TOPIC 4A Phase diagrams of pure substances

➤ **Why do you need to know this material?**

Phase diagrams summarize the behaviour of substances under different conditions, and identify which phase or phases are the most stable at a particular temperature and pressure. Such diagrams are important tools for understanding the behaviour of both pure substances and mixtures.

➤ **What is the key idea?**

A pure substance tends to adopt the phase with the lowest chemical potential.

➤ **What do you need to know already?**

This Topic builds on the fact that the Gibbs energy is a signpost of spontaneous change under conditions of constant temperature and pressure (Topic 3D).

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'. This material is also the basis of the discussion of mixtures in Focus 5.

4A.1 The stabilities of phases

Thermodynamics provides a powerful framework for describing and understanding the stabilities and transformations of phases, but the terminology must be used carefully. In particular, it is necessary to understand the terms 'phase', 'component', and 'degree of freedom'.

(a) The number of phases

A **phase** is a form of matter that is uniform throughout in chemical composition and physical state. Thus, there are the solid, liquid, and gas phases of a substance, as well as various solid phases, such as the white and black allotropes of phosphorus, or the aragonite and calcite polymorphs of calcium carbonate.

A note on good practice An *allotrope* is a particular molecular form of an element (such as O_2 and O_3) and may be solid, liquid, or gas. A *polymorph* is one of a number of solid phases of an element or compound.

The number of phases in a system is denoted P. A gas, or a gaseous mixture, is a single phase ($P = 1$), a crystal of a substance is a single phase, and two fully mixed liquids form a single phase.

Brief illustration 4A.1

A solution of sodium chloride in water is a single phase ($P = 1$). Ice is a single phase even though it might be chipped into small fragments. A slurry of ice and water is a two-phase system ($P = 2$) even though it is difficult to map the physical boundaries between the phases. A system in which calcium carbonate undergoes the thermal decomposition $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$ consists of two solid phases (one consisting of calcium carbonate and the other of calcium oxide) and one gaseous phase (consisting of carbon dioxide), so $P = 3$.

Two metals form a two-phase system ($P = 2$) if they are immiscible, but a single-phase system ($P = 1$), an alloy, if they are miscible (and actually mixed). A solution of solid B in solid A—a homogeneous mixture of the two miscible 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, even microscopically small, is representative of the composition of the whole. It is therefore a single phase.

A dispersion is uniform on a macroscopic scale but not on a microscopic scale, because it consists of grains or droplets of one substance in a matrix of the other (Fig. 4A.1). A small sample could come entirely from one of the minute grains of pure A and would not be representative of the whole. A dispersion therefore consists of two phases.

(b) Phase transitions

A **phase transition**, the spontaneous conversion of one phase into another phase, occurs at a characteristic **transition temperature**, T_{trs}, for a given pressure. At the transition temperature
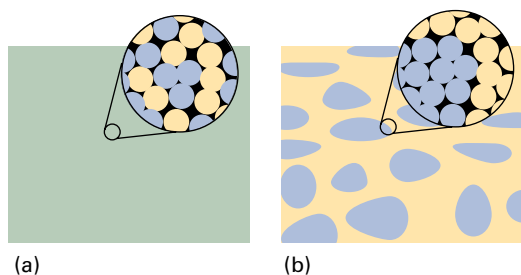
Figure 4A.1 The difference between (a) a single-phase solution, in which the composition is uniform on a molecular scale, and (b) a dispersion, in which microscopic regions of one component are embedded in a matrix of a second component.

the two phases are in equilibrium and the Gibbs energy of the system is a minimum at the prevailing pressure.

> **Brief illustration 4A.2**
>
> 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, but that above 0 °C the Gibbs energy decreases as ice changes into liquid water. The numerical values of the Gibbs energies are considered in the next *Brief illustration*.

The detection of a phase transition is not always straightforward as there may be nothing to see, especially if the two phases are both solids. **Thermal analysis**, which takes advantage of the heat that is evolved or absorbed during a transition, can be used. Thus, if the phase transition is exothermic and the temperature of a sample is monitored as it cools, the presence of the transition can be recognized by a pause in the otherwise steady fall of the temperature (Fig. 4A.2). Similarly, if a sample is heated steadily and the transition is endothermic, there will
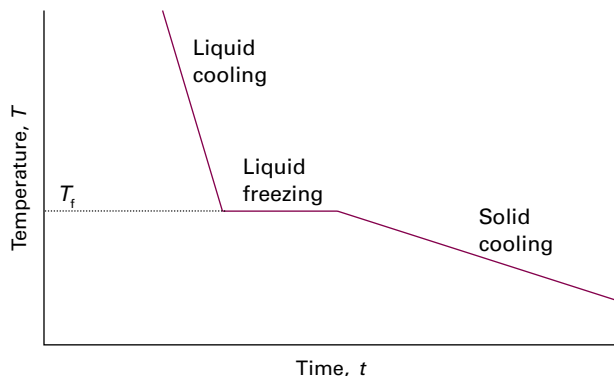
Figure 4A.2 A cooling curve at constant pressure. The flat section corresponds to the pause in the fall of temperature while an exothermic transition (freezing) occurs. This pause enables T_f to be located even if the transition cannot be observed visually.

be a pause in the temperature rise at the transition temperature. Differential scanning calorimetry (Topic 2C) is also used to detect phase transitions, and X-ray diffraction (Topic 15B) is useful for detecting phase transitions in a solid, because the two phases will have different structures.

As always, it is important to distinguish between the thermodynamic description of a process and the rate at which the process occurs. A phase transition that is predicted by thermodynamics to be spontaneous might 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, except at high temperatures, is an immeasurably slow process in a solid. 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 but persistent phase of carbon under normal conditions.

(c) Thermodynamic criteria of phase stability

All the following considerations are based on the Gibbs energy of a substance, and in particular on its molar Gibbs energy, G_m. In fact, this quantity plays such an important role in this Focus and elsewhere in the text that it is given a special name and symbol, the **chemical potential**, μ (mu). For a system that consists of a single substance, the 'molar Gibbs energy' and the 'chemical potential' are exactly the same: $\mu = G_m$. In Topic 5A the chemical potential is given a broader significance and a more general definition. The name 'chemical potential' is also instructive: as the concept is developed it will become clear that μ is a measure of the potential that a substance has for undergoing change. In this Focus, and in Focus 5, it reflects the potential of a substance to undergo physical change. In Focus 6, μ is the potential of a substance to undergo chemical change.

The discussion in this Topic is based on the following consequence of the Second Law (Fig. 4A.3):

> At equilibrium, the chemical potential of a substance is the same in and throughout every phase present in the system.

Criterion for phase equilibrium

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 infinitesimal amount dn of the substance is transferred from one location to the other, the Gibbs energy of the system changes by $-\mu_1 dn$ (i.e. $dG = -G_{m,1} dn$) when material is removed from location 1. It changes
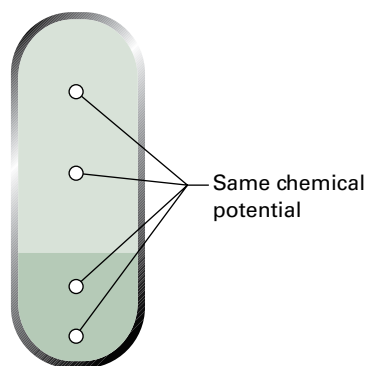
Figure 4A.3 When two or more phases are in equilibrium, the chemical potential of a substance (and, in a mixture, a component) is the same in each phase, and is the same at all points in each phase.

