4A Phase diagrams of pure substances

Contents

➤ Why do you need to know this material?

Phase diagrams summarize the behaviour of substances under different conditions. In metallurgy, the ability to control the microstructure resulting from phase equilibria makes it possible to tailor the mechanical properties of the materials to a particular application.

➤ 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 3C).

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 Chapter 5.

4A.1 The stabilities of phases

Thermodynamics provides a powerful language for describing and understanding the stabilities and transformations of phases, but to apply it we need to employ definitions carefully.

(a) The number of phases

A **phase** 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 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 miscible liquids form a single phase.

Brief illustration 4A.1 The number of phases

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 $P=3$.

Self-test 4A.1 How many phases are present in a sealed, half-full vessel containing water?

Answer: 2

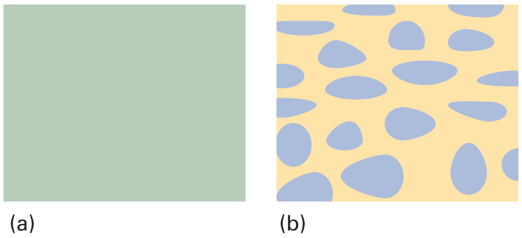

Figure 4A.1 The difference between (a) a single-phase solution, in which the composition is uniform on a microscopic scale, and (b) a dispersion, in which regions of one component are embedded in a matrix of a second component.

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. This example shows that it is not always easy to decide whether a system consists of one phase or of two. A solution of solid B in solid A—a homogeneous mixture of the two substances—is uniform on a molecular scale. In a solution, atoms of A are surrounded by atoms of A and B, and any sample cut from the sample, even microscopically small, is representative of the composition of the whole.

A dispersion is uniform on a macroscopic scale but not on a microscopic scale, for it consists of grains or droplets of one substance in a matrix of the other. A small sample could come entirely from one of the minute grains of pure A and would not be representative of the whole (Fig. 4A.1). Dispersions are important because, in many advanced materials (including steels), heat treatment cycles are used to achieve the precipitation of a fine dispersion of particles of one phase (such as a carbide phase) within a matrix formed by a saturated solid solution phase.

(b) Phase transitions

A **phase transition**, the spontaneous conversion of one phase into another phase, occurs at a characteristic temperature for a given pressure. The **transition temperature**, T_{trs}, is the temperature at which the two phases are in equilibrium and the Gibbs energy of the system is minimized at the prevailing pressure.

Brief illustration 4A.2 Phase transitions

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 numerical values of the Gibbs energies are considered in the next *Brief illustration*.

Self-test 4A.2 Which has the higher standard molar Gibbs energy at 105 °C, liquid water or its vapour?

Answer: Liquid water

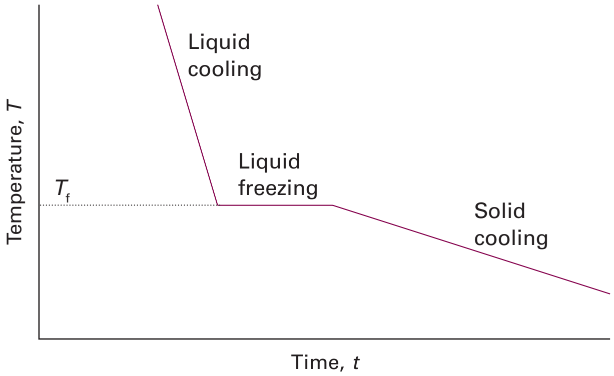

Figure 4A.2 A cooling curve at constant pressure. The flat section corresponds to the pause in the fall of temperature while the first-order exothermic transition (freezing) occurs. This pause enables T_f to be located even if the transition cannot be observed visually.

Detecting a phase transition is not always as simple as seeing water boil in a kettle, so special techniques have been developed. One technique is **thermal analysis**, which takes advantage of the heat that is evolved or absorbed during any transition. The transition is detected by noting that the temperature does not change even though heat is being supplied or removed from the sample (Fig. 4A.2). Differential scanning calorimetry (Topic 2C) is also used. Thermal techniques are useful for solid–solid transitions, where simple visual inspection of the sample may be inadequate. X-ray diffraction (Topic 18A) also reveals the occurrence of a phase transition in a solid, for different structures are found on either side of the transition temperature.

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 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 but persistent phase of carbon under normal conditions.

(c) Thermodynamic criteria of phase stability

All our considerations will be based on the Gibbs energy of a substance, and in particular on its molar Gibbs energy, G_m. In

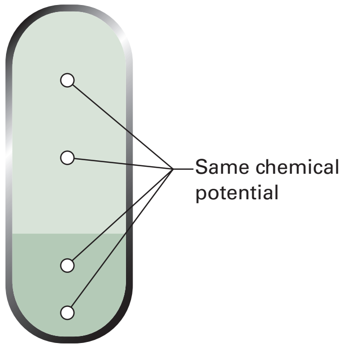

Figure 4A.3 When two or more phases are in equilibrium, the chemical potential of a substance (and, in a mixture, a component) is the same in each phase and is the same at all points in each phase.

fact, this quantity plays 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 Topic 5A we 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 and Chapter 5, it reflects the potential of a substance to undergo physical change. In Chapter 6, we see that μ is the potential of a substance to undergo chemical change.

We base the entire discussion on the following consequence of the Second Law (Fig. 4A.3):

> At equilibrium, the chemical potential of a substance is the same throughout a sample, regardless of how many phases are present.

Criterion of 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 $-\mu_1 \mathrm{d}n$ when material is removed from location 1, and it changes by $+\mu_2 \mathrm{d}n$ when that material is added to location 2. The overall change is therefore $\mathrm{d}G = (\mu_2 - \mu_1)\mathrm{d}n$. 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 Gibbs energy and phase transition

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).

Self-test 4A.3 The standard Gibbs energies of formation of HN_3 at 298 K are +327 kJ mol^{-1} and +328 kJ mol^{-1} for the liquid and gas phases, respectively. Which phase of hydrogen azide is the more stable at that temperature and 1 bar?

