without resistance. See Chapter 20 for more details.
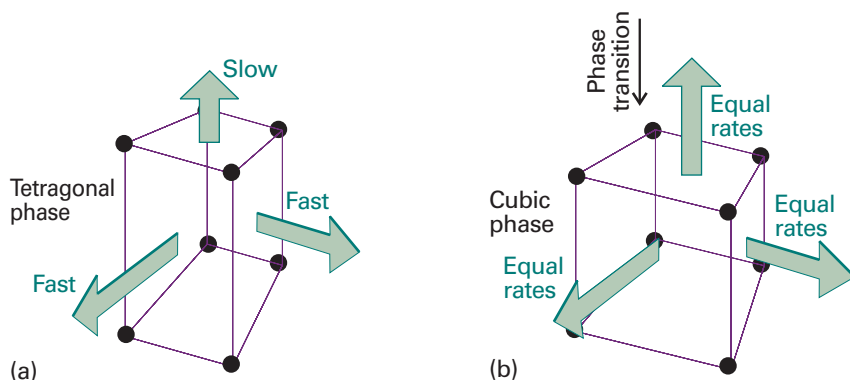
Fig. 4.18 One version of a second-order phase transition in which (a) a tetragonal phase expands more rapidly in two directions than a third, and hence becomes a cubic phase, which (b) expands uniformly in three directions as the temperature is raised. There is no rearrangement of atoms at the transition temperature, and hence no enthalpy of transition.

Fig. 4.19 An order–disorder transition. (a) At $T = 0$, there is perfect order, with different kinds of atoms occupying alternate sites. (b) As the temperature is increased, atoms exchange locations and islands of each kind of atom form in regions of the solid. Some of the original order survives. (c) At and above the transition temperature, the islands occur at random throughout the sample.

The order–disorder transition in β-brass (CuZn) is an example of a λ-transition. The low-temperature phase is an orderly array of alternating Cu and Zn atoms. The high-temperature phase is a random array of the atoms (Fig. 4.19). At $T = 0$ the order is perfect, but islands of disorder appear as the temperature is raised. The islands form because the transition is cooperative in the sense that, once two atoms have exchanged locations, it is easier for their neighbours to exchange their locations. The islands grow in extent, and merge throughout the crystal at the transition temperature (742 K). The heat capacity increases as the transition temperature is approached because the cooperative nature of the transition means that it is increasingly easy for the heat supplied to drive the phase transition rather than to be stored as thermal motion.

Checklist of key ideas

☐ 1. A phase is a form of matter that is uniform throughout in chemical composition and physical state.

☐ 2. A transition temperature is the temperature at which the two phases are in equilibrium.

☐ 3. A metastable phase is a thermodynamically unstable phase that persists because the transition is kinetically hindered.

☐ 4. A phase diagram is a diagram showing the regions of pressure and temperature at which its various phases are thermodynamically stable.

☐ 5. A phase boundary is a line separating the regions in a phase diagram showing the values of p and T at which two phases coexist in equilibrium.

☐ 6. The vapour pressure is the pressure of a vapour in equilibrium with the condensed phase.

☐ 7. Boiling is the condition of free vaporization throughout the liquid.

☐ 8. The boiling temperature is the temperature at which the vapour pressure of a liquid is equal to the external pressure.

☐ 9. The critical temperature is the temperature at which a liquid surface disappears and above which a liquid does not exist whatever the pressure. The critical pressure is the vapour pressure at the critical temperature.

☐ 10. A supercritical fluid is a dense fluid phase above the critical temperature.

☐ 11. The melting temperature (or freezing temperature) is the temperature at which, under a specified pressure, the liquid and solid phases of a substance coexist in equilibrium.

☐ 12. The triple point is a point on a phase diagram at which the three phase boundaries meet and all three phases are in mutual equilibrium.

☐ 13. The chemical potential μ of a pure substance is the molar Gibbs energy of the substance.

14. The chemical potential is uniform throughout a system at equilibrium.

15. The chemical potential varies with temperature as $(\partial\mu/\partial T)_p = -S_m$ and with pressure as $(\partial\mu/\partial p)_T = V_m$.