Figure 4A.4 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.

by $+\mu_2 dn$ (i.e. $dG = G_{m,2}dn$) 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.

Brief illustration 4A.3

The standard molar Gibbs energy of formation of water vapour at 298 K (25 °C) is $-229\,kJ\,mol^{-1}$, and that of liquid water at the same temperature is $-237\,kJ\,mol^{-1}$. It follows that there is a decrease in Gibbs energy when water vapour condenses to the liquid at 298 K, so condensation is spontaneous at that temperature (and 1 bar).

4A.2 Phase boundaries

The **phase diagram** of a pure substance shows the regions of pressure and temperature at which its various phases are thermodynamically stable (Fig. 4A.4). In fact, any two intensive variables may be used (such as temperature and magnetic field; in Topic 5A mole fraction is another variable), but this Topic focuses on pressure and temperature. The lines separating the regions, which are called **phase boundaries** (or *coexistence curves*), show the values of p and T at which two phases coexist in equilibrium and their chemical potentials are equal. A single phase is represented by an *area* on a phase diagram.

(a) Characteristic properties related to phase transitions

Consider a liquid sample of a pure substance in a closed vessel. The pressure of a vapour in equilibrium with the liquid
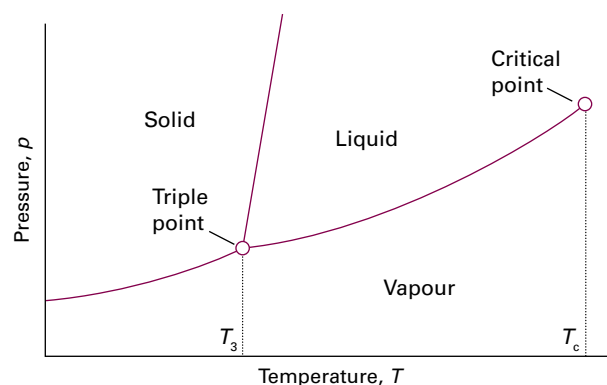
is its vapour pressure (the property introduced in Topic 1C; Fig. 4A.5). Therefore, the liquid–vapour phase boundary in a phase diagram shows how the vapour pressure of the liquid varies with temperature. Similarly, the solid–vapour phase boundary shows the temperature variation of the **sublimation 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.

When a liquid is in an open vessel and subject to an external pressure, it is possible for the liquid to vaporize from its surface. However, only when the temperature is such that the vapour pressure is equal to the external pressure will it be possible for vaporization to occur throughout the bulk of the liquid and for the vapour to expand freely into the surroundings. This condition of free vaporization throughout the liquid is called **boiling**. The temperature at which the vapour pres-
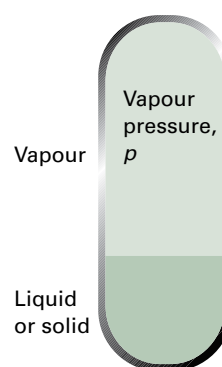

Figure 4A.5 The vapour pressure of a liquid or solid is the pressure exerted by the vapour in equilibrium with the condensed phase.

sure 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. For example, the normal boiling point of water is 100.0 °C, but 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, rises as the temperature is raised (Fig. 4A.6). 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. 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.

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 cannot be changed: it occurs at a single definite pressure and temperature characteristic of the substance.

As can be seen from Fig. 4A.4, 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.

Brief illustration 4A.4

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 was the basis of its use in the now superseded definition of the Kelvin scale of temperature (Topic 3A).
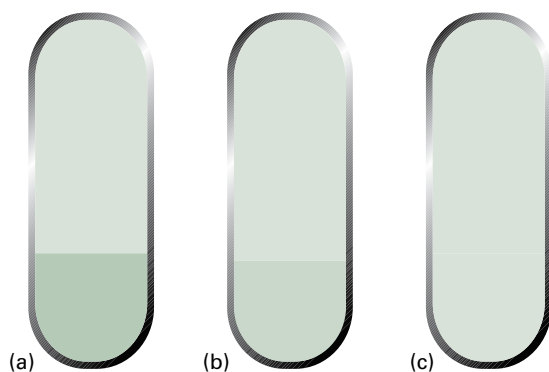
Figure 4A.6 (a) A liquid in equilibrium with its vapour. (b) When a liquid is heated in a sealed container, the density of the vapour phase increases and the density of the liquid decreases slightly. There comes a stage, (c), at which the two densities are equal and the interface between the fluids disappears. This disappearance occurs at the critical temperature.

(a)   (b)   (c)

(b) The phase rule

In one of the most elegant arguments in the whole of chemical thermodynamics, J.W. Gibbs deduced the **phase rule**, which gives the number of parameters that can be varied independently (at least to a small extent) while the number of phases in equilibrium is preserved. The phase rule is a general relation between the variance, F, the number of components, C, and the number of phases at equilibrium, P, for a system of any composition. Each of these quantities has a precisely defined meaning:

- The **variance** (or *number of degrees of freedom*), F, of a system is the number of intensive variables that can be changed independently without disturbing the number of phases in equilibrium.
- A **constituent** of a system is any chemical species that is present.
- A **component** is a *chemically independent* constituent of a system.
- The number of components, C, in a system is the minimum number of types of independent species (ions or molecules) necessary to define the composition of all the phases present in the system.

A mixture of ethanol and water has two constituents. A solution of sodium chloride has three constituents: water, Na^+ ions, and Cl^- ions, but only two components because the numbers of Na^+ and Cl^- ions are constrained to be equal by the requirement of charge neutrality.

The relation between these quantities, which is called the **phase rule**, is established by considering the conditions for equilibrium to exist between the phases in terms of the chemical potentials of all the constituents.

The argument that leads to the phase rule is most easily appreciated by first thinking about the simpler case when only one component is present and then generalizing the result to an arbitrary number of components.

Step 1 *Consider the case where only one component is present*

When only one phase is present ($P = 1$), both p and T can be varied independently, so $F = 2$. Now consider the case where two phases α and β are in equilibrium ($P = 2$). If the phases are in equilibrium at a given pressure and temperature, their chemical potentials must be equal:

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

This equation relates p and T: when the pressure changes, the changes in the chemical potentials are different in general, so in order to keep them equal, the temperature must change too. To keep the two phases in equilibrium only one variable can be changed arbitrarily, so $F = 1$.

If three phases of a one-component system are in mutual equilibrium, the chemical potentials of all three phases (α, β, and γ) must be equal:

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

This relation is actually *two* equations $\mu(\alpha; p,T) = \mu(\beta; p,T)$ and $\mu(\beta; p,T) = \mu(\gamma; p,T)$, in which there are *two* variables: pressure and temperature. With two equations for two unknowns, there is a single solution (just as the pair of algebraic equations $x + y = xy$ and $3x - y = xy$ have the single, fixed solutions $x = 2$ and $y = 2$). There is therefore only one single, unchangeable value of the pressure and temperature as a solution. The conclusion is that there is no freedom to choose these variables, so $F = 0$.

