CHAPTER10

# Changes of phase: background theory

## 10.1 Introduction

A collection of molecules of $H_2O$ are capable of smashing the steel hull of an ocean liner if their temperature is 272 K. If their temperature is increased by less than 1 % to 274 K they pose no danger at all. When ice melts some of its properties change dramatically even though the temperature changes by only a tiny amount. The phenomenon of 'sudden change' of properties is the most general, and the most striking, characteristic of *phase changes*.

In the preceding chapters we have examined the properties of gases, solids and liquids, and seen how it is possible to understand their behaviour in terms of the atoms and molecules of which they are made. The division into just three phases is natural, since in our experience solids, liquids and gases behave strikingly differently. However, the division raises several questions that we will address in this chapter.

§10.2 **Free energy:** It is frankly impossible to understand phase transitions in anything more than a qualitative sense without understanding the role of *free energy*. In this section we will introduce the concept and use it to estimate the melting and boiling temperatures of potassium metal. The key result (which is demonstrated explicitly in Appendix 3) is that the equilibrium phase of a substance is the phase with the lowest Gibbs free energy.

§10.3, §10.4 **Phase transitions** and **Enthalpy change on transformation:** In these sections we look at the key result from §10.2 and extend our analysis to enable us to estimate not only the temperatures at which transitions take place, but also the amount of heat energy required to make them happen.

§10.5 **The 'order' of a phase transition:** The transition temperature of a phase transition can mark one of two things depending on its *order*. It can mark the temperature below which one phase has *completely changed* into another. This is the 'normal' or *first-order* type of phase change. For example, on cooling below its melting temperature, a substance becomes *completely* solid. Alternatively, for so called *non-first order* or *continuous* transitions, the transition temperature marks the temperature below which one phase *begins to change* into another.

§10.6 **Nucleation: supercooling and superheating:** In order to change from one phase (e.g. liquid) to another (e.g. solid) a substance has to somehow 'know' that a solid has a lower free energy than a liquid. But how can a liquid 'know' anything about a solid?

§10.7 **Phase diagrams:** The transition temperatures between phases change with pressure in an interesting and complicated manner. Sometimes we wish to summarise a great deal of information about the general form of these changes and this can be achieved with a phase diagram. Here we learn what phase diagrams are, how they are constructed, and the significance of some of their special features.

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You will find copies of the figures and tables from this chapter.

## 10.2 Free energy

### 10.2.1 Questions and answers

Consider the following questions:

- What factors determine that at a particular temperature a substance should be a liquid, but that at slightly higher temperature the substance should become a gas?
- What factors determine that at a particular pressure a substance should be a liquid, but that at slightly higher pressure the substance should become a solid?

These changes of *phase* are certainly complex in nature and in any particular case we could imagine considering many detailed microscopic features of a substance in search of understanding. However, there exists a general formalism for determining which phase of matter a substance adopts under specified circumstances. The formalism discusses the *equilibrium* phase of material in terms of five quantities listed below:

- **Temperature**: We are already aware that temperature is key factor in determining the equilibrium phase of substance.
- **Pressure**: We will see in §11.4 that the temperature at which the liquid⇔vapour transition occurs depends strongly on pressure. Similarly we shall see in §11.3 that the temperature at which the solid⇔liquid transition occurs depends weakly on pressure. So pressure is also a factor in determining the equilibrium phase of a substance.
- **Volume**: In most experiments the volume of a substance is allowed to vary, being determined by the experimenter's choice of temperature and pressure.
- **Internal energy**: As students of physics we are used to explaining phenomena by stating that objects try to 'minimise their energy'. So for example we noted in §6.1 that solids formed from noble gas atoms chose particular crystal structures in order to minimise their internal energy. It is not surprising therefore that internal energy is a factor in determining the equilibrium phase of a substance.
- **Entropy**: Entropy has not previously been discussed in this book for the reason that there is no simple way of explaining what entropy is. Thus while we appreciate what heat, temperature, pressure and volume are, I have never met a scientist who had a 'sense of entropy'. This tends to make explanations of phenomena in terms of entropy confusing (at first). Now, however, we have no choice but to come to terms with entropy.

The five factors above that influence the equilibrium phase of a substance may be combined into a single mathematical function that reflects the balance between the various terms. The function is (to me at least) shockingly simple: as outlined in detail in Appendix 3, if a substance is in equilibrium at a temperature $T$ and pressure $P$, the phase of the substance which minimises the function:

$$G = U - TS + PV \qquad (10.1)$$

is the equilibrium phase of the substance. The function $G$ is called the *Gibbs free energy* of a substance and is an especially important quantity in understanding changes of phase. It is usually expressed in units of kJ mol$^{-1}$ but may also be expressed in several other formats, commonly as electron volts per molecule (eV molecule$^{-1}$)

**Entropy: an aside**

Microscopically, entropy is related to the amount of *order* in a substance. We can readily appreciate that heating a substance, i.e. adding heat energy $\Delta Q$ to a substance, will increase the amount of disordered motion of the constituent atoms of a substance. Macroscopically the quantitative measure of this disorder is the entropy $S$ of the substance. If an amount of heat $\Delta Q$ is added to a substance at temperature $T$ then the entropy $S$ of the substance is increased by $\Delta S$ given by the surprisingly simple formula:

$$\Delta S = \frac{\Delta Q}{T} \text{ joule kelvin}^{-1} \left(\mathrm{J\,K^{-1}}\right) \qquad (10.2)$$

The total entropy of a substance is conventionally assigned to be zero for a substance in equilibrium at absolute zero, and so the total entropy of a substance at temperature $T$ is given by:

$$S = S_o + \int_0^T \frac{\Delta Q}{T} \mathrm{d}T \qquad (10.3)$$

as shown in Example 10.2.

Entropy is discussed a little further in Appendix A3, but at this point we note the similarity between the entropy and the internal energy $U$

$$U = U_o + \int_0^T \Delta Q \mathrm{d}T \qquad (10.4)$$

**But what *is* entropy?**

Nature has provided we humans with a sense of temperature, albeit with rather non-linear sensors. Also, we can fairly easily develop concepts of thermal energy (heat) and mechanical energy (work). Developing an appreciation of what entropy *is*, or refers to, is more difficult. Each of us has to make this journey towards understanding alone, and so I offer the following paragraphs as a gesture of friendship to those of you struggling with the concept.

Consider a solid made of long chain polymers. By considering the shape of each molecule, it is possible to calculate the equilibrium structure of such a solid. We did this kind of thing in §6.2 for simple molecules. However, in practice the solid is unlikely ever to be found in this structure. This is because long molecules are easily tangled up. You can observe this process if you fill a box with electrical leads with a plug on either end. If you place the leads in carefully (make a crystal), then shake the box (increase the temperature), then you can be pretty sure to find that the leads are tangled in ways which are extremely complicated. It requires careful untangling to restore the leads to their pristine structure. In particular, once tangled, no amount of shaking will *ever* return the leads to their untangled state. What you have observed is analogous to the tendency of atoms and molecules to try out different ways of arranging themselves. You have also seen that this tendency becomes stronger at higher temperatures.

Another analogy for the action of entropy can be found in the game of snooker (or ‘pool’). Anyone who has ever played this game knows that the lowest energy state for the snooker balls is in the pockets. When they approach the pockets with just the right speed and from the correct angle, the balls are satisfyingly captured. However, this is irrelevant to the amateur snooker player for whom the balls just bounce around on the surface of the table without showing any tendency to be captured. The analogy with entropy is that molecules will only enter a low-energy state if they can find it. If there are many more high-energy ways of behaving, then molecules can essentially indefinitely resist the tendency to occupy low-energy states. This is the action and the effect of entropy.

### Example 10.1

**A quantity of heat $\Delta Q$= 0.2 J is added to a large amount of the substance at (a) 0.1 K, (b) 1 K, and (c) 10 K. Calculate the increase in entropy of the substance at each temperature.**

We assume the amount of substance is large enough that the temperature rise in each case is small. The increase in entropy in each case is given by Equation 10.2:

$$\Delta S = \frac{\Delta Q}{T}$$

So in case (a) we have:

$$\Delta S_a = \frac{0.2}{0.1} = 2 \ \mathrm{J\,K^{-1}}$$

and in cases (b) and (c) we have $\Delta S_b$ = 0.2 J K$^{-1}$ and $\Delta S_c$= 0.02 J K$^{-1}$ respectively. Notice that adding a given amount of heat at low temperatures causes a large increase in entropy (disorder), whereas the same quantity of heat added at higher temperature adds less entropy.

Colloquially we might consider that adding a certain amount of heat energy to a substance at low temperatures is the equivalent of placing an energetic bull into a calm shop selling porcelain: the result is a large increase in the disorder. Adding the same amount of energy to a substance at a higher temperature is the equivalent of placing another energetic bull into a shop already full of other energetic bulls: the amount of added disorder is less noticeable.

## 10.2.2 The Gibbs free energy

The circumstances in which we imagine an experiment being performed on a substance are usually such as to maintain the temperature constant in a cryostat or a furnace, and the pressure is either the ambient atmospheric pressure, or a controlled and stabilised pressure. Thus $P$ and $T$ are usually the controlled parameters of an experiment with the volume a 'free' parameter able to adjust itself appropriately to the temperature and pressure.

Let us look at each of the three terms on the right-hand side of Equation 10.4 and see how each contributes to $G$:

$$G = U - TS + PV \qquad (10.1^*)$$

$U$ The internal energy. Lowering $U$ helps to minimise $G$.

$TS$ The temperature times the entropy. In order to minimise $G$ the substance should try to *maximise* this product. At a given temperature this means choosing a state with maximum $S$. The requirement to maximise $S$ becomes less significant at low temperatures because $T$ is a multiplying factor.

$PV$ The pressure times the volume. In order to minimise $G$ the substance should try to minimise this product. At a given pressure this means choosing a state with the *minimum* volume.