16. The vapour pressure in the presence of applied pressure is given by $p = p^{\star}\mathrm{e}^{V_m\Delta P/RT}$.

17. The temperature dependence of the vapour pressure is given by the Clapeyron equation, $\mathrm{d}p/\mathrm{d}T = \Delta_{trs}S/\Delta_{trs}V$.

18. The temperature dependence of the vapour pressure of a condensed phase is given by the Clausius–Clapeyron equation, $\mathrm{d}\ln p/\mathrm{d}T = \Delta_{vap}H/RT^2$.

19. The Ehrenfest classification is a classification of phase transitions based on the behaviour of the chemical potential.

Further reading

Articles and texts

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Sources of data and information[3]

T. Boublik, V. Fried, and E. Hála, *The vapor pressures of pure substances*. Elsevier, Amsterdam (1984).

R.C. Weast (ed.), *Handbook of chemistry and physics*, Vol. 81. CRC Press, Boca Raton (2004).

Discussion questions

4.1 Discuss the implications for phase stability of the variation of chemical potential with temperature and pressure.

4.2 Suggest a physical interpretation of the phenomena of superheating and supercooling.

4.3 Discuss what would be observed as a sample of water is taken along a path that encircles and is close to its critical point.

4.4 Use the phase diagram in Fig. 4.4 to state what would be observed when a sample of carbon dioxide, initially at 1.0 atm and 298 K, is subjected to the following cycle: (a) isobaric (constant–pressure) heating to 320 K, (b) isothermal compression to 100 atm, (c) isobaric cooling to 210 K, (d) isothermal decompression to 1.0 atm, (e) isobaric heating to 298 K.

4.5 The use of supercritical fluids for the extraction of a component from a complicated mixture is not confined to the decaffeination of coffee. Consult library and internet resources and prepare a discussion of the principles, advantages, disadvantages, and current uses of supercritical fluid extraction technology.

4.6 Explain the significance of the Clapeyron equation and of the Clausius–Clapeyron equation.

4.7 Distinguish between a first-order phase transition, a second-order phase transition, and a λ-transition at both molecular and macroscopic levels.

Exercises

4.1(a) The vapour pressure of dichloromethane at 24.1°C is 53.3 kPa and its enthalpy of vaporization is 28.7 kJ mol^{-1}. Estimate the temperature at which its vapour pressure is 70.0 kPa.

4.1(b) The vapour pressure of a substance at 20.0°C is 58.0 kPa and its enthalpy of vaporization is 32.7 kJ mol^{-1}. Estimate the temperature at which its vapour pressure is 66.0 kPa.

4.2(a) The molar volume of a certain solid is 161.0 cm^3 mol^{-1} at 1.00 atm and 350.75 K, its melting temperature. The molar volume of the liquid at this temperature and pressure is 163.3 cm^3 mol^{-1}. At 100 atm the melting temperature changes to 351.26 K. Calculate the enthalpy and entropy of fusion of the solid.

4.2(b) The molar volume of a certain solid is 142.0 cm^3 mol^{-1} at 1.00 atm and 427.15 K, its melting temperature. The molar volume of the liquid at this temperature and pressure is 152.6 cm^3 mol^{-1}. At 1.2 MPa the melting temperature changes to 429.26 K. Calculate the enthalpy and entropy of fusion of the solid.

4.3(a) The vapour pressure of a liquid in the temperature range 200 K to 260 K was found to fit the expression $\ln(p/\text{Torr}) = 16.255 - 2501.8/(T/\text{K})$. Calculate the enthalpy of vaporization of the liquid.

4.3(b) The vapour pressure of a liquid in the temperature range 200 K to 260 K was found to fit the expression $\ln(p/\text{Torr}) = 18.361 - 3036.8/(T/\text{K})$. Calculate the enthalpy of vaporization of the liquid.

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[3] See *Further reading* in Chapter 2 for additional sources of thermochemical data.

4.4(a) The vapour pressure of benzene between 10°C and 30°C fits the expression $\log(p/\mathrm{Torr}) = 7.960 - 1780/(T/\mathrm{K})$. Calculate (a) the enthalpy of vaporization and (b) the normal boiling point of benzene.