Four phases cannot be in mutual equilibrium in a one-component system because the three equalities

$$\mu(\alpha; p,T) = \mu(\beta; p,T), \ \mu(\beta; p,T) = \mu(\gamma; p,T),$$
$$\text{and } \mu(\gamma; p,T) = \mu(\delta; p,T)$$

are three equations with only two unknowns (p and T), which are not consistent because no values of p and T satisfy all three

equations (just as the three equations $x + y = xy$, $3x - y = xy$, and $4x - y = 2xy^2$ have no solution).

In summary, for a one-component system ($C = 1$) it has been shown that: $F = 2$ when $P = 1$; $F = 1$ when $P = 2$; and $F = 0$ when $P = 3$. The general result is that for $C = 1$, $F = 3 - P$.

Step 2 *Consider the general case of any number of components, C*

Begin by counting the total number of intensive variables. The pressure, p, and temperature, T, count as 2. The composition of a phase is specified by giving the mole fractions of the C components, but as the sum of the mole fractions must be 1, only $C - 1$ mole fractions are independent. 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 is the same in every phase:

$$\mu_J(\alpha; p,T) = \mu_J(\beta; p,T) = \cdots \text{ for } P \text{ phases}$$

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

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

The right-hand side simplifies to give the phase rule in the form derived by Gibbs:

$$F = C - P + 2 \qquad \text{(4A.1)}$$

The phase rule

The implications of the phase rule for a one-component system, when

$$F = 3 - P \qquad \qquad \text{(4A.2)}$$

The phase rule [C = 1]

are summarized in Fig. 4A.7. When only one phase is present in a one-component system, $F = 2$ and both p and T can be varied independently (at least over a small range) without changing the number of phases. The system is said to be **bivariant**, meaning having two degrees of freedom. 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, the pressure could be selected, but having done so the two phases would be in equilibrium only 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**, meaning that it has no degrees of freedom. This
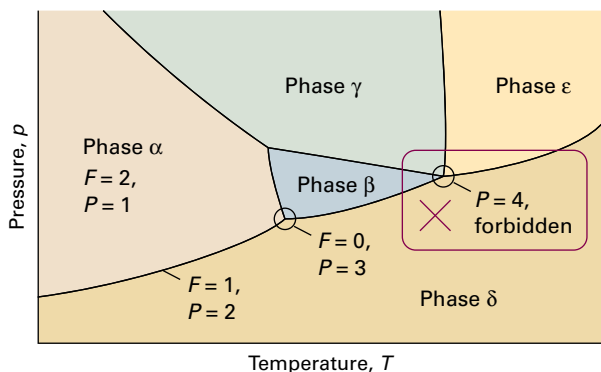
Figure 4A.7 The typical regions of a one-component phase diagram. The lines represent conditions under which the two adjoining phases are in equilibrium. A point represents the unique set of conditions under which three phases coexist in equilibrium. Four phases cannot mutually coexist in equilibrium when only one component is present.

Figure 4A.8 The experimental phase diagram for carbon dioxide; note the break in the vertical scale. 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 for liquid to be formed. The path ABCD is discussed in *Brief illustration* 4A.6.
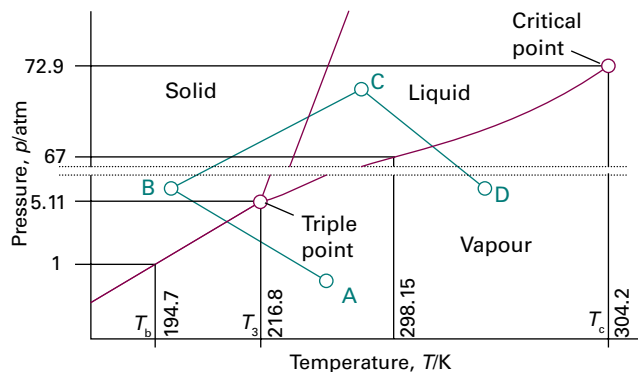
special condition can be established only at a definite temperature and pressure that is characteristic of the substance and cannot be changed. The equilibrium of three phases is therefore represented by a *point*, the triple point, on a phase diagram. Four phases cannot be in equilibrium in a one-component system because F cannot be negative.

4A.3 Three representative phase diagrams

Carbon dioxide, water, and helium illustrate the significance of the various features of a phase diagram.

(a) Carbon dioxide

Figure 4A.8 shows the phase diagram for carbon dioxide. The features to notice include the positive slope (up from left to right) of the solid–liquid phase boundary; the direction of this line is characteristic of most substances. This slope 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. As a result, 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 is released through a tap (which acts as a throttle) the gas 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. That carbon

dioxide gas cannot be liquefied except by applying high pressure reflects the weakness of the intermolecular forces between the nonpolar carbon dioxide molecules (Topic 14B).

Brief illustration 4A.6

Consider the path ABCD in Fig. 4A.8. At A the carbon dioxide is a gas. When the temperature and pressure are adjusted to B, the vapour condenses directly to a solid. Increasing the pressure and temperature to C results in the formation of the liquid phase, which evaporates to the vapour when the conditions are changed to D.

(b) Water

Figure 4A.9 shows 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: simply read off the temperature at which the vapour pressure is equal to the prevailing atmospheric pressure. The solid (ice I)–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 (down from left to right) 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: it is 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 open structure of ice: as shown in Fig. 4A.10, the water molecules are held apart, as well as together, by the hydrogen bonds
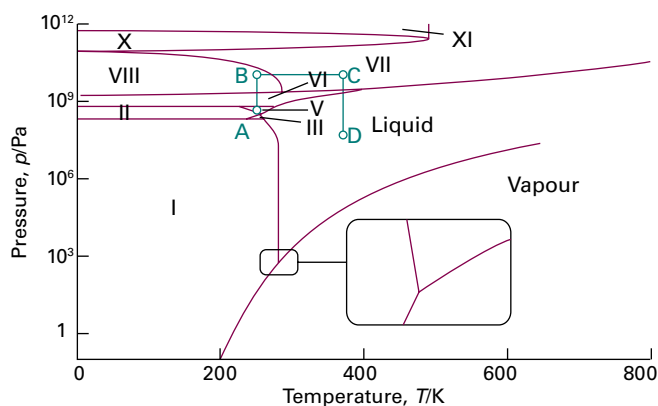
Figure 4A.9 The phase diagram for water showing the different solid phases, which are indicated with Roman numerals I, II, …; solid phase I (ice I) is ordinary ice. The path ABCD is discussed in *Brief illustration* 4A.7.

between them, but the hydrogen-bonded structure partially collapses on melting and the liquid is denser than the solid. Other consequences of its extensive hydrogen bonding are the anomalously high boiling point of water for a molecule of its molar mass and its high critical temperature and pressure.