Consider a substance at a particular temperature $T$ and pressure $P$, and imagine that the substance is able to 'try out' different phases in order to determine which phase minimises its *Gibbs free energy*. Let us consider the three terms in Equation 10.1 for each state: solid, liquid and gas. As we show in Appendix 3 the state which minimises $G$ will form the equilibrium state of the system.

The factors which favour of one state or another are summarised in Tables 10.1. We see that at a given temperature and pressure, a substance may seek to minimise $G$ in any of several ways. For example it may:

- minimise its internal energy: this is best achieved in the solid or liquid state
- maximise its entropy: this is best achieved in the liquid or gaseous state
- minimise its volume: this is best achieved in the solid or liquid state.

The state which minimises the *sum* of the three terms will depend on the balance of the terms.

## Example 10.2

**A substance is heated from $T_1$ to $T_2$. Neglecting thermal expansion, deduce an expression for the increase in entropy and internal energy of the substance.**

**Internal energy**

Consider the temperature rise d$T$ due to an infinitesimal input of heat d$Q$. If the substance expands only negligibly the work done by the substance on its environment d$W$ is negligible. The first law of thermodynamics (d$U$ = d$Q$ + d$W$) then tells us that the heat input d$Q$ goes entirely to increasing the internal energy of the substance d$U$. The heat input d$Q$ is related to the temperature rise d$T$ by the heat capacity d$Q$ = $C$d$T$. So the change in internal energy d$U$ due to d$Q$ is given by d$U$ = $C$d$T$. If $C$ varies with temperature (as it generally does) then the total change in internal energy on heating from temperature $T_1$ to $T_2$ is given by:

$$\Delta U = \int_{T_1}^{T_2} C(T)\mathrm{d}T$$

Putting $T_1$ =0 and $T$ =$T_2$ we arrive at:

$$U(T) = U_0 + \int_0^T C(T)\mathrm{d}T$$

where $U_0$ is the cohesive energy of the substance in the solid state at $T$= 0.

**Entropy**

Consider the temperature rise d$T$ due to an infinitesimal input of heat d$Q$. As above, we assume that d$W$ is negligible so that d$U$ = d$Q$ By the definition of entropy (Equation 10.2) the heat d$Q$ carries with it entropy d$S$ given by:

$$\mathrm{d}S = \frac{\mathrm{d}Q}{T}$$

By the definition of the heat capacity d$Q$ = $C$d$T$ and so:

$$\mathrm{d}S = \frac{C\mathrm{d}T}{T}$$

Thus the total change in entropy on heating from temperature $T_1$ to $T_2$ is given by:

$$\Delta S = \int_{T_1}^{T_2} \frac{C(T)}{T}\mathrm{d}T$$

Putting $T_1$ =0 and $T$ =$T_2$ we arrive at:

$$\Delta S = S_0 + \int_{T_1}^{T_2} \frac{C(T)}{T}\mathrm{d}T$$

where $S_0$ is the entropy of the substance in the solid state at $T$= 0. Conventionally $S_0$ is take to be zero.

**Table 10.1** Summary of the contributions to the Gibbs free energy in each of the possible states of matter.

| | *U* | *−TS* | *+PV* |
|---|---|---|---|
| **Solid** | In a solid atoms are close together and interact strongly. This terms is therefore large and negative. | The entropy of a solid is very low. This is because solids are highly ordered, which is *a priori* a very unlikely state for matter to be in. However, the entropy is multiplied by temperature. If the temperature is low, *TS* will be small, but if the temperature is large this term will be very significant. | At a given pressure the volume of a solid is close to the minimum volume that a substance can occupy. This makes this term small. |
| **Gas** | The interaction between atoms is many orders of magnitude weaker in gases than in solids. In the Ideal Gas theory it is neglected entirely. | The entropy of a gas is very high. This is because gases are completely disordered collections of atoms. | At a given pressure the volume of a gas is as large as it is able to be. |
| **Liquid** | The interaction between atoms is of the same order as in the solid state, but the lack of organisation means that the internal energy is generally not quite as low as in a solid. | The entropy of a liquid is a little larger than a solid. | At a given pressure the volume of a liquid is similar to that of a solid. |

### At absolute zero

At absolute zero matters are relatively straightforward. The internal energy term is just $U_o$, the *cohesive energy* of the substance. The term $TS$ containing the entropy is zero because $T = 0$. And the term $PV$ is negligible in comparison with $U_o$. Considering all these factors we see that at $T = 0$, the equilibrium state of the substance (i.e. the state with minimum $G$) will be the state which minimises the internal energy of the substance. With the sole exception of helium, this state is always the solid state. This is the justification for our calculations in §6.2. There we tried to determine which crystal structure a substance would adopt by considering only the internal energy of the solid. If we wished to repeat that procedure at higher temperatures, we would need to consider the minimum value of $G$, which would be considerably more complicated to estimate.

If we consider a substance to have a cohesive energy per atom of $u_o$ electron volts, then the internal energy of substance at $T = 0$ K will be just:

$$U_o = -u_o e N_A \;\; \text{J mol}^{-1} \tag{10.5}$$

where $e$ is the charge on the proton, $N_A$ is the Avogadro number, and the minus sign indicates that the energy is negative with respect to the state in which the atoms are widely separated from one another.

$$\begin{aligned} U_o &= -u_o \times 1.6\times10^{-19} \times 6.02\times10^{23} \\ &\approx -96 u_o \;\; \text{kJ mol}^{-1} \end{aligned} \tag{10.6}$$

### At finite temperature

Above absolute zero the other terms in the Gibbs free energy must be taken into account. As outlined in Example 10.2, we can estimate the internal energy $U(T)$ by:

$$U(T) = U_o + \int_0^T C(T)\mathrm{d}T \tag{10.7}$$

where $U_o$ is the cohesive energy of the substance in the solid state at $T = 0\,\text{K}$. Similarly we can estimate the entropy $S(T)$:

$$S(T) = S_o + \int_0^T \frac{C(T)}{T}\mathrm{d}T \tag{10.8}$$

However the calculations involved require two key pieces of information:

### Example 10.3

**Compare the terms $U$ and $PV$ in the Gibbs free energy for a solid at absolute zero.**

Cohesive energies range from around 0.1 eV per atom for molecularly bonded substances to around 10 eV per atom for substances such as diamond. A typical figure of around 1 eV per atom yields a cohesive energy of $U_o \approx -100$ kJ mol$^{-1}$.

We can compare this with the $PV$ term at atmospheric pressure. The volume of one mole of substance in the solid or liquid states is just the mass of one mole divided by the density of the substance. Using typical figures of $m \approx 100 \times 10^{-3}$ kg and $\rho \approx 10 \times 10^{3}$ kg m$^{-3}$ indicates a molar volume of $\approx 10^{-5}$ m$^3$ mol$^{-1}$(i.e around 10 cm$^3$). At atmospheric pressure, the $PV$ term evaluates to:

$$1.013 \times 10^5 \text{ Pa} \times 10^{-5} \text{ m}^3 \text{ mol}^{-1} \approx 1 \text{ J mol}^{-1}$$

Thus at zero temperature, the $PV$ term in the Gibbs free energy amounts to only $\approx 10^{-5}$ of the cohesive energy.

- We must know the heat capacity as function of temperature $C(T)$ in order to calculate either $U(T)$ or $S(T)$
- We must know the cohesive energy $U_o$. In general, this involves rather complicated calculations, or complex inferences from experimental data.

So although straightforward in principle, accurately calculating $G$ as a function of temperature is in practice rather difficult.

### 10.2.3 Gibbs free energy: an example

Let us examine the balance between contributions to the Gibbs free energy by means of an example. We will attempt to calculate the Gibbs free energy for potassium as a function of temperature. We do not have full data available for this element, but this will force us to rely on our general knowledge of the properties of matter. We shall have to make assumptions about what is typical for a substance, based on the data in Chapters 5, 7 and 9.

To determine the temperature at which a phase transition takes place, we need to estimate *all* of the terms in $G$ for each of the phases under consideration. In Table 10.2 we summarise the contributions to $G = U - TS + PV$ in the solid and gaseous phases and suggests how we may estimate these. The liquid state is considered later in Table 10.3.

In compiling Table 10.2 the following assumptions have been made. $U_o$ for the solid is taken from Table 11.5 and $U_o$ for the gas is taken as zero. $S_o$ for the solid is (in line with convention) taken as zero and $S_o$ for the gas is chosen so as to agree with the thermodynamic data from *Emsley*.

To compound the difficulty of estimating $S$ for the gas phase, the behaviour of the heat capacity of the gas at low temperatures is not known either. This problem is overcome by considering the heat capacity of the gas to be that of an ideal gas, and then adding the $S_o$ constant so as to achieve agreement with the data from *Emsley*.

The results of calculations of these quantities have been evaluated using a spreadsheet computer program and are shown in Figure 10.1. We see that the balance of terms in $G$ is such that at low temperatures, the $U + PV$ terms dominate and the substance seeks to have a low internal energy and a low volume. At higher temperatures however, the more disordered state minimises $G$.

We can consider the entropy $S$ to be weighted by a factor $T$ in the expression for $G$. So at low temperatures the $TS$ term is weighted rather little, and substances choose phases which minimise $U + PV$, of which the internal energy term usually dominates. This is the situation which we met in §6.2, where we predicted the equilibrium crystal structure of argon from a consideration of its internal energy alone. At high temperatures the $TS$ term is weighted more strongly and at high enough temperatures substances choose phases which maximise $TS$ (or minimise $-TS$), i.e. phases which have a high degree of disorder.

In the case of potassium, the balance between terms is such that we predict that at atmospheric pressure, the solid state should transform into the gaseous state at around 824 K.

In fact, potassium transforms into the *liquid state* at around 336 K and then into the gaseous state at around 1033 K (Table 11.1): not a very good agreement.