Answer: Liquid

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 in this Topic we concentrate 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) 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 called the **vapour pressure** of the substance (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

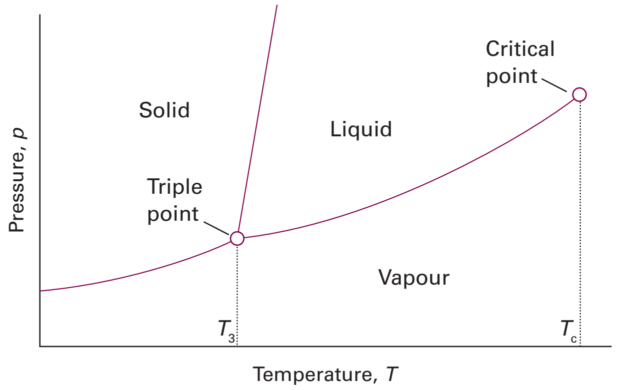

Figure 4A.4 The general regions of pressure and temperature where solid, liquid, or gas is stable (that is, has minimum molar Gibbs energy) are shown on this phase diagram. For example, the solid phase is the most stable phase at low temperatures and high pressures. In the following paragraphs we locate the precise boundaries between the regions.

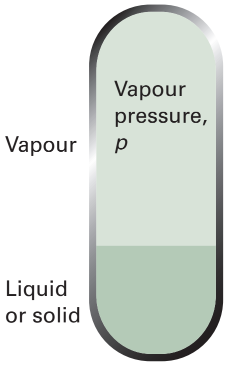

Figure 4A.5 The vapour pressure of a liquid or solid is the pressure exerted by the vapour in equilibrium with the condensed phase.

more molecules have sufficient energy to escape from their neighbours.

When a liquid is heated in an open vessel, the liquid vaporizes from its surface. When the vapour pressure is 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. We need to distinguish normal and standard properties only for precise work in thermodynamics because any thermodynamic properties that we intend to add together must refer to the same conditions.

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. 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.

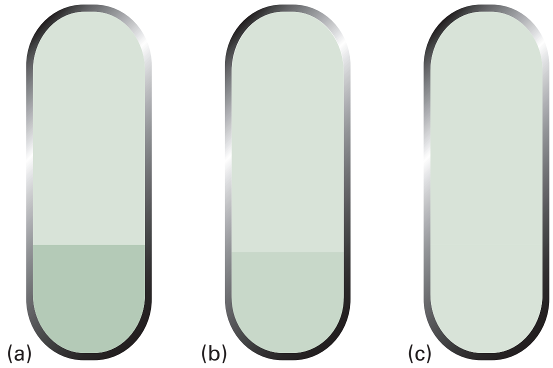

Figure 4A.6 (a) A liquid in equilibrium with its vapour. (b) When a liquid is heated in a sealed container, the density of the vapour phase increases and that of the liquid decreases slightly. There comes a stage (c) at which the two densities are equal and the interface between the fluids disappears. 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.

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.

As we can see 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; the critical temperature is the upper limit.

Brief illustration 4A.4 The triple point

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 about-to-be superseded definition of the Kelvin scale of temperature (Topic 3A).

Self-test 4A.4 How many triple points are present (as far as it is known) in the full phase diagram for water shown later in this Topic in Fig. 4A.9?

Answer: 6

(b) The phase rule

In one of the most elegant arguments of the whole of chemical thermodynamics, which is presented in the following *Justification*, 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:

$$F = C - P + 2 \qquad \text{The phase rule} \tag{4A.1}$$

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. In this chapter we deal only with one-component systems ($C=1$), so for this chapter

$$F = 3 - P \qquad \textit{A one-component system} \qquad \text{The phase rule} \tag{4A.2}$$

By a **constituent** of a system we mean a chemical species that is present. 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.

Brief illustration 4A.5 The number of components

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.

Self-test 4A.5 How many components are present in an aqueous solution of acetic acid, allowing for its partial deprotonation and the autoprotolysis of water?

Answer: 2

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

Justification 4A.1 The phase rule

Consider first the special case of a one-component system for which the phase rule is $F=3-P$. For two phases α and β in equilibrium ($P=2$, $F=1$) at a given pressure and temperature, we can write

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

(For instance, when ice and water are in equilibrium, we have $\mu(\mathrm{s};p,T)=\mu(\mathrm{l};p,T)$ for H_2O.) This is an equation relating p and T, so only one of these variables is independent (just as the equation $x+y=xy$ is a relation for y in terms of x: $y=x/(x-1)$). That conclusion is consistent with $F=1$. For three phases of a one-component system in mutual equilibrium ($P=3$, $F=0$),

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

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

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

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

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

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

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

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

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

which is eqn 4A.1.

4A.3 Three representative phase diagrams

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

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

Brief illustration 4A.6 Characteristics of phase diagrams

Figure 4A.7 shows a reasonably typical phase diagram of a single pure substance, with one forbidden feature, the 'quadruple point' where phases β, γ, δ, and ε are said to be in equilibrium. Two triple points are shown (for the equilibria $\alpha \rightleftharpoons \beta \rightleftharpoons \gamma$ and $\alpha \rightleftharpoons \beta \rightleftharpoons \delta$, respectively), corresponding to $P=3$ and $F=0$. The lines represent various equilibria, including $\alpha \rightleftharpoons \beta$, $\alpha \rightleftharpoons \delta$, and $\gamma \rightleftharpoons \varepsilon$.

Self-test 4A.6 What is the minimum number of components necessary before five phases can be in mutual equilibrium in a system?

Answer: 3

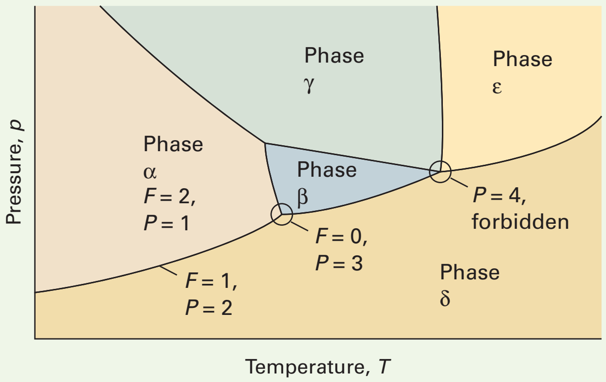

Figure 4A.7 The typical regions of a one-component phase diagram. The lines represent conditions under which the two adjoining phases are in equilibrium. A point represents the unique set of conditions under which three phases coexist in equilibrium. Four phases cannot mutually coexist in equilibrium.