The diagram shows that water has one liquid phase but many different solid phases other than ordinary ice ('ice I'). Some of these phases melt at high temperatures. Ice VII, for instance, melts at 100 °C but exists only above 25 kbar. Two further phases, Ice XIII and XIV, were identified in 2006 at −160 °C but have not yet been allocated regions in the phase diagram. 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 of ice may contribute to the advance of glaciers, for ice at the bottom of glaciers experiences very high pressures where it rests on jagged rocks.
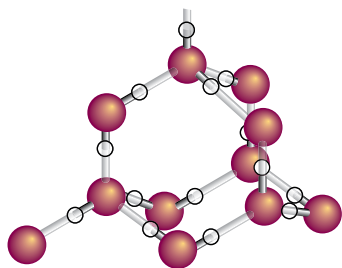

Figure 4A.10 A fragment of the structure of ice I. Each O atom is linked by two covalent bonds to H atoms and by two hydrogen bonds to a neighbouring O atom, in a tetrahedral array.

Brief illustration 4A.7

Consider the path ABCD in Fig. 4A.9. Water is present at A as ice V. Increasing the pressure to B at the same temperature results in the formation of ice VIII. Heating to C leads to the formation of ice VII, and reduction in pressure to D results in the solid melting to liquid.

(c) Helium

The two isotopes of helium, ³He and ⁴He, behave differently at low temperatures because ⁴He is a boson whereas ³He is a fermion, and are treated differently by the Pauli principle (Topic 8B). Figure 4A.11 shows the phase diagram of helium-4. Helium behaves unusually at low temperatures because the mass of its atoms is so low and there are only very weak interactions between neighbours. At 1 atm, 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.

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.** It is so called because it flows without viscosity.[1] The liquid–liquid phase boundary is called the λ-**line** (lambda line) for reasons related to the shape of a
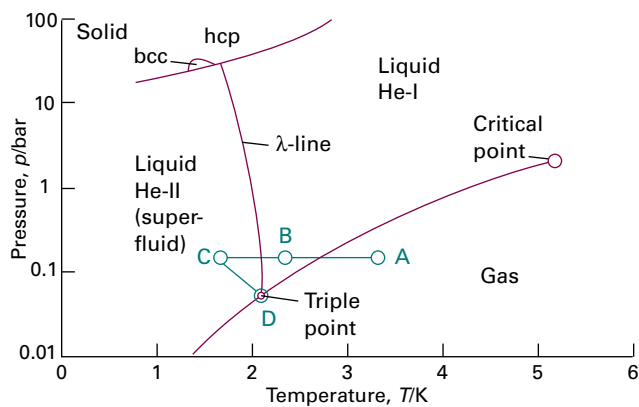

Figure 4A.11 The phase diagram for helium (⁴He). The λ-line marks the conditions under which the two liquid phases are in equilibrium; He-II is the superfluid phase. Note that a pressure of over 20 bar must be exerted before solid helium can be obtained. The labels hcp and bcc denote different solid phases in which the atoms pack together differently: hcp denotes hexagonal closed packing and bcc denotes body-centred cubic (Topic 15A). The path ABCD is discussed in *Brief illustration* 4A.8.

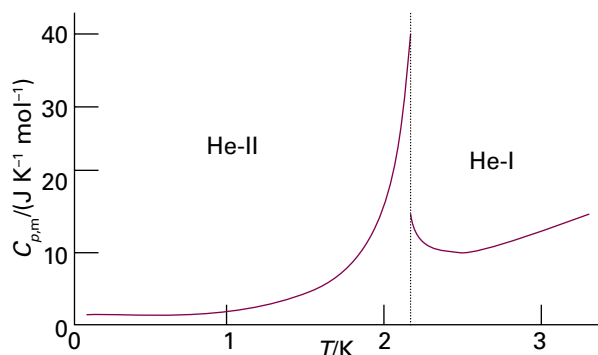[1] Water might also have a superfluid liquid phase.

Figure 4A.12 The heat capacity of superfluid He-II increases with temperature and rises steeply as the transition temperature to He-I is approached. The appearance of the plot has led the transition to be described as a λ-transition and the line on the phase diagram to be called a λ-line.

plot of the heat capacity of helium-4 against temperature at the transition temperature (Fig. 4A.12).

Helium-3 also has a superfluid phase. Helium-3 is unusual in that melting is exothermic ($\Delta_{fus}H < 0$) and therefore (from $\Delta_{fus}S = \Delta_{fus}H/T_f$) at the melting point the entropy of the liquid is lower than that of the solid.

> **Brief illustration 4A.8**
>
> Consider the path ABCD in Fig. 4A.11. At A, helium is present as a vapour. On cooling to B it condenses to helium-I, and further cooling to C results in the formation of helium-II. Adjustment of the pressure and temperature to D results in a system in which three phases, helium-I, helium-II, and vapour are in mutual equilibrium.

Checklist of concepts

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

☐ **2.** A **phase transition** is the spontaneous conversion of one phase into another.

☐ **3.** The thermodynamic analysis of phases is based on the fact that at equilibrium, the chemical potential of a substance is the same throughout a sample.

☐ **4.** A **phase diagram** indicates the values of the pressure and temperature at which a particular phase is most stable, or is in equilibrium with other phases.

☐ **5.** The **phase rule** relates the number of variables that may be changed while the phases of a system remain in mutual equilibrium.

Checklist of equations

Property	Equation	Comment	Equation number
Chemical potential	$\mu = G_m$	For a single substance	
Phase rule	$F = C - P + 2$	F is the variance, C the number of components, and P the number of phases	4A.1

TOPIC 4B Thermodynamic aspects of phase transitions

➤ **Why do you need to know this material?**

Thermodynamic arguments explain the appearance of phase diagrams and can be used to make predictions about the effect of pressure on phase transitions. They provide insight into the properties that account for the behaviour of matter under different conditions.

➤ **What is the key idea?**

The effect of temperature and pressure on the chemical potential of a substance in each phase depends on its molar entropy and molar volume, respectively.

➤ **What do you need to know already?**

You need to be aware that phases are in equilibrium when their chemical potentials are equal (Topic 4A) and that the variation of the molar Gibbs energy of a substance depends on its molar volume and entropy (Topic 3E). The Topic makes use of expressions for the entropy of transition (Topic 3B) and of the perfect gas law (Topic 1A).

As explained in Topic 4A, the thermodynamic criterion for phase equilibrium is the equality of the chemical potentials of each substance in each phase. For a one-component system, the chemical potential is the same as the molar Gibbs energy ($\mu = G_m$). In Topic 3E it is explained how the Gibbs energy varies with temperature and pressure:

dG = −SdT at constant pressure;
dG = Vdp at constant temperature

These expressions also apply to the molar Gibbs energy, and therefore to the chemical potential. By using the notation of partial derivatives (*The chemist's toolkit* 9 in Topic 2A) they can be expressed as

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

Variation of chemical potential with T [constant p]   (4B.1a)

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

Variation of chemical potential with p [constant T]   (4B.1b)

By combining the equality of chemical potentials of a substance in each phase with these expressions for the variation of μ with temperature and pressure it is possible to deduce how phase equilibria respond to changes in the conditions.

4B.1 The dependence of stability on the conditions

At sufficiently low temperatures the solid phase of a substance commonly has the lowest chemical potential and is therefore the most stable phase. However, the chemical potentials of different phases depend on temperature to different extents (because the molar entropy of each phase is different), and above a certain temperature the chemical potential of another phase (perhaps another solid phase, a liquid, or a gas) might turn out to be lower. Then a transition to the second phase becomes spontaneous and occurs if it is kinetically feasible.