**Table 10.2** Summary of the contributions to the Gibbs free energy $G = U - TS + PV$ in the solid and gas phases. The results of the sum are plotted as a function of temperature in Figure 10.1.

| | ***U*** **(mol$^{-1}$)** | ***TS*** **(mol$^{-1}$)** | ***PV*** **(mol$^{-1}$)** |
|---|---|---|---|
| **Solid** | The cohesive binding energy is given by Table 11.5 as –90.1 kJ mol$^{-1}$. To estimate *U* we evaluate:<br>$-90.1\times10^3+\int C_V(T)\mathrm{d}T$<br>where $C_V(T)$ is estimated from a Debye model of a solid with a Debye temperature of 100 K. | Estimated from:<br>$T\left[\int\frac{C_V(T)}{T}\mathrm{d}T\right]$<br>with $C_V(T)$ estimated from a Debye model of a solid with a Debye temperature of 100 K.<br>The entropy at $T = 0$ K is taken as zero. | We neglect thermal expansion and estimate *PV* from the density and atomic mass (Table 7.2).<br>At atmospheric pressure we find:<br>$PV = 1.013\times10^5\times\frac{39\times10^{-3}}{830}$<br>This term is very small. |
| **Gas** | Assuming perfect gas behaviour, we have no binding energy and so we estimate U as:<br>$0+\int C_V(T)\mathrm{d}T$<br>where $C_V(T)$ is estimated from an assumption of perfect gas behaviour as $C_V = 1.5R$ independent of temperature. | Estimated from:<br>$T\left[\int\frac{C_V(T)}{T}\mathrm{d}T\right]$<br>with $C_V(T)$ estimated from an assumption of perfect gas behaviour as $C_V = 1.5R$ independent of temperature.<br>The entropy at T = 0 K is chosen so as make the entropy of potassium vapour at 298 K agree with the data from *Emsley*. | We use the perfect gas equation for 1 mole of substance to evaluate :<br>$PV = RT$ |

Let us see if matters are improved if we make a calculation of *G* for the liquid state. Unfortunately, this is a difficult thing to do realistically because we have no simple universal theory of the liquid state from which we can deduce the properties of liquids. However we do have sufficient information in Chapter 9 to make an informed guess at the behaviour of $G_{\text{liquid}}$.

- We know that $|U_{\text{liquid}}|$ is less than $|U_{\text{solid}}|$, because the atoms are not so efficiently packed in a liquid. We assume that if the potassium existed in its liquid phase at absolute zero its cohesive energy would be only around 90% of that found in crystalline potassium.
- Furthermore we know from §9.10.1 that at high temperatures the heat capacity of liquids is roughly temperature-independent and typically around 10% higher than that of solids.
- We do not know the residual entropy of the liquid state as compared with the solid state at $T = 0$ K. For the sake of simplicity we set this constant equal to zero, and merely acknowledge that this detracts from the accuracy of the results.
- We know (§9.2) that the volume of liquids is typically 10 % higher than that of the equivalent solid. However the *PV* term is not large for either liquids or solids.

Our estimates for the three terms in $G_{\text{liquid}}$ are shown in Table 10.3 and the results of this calculation performed on a spreadsheet are plotted along with those of Figure 10.1 in Figure 10.2

The calculated results shown in Figure 10.2 indicate that it is possible to understand how the liquid state can become more stable In a limited temperature range. This range can be thought of as a ‘bridging region’ linking the low entropy, high cohesive energy state at low temperatures with the high entropy, low cohesive energy state at high temperatures. Our only input to this calculation has been some plausible assumptions about the entropy, internal energy and heat capacity in the liquid state.

**Table 10.3** Summary of the contributions to the Gibbs free energy $G = U - TS + PV$ in the liquid phase. The results are plotted as a function of temperature along with the results from Table 10.1 in Figure 10.2.

| | ***U***<br>**(mol$^{-1}$)** | ***TS***<br>**(mol$^{-1}$)** | ***PV***<br>**(mol$^{-1}$)** |
|---|---|---|---|
| **Liquid** | The cohesive binding energy of the solid is given by *Kittel* as –90.1 kJ mol$^{-1}$. Assuming a value of around 90% of this figure we estimate *U* as:<br>$-81\times10^3 + \int C_V(T)\mathrm{d}T$<br>where $C_V(T)$ is estimated to be 10% greater than the equivalent solid and to have a lower Debye temperature. | Estimated from:<br>$T\left[\int \frac{C_P(T)}{T}\mathrm{d}T\right]$<br>where $C_V(T)$ is estimated to be 10% greater than the equivalent solid and to have a lower Debye temperature.<br>The entropy at $T = 0$ is set equal to zero as for a solid. This will underestimate the entropy of the liquid state. | We consider this term to be the same as the solid. |

## Sensitivity of transition temperatures to assumptions

Notice that at zero temperature $G_{\text{liquid}}$ is just a little above $G_{\text{solid}}$. As we have seen, the heat capacities of liquids are only a little greater than solids and so the entropy rises at only a slightly greater rate than for solids. Because $G_{\text{solid}}$ varies in a similar manner to $G_{\text{liquid}}$, the predicted transition temperature is sensitive to the assumptions made in the calculation.

Small changes in our assumptions lead to large changes in transition temperatures. For example, the calculation illustrated in Figure 10.2 predicts that potassium will melt at 498 K (experimental value 336 K) and that potassium will boil at 922 K (experimental value 1033 K). In Figure 10.3 we illustrate the result of a calculation assuming that the cohesive energy of the liquid state at $T = 0$ K would be 95 % of the solid value, instead of 90 % as assumed in Figure 10.2. This calculation pre-

**Figure 10.1** The result of a calculation of the Gibbs free energy *G* for potassium in its solid and gaseous states. The simplest assumptions possible have been made about the behaviour of *U*, *S* and *V* in this temperature range. Notice that at zero temperature $G_{\text{gas}}$ is zero but $G_{\text{solid}}$ is large and negative. This arises because at low temperatures the internal energy *U* is the main contributor to *G*.

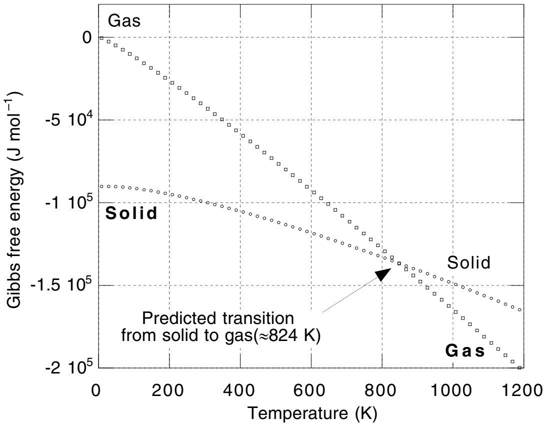
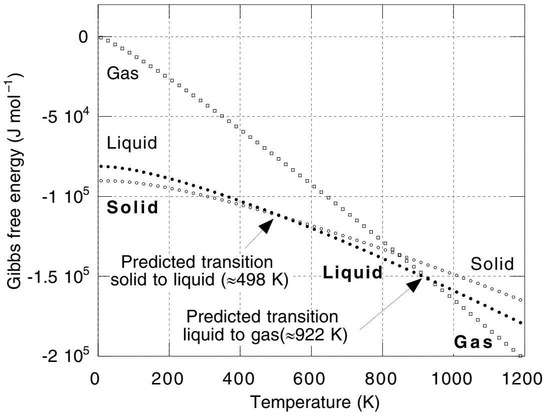


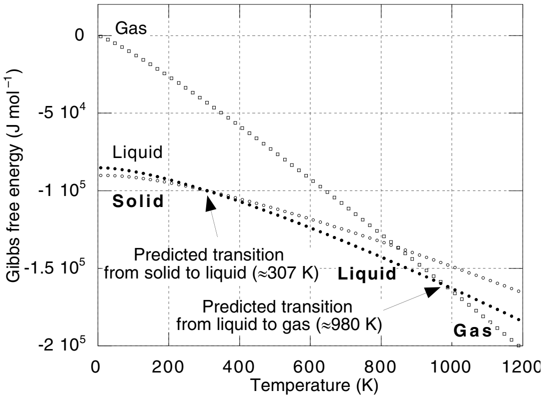
**Figure 10.2** The result of a calculation of the Gibbs free energy *G* for potassium in its solid, liquid and gaseous phases. See also Figure 10.1. Notice that at zero temperature $G_{\text{liquid}}$ is just a little above $G_{\text{solid}}$. As we have seen, the heat capacities of liquids are only a little greater than solids and so the entropy rises at only a slightly greater rate than for solids. The similar variation of $G_{\text{solid}}$ and $G_{\text{liquid}}$ means that the predicted transition temperature is sensitive to the assumptions made in the calculations.



dicts that potassium will melt at 307 K and boil at 980 K, much closer to experimental values.

The better agreement between predicted and experimental values of $T_M$ and $T_B$ in Figure 10.3 should not be taken to indicate that the assumptions of the second calculation are any more realistic than the first. The two calculations are presented merely to indicate how sensitive the calculations are to assumptions made about the states involved. The success of both these calculations is that they predict a liquid state at all! Determining realistic values for $T_M$ and $T_B$ requires a good deal of attention to details that we have neglected to consider here.

**Figure 10.3** The result of a calculation of the Gibbs free energy *G* for potassium in its solid, liquid and gaseous phases. See also Figure 10.2 above. In this figure we have assumed a cohesive energy in the liquid state of 95% of the solid value rather than 90% as assumed in Figure 10.2. The resulting predictions for $T_M$ and $T_B$ have changed significantly.



## 10.3 Phase transitions

We can now state in a general sense why phase transitions occur: they occur because the Gibbs free energy of one state of matter becomes less than that of another. It is important to realise that the free energy is a function which combines *both* the internal energy of the substance *and* the natural tendency of all states towards disorder. So the equilibrium state of substance is *not* (as students frequently maintain) the state which minimise the internal energy. If this were true, substances would remain solids at all temperatures.