4.4(b) The vapour pressure of a liquid between 15°C and 35°C fits the expression $\log(p/\mathrm{Torr}) = 8.750 - 1625/(T/\mathrm{K})$. Calculate (a) the enthalpy of vaporization and (b) the normal boiling point of the liquid.

4.5(a) When benzene freezes at 5.5°C its density changes from 0.879 g cm^{-3} to 0.891 g cm^{-3}. Its enthalpy of fusion is 10.59 kJ mol^{-1}. Estimate the freezing point of benzene at 1000 atm.

4.5(b) When a certain liquid freezes at −3.65°C its density changes from 0.789 g cm^{-3} to 0.801 g cm^{-3}. Its enthalpy of fusion is 8.68 kJ mol^{-1}. Estimate the freezing point of the liquid at 100 MPa.

4.6(a) In July in Los Angeles, the incident sunlight at ground level has a power density of 1.2 kW m^{-2} at noon. A swimming pool of area 50 m^2 is directly exposed to the sun. What is the maximum rate of loss of water? Assume that all the radiant energy is absorbed.

4.6(b) Suppose the incident sunlight at ground level has a power density of 0.87 kW m^{-2} at noon. What is the maximum rate of loss of water from a lake of area 1.0 ha? (1 ha = 10^4 m^2.) Assume that all the radiant energy is absorbed.

4.7(a) An open vessel containing (a) water, (b) benzene, (c) mercury stands in a laboratory measuring 5.0 m × 5.0 m × 3.0 m at 25°C. What mass of each

substance will be found in the air if there is no ventilation? (The vapour pressures are (a) 3.2 kPa, (b) 13.1 kPa, (c) 0.23 Pa.)

4.7(b) On a cold, dry morning after a frost, the temperature was −5°C and the partial pressure of water in the atmosphere fell to 0.30 kPa. Will the frost sublime? What partial pressure of water would ensure that the frost remained?

4.8(a) Naphthalene, $C_{10}H_8$, melts at 80.2°C. If the vapour pressure of the liquid is 1.3 kPa at 85.8°C and 5.3 kPa at 119.3°C, use the Clausius–Clapeyron equation to calculate (a) the enthalpy of vaporization, (b) the normal boiling point, and (c) the enthalpy of vaporization at the boiling point.

4.8(b) The normal boiling point of hexane is 69.0°C. Estimate (a) its enthalpy of vaporization and (b) its vapour pressure at 25°C and 60°C.

4.9(a) Calculate the melting point of ice under a pressure of 50 bar. Assume that the density of ice under these conditions is approximately 0.92 g cm^{-3} and that of liquid water is 1.00 g cm^{-3}.

4.9(b) Calculate the melting point of ice under a pressure of 10 MPa. Assume that the density of ice under these conditions is approximately 0.915 g cm^{-3} and that of liquid water is 0.998 g cm^{-3}.

4.10(a) What fraction of the enthalpy of vaporization of water is spent on expanding the water vapour?

4.10(b) What fraction of the enthalpy of vaporization of ethanol is spent on expanding its vapour?

Problems*

Numerical problems

4.1 The temperature dependence of the vapour pressure of solid sulfur dioxide can be approximately represented by the relation $\log(p/\mathrm{Torr}) = 10.5916 - 1871.2/(T/\mathrm{K})$ and that of liquid sulfur dioxide by $\log(p/\mathrm{Torr}) = 8.3186 - 1425.7/(T/\mathrm{K})$. Estimate the temperature and pressure of the triple point of sulfur dioxide.

4.2 Prior to the discovery that freon-12 (CF_2Cl_2) was harmful to the Earth's ozone layer, it was frequently used as the dispersing agent in spray cans for hair spray, etc. Its enthalpy of vaporization at its normal boiling point of −29.2°C is 20.25 kJ mol^{-1}. Estimate the pressure that a can of hair spray using freon-12 had to withstand at 40°C, the temperature of a can that has been standing in sunlight. Assume that $\Delta_{vap}H$ is a constant over the temperature range involved and equal to its value at −29.2°C.