(a) The temperature dependence of phase stability

Because $S_m > 0$ for all substances above $T = 0$, eqn 4B.1a shows that the chemical potential of a pure substance decreases as the temperature is raised. That is, a plot of chemical potential against temperature slopes down from left to right. It also implies that because $S_m(g) > S_m(l)$, the slope is steeper for gases than for liquids. Because it is almost always the case that $S_m(l) > S_m(s)$, the slope is also steeper for a liquid than the corresponding solid. These features are illustrated in Fig. 4B.1. The steeper slope of $\mu(l)$ compared with that of $\mu(s)$ results in $\mu(l)$ falling below $\mu(s)$ when the temperature is high enough; then the liquid becomes the stable phase, and melting is spontaneous. 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 below that of the liquid. Then the gas is the stable phase and vaporization is spontaneous.
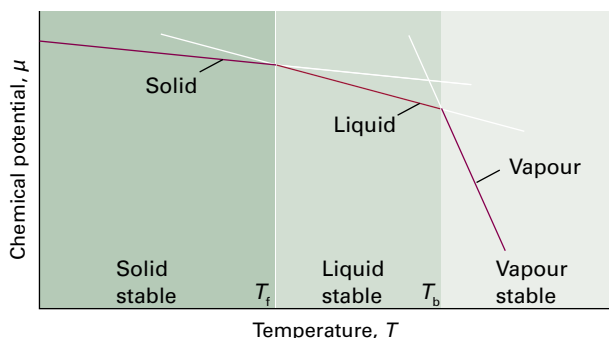
Figure 4B.1 The schematic temperature dependence of the chemical potential of the solid, liquid, and gas phases of a substance (in practice, the lines are curved). The phase with the lowest chemical potential at a specified temperature is the most stable one at that temperature. The transition temperatures, the freezing (melting) and boiling temperatures (T_f and T_b, respectively), are the temperatures at which the chemical potentials of the two phases are equal.
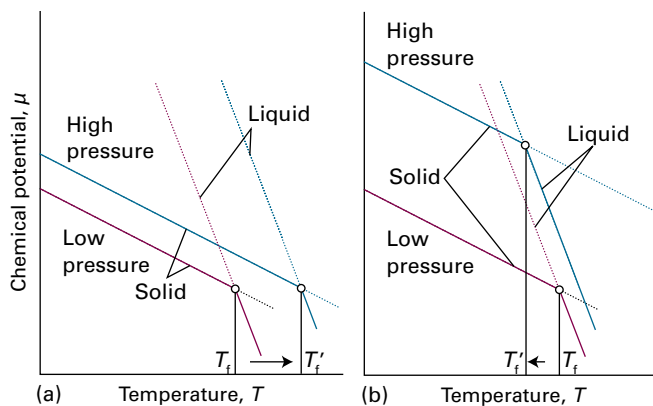

Figure 4B.2 The pressure dependence of the chemical potential of a substance depends on the molar volume of the phase. The lines show schematically the effect of increasing pressure on the chemical potential of the solid and liquid phases (in practice, the lines are curved), and the corresponding effects 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.

Brief illustration 4B.1

The standard molar entropy of liquid water at $100\,°C$ is $86.8\,J\,K^{-1}\,mol^{-1}$ and that of water vapour at the same temperature is $195.98\,J\,K^{-1}\,mol^{-1}$. It follows that when the temperature is raised by $1.0\,K$ the changes in chemical potential are

$$\Delta\mu(l) \approx -S_m(l)\Delta T = -87\,J\,mol^{-1}$$
$$\Delta\mu(g) \approx -S_m(g)\Delta T = -196\,J\,mol^{-1}$$

At $100\,°C$ the two phases are in equilibrium with equal chemical potentials. At $101\,°C$ the chemical potential of both vapour and liquid are lower than at $100\,°C$, but the chemical potential of the vapour has decreased by a greater amount. It follows that the vapour is the stable phase at the higher temperature, so vaporization will be spontaneous.

(b) The response of melting to applied pressure

Equation 4B.1b shows that because $V_m > 0$, an increase in pressure raises the chemical potential of any pure substance. In most cases, $V_m(l) > V_m(s)$, so an increase in pressure increases the chemical potential of the liquid phase of a substance more than that of its solid phase. As shown in Fig. 4B.2(a), the effect of pressure in such a case is to raise the freezing 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 freezing temperature is lowered slightly (Fig. 4B.2(b)).

Example 4B.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 mass density of ice is $0.917\,g\,cm^{-3}$ and that of liquid water is $0.999\,g\,cm^{-3}$ under these conditions.

Collect your thoughts From $d\mu = V_m dp$, you can infer 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, you 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 $V_m = M/\rho$. Then $\Delta\mu = M\Delta p/\rho$. To keep the units straight, you will need to express the mass densities in kilograms per cubic metre ($kg\,m^{-3}$) and the molar mass in kilograms per mole ($kg\,mol^{-1}$), and use $1\,Pa\,m^3 = 1\,J$.

The solution The molar mass of water is $18.02\,g\,mol^{-1}$ (i.e. $1.802\times10^{-2}\,kg\,mol^{-1}$); therefore, when the pressure is increased by $1.00\,bar$ ($1.00\times10^5\,Pa$)

$$\Delta\mu(ice) = \frac{(1.802\times10^{-2}\,kg\,mol^{-1})\times(1.00\times10^5\,Pa)}{917\,kg\,m^{-3}} = +1.97\,J\,mol^{-1}$$

$$\Delta\mu(water) = \frac{(1.802\times10^{-2}\,kg\,mol^{-1})\times(1.00\times10^5\,Pa)}{999\,kg\,m^{-3}}$$
$$= +1.80\,J\,mol^{-1}$$

Comment. The chemical potential of ice rises by more than that of water, so if they are initially in equilibrium at 1 bar, then there is a tendency for the ice to melt at 2 bar.

Self-test 4B.1 Calculate the effect of an increase in pressure of 1.00 bar on the liquid and solid phases of carbon dioxide (molar mass 44.0 g mol^{-1}) in equilibrium with mass densities 2.35 g cm^{-3} and 2.50 g cm^{-3}, respectively.

Answer: $\Delta\mu$(l) = +1.87 J mol^{-1}, $\Delta\mu$(s) = +1.76 J mol^{-1}; solid tends to form.

## (c) The vapour pressure of a liquid subjected to pressure

Pressure can be exerted on the condensed phase mechanically or by subjecting it to the applied pressure of an inert gas (Fig. 4B.3). In the latter case, the **partial vapour pressure** is the partial pressure of the vapour in equilibrium with the condensed phase. 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. The effect can be explored thermodynamically and a relation established between the applied pressure P and the vapour pressure p.

How is that done? 4B.1   Deriving an expression for the vapour pressure of a pressurized liquid

At equilibrium the chemical potentials of the liquid and its vapour are equal: μ(l) = μ(g). It follows that, for any change that preserves equilibrium, the resulting change in μ(l) must be equal to the change in μ(g); therefore, dμ(g) = dμ(l).