Our general picture of solid ⇔ liquid ⇔ gas phase transitions is summarised in Figure 10.4. Notice that at each transition temperature the *slope* of the Gibbs free energy changes suddenly from one value to another. Let us perform some manipulations on the Gibbs free energy in order to look at its gradient with respect to temperature. In general we have:

$$G = U - TS + PV \qquad (10.1^*)$$

Changes in *G* result from changes in internal energy, temperature, entropy, pressure, and volume. Thus we may write a small (differential) change in *G* as:

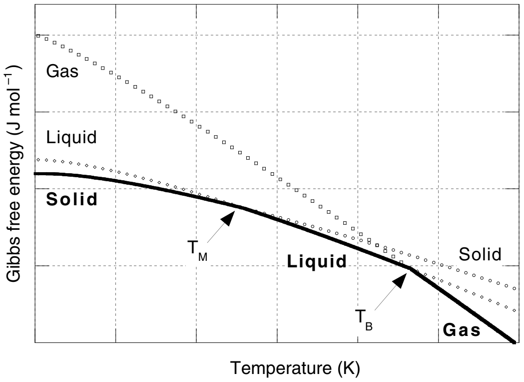
$$\mathrm{d}G = \mathrm{d}U + P\mathrm{d}V + V\mathrm{d}P - T\mathrm{d}S - S\mathrm{d}T \qquad (10.9)$$

This is a complicated expression. However, the first law of thermodynamics asserts that:

$$\Delta U = \Delta Q + \Delta W \qquad (2.41^*)$$

From the definition of entropy we can substitute

**Figure 10.4** A substance seeking to minimise its Gibbs free energy will jump from one curve to another at the temperature at which the Gibbs free energy of one phase becomes lower than another. In this case the substance jumps from the solid to the liquid curve at $T_M$ and then to the gaseous curve at $T_B$.



for $\Delta Q$:

$$\Delta Q = T\Delta S \tag{10.2*}$$

If we are careful to account of the sign of the work done *on* the gas in expanding by $\Delta V$ we write the first law as:

$$\Delta U = T\Delta S - P\Delta V \tag{10.10}$$

which in differential limit is:

$$\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V \tag{10.11}$$

We now re-arrange this so that all the terms are on the same side to find that:

$$\mathrm{d}U + P\mathrm{d}V - T\mathrm{d}S = 0 \tag{10.12}$$

We can now apply this result to Equation 10.5:

$$\mathrm{d}G = \underbrace{\mathrm{d}U + P\mathrm{d}V - T\mathrm{d}S}_{=0} + V\mathrm{d}P - S\mathrm{d}T \tag{10.13}$$

which simplifies the equation considerably:

$$\mathrm{d}G = V\mathrm{d}P - S\mathrm{d}T \tag{10.14}$$

Now if the changes of phase in which we are interested take place at constant pressure (as they usually do) the alterations in $G$ are not due to changes in pressure. So we put $\mathrm{d}P = 0$. In this case we have:

$$\mathrm{d}G = -S\mathrm{d}T \tag{10.15}$$

which amounts to:

$$\left.\frac{\mathrm{d}G}{\mathrm{d}T}\right|_{\mathrm{P}} = -S \tag{10.16}$$

This equation tells us that the slope of the Gibbs free energy with respect to temperature at constant pressure is just the negative of the entropy $S$. Thus all curves on graphs of $G$ versus $T$ (such as Figures 10.1 to 10.4) must have negative slopes. Also high entropy states have steeper slopes than low entropy states. This allows us to understand analytically what we already appreciate physically: the phase of matter with the highest entropy (colloquially the least amount or ‘order’ or ‘structure’) will eventually become the equilibrium phase of the substance. The steepness of the curve will eventually overtake *any* amount of advantage given to a phase which has an large cohesive energy. Ultimately everything will enter the gaseous phase.

Around a phase transition point, we can apply Equation 10.10 to produce a particularly useful and interesting result. In what follows we use the subscripts ‘1’ to indicate the lower temperature phase (which might be a solid or a liquid) and ‘2’ to indicate the higher temperature phase (which might be a liquid or a gas).

At temperatures infinitesimally below and infinitesimally above a phase transition we have:

$$\left(\frac{\mathrm{d}G}{\mathrm{d}T}\right)_1 = -S_1 \quad \text{and} \quad \left(\frac{\mathrm{d}G}{\mathrm{d}T}\right)_2 = -S_2 \tag{10.17}$$

Thus the difference in the slopes is given by

$$\left(\frac{\mathrm{d}G}{\mathrm{d}T}\right)_2 - \left(\frac{\mathrm{d}G}{\mathrm{d}T}\right)_1 = \left[-S_2\right] - \left[-S_1\right] \tag{10.18}$$

$$\begin{aligned}\left(\frac{\mathrm{d}G}{\mathrm{d}T}\right)_2 - \left(\frac{\mathrm{d}G}{\mathrm{d}T}\right)_1 &= S_1 - S_2 \\ &= -\Delta S\end{aligned} \tag{10.19}$$

Since we are at a phase transition, we have $S_2 > S_1$ so $\Delta S$ in Equation 10.13 is a positive quantity. Thus in order to move from the lower temperature curve (1) to the higher temperature curve (2) and so accomplish the phase transition, a quantity of entropy must be supplied at the constant temperature of the transition temperature. In order to supply this entropy at the transition temperature $T_{\mathrm{T}}$ we must, from the definition of entropy (Equation 10.1), supply an amount of heat:

$$\Delta Q_{\mathrm{T}} = T_{\mathrm{T}}\Delta S \tag{10.20}$$

This heat energy $\Delta Q_{\mathrm{T}}$ transforms the substance at constant temperature from one phase to another, increasing the internal energy of the substance and (usually) its volume. The combination of terms

$U + PV$ is known as the *enthalpy* of a substance, and the heat $\Delta Q_T$ supplied at a transition is known as the *enthalpy change on vaporisation* or *fusion*. This is often shortened to *enthalpy of vaporisation* or *fusion*, or less commonly nowadays to *latent heat of vaporisation* or *fusion*. The terms are all equivalent. *Fusion* is an old-fashioned term for melting.

## 10.4 Enthalpy change on transformation

### 10.4.1 Introduction

Based on the theory outlined above we ought to be able to arrive at some general estimates about the typical magnitude of the enthalpies of fusion and vaporisation.

Let us pause to review our results so far. We saw in §10.3 that with some plausible assumptions, we could estimate $U$ and $S$ as a function of temperature and hence estimate the phase transition temperatures for potassium. In §10.3 we predicted that at a phase transition, we must supply an amount of entropy $\Delta S$ given by:

$$\begin{aligned}\left(\frac{dG_2}{dT}\right)-\left(\frac{dG_1}{dT}\right)&=S_1-S_2\\&=-\Delta S\end{aligned} \qquad (10.19^*)$$

which requires an amount of heat $\Delta Q_T$:

$$\Delta Q_T = T_T \Delta S \qquad (10.20^*)$$

Further, at the transformation temperature, we know (by definition) that $G_2 = G_1$ and so:

$$U_1 - T_T S_1 + P_T V_1 = U_2 - T_T S_2 + P_T V_2 \qquad (10.21)$$

Re-arranging this yields:

$$\begin{aligned}\left(U_1-U_2\right)+P_T\left(V_1-V_2\right)&=T_T\left(S_1-S_2\right)\\&=-T_T\Delta S\end{aligned} \qquad (10.22)$$

which may be compared to Equation 10.20 to give an expression for $\Delta Q_T$:

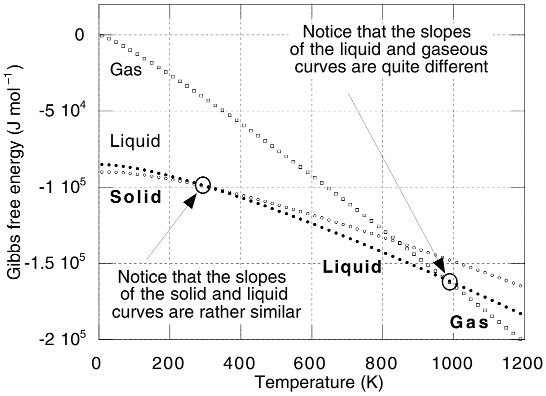
$$\Delta Q_T = \left(U_2 - U\right)_1 + P_T\left(V_2 - V_1\right) \qquad (10.23)$$

In the next two sections we will move on from the calculations in §10.3 to try to estimate $\Delta Q_T$, the enthalpy changes on phase transformation.

#### The relative values of $\Delta Q_M$ and $\Delta Q_B$

One feature of calculations shown in Figure 10.2 and reproduced below in Figure 10.5 is already clear. The difference between the slope of the liquid and solid curves at the predicted melting temperature is rather small: the two curves run close to one another over a considerable range of temperature. In contrast, the difference between the slope of the gas and liquid curves at the predicted vaporisation temperature is rather large: the gas curve cuts the liquid curve rather steeply. Thus according to Equations 10.17 and 10.18 we should expect that the enthalpy change on vaporisation $\Delta Q_B$ should be considerably larger than the enthalpy change on fusion $\Delta Q_M$. Here and in the following sections, I have used the subscript 'B' to stand for 'boiling' and the subscript 'M' to stand for 'melting'.

**Figure 10.5** According to the considerations of sections 10.1 and 10.2, a general feature of the enthalpy changes on transformation is that the enthalpy change on fusion (melting) is less than the enthalpy change on vaporisation (boiling). On the *G*(*T*) graph, the enthalpy changes are related to the differences in the *gradient* of the curves at their intersections.



In the next two sections the enthalpy change at each of the melting and boiling transformations will be considered in turn.