(a) Carbon dioxide

The phase diagram for carbon dioxide is shown in Fig. 4A.8. The features to notice include the positive slope (up from left to right) of the solid–liquid 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

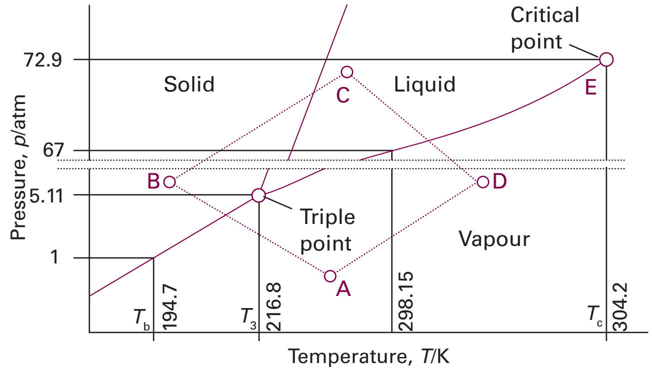

Figure 4A.8 The experimental phase diagram for carbon dioxide. Note that, as the triple point lies at pressures well above atmospheric, liquid carbon dioxide does not exist under normal conditions (a pressure of at least 5.11 atm must be applied). The path ABCD is discussed in *Brief illustration* 4A.7

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. 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 16B).

Brief illustration 4A.7 A phase diagram 1

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.

Self-test 4A.7 Describe what happens on circulating around the critical point, Path E.

Answer: Liquid → $scCO_2$ → vapour → liquid

(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: 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 (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 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.

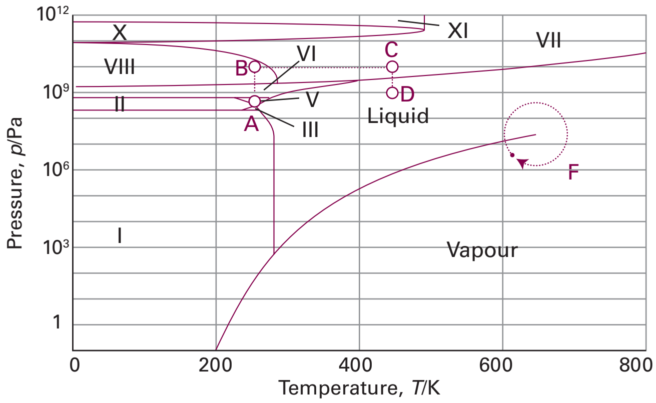

Figure 4A.9 The experimental phase diagram for water showing the different solid phases. The path ABCD is discussed in *Brief illustration* 4A.8.

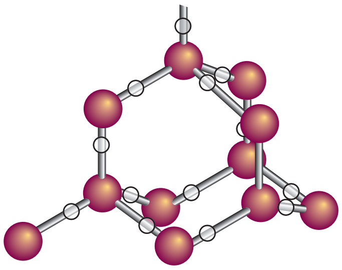

Figure 4A.10 A fragment of the structure of ice (ice-I). Each O atom is linked by two covalent bonds to H atoms and by two hydrogen bonds to a neighbouring O atom, in a tetrahedral array.

Figure 4A.9 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.

Brief illustration 4A.8 A phase diagram 2

Consider the path ABCD in Fig. 4A.9. At A, water is present as ice V. Increasing the pressure to B at the same temperature results in the formation of a polymorph, 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.

Self-test 4A.8 Describe what happens on circulating around the critical point, Path F.

Answer: Vapour → liquid → scH_2O → vapour

(c) Helium

When considering helium at low temperatures it is necessary to distinguish between the isotopes ^{3}He and ^{4}He. 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 their small number of electrons results in them interacting only very weakly with their neighbours. 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. The isotopes of helium behave differently for quantum mechanical reasons that are explained in Part 2. (The difference stems from the different nuclear spins of the isotopes and the role of the Pauli exclusion principle: helium-4 has $I=0$ and is a boson; helium-3 has $I=\frac{1}{2}$ and is a fermion.)

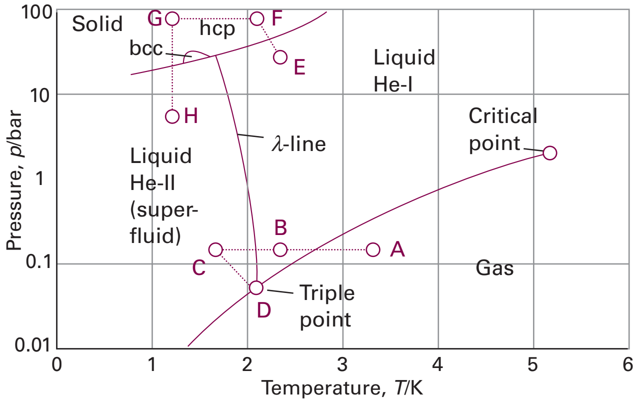

Figure 4A.11 The phase diagram for helium (^{4}He). The λ-line marks the conditions under which the two liquid phases are in equilibrium. Helium-II is the superfluid phase. Note that a pressure of over 20 bar must be exerted before solid helium can be obtained. The labels hcp and bcc denote different solid phases in which the atoms pack together differently: hcp denotes hexagonal closed packing and bcc denotes body-centred cubic (see Topic 18B for a description of these structures). The path ABCD is discussed in *Brief illustration* 4A.9.

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] Provided we discount the liquid crystalline substances discussed in *Impact* I5.1 on line, helium is the only known substance with a liquid–liquid boundary, shown as the **λ-line** (lambda line) in Fig. 4A.11.

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 melting is exothermic ($\Delta_{\text{fus}}H<0$) and therefore (from $\Delta_{\text{fus}}S=\Delta_{\text{fus}}H/T_{\text{f}}$) at the melting point the entropy of the liquid is lower than that of the solid.

Brief illustration 4A.9 A phase diagram 3

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.

Self-test 4A.9 Describe what happens on the path EFGH.

Answer: He-I → solid → solid → He-II

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

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 and may be studied by techniques that include thermal analysis.

☐ **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 substance is characterized by a variety of parameters that can be identified on its **phase diagram**.

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

☐ **6.** Carbon dioxide is a typical substance but shows features that can be traced to its weak intermolecular forces.

☐ **7.** Water shows anomalies that can be traced to its extensive hydrogen bonding.

☐ **8.** Helium shows anomalies that can be traced to its low mass and weak interactions.

Checklist of equations

Property	Equation	Comment	Equation number
Chemical potential	$\mu = G_m$	For a pure substance	
Phase rule	$F = C - P + 2$		4A.1

4B Thermodynamic aspects of phase transitions

Contents

➤ Why do you need to know this material?