Step 1 *Express changes in the chemical potentials that arise from changes in pressure*

When the pressure P on the liquid is increased by dP, the chemical potential of the liquid changes by dμ(l) = V_m(l)dP.
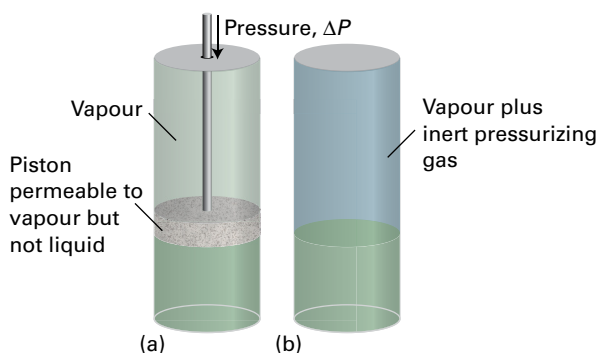
Figure 4B.3 Pressure may be applied to a condensed phase either (a) by compressing it or (b) by subjecting it to an inert pressurizing gas. When pressure is applied, the vapour pressure of the condensed phase increases.

The chemical potential of the vapour changes by dμ(g) = V_m(g)dp, where dp is the change in the vapour pressure. If the vapour is treated as a perfect gas, the molar volume can be replaced by V_m(g) = RT/p, to give dμ(g) = (RT/p)dp.

Step 2 *Equate the changes in chemical potentials of the vapour and the liquid*

Equate dμ(l) = V_m(l)dP and dμ(g) = (RT/p)dp:

$$\frac{RT\,\mathrm{d}p}{p} = V_m(l)\,\mathrm{d}P$$

Be careful to distinguish between P, the total pressure, and p, the partial vapour pressure.

Step 3 *Set up the integration of this expression by identifying the appropriate limits*

When there is no additional pressure acting on the liquid, P (the pressure experienced by the liquid) is equal to the normal vapour pressure $p^\star$, so when $P = p^\star$, $p = p^\star$ too. When there is an additional pressure ΔP on the liquid, so $P = p + \Delta P$, the vapour pressure is p (the value required). 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 $p^\star$ itself, and to set the upper limit of the integral to $p^\star + \Delta P$. The integrations required are therefore as follows:

$$RT\int_{p^\star}^{p}\frac{\mathrm{d}p'}{p'} = \int_{p^\star}^{p^\star+\Delta P} V_m(l)\,\mathrm{d}P$$

(In the first integral, the variable of integration has been changed from p to p' to avoid confusion with the p at the upper limit.)

Step 4 *Carry out the integrations*

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

$$\overbrace{\int_{p^\star}^{p}\frac{\mathrm{d}p'}{p'}}^{\text{Integral A.2}} = \frac{1}{RT}\int_{p^\star}^{p^\star+\Delta P} V_m(l)\,\mathrm{d}P = \frac{V_m(l)}{RT}\overbrace{\int_{p^\star}^{p^\star+\Delta P}\mathrm{d}P}^{\text{Integral A.1}}$$

Both integrations are straightforward, and lead to

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

which (by using $e^{\ln x} = x$) rearranges to

$$p = p^\star e^{V_m(l)\Delta P/RT} \qquad\qquad (4B.2)$$

Effect of applied pressure ΔP on partial vapour pressure p

One complication that has been ignored is that, if the condensed phase is a liquid, then the pressurizing gas might dissolve and change its properties. 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.

Brief illustration 4B.2

For water, which has mass density $0.997\,\mathrm{g\,cm^{-3}}$ at $25\,^\circ\mathrm{C}$ and therefore molar volume $18.1\,\mathrm{cm^3\,mol^{-1}}$, when the applied pressure is increased by 10 bar (i.e. $\Delta P = 1.0 \times 10^6\,\mathrm{Pa}$)

$$\ln\frac{p}{p^\star} = \frac{V_m(1)\Delta P}{RT} = \frac{(1.81\times10^{-5}\,\mathrm{m^3\,mol^{-1}})\times(1.0\times10^6\,\mathrm{Pa})}{(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})\times(298\,\mathrm{K})}$$
$$= 0.0073\ldots$$

where $1\,\mathrm{J} = 1\,\mathrm{Pa\,m^3}$. It follows that $p = 1.0073p^\star$, an increase of only 0.73 per cent.

4B.2 The location of phase boundaries

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

$$\mu(\alpha; p,T) = \mu(\beta; p,T) \tag{4B.3}$$

Solution of this equation for p in terms of T gives an equation for the phase boundary (the coexistence curve).

(a) The slopes of the phase boundaries

Imagine that at some particular pressure and temperature the two phases are in equilibrium: their chemical potentials are then equal. Now p and T are changed infinitesimally, but in such a way that the phases remain in equilibrium: after these changes, the chemical potentials of the two phases change but remain equal (Fig. 4B.4). It follows that the change in the
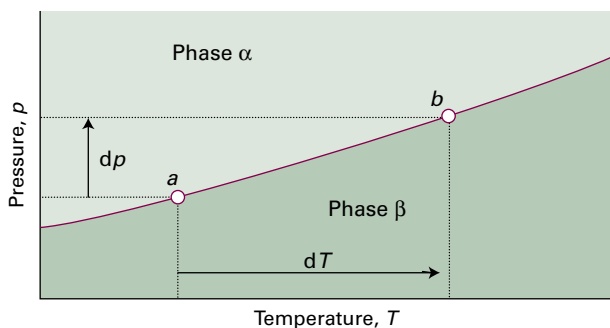

Figure 4B.4 When pressure is applied to a system in which two phases are in equilibrium (at *a*), the equilibrium is disturbed. It can be restored by changing the temperature, so moving the state of the system to *b*. It follows that there is a relation between d*p* and d*T* that ensures that the system remains in equilibrium as either variable is changed.

chemical potential of phase α must be the same as the change in chemical potential of phase β, so $d\mu(\alpha) = d\mu(\beta)$.

Equation 3E.7 ($dG = Vdp - SdT$) gives the variation of G with p and T, so with $\mu = G_m$, it follows that $d\mu = V_m dp - S_m dT$ for each phase. Therefore the relation $d\mu(\alpha) = d\mu(\beta)$ can be written

$$V_m(\alpha)dp - S_m(\alpha)dT = V_m(\beta)dp - S_m(\beta)dT$$

where $S_m(\alpha)$ and $S_m(\beta)$ are the molar entropies of the two phases, and $V_m(\alpha)$ and $V_m(\beta)$ are their molar volumes. Hence

$$\{S_m(\beta) - S_m(\alpha)\}dT = \{V_m(\beta) - V_m(\alpha)\}dp$$

The change in (molar) entropy accompanying the phase transition, $\Delta_{trs}S$, is the difference in the molar entropies $\Delta_{trs}S = S_m(\beta) - S_m(\alpha)$, and likewise for the change in (molar) volume, $\Delta_{trs}V = V_m(\beta) - V_m(\alpha)$. Therefore,

$$\Delta_{trs}S\,dT = \Delta_{trs}V\,dp$$

This relation turns into the **Clapeyron equation**:

$$\frac{dp}{dT} = \frac{\Delta_{trs}S}{\Delta_{trs}V} \qquad \text{Clapeyron equation} \tag{4B.4a}$$

The Clapeyron equation is an exact expression for the slope of the tangent to the phase boundary at any point and applies to any phase equilibrium of any pure substance. It implies that thermodynamic data can be used 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, when it can be used in the form obtained by inverting both sides:

$$\frac{dT}{dp} = \frac{\Delta_{trs}V}{\Delta_{trs}S} \tag{4B.4b}$$

Brief illustration 4B.3

For water at $0\,^\circ\mathrm{C}$, the standard volume of transition of ice to liquid is $-1.6\,\mathrm{cm^3\,mol^{-1}}$, and the corresponding standard entropy of transition is $+22\,\mathrm{J\,K^{-1}\,mol^{-1}}$. The slope of the solid–liquid phase boundary at that temperature is therefore

$$\frac{dT}{dp} = \frac{-1.6\times10^{-6}\,\mathrm{m^3\,mol^{-1}}}{22\,\mathrm{J\,K^{-1}\,mol^{-1}}} = -7.3\times10^{-8}\,\frac{\mathrm{K}}{\mathrm{J\,m^{-3}}}$$
$$= -7.3\times10^{-8}\,\mathrm{K\,Pa^{-1}}$$

which corresponds to $-7.3\,\mathrm{mK\,bar^{-1}}$. An increase of 100 bar therefore results in a lowering of the freezing point of water by 0.73 K.