### 10.4.2 Enthalpy change on fusion $\Delta Q_M$

In order to estimate the enthalpy change on fusion (melting) $\Delta Q_M$, we can make use of Equation 10.17 $\Delta Q_M = T_M \Delta S$ and estimate the melting temperature $T_M$, $S_{\text{liquid}}$ for the liquid state at $T_M$ and $S_{\text{solid}}$ for the solid state at $T_M$. Alternatively, we can use Equation 10.23:

$$\Delta Q_M = \left(U_{\text{liquid}} - U_{\text{solid}}\right) + P_M\left(V_{\text{liquid}} - V_{\text{solid}}\right) \tag{10.24}$$

and estimate the internal energy and volume of the liquid state at $T_M$, and the internal energy and volume of solid state at $T_M$. Given the uncertainty in estimating the residual entropy of a liquid at $T = 0$ K, it is a more profitable to follow the second of these two options.

For the solid and liquid states, the $PV$ term is negligible in comparison with the internal energy term and Equation 10.24 becomes:

$$\Delta Q_M \approx U_{\text{liquid}} - U_{\text{solid}} \tag{10.25}$$

As in Example 10.2, we can estimate $U$ by integrating the heat capacity:

$$\begin{aligned}\Delta Q_M = &\left[U_o(\text{liquid}) + \int_{T=0}^{T} C_{\text{liquid}}(T)dT\right] \\ &- \left[U_o(\text{solid}) + \int_{T=0}^{T} C_{\text{solid}}(T)dT\right]\end{aligned} \tag{10.26}$$

which becomes:

$$\begin{aligned}\Delta Q_M = &\left[U_o(\text{liquid}) - U_o(\text{solid})\right] \\ &+ \int_{\mathrm{T}=0}^{\mathrm{T}} [C_{\text{liquid}}(T) - C_{\text{solid}}(T)]\mathrm{d}T\end{aligned} \tag{10.27}$$

Equation 10.27 is evaluated for potassium in Example 10.4. The result ($5.22\ \text{kJ mol}^{-1}$) does not compare particularly well with the experimental value (Table 11.1) of $2.4\ \text{kJ mol}^{-1}$. However, we clearly have the correct order of magnitude, and the poor detailed agreement is due mainly to the generality of the assumptions made in our estimates of the heat capacities of the liquid and solid state. We will consider the experimental data on the enthalpy change on melting in §11.3.

**Example 10.4**

**Estimate $Q_M$ for potassium.**

Following on from the calculations of §10.2. We note that:

- The zero temperature cohesive energy of the liquid state amounts to only a fraction (typically 90%–95%) of the cohesive energy of the solid. The 95% yielded slightly better values for $T_M$ so we use this estimate that $U_o(\text{liquid}) \approx 0.95\ U_o(\text{solid})$ .
- The heat capacity in the liquid state is generally greater than in the solid state typically by around 10%.

We thus find:

$$Q_M = -0.05 U_o(solid) + 0.1 \times \int_0^T C_{\text{solid}}(T)\mathrm{d}T$$

Now $U_o(\text{solid}) = 90.1\ \text{kJ mol}^{-1}$ (Table 11.5) and estimating the integral numerically as we did for the previous examples we find that at the experimentally determined melting temperature $T_M = 336$ K

$$\begin{aligned}Q_M &\approx -0.05 \times \left(-90.1 \times 10^3\right) + 0.1 \times 7198 \\ &\approx 5.22\ \ \text{kJ mol}^{-1}\end{aligned}$$

### 10.4.3 Enthalpy change on vaporisation $\Delta Q_B$

Following a similar scheme to that outlined in the previous §10.4.2, we can estimate the enthalpy change on vaporisation by using Equation 10.23:

$$\Delta Q_B = \left(U_{\text{gas}} - U_{\text{liquid}}\right) + P_B\left(V_{\text{gas}} - V_{\text{liquid}}\right) \tag{10.28}$$

For the liquid state, the $PV$ term is negligible, but for the gaseous state this is not so. Including the $PV$ term only for the gaseous state, this equation becomes:

$$\Delta Q_B = \left(U_{\text{gas}} - U_{\text{liquid}}\right) + P_B V_{\text{gas}} \tag{10.29}$$

As in Example 10.4, we can estimate $U$ by integrating the heat capacity:

$$\Delta Q_\mathrm{B} = \left[ U_\mathrm{o}(gas) + \int_{\mathrm{T}=0}^{\mathrm{T}} C_\mathrm{gas}(T)\mathrm{d}T \right] - \left[ U_\mathrm{o}(liquid) + \int_{\mathrm{T}=0}^{\mathrm{T}} C_\mathrm{liquid}(T)\mathrm{d}T \right] + P_\mathrm{B} V_\mathrm{gas} \qquad (10.30)$$

which becomes:

$$\Delta Q_\mathrm{B} = \left[ U_\mathrm{o}(gas) - U_\mathrm{o}(liquid) \right] + \left[ \int_{\mathrm{T}=0}^{\mathrm{T}} C_\mathrm{gas}(T)dT - \int_{\mathrm{T}=0}^{\mathrm{T}} C_\mathrm{liquid}(T)\mathrm{d}T \right] + RT_\mathrm{B} \qquad (10.31)$$

Equation 10.31 is evaluated for potassium in Example 10.5. The result (88.6 kJ mol$^{-1}$) does not compare particularly well with the experimental value (Table 11.1) of 77.5 kJ mol$^{-1}$. However we again have the correct order of magnitude, and attribute the poor detailed agreement to the generality of the assumptions made in our estimates of the heat capacities of the liquid and gaseous states. We will consider the experimental data on the enthalpy change on vaporisation for the elements in §11.3.

**Example 10.5**

**Estimate $Q_\mathrm{B}$ for potassium.**

Following on from the calculations of §10.1. If we make ideal gas assumptions for the gaseous phase we note that:

- The zero temperature cohesive energy of the gaseous state is zero
- The heat capacity in the liquid state is generally greater than in the solid state typically by around 10%
- The heat capacity in the gaseous state is $C_\mathrm{P} = 2.5R$ (§5.3).

We thus find:

$$Q_\mathrm{B} = \left[0 - 0.95U_\mathrm{o}(solid)\right] + 2.5RT_\mathrm{B} - 1.1 \times \int_0^T C_\mathrm{solid}(T)\mathrm{d}T + RT_\mathrm{B}$$

Recalling $U_\mathrm{O}$(solid) = 90.1 kJ mol$^{-1}$ and estimating the liquid integral numerically as we did for the previous examples, we find that at the experimentally determined boiling temperature $T_\mathrm{M}$ = 1047 K

$$\begin{aligned} Q_\mathrm{B} &\approx \left[-0.95 \times \left(-90.1 \times 10^3\right)\right] + 2.5 \times 8.31 \times 1047 \\ &\quad - 1.1 \times 24914 + 8.31 \times 1047 \\ &\approx 85595 + 21751 - 27405 + 8700 \\ &\approx 88.6 \ \text{kJ mol}^{-1} \end{aligned}$$

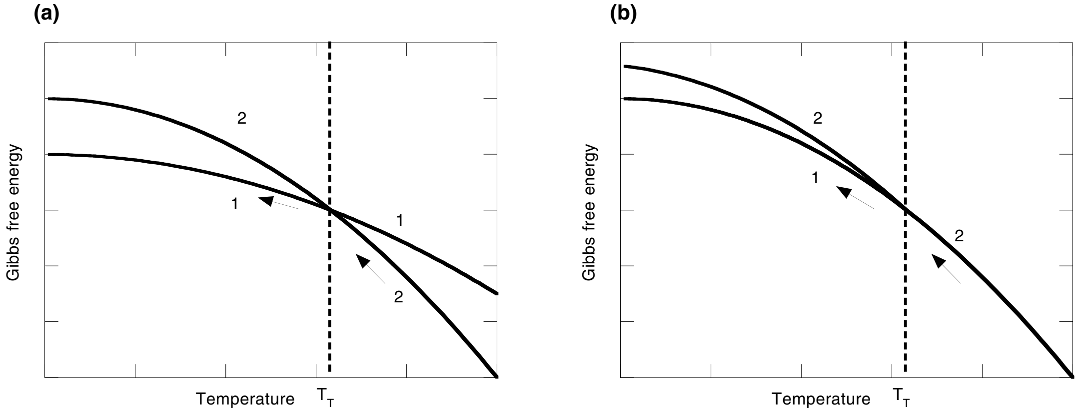
## 10.5 The ‘order’ of a phase transition

### 10.5.1 Introduction

At the transitions discussed in §10.3.1 and §10.3.2, a substance changes completely from one phase to another. For example at 0.01 K above $T_\mathrm{M}$ the substance is *completely* liquid; at 0.01 K below $T_\mathrm{M}$ the substance is *completely* solid. These transitions are characterised by a discontinuous change in the *gradient* of the Gibbs free energy. However, not all phase transitions take place in this way. Imagine cooling a substance slowly in its solid or liquid phases: it is conceivable that at a certain temperature some processes or behaviours *begin* to be possible. Below the transition temperature, the substance does not completely transform, but *begins* to show a new property, and the strength of this property grows as the substance is cooled further below the transition temperature.

At such a transition there is no discontinuity in the *gradient* of $G$, but there is a discontinuity in the *curvature* of $G$. This leads to a general technique of categorising phase transitions according to whether $G$ has a discontinuity in its gradient or its curvature.

**Figure 10.6** Schematic illustration of the changes in the Gibbs free energy $G$ at (a) a first-order and (b) a second-order phase transition at temperature $T_T$. In a first-order transition, entropy (and hence heat energy) equal to the difference in gradients must be supplied. In a second-order transition there is no discontinuity in gradient, but there is a discontinuity in the *curvature* of $G$.