4.3 The enthalpy of vaporization of a certain liquid is found to be 14.4 kJ mol^{-1} at 180 K, its normal boiling point. The molar volumes of the liquid and the vapour at the boiling point are 115 cm^3 mol^{-1} and 14.5 dm^3 mol^{-1}, respectively. (a) Estimate dp/dT from the Clapeyron equation and (b) the percentage error in its value if the Clausius–Clapeyron equation is used instead.

4.4 Calculate the difference in slope of the chemical potential against temperature on either side of (a) the normal freezing point of water and (b) the normal boiling point of water. (c) By how much does the chemical potential of water supercooled to −5.0°C exceed that of ice at that temperature?

4.5 Calculate the difference in slope of the chemical potential against pressure on either side of (a) the normal freezing point of water and (b) the normal

boiling point of water. The densities of ice and water at 0°C are 0.917 g cm^{-3} and 1.000 g cm^{-3}, and those of water and water vapour at 100°C are 0.958 g cm^{-3} and 0.598 g dm^{-3}, respectively. By how much does the chemical potential of water vapour exceed that of liquid water at 1.2 atm and 100°C?

4.6 The enthalpy of fusion of mercury is 2.292 kJ mol^{-1}, and its normal freezing point is 234.3 K with a change in molar volume of +0.517 cm^3 mol^{-1} on melting. At what temperature will the bottom of a column of mercury (density 13.6 g cm^{-3}) of height 10.0 m be expected to freeze?

4.7 50.0 dm^3 of dry air was slowly bubbled through a thermally insulated beaker containing 250 g of water initially at 25°C. Calculate the final temperature. (The vapour pressure of water is approximately constant at 3.17 kPa throughout, and its heat capacity is 75.5 J K^{-1} mol^{-1}. Assume that the air is not heated or cooled and that water vapour is a perfect gas.)

4.8 The vapour pressure, p, of nitric acid varies with temperature as follows:

θ/°C	0	20	40	50	70	80	90	100
p/kPa	1.92	6.38	17.7	27.7	62.3	89.3	124.9	170.9

What are (a) the normal boiling point and (b) the enthalpy of vaporization of nitric acid?

4.9 The vapour pressure of the ketone carvone ($M = 150.2$ g mol^{-1}), a component of oil of spearmint, is as follows:

θ/°C	57.4	100.4	133.0	157.3	203.5	227.5
p/Torr	1.00	10.0	40.0	100	400	760

What are (a) the normal boiling point and (b) the enthalpy of vaporization of carvone?

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

4.10 Construct the phase diagram for benzene near its triple point at 36 Torr and 5.50°C using the following data: $\Delta_{fus}H = 10.6$ kJ mol^{-1}, $\Delta_{vap}H = 30.8$ kJ mol^{-1}, $\rho(s) = 0.891$ g cm^{-3}, $\rho(l) = 0.879$ g cm^{-3}.

4.11‡ In an investigation of thermophysical properties of toluene (R.D. Goodwin *J. Phys. Chem. Ref. Data* **18**, 1565 (1989)) presented expressions for two coexistence curves (phase boundaries). The solid–liquid coexistence curve is given by

$$p/\text{bar} = p_3/\text{bar} + 1000 \times (5.60 + 11.727x)x$$

where $x = T/T_3 - 1$ and the triple point pressure and temperature are $p_3 = 0.4362$ μbar and $T_3 = 178.15$ K. The liquid–vapour curve is given by:

$$\ln(p/\text{bar}) = -10.418/y + 21.157 - 15.996y + 14.015y^2 - 5.0120y^3 + 4.7224(1-y)^{1.70}$$

where $y = T/T_c = T/(593.95 \text{ K})$. (a) Plot the solid–liquid and liquid–vapour phase boundaries. (b) Estimate the standard melting point of toluene. (c) Estimate the standard boiling point of toluene. (d) Compute the standard enthalpy of vaporization of toluene, given that the molar volumes of the liquid and vapour at the normal boiling point are 0.12 dm^3 mol^{-1} and 30.3 dm^3 mol^{-1}, respectively.