This Topic illustrates how thermodynamics is used to discuss the equilibria of the phases of one-component systems and shows how to make predictions about the effect of pressure on freezing and boiling points.

➤ What is the key idea?

The effect of temperature and pressure on the chemical potentials of phases in equilibrium is determined by the molar entropy and molar volume, respectively, of the phases.

➤ 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 3D). We draw on expressions for the entropy of transition (Topic 3B) and the perfect gas law (Topic 1A).

As explained in Topic 4A, the thermodynamic criterion of phase equilibrium is the equality of the chemical potentials of each phase. For a one-component system, the chemical potential is the same as the molar Gibbs energy of the phase. As Topic 3D explains how the Gibbs energy varies with temperature and pressure, by combining these two aspects, we can expect to be able to deduce how phase equilibria vary as the conditions are changed.

4B.1 The dependence of stability on the conditions

At very 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.

(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 3D.8 ($(\partial G/\partial T)_p = -S$). Because the chemical potential of a pure substance is just another name for its molar Gibbs energy, it follows that

$$\left(\frac{\partial \mu}{\partial T}\right)_p = -S_\mathrm{m} \qquad \text{Variation of chemical potential with } T \tag{4B.1}$$

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

Equation 4B.1 implies that because $S_\mathrm{m}(\mathrm{g}) > S_\mathrm{m}(\mathrm{l})$ the slope of a plot of μ against temperature is steeper for gases than for liquids. Because $S_\mathrm{m}(\mathrm{l}) > S_\mathrm{m}(\mathrm{s})$ almost always, the slope is also steeper for a liquid than the corresponding solid. These features are illustrated in Fig. 4B.1. The steep negative slope of $\mu(\mathrm{l})$ results in it falling below $\mu(\mathrm{s})$ 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.

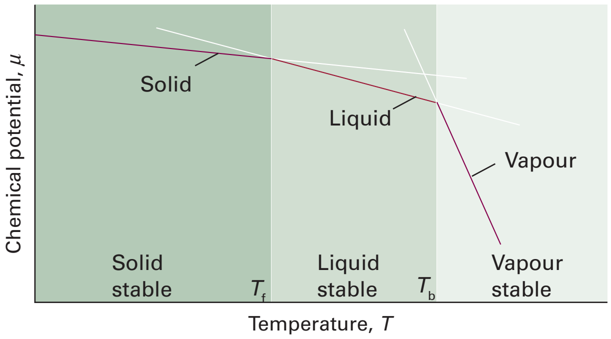

Figure 4B.1 The schematic temperature dependence of the chemical potential of the solid, liquid, and gas phases of a substance (in practice, the lines are curved). The phase with the lowest chemical potential at a specified temperature is the most stable one at that temperature. The transition temperatures, the melting and boiling temperatures (T_f and T_b, respectively), are the temperatures at which the chemical potentials of the two phases are equal.

Brief illustration 4B.1 The temperature variation of μ

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

$$\delta\mu(\mathrm{l}) \approx S_\mathrm{m}(\mathrm{l})\delta T = 87\,\mathrm{J\,mol^{-1}} \qquad \delta\mu(\mathrm{g}) \approx S_\mathrm{m}(\mathrm{g})\delta T = 196\,\mathrm{J\,mol^{-1}}$$

At 100 °C the two phases are in equilibrium with equal chemical potentials, so at 1.0 K higher the chemical potential of the vapour is lower (by 109 J mol⁻¹) than that of the liquid and vaporization is spontaneous.

Self-test 4B.1 The standard molar entropy of liquid water at 0 °C is 65 J K⁻¹ mol⁻¹ and that of ice at the same temperature is 43 J K⁻¹ mol⁻¹. What is the effect of increasing the temperature by 1.0 K?

Answer: $\delta\mu(\mathrm{l}) \approx -65\,\mathrm{J\,mol^{-1}}$, $\delta\mu(\mathrm{s}) \approx -43\,\mathrm{J\,mol^{-1}}$; ice melts

(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 and ice melts 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 eqns 3D.8, $(\partial G/\partial p)_T = V$) by

$$\left(\frac{\partial \mu}{\partial p}\right)_T = V_\mathrm{m} \qquad \text{Variation of chemical potential with } p \tag{4B.2}$$

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 $V_\mathrm{m} > 0$). In most cases, $V_\mathrm{m}(\mathrm{l}) > V_\mathrm{m}(\mathrm{s})$ 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. 4B.2a, the effect of pressure in such a case is to raise the melting temperature slightly. For water, however, $V_\mathrm{m}(\mathrm{l}) < V_\mathrm{m}(\mathrm{s})$, 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. 4B.2b).

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 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 4B.2 in the form $d\mu = V_m dp$, 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,

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

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

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 4B.2 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 densities 2.35 g cm⁻³ and 2.50 g cm⁻³, respectively.

Answer: $\Delta\mu(\text{l}) = +1.87$ J mol⁻¹, $\Delta\mu(\text{s}) = +1.76$ J mol⁻¹; solid forms

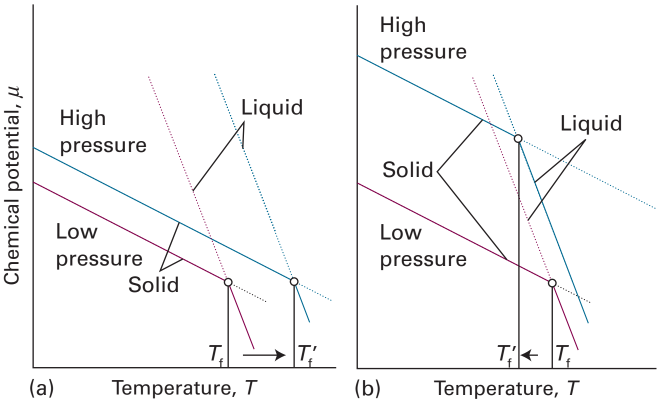

Figure 4B.2 The pressure dependence of the chemical potential of a substance depends on the molar volume of the phase. The lines show schematically the effect of increasing pressure on the chemical potential of the solid and liquid phases (in practice, the lines are curved), and the corresponding effects on the freezing temperatures. (a) In this case the molar volume of the solid is smaller than that of the liquid and μ(s) increases less than μ(l). As a result, the freezing temperature rises. (b) Here the molar volume is greater for the solid than the liquid (as for water), μ(s) increases more strongly than μ(l), and the freezing temperature is lowered.