(b) The solid–liquid boundary

Melting (fusion) is accompanied by a molar enthalpy change $\Delta_{fus}H$, and if it occurs at a temperature T the molar entropy of melting is $\Delta_{fus}H/T$ (Topic 3B); all points on the phase boundary correspond to equilibrium, so T is in fact a transition temperature, T_{trs}. The Clapeyron equation for this phase transition then becomes

$$\frac{dp}{dT} = \frac{\Delta_{fus}H}{T\Delta_{fus}V}$$
<div style="text-align:right">Slope of solid–liquid boundary   (4B.5)</div>

where $\Delta_{fus}V$ is the change in molar volume that accompanies melting. The enthalpy of melting is positive (the only exception is helium-3); the change in molar volume is usually positive and always small. Consequently, the slope dp/dT is steep and usually positive (Fig. 4B.5).

The equation for the phase boundary is found by integrating dp/dT and 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 $T^{\star}$ when the pressure is $p^{\star}$, and T when the pressure is p, the integration required is

$$\int_{p^{\star}}^{p} dp = \frac{\Delta_{fus}H}{\Delta_{fus}V} \overbrace{\int_{T^{\star}}^{T} \frac{dT}{T}}^{\text{Integral A.2}}$$

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

$$p = p^{\star} + \frac{\Delta_{fus}H}{\Delta_{fus}V} \ln \frac{T}{T^{\star}} \qquad (4B.6)$$

This equation was originally obtained by yet another Thomson—James, the brother of William, Lord Kelvin.

When T is close to $T^{\star}$, the logarithm can be approximated by using the expansion $\ln(1 + x) = x - \tfrac{1}{2}x^2 + \cdots$ (see *The*
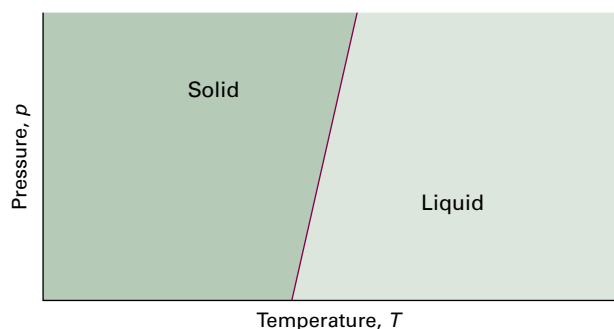
Figure 4B.5 A typical solid–liquid phase boundary slopes steeply upwards. This slope implies that, as the pressure is raised, the melting temperature rises. Most substances behave in this way, water being the notable exception.

chemist's toolkit 12 in Topic 5B) and neglecting all but the leading term:

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

Therefore

$$p \approx p^{\star} + \frac{\Delta_{fus}H}{T^{\star}\Delta_{fus}V}(T-T^{\star}) \qquad (4B.7)$$

This expression is the equation of a steep straight line when p is plotted against T (as in Fig. 4B.5).

<div style="border:1px solid green; padding:4px">**Brief illustration 4B.4**</div>

The enthalpy of fusion of ice at $0\,°C$ ($273\,K$) and $1\,bar$ is $6.008\,kJ\,mol^{-1}$ and the volume of fusion is $-1.6\,cm^3\,mol^{-1}$. It follows that the solid–liquid phase boundary is given by the equation

$$p \approx 1.0\times10^5\,Pa + \frac{6.008\times10^3\,J\,mol^{-1}}{(273\,K)\times(-1.6\times10^{-6}\,m^3\,mol^{-1})}(T-T^{\star})$$

$$\approx 1.0\times10^5\,Pa - 1.4\times10^7\,Pa\,K^{-1}(T-T^{\star})$$

That is,

$$p/bar = 1 - 140(T-T^{\star})/K$$

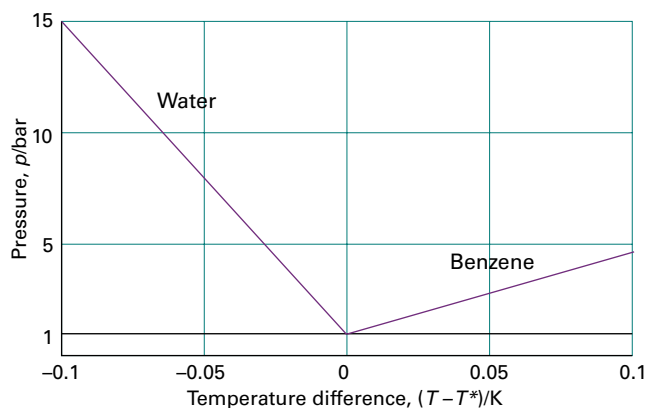with $T^{\star} = 273\,K$. This expression is plotted in Fig. 4B.6.

Figure 4B.6 The solid–liquid phase boundary (the melting point curve) for water as calculated in *Brief illustration* 4B.4. For comparison, the boundary for benzene is included.

(c) The liquid–vapour boundary

The entropy of vaporization at a temperature T is equal to $\Delta_{vap}H/T$ (as before, all points on the phase boundary correspond to equilibrium, so T is a transition temperature, T_{trs}), so

the Clapeyron equation for the liquid–vapour boundary can therefore be written

$$\frac{dp}{dT} = \frac{\Delta_{vap}H}{T\Delta_{vap}V}$$

Slope of liquid–vapour boundary (4B.8)

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

Example 4B.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.

Collect your thoughts To use eqn 4B.8 you need to estimate the right-hand side. At the boiling point, the term $\Delta_{vap}H/T$ is Trouton's constant (Topic 3B). Because the molar volume of a gas is so much greater than the molar volume of a liquid, you 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). You will need to use $1\,J = 1\,Pa\,m^3$.

The solution 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,

$$\frac{dp}{dT} \approx \frac{85\,J\,K^{-1}\,mol^{-1}}{2.5\times10^{-2}\,m^3\,mol^{-1}} = 3.4\times10^3\,Pa\,K^{-1}$$

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 4B.2 Estimate dT/dp for water at its normal boiling point using the information in Table 3B.2 and $V_m(g) = RT/p$.