4.12‡ In a study of the vapour pressure of chloromethane, A. Bah and N. Dupont-Pavlovsky (*J. Chem. Eng. Data* **40**, 869 (1995)) presented data for the vapour pressure over solid chloromethane at low temperatures. Some of that data is shown below:

T/K	145.94	147.96	149.93	151.94	153.97	154.94
p/Pa	13.07	18.49	25.99	36.76	50.86	59.56

Estimate the standard enthalpy of sublimation of chloromethane at 150 K. (Take the molar volume of the vapour to be that of a perfect gas, and that of the solid to be negligible.)

Theoretical problems

4.13 Show that, for a transition between two incompressible solid phases, ΔG is independent of the pressure.

4.14 The change in enthalpy is given by $dH = C_p dT + V dp$. The Clapeyron equation relates dp and dT at equilibrium, and so in combination the two equations can be used to find how the enthalpy changes along a phase boundary as the temperature changes and the two phases remain in equilibrium. Show that $d(\Delta H/T) = \Delta C_p \, d \ln T$.

4.15 In the 'gas saturation method' for the measurement of vapour pressure, a volume V of gas (as measured at a temperature T and a pressure p) is bubbled slowly through the liquid that is maintained at the temperature T, and a mass loss m is measured. Show that the vapour pressure, p, of the liquid is related to its molar mass, M, by $p = AmP/(1 + Am)$, where $A = RT/MPV$. The vapour pressure of geraniol ($M = 154.2$ g mol^{-1}), which is a component of oil of roses, was measured at 110°C. It was found that, when 5.00 dm^3 of nitrogen at 760 Torr was passed slowly through the heated liquid, the loss of mass was 0.32 g. Calculate the vapour pressure of geraniol.

4.16 Combine the barometric formula (stated in *Impact I1.1*) for the dependence of the pressure on altitude with the Clausius–Clapeyron equation, and predict how the boiling temperature of a liquid depends on the altitude and the ambient temperature. Take the mean ambient temperature as 20°C and predict the boiling temperature of water at 3000 m.

4.17 Figure 4.9 gives a schematic representation of how the chemical potentials of the solid, liquid, and gaseous phases of a substance vary with temperature. All have a negative slope, but it is unlikely that they are truly straight lines as indicated in the illustration. Derive an expression for the curvatures (specifically, the second derivatives with respect to temperature) of these lines. Is there a restriction on the curvature of these lines? Which state of matter shows the greatest curvature?

4.18 The Clapeyron equation does not apply to second-order phase transitions, but there are two analogous equations, the *Ehrenfest equations*, that do. They are:

$$\frac{dp}{dT} = \frac{\alpha_2 - \alpha_1}{\kappa_{T,2} - \kappa_{T,1}} \qquad \frac{dp}{dT} = \frac{C_{p,m2} - C_{p,m1}}{TV_m(\alpha_2 - \alpha_1)}$$

where α is the expansion coefficient, κ_T the isothermal compressibility, and the subscripts 1 and 2 refer to two different phases. Derive these two equations. Why does the Clapeyron equation not apply to second-order transitions?

4.19 For a first-order phase transition, to which the Clapeyron equation does apply, prove the relation

$$C_S = C_p - \frac{\alpha V \Delta_{trs} H}{\Delta_{trs} V}$$

where $C_S = (\partial q/\partial T)_S$ is the heat capacity along the coexistence curve of two phases.

Applications: to biology and engineering

4.20 Proteins are *polypeptides*, polymers of amino acids that can exist in ordered structures stabilized by a variety of molecular interactions. However, when certain conditions are changed, the compact structure of a polypeptide chain may collapse into a random coil. This structural change may be regarded as a phase transition occurring at a characteristic transition temperature, the *melting temperature*, T_m, which increases with the strength and number of intermolecular interactions in the chain. A thermodynamic treatment allows predictions to be made of the temperature T_m for the unfolding of a helical polypeptide held together by hydrogen bonds into a random coil. If a polypeptide has n amino acids, $n - 4$ hydrogen bonds are formed to form an α-helix, the most common type of helix in naturally occurring proteins (see Chapter 19). Because the first and last residues in the chain are free to move, $n - 2$ residues form the compact helix and have restricted motion. Based on these ideas, the molar Gibbs energy of unfolding of a polypeptide with $n \geq 5$ may be written as