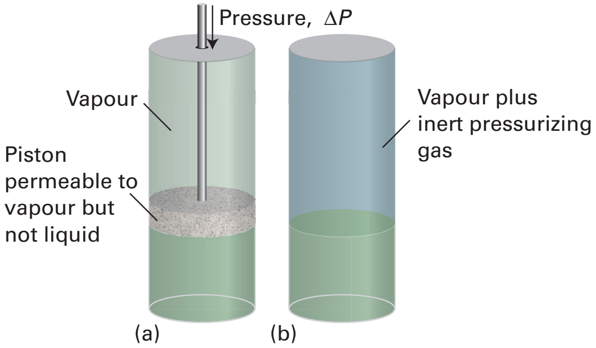

Figure 4B.3 Pressure may be applied to a condensed phase either (a) by compressing the condensed phase or (b) by subjecting it to an inert pressurizing gas. When pressure is applied, the vapour pressure of the condensed phase increases.

(c) The vapour pressure of a liquid subjected to 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 phase mechanically or by subjecting it to the applied pressure of an inert gas (Fig. 4B.3). In the latter case, the vapour pressure is the partial pressure of the vapour in equilibrium with the condensed phase. We then 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^*, of the liquid in the absence of an additional pressure is

$$p = p^{*}e^{V_m(\text{l})\Delta P/RT} \qquad (4\text{B}.3)$$

Effect of applied pressure ΔP on vapour pressure p

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

Justification 4B.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: $\mu(\text{l}) = \mu(\text{g})$. 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, we can write $d\mu(\text{g}) = d\mu(\text{l})$. When the pressure P on the liquid is increased by dP, the chemical potential of the liquid changes by $d\mu(\text{l}) = V_m(\text{l})dP$. 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 $d\mu(g)=RTdp/p$. 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:

$$\int_{p^*}^{p}\frac{dp}{p}=\frac{1}{RT}\int_{p^*}^{p^*+\Delta P}V_m(l)\,dP=\frac{V_m(l)}{RT}\int_{p^*}^{p^*+\Delta P}dP$$

Then both integrations are straightforward, and lead to

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

which rearranges to eqn 4B.3 because $e^{\ln x}=x$.

Brief illustration 4B.2 The effect of pressurization

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, $\Delta P=1.0\times10^6\,Pa$)

$$\frac{V_m(l)\Delta P}{RT}=\frac{(1.81\times10^{-5}\,m^3\,mol^{-1})\times(1.0\times10^6\,Pa)}{(8.3145\,J\,K^{-1}\,mol^{-1})\times(298\,K)}$$
$$=\frac{1.81\times1.0\times10^{1}}{8.3145\times298}=0.0073\ldots$$

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 4B.3 Calculate the effect of an increase in pressure of 100 bar on the vapour pressure of benzene at 25 °C, which has density $0.879\,g\,cm^{-3}$.

Answer: 43 per cent increase

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 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,

$$\mu(\alpha;p,T)=\mu(\beta;p,T) \qquad (4B.4)$$

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. 4B.4). 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 3D.7 ($dG=Vdp-SdT$), we know that $d\mu=-S_mdT+V_mdp$ for each phase, it follows that

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

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

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

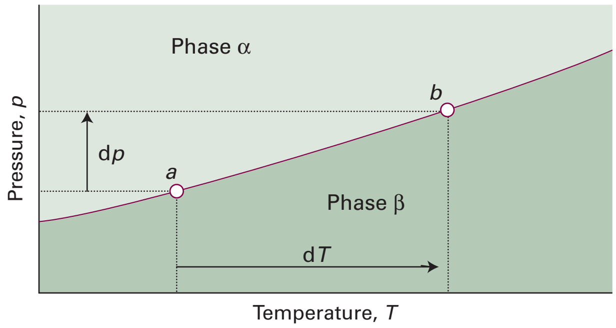

Figure 4B.4 When pressure is applied to a system in which two phases are in equilibrium (at *a*), the equilibrium is disturbed. It can be restored by changing the temperature, so moving the state of the system to *b*. It follows that there is a relation between d*p* and d*T* that ensures that the system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

Then, with $\Delta_{\rm trs}S = S_{\rm m}(\beta) - S_{\rm m}(\alpha)$ and $\Delta_{\rm trs}V = V_{\rm m}(\beta) - V_{\rm m}(\alpha)$, which are the (molar) entropy and volume of transition, respectively,

$$\Delta_{\rm trs}S\,{\rm d}T = \Delta_{\rm trs}V\,{\rm d}p$$

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

$$\frac{{\rm d}p}{{\rm d}T} = \frac{\Delta_{\rm trs}S}{\Delta_{\rm trs}V} \qquad \text{Clapeyron equation} \qquad (4B.5a)$$

The Clapeyron equation is an exact expression for the slope of the tangent to the boundary at any point 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, when it can be used in the form obtained by inverting both sides:

$$\frac{{\rm d}T}{{\rm d}p} = \frac{\Delta_{\rm trs}V}{\Delta_{\rm trs}S} \qquad (4B.5b)$$

Brief illustration 4B.3 The Clapeyron equation

The standard volume and entropy of transition of water from ice to liquid are −1.6 cm³ mol⁻¹ and +22 J K⁻¹ mol⁻¹, respectively, at 0 °C. The slope of the solid–liquid phase boundary at that temperature is therefore

$$\frac{{\rm d}T}{{\rm d}p} = \frac{-1.6\times10^{-6}\,{\rm m^3\,mol^{-1}}}{22\,{\rm J^{-1}\,mol^{-1}}} = -7.3\times10^{-8}\,\frac{\rm K}{\rm J\,m^{-3}} = -7.3\times10^{-8}\,{\rm K\,Pa^{-1}}$$

which corresponds to −7.3 mK bar⁻¹. An increase of 100 bar therefore results in a lowering of the freezing point of water by 0.73 K.

Self-test 4B.4 The standard volume and entropy of transition of water from liquid to vapour are +30 dm³ mol⁻¹ and +109 J K⁻¹ mol⁻¹, respectively, at 100 °C. By how much does the boiling temperature change when the pressure is reduced from 1.0 bar to 0.80 bar?