- Recalling that the gradient $\partial G/\partial T$ is the *first* derivative of $G$, transitions in which there is a discontinuity in gradient are called *first-order transitions*. These are characterised by the phenomena of an enthalpy of transformation, colloquially a *latent heat*.
- Recalling that the curvature $\partial^2 G/\partial T^2$ is the *second* derivative of $G$, transitions in which there is a discontinuity in curvature are called *second-order transitions*. These are characterised by the absence of any enthalpy of transformation, which means there is no latent heat associated with such a transition.

The characteristic behaviour of the Gibbs free energy close to first- and second-order transitions is illustrated schematically in Figure 10.6.

Now we might imagine that, having gone to the trouble of establishing this general framework for phase transitions, there must be a great many examples of both types of phase transition: not so. The vast majority of phase transitions are first-order, and only one or two examples of second-order phase transitions. It is possible to continue the sequence of categorising to ever more subtle degree. For example, for a third-order phase change, the transition temperatures would indicate the temperature at which the Gibbs free energy begins 'to begin' to change! In general, the categorisation of any phase transition as third-order is specious and is no longer made. So in general we simply categorise transitions as either first-order, or 'not first-order'. Transitions which are not first-order are called *continuous*.

In practice, it is often difficult to distinguish between first-order and continuous transitions. If a substance is not homogeneous, or there is a temperature gradient across it, then a transition may appear continuous, when it is in fact first-order. It usually requires careful experiments to distinguish the two cases. Notice that I have referred to phase transitions other than solid⇔liquid⇔gas transitions, something I shall justify in Chapter 11. However, structural phase transitions such as those between solids, liquids and gases are nearly always first-order.

**Table 10.4** The orders of some phase transitions.

| First-order | Continuous |
|---|---|
| Melting/freezing | Superconducting<br>(in zero magnetic field) |
| Boiling/condensing | Ferromagnetic |
| Liquid crystals | |
| Superconducting<br>(in a magnetic field) | |

## 10.6 Nucleation: supercooling and superheating

### 10.6.1 The mechanism of a phase transition

So far in our discussion of phase changes we have assumed that a substance changes from one phase to another when the Gibbs free energy of one phase becomes lower than the Gibbs free energy of the other phase. However this raises the question of how the substance 'knows' what the Gibbs free energy of the other phase is going to be when it is not actually in that phase already! In other words how is a phase transition is initiated?

Microscopically, all phase transitions may be considered to occur in two stages: *nucleation* and *growth*.

#### Nucleation

In the *nucleation* stage, the random motions of the atoms or molecules conspire to create a local situation which is atypical of the *average* properties of the substance. These locally atypical regions (perhaps just a few atoms in size initially) are known variously as *nuclei*, *embryos* or *seeds*. The process of embryo formation occurs at all temperatures, although the rate of formation varies strongly with temperature. Alternatively some small irregularity within the substance, perhaps an impurity, or some feature of the container for the substance, provides a locally anomalous region capable of supporting a nucleus of a different phase.

#### Growth

In the *growth* stage, the nucleus of the second phase either (a) grows in size, (b) stays the same size, or (c) shrinks. In general, nuclei will not grow spontaneously even when the Gibbs free energy of the second phase becomes lower than the Gibbs free energy of the first phase. This is because for small nuclei the *surface energy* of the nuclei may be very high. Eventually the nucleus becomes able to grow in size and the macroscopic phase transition commences.

If there are no suitable nuclei available, a substance may pass its appropriate transition temperature and continue in the 'wrong' (or non-equilibrium) phase. This phenomenon is known as either *supercooling* or *superheating* depending on the direction of temperature change. Note that these phenomena are not caused by the experimental 'error' of heating or cooling 'too quickly' into a transient state. The supercooled or superheated substances may be quite stable until supplied with an appropriate 'seed' on which the second phase may grow.

Let us examine the process of nucleation and growth for each of the phase transitions we have considered so far.

### 10.6.1 Solid ⇒ liquid: melting

Superheating past the bulk melting temperature is extremely unusual in the solid ⇒ liquid transition. In terms of the nucleation and growth theory outlined above, this implies that suitable liquid nuclei exist in the solid phase near the melting temperature. There is considerable evidence that these nuclei exist at solid surfaces and cause solids to tend to melt from their surfaces inwards. Indeed it is possible that in equilibrium, even well below $T_M$ there may be an atomic layer or two of essentially liquid substance present on the surface of a solid. The equilibrium thickness of this layer grows rapidly as the temperature approaches $T_M$ and then grows without limit. In this theory we can understand the reluctance of solids to superheat, because liquid nuclei would always be available due to the so-called *pre-melting* of the surface. This theory predicts that, in general, solids should melt from their surfaces rather than from within the solid.

### 10.6.2 Liquid ⇒ solid: freezing

In contrast with the melting transition, the solid ⇒ liquid transition frequently shows significant supercooling. In line with the theory above, we can interpret this as being either due to a lack of nuclei, or to the presence of a strong barrier to the growth of nuclei.

Considering our simple conceptions of liquid and solid structures as envisaged in Figures 6.2 and 8.2, it seems unlikely that there will be any lack of nuclei. We expect that there will be many regions of liquid structure that are (transiently) similar to the solid structure. It seems that once such solid nuclei form they fail to grow either because the nuclei has a large surface energy or because the nuclei has broken apart before it had time to grow.

Suppose that a spherical nucleus of ‘solid’ of radius $a$ exists in the liquid state. The nucleus will grow if increasing its size from $a$ to $a + \mathrm{d}a$ lowers the free energy of the substance. There are two factors which determine whether this is so.

- The first is the free energy difference between the solid and liquid states $\Delta G_{\mathrm{LS}}(T)$. At the melting temperature $\Delta G_{\mathrm{LS}}(T_{\mathrm{M}})$ is zero by definition. If the temperature is lowered below $T_{\mathrm{M}}$, then the solid state becomes increasingly favoured over the liquid state. However, as Figure 10.5 indicates, the *gradients* ($\mathrm{d}G/\mathrm{d}T$) of the free energies of liquid and solid states differ only slightly. So the free energy benefit of the solid state increases only slowly as the temperature is lowered below $T_{\mathrm{M}}$. Notice that $\Delta G_{\mathrm{LS}}(T)$ is proportional to the *volume* of the nucleus.
- The second factor is the energy cost of forming an interface between the solid and liquid states. Around the nucleus may be a region of strained material which is not optimally arranged for either the solid or the liquid states. If this surface layer has a cost $G_{\mathrm{surface}}$ per unit area, then there will be a cost of allowing the nucleus to grow which will be proportional to the *surface area* of the nucleus.

We can write the total energy as:

$$G_{\mathrm{nucleus}} = -[\mathrm{volume}] \times \Delta G_{\mathrm{LS}}(T) + [\mathrm{surface\ area}] \times G_{\mathrm{surface}} \tag{10.32}$$

$$G_{\mathrm{nucleus}} = -\left[\frac{4}{3}\pi a^3\right] \times \Delta G_{\mathrm{LS}}(T) + \left[4\pi a^2\right] \times G_{\mathrm{surface}} \tag{10.33}$$

Note that in Equation 32 we have defined $\Delta G_{\mathrm{LS}}$ as positive if the $G_{\mathrm{solid}}$ is less than $G_{\mathrm{liquid}}$. Evaluating $\partial G_{\mathrm{nucleus}} / \partial a$ we find:

$$\frac{\partial G_{\mathrm{nucleus}}}{\partial a} = -\left[4\pi a^2\right] \times \Delta G_{\mathrm{LS}}(T) + [8\pi a] \times G_{\mathrm{surface}} \tag{10.34}$$

Now the nucleus will grow if its total energy decreases as $a$ increases, i.e. if $\partial G_{\mathrm{nucleus}} / \partial a < 0$. This is true when:

$$-4\pi a^2 \times \Delta G_{\mathrm{LS}}(T) + 8\pi a \times G_{\mathrm{surface}} < 0 \tag{10.35}$$

i.e. when:

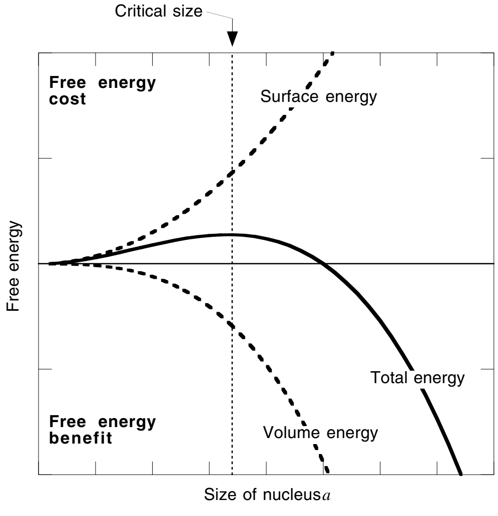
$$4\pi a^2 \times \Delta G_{\mathrm{LS}}(T) > 8\pi a \times G_{\mathrm{surface}} \tag{10.36}$$

which simplifies to:

$$a > \frac{2G_{\mathrm{surface}}}{\Delta G_{\mathrm{LS}}(T)} \tag{10.37}$$

This defines a critical size for a nucleus, $a_{\mathrm{critical}}$, below which the surface energy cost of the nu-

**Figure 10.7** The origin of the phenomena of supercooling. Nuclei of the solid state within the liquid state will not grow unless doing so lowers the free energy. This leads to the phenomenon of a critical size of nucleus. As the temperature falls below the melting temperature (at which the free energies of the bulk liquid and solid states are equal by definition), the free energy difference between liquid and solid states increases and causes a decrease in the critical nuclear size. Eventually, the critical size is reduced to the size of the nuclei that are spontaneously formed in the liquid state and the substance freezes.



cleus impedes the transformation from liquid to solid. Notice that:

- At the melting temperature $a_{\text{critical}}$ is infinite since $\Delta G_{LS}(T_M)$ is zero by definition. Thus unless some external process initiates the transition, liquids will always supercool to some extent.
- As the temperature falls below $T_M$, $\Delta G_{LS}(T)$ increases, and thus decreases the critical size of a nucleus. When the temperature is sufficiently far below $T_M$ that the critical size is less than the size of the nuclei actually formed in the liquid, then the nuclei will grow and the substance will freeze. Because $\partial G/\partial T$ for both solid and liquid are similar (Figure 10.5) it is possible for the temperature to fall considerably (several kelvin) below $T_M$ before $\Delta G_{LS}$ becomes large enough to cause nuclear growth.