Answer: 28 K atm⁻¹

Because the molar volume of a gas is so much greater than the molar volume of a liquid, $\Delta_{vap}V \approx V_m(g)$ (as in Example 4B.2). Moreover, if the gas behaves perfectly, $V_m(g) = RT/p$. These two approximations turn the exact Clapeyron equation into

$$\frac{dp}{dT} = \frac{\Delta_{vap}H}{T(RT/p)} = \frac{p\Delta_{vap}H}{RT^2}$$

By using $dx/x = d\ln x$, this expression can be rearranged into the **Clausius–Clapeyron equation** for the variation of vapour pressure with temperature:

$$\frac{d\ln p}{dT} = \frac{\Delta_{vap}H}{RT^2}$$
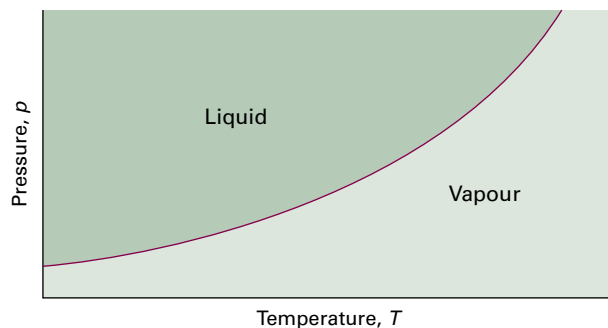
Clausius–Clapeyron equation (4B.9)

Figure 4B.7 A typical liquid–vapour phase boundary. The boundary can be interpreted as a plot of the vapour pressure against the temperature. This phase boundary terminates at the critical point (not shown).

Like the Clapeyron equation (which is exact), the Clausius–Clapeyron equation (which is an approximation) is important for understanding the appearance of phase diagrams, particularly the location and shape of the liquid–vapour and solid–vapour phase boundaries. It can be used to predict how the vapour pressure varies with temperature and how the boiling temperature varies with pressure. For instance, if it is also assumed that the enthalpy of vaporization is independent of temperature, eqn 4B.9 can be integrated as follows:

$$\overbrace{\int_{\ln p^\star}^{\ln p} d\ln p}^{\text{Integral A.1, with } x = \ln p} = \frac{\Delta_{vap}H}{R}\overbrace{\int_{T^\star}^{T}\frac{dT}{T^2}}^{\text{Integral A.1}}$$

hence

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

where $p^\star$ is the vapour pressure when the temperature is $T^\star$, and p the vapour pressure when the temperature is T. It follows that

$$p = p^\star e^{-\chi} \quad \chi = \frac{\Delta_{vap}H}{R}\left(\frac{1}{T} - \frac{1}{T^\star}\right)$$ (4B.10)

Equation 4B.10 is plotted as the liquid–vapour boundary in Fig. 4B.7. The line does not extend beyond the critical temperature, T_c, because above this temperature the liquid does not exist.

Brief illustration 4B.5

Equation 4B.10 can be used to estimate the vapour pressure of a liquid at any temperature from knowledge of its normal boiling point, the temperature at which the vapour pressure is $1.00\,atm$ ($101\,kPa$). The normal boiling point of benzene is $80\,°C$ ($353\,K$) and (from Table 3B.2) $\Delta_{vap}H^\ominus = 30.8\,kJ\,mol^{-1}$.

Therefore, to calculate the vapour pressure at 20 °C (293 K), write

$$\chi = \frac{3.08\times10^4\,\text{J mol}^{-1}}{8.3145\,\text{JK}^{-1}\,\text{mol}^{-1}}\left(\frac{1}{293\text{K}} - \frac{1}{353\text{K}}\right)$$

$$= 2.14\ldots$$

and substitute this value into eqn 4B.10 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 the solid–vapour and the liquid–vapour boundary 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 (recall that $\Delta_{sub}H = \Delta_{fus}H + \Delta_{vap}H$), at similar temperatures the equation predicts a steeper slope for the sublimation curve than for the vaporization curve. These two boundaries meet at the triple point (Fig. 4B.8).

Brief illustration 4B.6

The enthalpy of fusion of ice at the triple point of water (6.1 mbar, 273 K) is negligibly different from its standard enthalpy of fusion at its freezing point, which is 6.008 kJ mol^{-1}. The enthalpy of vaporization at that temperature is 45.0 kJ mol^{-1}

(once again, ignoring differences due to the pressure not being 1 bar). The enthalpy of sublimation is therefore 51.0 kJ mol^{-1}. Therefore, the equations for the slopes of (a) the liquid–vapour and (b) the solid–vapour phase boundaries at the triple point are

(a) $\dfrac{\text{d}\ln p}{\text{d}T} = \dfrac{45.0\times10^3\,\text{J mol}^{-1}}{(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})\times(273\text{K})^2} = 0.0726\,\text{K}^{-1}$

(b) $\dfrac{\text{d}\ln p}{\text{d}T} = \dfrac{51.0\times10^3\,\text{J mol}^{-1}}{(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})\times(273\text{K})^2} = 0.0823\,\text{K}^{-1}$

The slope of $\ln p$ plotted against T is greater for the solid–vapour boundary than for the liquid–vapour boundary at the triple point.
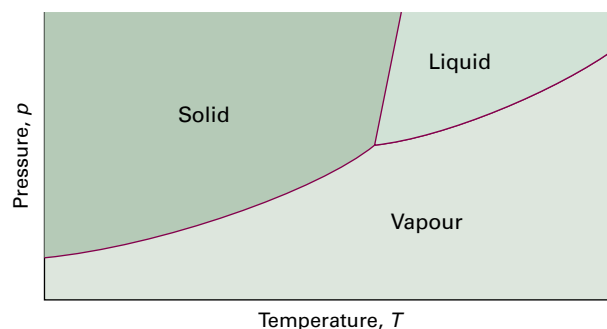

Figure 4B.8 At temperatures close to the triple point the solid–vapour boundary is steeper than the liquid–vapour boundary because the enthalpy of sublimation is greater than the enthalpy of vaporization.

Checklist of concepts

☐ **1.** The chemical potential of a substance decreases with increasing temperature in proportion to its molar entropy.

☐ **2.** The chemical potential of a substance increases with increasing pressure in proportion to its molar volume.

☐ **3.** The vapour pressure of a condensed phase increases when pressure is applied.

☐ **4.** The **Clapeyron equation** is an exact expression for the slope of a phase boundary.

☐ **5.** The **Clausius–Clapeyron equation** is an approximate expression for the boundary between a condensed phase and its vapour.

Checklist of equations

Property	Equation	Comment	Equation number
Variation of μ with temperature	$(\partial\mu/\partial T)_p = -S_m$	$\mu = G_m$	4B.1a
Variation of μ with pressure	$(\partial\mu/\partial p)_T = V_m$		4B.1b
Vapour pressure in the presence of applied pressure	$p = p^* e^{V_m(l)\Delta P/RT}$	$\Delta P = P - p^*$	4B.2
Clapeyron equation	$\text{d}p/\text{d}T = \Delta_{trs}S/\Delta_{trs}V$		4B.4a
Clausius–Clapeyron equation	$\text{d}\ln p/\text{d}T = \Delta_{vap}H/RT^2$	Assumes $V_m(g) \gg V_m(l)$ or $V_m(s)$, and vapour is a perfect gas	4B.9