Answer: −5.5 K

(b) The solid–liquid boundary

Melting (fusion) is accompanied by a molar enthalpy change $\Delta_{\rm fus}H$ and occurs at a temperature T. The molar entropy of melting at T is therefore $\Delta_{\rm fus}H/T$ (Topic 3B), and the Clapeyron equation becomes

$$\frac{{\rm d}p}{{\rm d}T} = \frac{\Delta_{\rm fus}H}{T\Delta_{\rm fus}V} \qquad \text{Slope of solid–liquid boundary} \qquad (4B.6)$$

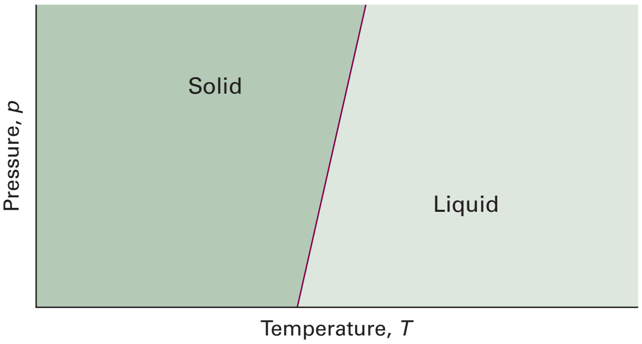

Figure 4B.5 A typical solid–liquid phase boundary slopes steeply upwards. This slope implies that, as the pressure is raised, the melting temperature rises. Most substances behave in this way.

where $\Delta_{\rm fus}V$ 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 ${\rm d}p/{\rm d}T$ is steep and usually positive (Fig. 4B.5).

We can obtain the formula for the phase boundary by integrating ${\rm d}p/{\rm d}T$, assuming that $\Delta_{\rm fus}H$ and $\Delta_{\rm fus}V$ 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

$$\int_{p^*}^{p} {\rm d}p = \frac{\Delta_{\rm fus}H}{\Delta_{\rm fus}V}\int_{T^*}^{T}\frac{{\rm d}T}{T}$$

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

$$p = p^* + \frac{\Delta_{\rm fus}H}{\Delta_{\rm fus}V}\ln\frac{T}{T^*} \qquad (4B.7)$$

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

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

where we have used the expansion $\ln(1+x) = x - \frac{1}{2}x^2 + \cdots$ (*Mathematical background* 1) and neglected all but the leading term; therefore

$$p \approx p^* + \frac{\Delta_{\rm fus}H}{T^*\Delta_{\rm fus}V}(T - T^*) \qquad (4B.8)$$

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

Brief illustration 4B.4 The solid–liquid boundary

The enthalpy of fusion of ice at 0 °C and 1 bar (273 K) 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

$$\begin{aligned} p &\approx 1\,\mathrm{bar} + \frac{6.008\times10^3\ \mathrm{J\,mol^{-1}}}{(273\,\mathrm{K})\times(-1.6\times10^{-6}\ \mathrm{m^3\,mol^{-1}})}(T-T^*) \\ &\approx 1\,\mathrm{bar} - 1.4\times10^7\ \mathrm{Pa\,K^{-1}}(T-T^*) \end{aligned}$$

That is,

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

with $T^* = 273$ K. This expression is plotted in Fig. 4B.6.

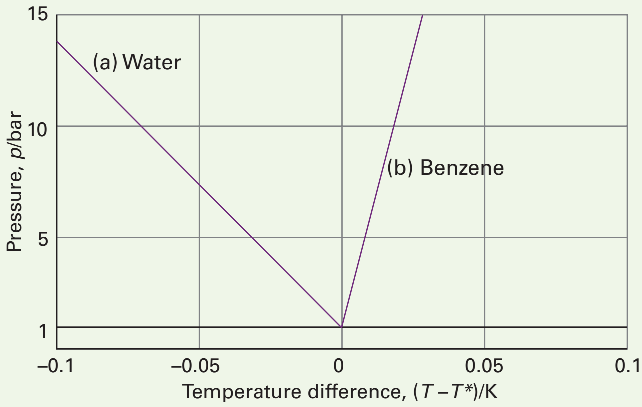

Figure 4B.6 The solid–liquid phase boundaries (the melting point curves) for water and benzene, as calculated in *Brief illustration* 4B.4.

Self-test 4B.5 The enthalpy of fusion of benzene is 10.59 kJ mol^{-1} at its melting point of 279 K and its volume of fusion is close to +0.50 cm^3 mol^{-1} (an estimated value). What is the equation of its solid–liquid phase boundary?

Answer: $p/\mathrm{bar} = 1 + 760(T - T^*)$, as in Fig. 4B.6

(c) The liquid–vapour boundary

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

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta_{\mathrm{vap}}H}{T\Delta_{\mathrm{vap}}V} \qquad \text{Slope of liquid–vapour boundary} \tag{4B.9}$$

The enthalpy of vaporization is positive; $\Delta_{\mathrm{vap}}V$ is large and positive. Therefore, $\mathrm{d}p/\mathrm{d}T$ is positive, but it is much smaller than for the solid–liquid boundary. It follows that $\mathrm{d}T/\mathrm{d}p$ is large, and hence that 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.

Method To use eqn 4B.9 we need to estimate the right-hand side. At the boiling point, the term $\Delta_{\mathrm{vap}}H/T$ is Trouton's constant (Topic 3B). Because the molar volume of a gas is so much greater than the molar volume of a liquid, we can write $\Delta_{\mathrm{vap}}V = V_{\mathrm{m}}(\mathrm{g}) - V_{\mathrm{m}}(\mathrm{l}) \approx V_{\mathrm{m}}(\mathrm{g})$ and take for $V_{\mathrm{m}}(\mathrm{g})$ 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,

$$\frac{\mathrm{d}p}{\mathrm{d}T} \approx \frac{85\ \mathrm{J\,K^{-1}\,mol^{-1}}}{2.5\times10^{-2}\ \mathrm{m^3\,mol^{-1}}} = 3.4\times10^3\ \mathrm{Pa\,K^{-1}}$$

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

Self-test 4B.6 Estimate $\mathrm{d}T/\mathrm{d}p$ for water at its normal boiling point using the information in Table 3A.2 and $V_{\mathrm{m}}(\mathrm{g}) = RT/p$.