### 10.6.3 Liquid ⇒ gas: boiling/vaporisation

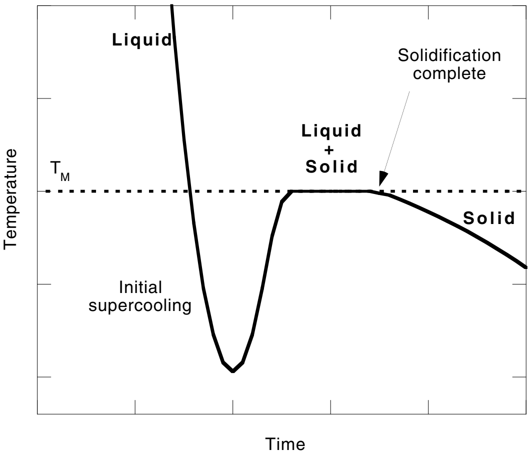
Superheating at the liquid ⇒ gas transition is also relatively common. Here a liquid may be heated to above its normal boiling temperature, but fails to boil because of the lack of suitable nuclei. Notice that at any free surface the vapour pressure will continue to increase exponentially with temperature (§9.8) above the normal boiling temperature. The process which is inhibited is the formation of bubbles of gas within the body of the liquid.

This is relatively easy to understand: to form a bubble it is necessary to form a new surface on the inside of the bubble and this requires a large surface energy. Since forming surfaces requires extra energy, this must be supplied in excess of the normal free energy difference between the liquid and gas phases. For this reason the presence of external nuclei (which minimise the initial surface energy required) is often critical to establishing boiling close to the equilibrium $T_B$.

### 10.6.4 Gas ⇒ liquid: condensation

Supercooling at the gas ⇒ liquid transition is considerably less common than superheating at the liquid ⇒ gas transition. Once again this requires that we have a large number of nuclei, or a low barrier to growth.

**Figure 10.8** Schematic illustration of the variation of temperature with time during the slow cooling of a pure substance through its equilibrium melting temperature. As discussed in the text, the liquid always supercools to some extent. This continues until the critical radius reduces to the same size as the typical nucleus size present in the liquid, at which point the nuclei begin to grow spontaneously. This causes the release of enthalpy of fusion, which (if the external cooling rate is slow enough) will reheat the solid/liquid melt back to the equilibrium melting temperature. The melt remains at this temperature until all the liquid is transformed to solid, after which cooling recommences.



In a gas, large numbers of nuclei are constantly formed when molecules collide. Notice however, for simple molecules at least, it requires at least *three* molecules to interact in order to form a two-molecule ‘droplet’, technically called a *dimer*. The reason for this can be seen if we consider simple molecules such as argon, which consist of just a single atom. If two molecules collide, without any interactions with other molecules, then they will never stick together. This is because no matter how slowly they are moving when they collide, their interactions conserve energy and so they will always move apart again. In order to form a dimer, they must interact in the presence of a third molecule, which will take away some fraction of their total energy and leave the pair with less than they started with. For more complex molecules consisting of many atoms, it is possible for collisions between two molecules to result in dimer formation. This is because energy can be lost from their kinetic energy into other degrees of freedom of the molecules.

## 10.7 Phase diagrams

### 10.7.1 Introduction

It is often instructive to present information about the transitions between substances pictorially on what is known as a *phase diagram*. There are many different types of phase diagram but the aim of all such diagrams is to *summarise* the tremendous amount of information about the phases adopted by substance, in a way that can be readily appreciated. A schematic phase diagram is shown in Figure 10.9 below.

Consider a substance at atmospheric pressure: at absolute zero the substance will, with the sole exception of helium, be solid. As the temperature is increased at constant pressure, typically the substance will eventually melt at $T_M$ and then boil at $T_B$. (Note that the volume of the substance will change significantly as it transforms from solid to gas, but this is not shown on this type of diagram.) This heating process, represented by the dotted line on Figure 10.9, seems fairly straightforward to interpret. However other paths are not so straightforward to interpret. Consider for example that shown in Figure 10.10 which represents heating a solid in a vacuum.

The phase boundaries (lines) on Figures 10.9 and 10.10 represent sets of points at which a phase transition takes place. Thus traversing any of the solid lines in these figures takes us from one phase to another. We know, from our analysis of the changes in Gibbs free energy at transitions (§10.1.1), that at any point on the phase boundary, the Gibbs free energies of the two phases on either side of the boundary are equal. Let us consider two points $A$ and $B$ on a phase boundary at slightly different temperatures and pressures (Figure 10.11).

The Gibbs free energy at point $A$ is $G_A$ and the

**Figure 10.9** Schematic phase diagram of a typical substance on the *PT* plane. Note: The drawing is not to scale. This type of diagram refers to the state of a fixed amount of a substance, usually one mole. The volume of the substance is free to take any value and is not recorded on this type of diagram. The diagram must be interpreted subtly as discussed in the text. The solid lines connect temperatures and pressures at which more than one phase exists in equilibrium. The point *A* represents the so-called *triple point* (§10.7.3) of the substance and point *C* represents the so-called *critical point* (§10.7.2).

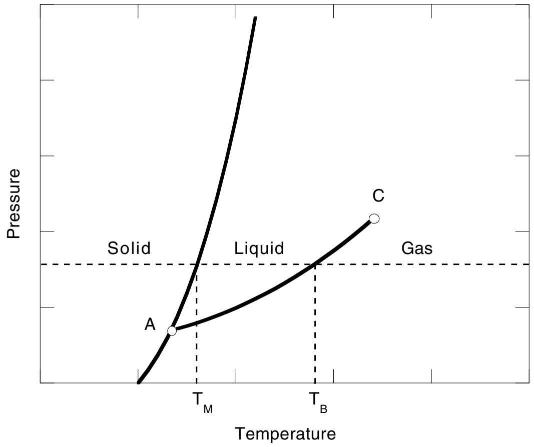
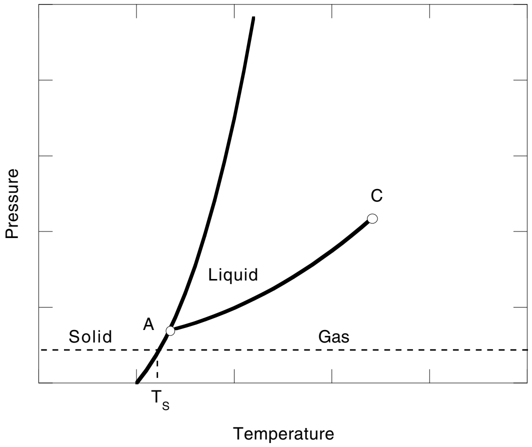


**Figure 10.10** Schematic phase diagram of a typical substance on the *PT* plane. Note: The drawing is not to scale. If a solid is heated at low pressure, i.e. the pressure is not allowed to rise on heating, then at ‘low enough pressure’ the solid always transforms directly into the gas phase. This can be understood as being because the liquid phase always has a minimum vapour pressure above it, whereas a solid can sustain a much lower vapour pressure above its surface. The point *A* represents the so-called *triple point* (§10.7.3) of the substance and point *C* represents the so-called *critical point* (§10.7.2).



difference in free energy between $A$ and $B$ is $\Delta G$. The free energy difference $\Delta G$ is due to differences in $U$, $T$, $S$, $P$ and $V$ and, as outlined in Equation 10.14, this may be simplified to:

$$\Delta G = V\Delta P - S\Delta T \tag{10.38}$$

Now the change $\Delta G$ is the same for both phases, so using subscripts 1 and 2 for the two phases:

$$\Delta G_1 = \Delta G_2 \tag{10.39}$$

or

$$V_1\Delta P - S_1\Delta T = V_2\Delta P - S_2\Delta T \tag{10.40}$$

Rearranging this we have:

$$\Delta P(V_1 - V_2) = \Delta T(S_1 - S_2) \tag{10.41}$$

$$\frac{\Delta P}{\Delta T} = \frac{(S_1 - S_2)}{(V_1 - V_2)} \tag{10.42}$$

Or taking the differential limit we arrive at an equation known as the *Clausius–Clapeyron* equation:

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{(S_1 - S_2)}{(V_1 - V_2)} \tag{10.43}$$

This is a very important equation!

## Example 10.6

**Work out the rate of change of boiling temperature with pressure for water.**

Consider 1 mole of water at around its normal boiling temperature of 100 °C. From Table 11.2 we find that the molar enthalpy change on vaporisation is around $40.6 \times 10^3$ J K$^{-1}$ mol$^{-1}$. One mole of liquid has a mass of $18 \times 10^{-3}$ kg and a volume of roughly $V_L = 18 \times 10^{-6}$ m$^3$ (Table 9.1). Assuming the gas to behave as a perfect gas, we can estimate the volume of one mole of gas as:

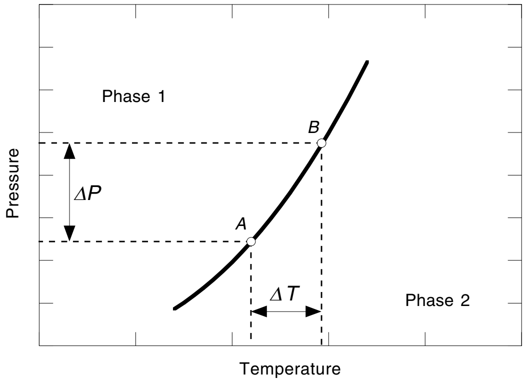
$$V_G = \frac{RT}{P} = \frac{8.3 \times 373}{10^5} = 0.031 \text{ m}^3$$

or around 1700 times the liquid volume. Neglecting the liquid volume in comparison with the gas volume we can use Equation 10.47 to estimate d$P$/d$T$ :

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{40.6 \times 10^3}{373 \times 0.031} = 3511 \text{ Pa K}^{-1}$$

Thus if we increase the pressure above the liquid by 3511 Pa we increase the boiling temperature by 1 K.