$$\Delta G_m = (n-4)\Delta_{hb}H_m - (n-2)T\Delta_{hb}S_m$$

where $\Delta_{hb}H_m$ and $\Delta_{hb}S_m$ are, respectively, the molar enthalpy and entropy of dissociation of hydrogen bonds in the polypeptide. (a) Justify the form of the equation for the Gibbs energy of unfolding. That is, why are the enthalpy and entropy terms written as $(n-4)\Delta_{hb}H_m$ and $(n-2)\Delta_{hb}S_m$, respectively? (b) Show that T_m may be written as

$$T_m = \frac{(n-4)\Delta_{hb}H_m}{(n-2)\Delta_{hb}S_m}$$

(c) Plot $T_m/(\Delta_{hb}H_m/\Delta_{hb}S_m)$ for $5 \leq n \leq 20$. At what value of n does T_m change by less than 1% when n increases by one?

4.21‡ The use of supercritical fluids as mobile phases in SFC depends on their properties as nonpolar solvents. The solubility parameter, δ, is defined as $(\Delta U_{cohesive}/V_m)^{1/2}$, where $\Delta U_{cohesive}$ is the cohesive energy of the solvent, the energy per mole needed to increase the volume isothermally to an infinite value. Diethyl ether, carbon tetrachloride, and dioxane have solubility parameter ranges of 7–8, 8–9, and 10–11, respectively. (a) Derive a practical equation for the computation of the isotherms for the reduced internal energy change, $\Delta U_r(T_r, V_r)$ defined as

$$\Delta U_r(T_r, V_r) = \frac{U_r(T_r, V_r) - U_r(T_r, \infty)}{p_c V_c}$$

(b) Draw a graph of ΔU_r against p_r for the isotherms $T_r = 1, 1.2$, and 1.5 in the reduced pressure range for which $0.7 \leq V_r \leq 2$. (c) Draw a graph of δ against p_r for the carbon dioxide isotherms $T_r = 1$ and 1.5 in the reduced pressure range for which $1 \leq V_r \leq 3$. In what pressure range at $T_r = 1$ will carbon dioxide have

solvent properties similar to those of liquid carbon tetrachloride? *Hint.* Use mathematical software or a spreadsheet.

4.22‡ A substance as well–known as methane still receives research attention because it is an important component of natural gas, a commonly used fossil fuel . Friend *et al.* have published a review of thermophysical properties of methane (D.G. Friend, J.F. Ely, and H. Ingham, *J. Phys. Chem. Ref. Data* **18**, 583 (1989)), which included the following data describing the liquid–vapour phase boundary.

T/K	100	108	110	112	114	120	130	140	150	160	170	190
p/MPa	0.034	0.074	0.088	0.104	0.122	0.192	0.368	0.642	1.041	1.593	2.329	4.521

(a) Plot the liquid–vapour phase boundary. (b) Estimate the standard boiling point of methane. (c) Compute the standard enthalpy of vaporization of methane, given that the molar volumes of the liquid and vapour at the standard boiling point are 3.80×10^{-2} and $8.89 \ \mathrm{dm^3 \ mol^{-1}}$, respectively.

4.23‡ Diamond, an allotrope of carbon, is the hardest substance and the best conductor of heat yet characterized. For these reasons, diamond is used widely in industrial applications that require a strong abrasive. Unfortunately, it is difficult to synthesize diamond from the more readily available allotropes of carbon, such as graphite. To illustrate this point, calculate the pressure required to convert graphite into diamond at 25°C. The following data apply to 25°C and 100 kPa. Assume the specific volume, V_s, and κ_T are constant with respect to pressure changes.

	Graphite	Diamond
$\Delta_f G^{\ominus}/(\mathrm{kJ \ mol^{-1}})$	0	+2.8678
$V_s/(\mathrm{cm^3 \ g^{-1}})$	0.444	0.284
κ_T/kPa	3.04×10^{-8}	0.187×10^{-8}