Answer: 28 K atm^{-1}

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

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

which, by using $\mathrm{d}x/x = \mathrm{d}\ln x$, rearranges into the **Clausius–Clapeyron equation** for the variation of vapour pressure with temperature:

$$\frac{\mathrm{d}\ln p}{\mathrm{d}T} = \frac{\Delta_{\mathrm{vap}}H}{RT^2} \qquad \textit{Vapour is a perfect gas} \qquad \text{Clausius–Clapeyron equation} \tag{4B.10}$$

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 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, eqn 4B.10 can be integrated as follows:

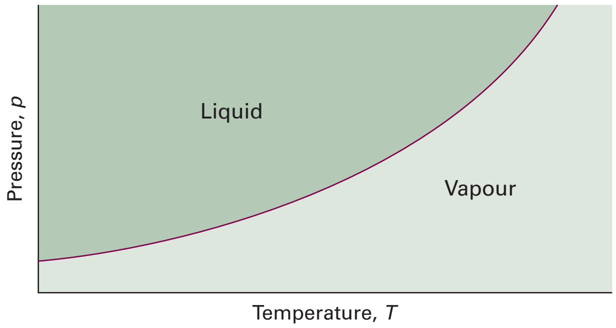

Figure 4B.7 A typical liquid–vapour phase boundary. The boundary can be regarded as a plot of the vapour pressure against the temperature. Note that, in some depictions of phase diagrams in which a logarithmic pressure scale is used, the phase boundary has the opposite curvature (see Fig. 4B.8). This phase boundary terminates at the critical point (not shown).

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

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

$$p = p^* \mathrm{e}^{-\chi} \qquad \chi = \frac{\Delta_{\mathrm{vap}}H}{R}\left(\frac{1}{T}-\frac{1}{T^*}\right) \tag{4B.11}$$

Equation 4B.11 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 The Clausius–Clapeyron equation

Equation 4B.11 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). The normal boiling point of benzene is 80 °C (353 K) and (from Table 3A.2), $\Delta_{\mathrm{vap}}H^{\ominus} = 30.8\,\mathrm{kJ\,mol^{-1}}$. Therefore, to calculate the vapour pressure at 20 °C (293 K), we write

$$\chi = \frac{3.08\times10^4\,\mathrm{J\,mol^{-1}}}{8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}}\left(\frac{1}{293\,\mathrm{K}}-\frac{1}{353\,\mathrm{K}}\right) = 2.14\ldots$$

and substitute this value into eqn 4B.11 with $p^* = 101\,\mathrm{kPa}$. 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, $\Delta_{\mathrm{sub}}H$. Because the enthalpy of sublimation is greater than the enthalpy of vaporization (recall that $\Delta_{\mathrm{sub}}H = \Delta_{\mathrm{fus}}H + \Delta_{\mathrm{vap}}H$), 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. 4B.8).

Brief illustration 4B.6 The solid–vapour boundary

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

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

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

We see that 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.

Self-test 4B.7 Confirm that the same may be said for the plot of p against T at the triple point.

Answer: $\mathrm{d}p/\mathrm{d}T = p\,\mathrm{d}\ln p/\mathrm{d}T$, $p = p_3 = 6.1\,\mathrm{mbar}$

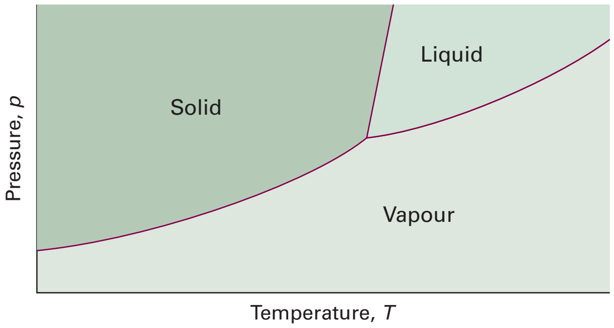

Figure 4B.8 Near the point where they coincide (at the triple point), the solid–vapour boundary has a steeper slope than the liquid–vapour boundary because the enthalpy of sublimation is greater than the enthalpy of vaporization and the temperatures that occur in the Clausius–Clapeyron equation for the slope have similar values.

4B.3 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. Classification is commonly a first step towards a molecular interpretation and the identification of common features. The classification scheme was originally proposed by Paul Ehrenfest, and is known as the **Ehrenfest classification**.

(a) The thermodynamic basis

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,

$$\left(\frac{\partial\mu(\beta)}{\partial p}\right)_T-\left(\frac{\partial\mu(\alpha)}{\partial p}\right)_T=V_\mathrm{m}(\beta)-V_\mathrm{m}(\alpha)=\Delta_\mathrm{trs}V$$
$$\left(\frac{\partial\mu(\beta)}{\partial T}\right)_p-\left(\frac{\partial\mu(\alpha)}{\partial T}\right)_p=-S_\mathrm{m}(\beta)+S_\mathrm{m}(\alpha)=-\Delta_\mathrm{trs}S=-\frac{\Delta_\mathrm{trs}H}{T_\mathrm{trs}} \qquad (4B.12)$$

Because $\Delta_\mathrm{trs}V$ and $\Delta_\mathrm{trs}H$ 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. 4B.9a). In other words, the first derivatives of the chemical potentials with respect to pressure and temperature are discontinuous at the transition.

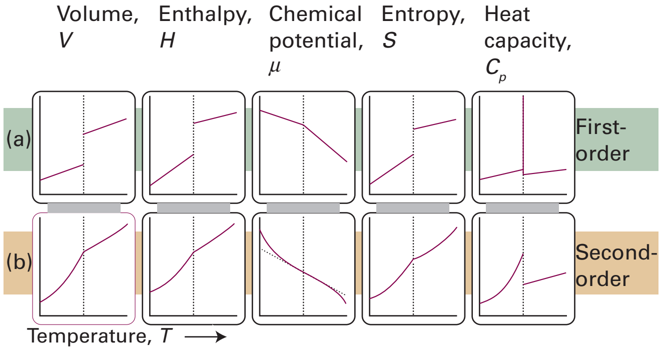

Figure 4B.9 The changes in thermodynamic properties accompanying (a) first-order and (b) second-order phase transitions.

Brief illustration 4B.7 Discontinuities of the transitions

The melting of water at its normal melting point of 0 °C has $\Delta_\mathrm{trs}V=-1.6\,\mathrm{cm^3\,mol^{-1}}$ and $\Delta_\mathrm{trs}H=6.008\,\mathrm{kJ\,mol^{-1}}$, so

$$\left(\frac{\partial\mu(\mathrm{l})}{\partial p}\right)_T-\left(\frac{\partial\mu(\mathrm{s})}{\partial p}\right)_T=\Delta_\mathrm{fus}V=-1.6\,\mathrm{cm^3\,mol^{-1}}$$
$$\left(\frac{\partial\mu(\mathrm{l})}{\partial T}\right)_p-\left(\frac{\partial\mu(\mathrm{s})}{\partial T}\right)_p=-\frac{\Delta_\mathrm{fus}H}{T_\mathrm{fus}}=-\frac{6.008\times10^3\,\mathrm{J\,mol^{-1}}}{273\,\mathrm{K}}$$
$$=-22.0\,\mathrm{J\,mol^{-1}}$$

and both slopes are discontinuous.

Self-test 4B.8 Evaluate the difference in slopes at the normal boiling point.

Answer: $+31\,\mathrm{dm^3\,mol^{-1}}$, $-109\,\mathrm{J\,mol^{-1}}$

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.

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. 4B.9b). 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.[1]

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. 4B.10), and the shape of the heat capacity curve resembles the Greek letter lambda. Examples of λ-transitions include order–disorder transitions in alloys, the onset of ferromagnetism, and the fluid–superfluid transition of liquid helium.

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[1] 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 Topic 18C for more details.

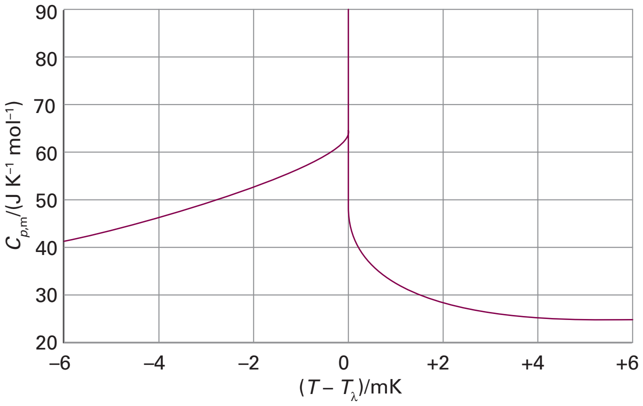

Figure 4B.10 The λ-curve for helium, where the heat capacity rises to infinity. The shape of this curve is the origin of the name λ-transition.

(b) Molecular interpretation

First-order transitions typically involve the relocation of atoms, molecules, or ions with a consequent change in the energies of their interactions. Thus, vaporization eliminates the attractions between molecules and a first-order phase transition from one ionic polymorph to another (as in the conversion of calcite to aragonite) involves the adjustment of the relative positions of ions.

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. 4B.11a, 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 Topic 18A). 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. 4B.11b), 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.

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. 4B.12). 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.

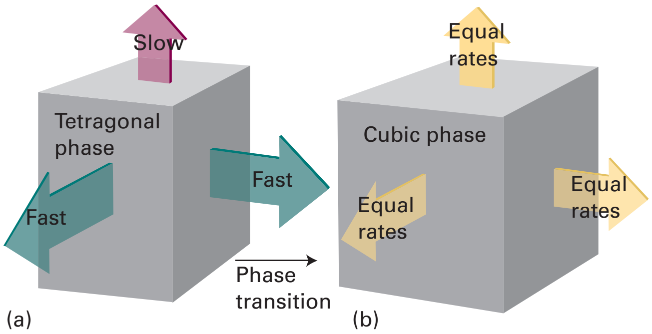

Figure 4B.11 One version of a second-order phase transition in which (a) a tetragonal phase expands more rapidly in two directions than a third, and hence becomes a cubic phase, which (b) expands uniformly in three directions as the temperature is raised. There is no rearrangement of atoms at the transition temperature, and hence no enthalpy of transition.

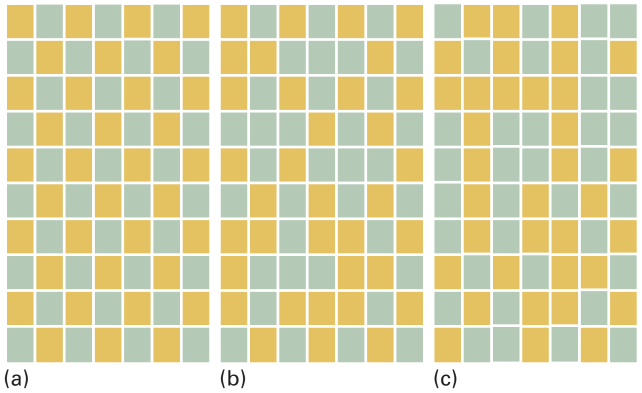

Figure 4B.12 An order–disorder transition. (a) At $T=0$, there is perfect order, with different kinds of atoms occupying alternate sites. (b) As the temperature is increased, atoms exchange locations and islands of each kind of atom form in regions of the solid. Some of the original order survives. (c) At and above the transition temperature, the islands occur at random throughout the sample.

Checklist of concepts

- ☐ **1.** The chemical potential of a substance decreases with increasing temperature at a rate determined by its molar entropy.
- ☐ **2.** The chemical potential of a substance increases with increasing pressure at a rate determined by its molar volume.
- ☐ **3.** When pressure is applied to a condensed phase, its vapour pressure rises.
- ☐ **4.** The **Clapeyron equation** is an expression for the slope of a phase boundary.
- ☐ **5.** The **Clausius–Clapeyron equation** is an approximation that relates the slope of the liquid–vapour boundary to the enthalpy of vaporization.
- ☐ **6.** According to the **Ehrenfest classification**, different types of phase transition are identified by the behaviour of thermodynamic properties at the transition temperature.
- ☐ **7.** The classification reveals the type of molecular process occurring at the phase transition.

Checklist of equations

Property	Equation	Comment	Equation number
Variation of μ with temperature	$(\partial\mu/\partial T)_p = -S_\mathrm{m}$		4B.1
Variation of μ with pressure	$(\partial\mu/\partial p)_T = V_\mathrm{m}$		4B.2
Vapour pressure in the presence of applied pressure	$p = p^{*}\mathrm{e}^{V_\mathrm{m}(\mathrm{l})\Delta P/RT}$	$\Delta P = P_\mathrm{applied} - p^{*}$	4B.3
Clapeyron equation	$\mathrm{d}p/\mathrm{d}T = \Delta_\mathrm{trs}S/\Delta_\mathrm{trs}V$		4B.5a
Clausius–Clapeyron equation	$\mathrm{d}\ln p/\mathrm{d}T = \Delta_\mathrm{vap}H/RT^2$	Assumes $V_\mathrm{m}(\mathrm{g}) \gg V_\mathrm{m}(\mathrm{l})$ and vapour is a perfect gas	4B.10