**Figure 10.11** A detailed view of the phase boundary between two phases 1 and 2 which might, for example, refer to a liquid⇔solid phase boundary. At each point along the phase boundary the Gibbs free energies of the phases on either side of the phase boundary are equal. At point *A* the Gibbs free energy of each phase is $G_A$ and at point *B* (which is at a slightly different temperature and pressure) the Gibbs free energy of each phase is $G_B$.



## Example 10.7

**Work out the rate of change of boiling temperature with pressure for water.**

Consider 1 mole of water at around its normal melting temperature of 0 °C. From Table 11.2 we find that the molar enthalpy change on fusion is around $5.99 \times 10^3$ J K$^{-1}$ mol$^{-1}$. One mole of liquid has a mass of $18 \times 10^{-3}$ kg and a volume of approximately $V_L = 18 \times 10^{-6}$ m$^3$ (Table 9.1). One mole of solid (ice) has a volume roughly 8% larger or around $V_S = 19.4 \times 10^{-6}$ m$^3$ (Figure 9.3). Using Equation 11.47 to estimate d$P$/d$T$ :

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{5.99 \times 10^3}{273 \times \left[18 \times 10^{-6} - 19.4 \times 10^{-6}\right]}$$
$$= -15.6 \times 10^6 \text{ Pa K}^{-1}$$

Thus if we increase the pressure above the solid by around $15.6 \times 10^6$ Pa which is around 150 times atmospheric pressure, i.e. we *decrease* the melting temperature by 1 K.

Notice (a) the relative insensitivity of the melting temperature to external pressure: this is typical of most solid⇔liquid transitions, and (b) the fact that increasing the pressure *decreases* the melting temperature: this is highly unusual. This depression of the melting temperature by pressure is a consequence of the unusual contraction of the substance as it enters the liquid phase. (Figure 9.3)

The Clausius–Clapeyron equation relates the slope of a phase boundary to the difference in entropy and volume of the phases on either side of the phase boundary. We have already seen that the difference in entropy between the two phases is the origin of the *enthalpy change on transformation (or latent heat)* $Q_T$ and so we may write:

$$\begin{aligned}\frac{dP}{dT} &= \frac{Q_T/T_T}{(V_1 - V_2)} \\ &= \frac{Q_T}{T_T(V_1 - V_2)}\end{aligned} \qquad (10.44)$$

The usefulness of the Clausius–Clapeyron equation is best illustrated by some examples, but we will return to Equations 10.43 and 10.44 several times in the following sections.

## 10.7.2 The critical point

The *critical point* is a special point on the liquid ⇔ gas phase boundary. It marks the point at which the densities of the phases on the liquid side and the gas side of the phase boundary become equal. Let us calculate the general shape of the liquid ⇔ gas phase boundary and then consider how the densities of the two terms vary as one moves along the boundary.

**The liquid–gas phase boundary**

In §9.8 we considered a microscopic model of evaporation and condensation, and came to the conclusion that we may reasonably expect the vapour pressure of a gas in equilibrium to vary like:

$$P \approx A \exp\left[\frac{-\alpha}{T}\right] \qquad (10.45)$$

where $\alpha$ is a constant. A similar result also follows from the Clausius–Clapeyron equation with rather fewer assumptions about a particular liquid model. At the liquid ⇔ gas phase boundary we have:

$$\frac{dP_B}{dT_B} = \frac{\Delta Q_B}{T_B(V_G - V_L)} \qquad (10.46)$$

where the subscript 'B' indicates that $P_B$ and $T_B$ are the boiling pressure and temperature of the liquid, and 'L' and 'G' indicate liquid and gas phases respectively. Let us first assume that:

- in the gas phase the substance behaves as an ideal gas
- has a volume very much greater than in the liquid phase, and
- the latent heat $Q_B$ does not vary with temperature.

Under these assumptions, and remembering that the volume of one mole of ideal gas is:

$$V_G = \frac{RT}{P} \qquad (10.47)$$

we find that Equation 10.46 becomes:

$$\begin{aligned}\frac{dP_B}{dT_B} &= \frac{Q_B}{T_B\left[\frac{RT_B}{P_B}\right]} \\ &= \frac{P_B Q_B}{RT_B^2}\end{aligned} \qquad (10.48)$$

Rearranging this yields:

$$\frac{dP_B}{P_B} = \left[\frac{Q_{LG}}{R}\right]\frac{dT_B}{T_B^2} \qquad (10.49)$$

If we integrate this equation, we find:

$$\int \frac{dP_B}{P_B} = \left[\frac{Q_B}{R}\right]\int \frac{dT_B}{T_B^2} \qquad (10.50)$$

which yields:

$$\ln\left[\frac{P_B}{P_o}\right] = \left[\frac{-Q_B}{RT_B}\right] \qquad (10.51)$$

or:

$$P_B = P_o \exp\left[\frac{-Q_B}{RT_B}\right] \qquad (10.52)$$

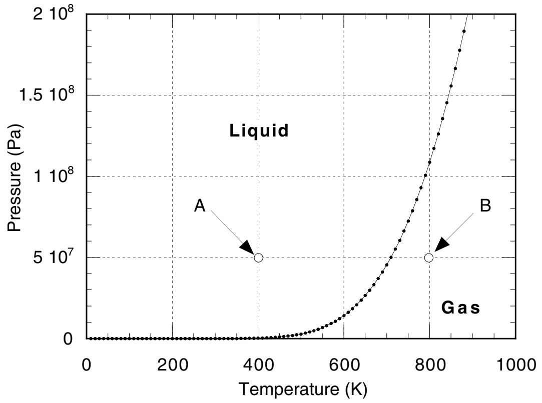
This equation has a form similar to that derived with the aid of a microscopic model of a liquid (Equation 9.35). Figure 10.12 shows a plot of Equation 10.56 for water using the value $Q_B = 40.6$ kJ mol$^{-1}$ from Table 11.2 and a value of $P_o = 4.89 \times 10^{10}$ Pa chosen to give a vapour pressure of 1 atmosphere ($1.013 \times 10^5$ Pa) at 373.15 K.

### The volume of gas at the phase boundary

Figure 10.12 and Equation 10.52 indicate that the pressure at the liquid ⇔ gas phase boundary rises exponentially with temperature. This rapid variation causes some of the assumptions on which this equation was based to relatively quickly become invalid. In particular we assumed that the gas behaved like a perfect gas and we neglected the volume of the liquid in comparison with the gas. While this assumption was valid at 373 K where the vapour pressure was 1 atmosphere, it is unlikely to be valid at around 800 K where the vapour pressure is around 1000 times higher. Using the perfect gas equation to derive a rough estimate of the volume of one mole of substance in the gas phase we find:

$$\begin{aligned} V_{\mathrm{G}} &= \frac{RT}{P} \\ &= \frac{RT}{P_{\mathrm{o}} \exp\left[ {}^{-Q_{\mathrm{B}}}\!\big/\!{}_{RT_{\mathrm{B}}} \right]} \qquad (10.53) \end{aligned}$$

**Figure 10.12** The equilibrium vapour pressure above liquid water predicted according to Equation 10.52. Consider point *A* on the graph which refers to water at a pressure of $5 \times 10^7$ Pa and a temperature of 400 K (127 °C). The graph tells us that the water would be in the liquid phase. At point *B*, which refers to water under a pressure of $5 \times 10^7$ Pa and a temperature of 800 K (527 °C) the graph tells us that the water would be in the gas phase. The line indicates temperatures and pressures in which water can co-exist as a liquid and as a gas, i.e. it defines the boiling temperature. Atmospheric pressure (≈ $10^5$ Pa) is very close to the *x*-axis on this graph.



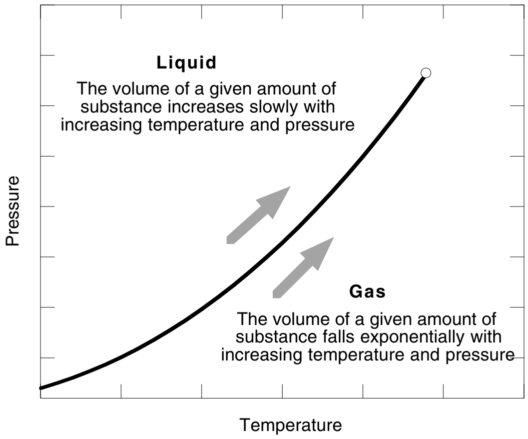
To see what this equation implies, consider a container with both liquid and gas present in equilibrium. Since both phases are present, we are by definition, at the phase boundary. As we increase the temperature, the pressure increases and we move along the phase boundary. Equation 10.53 tells us that for the material present in the gas phase, the volume of one mole of substance falls *exponentially*.

However, for the material present in the liquid phase, the molar volume does not vary so dramatically. In general the volume of liquid held on the co-existence curve increases slightly with temperature. The *critical point* refers to a point along the co-existence curve at which the volumes of the liquid and gas phases become equal. At this point it becomes impossible to distinguish between the two phases

### Estimating the critical temperature and pressure

At what pressure the volume of one mole of gas will become equal to the volume of one mole of liquid? The ideal gas equation is obviously not going to produce a good estimate for this. Remember that the ideal gas equation ignores two key features of real molecules: the interactions between molecules, and the volume of the molecules themselves. We will first use the ideal gas

**Figure 10.13** At the critical point the volume of a substance is the same in either the 'liquid' or the 'gas' phase.



equation to make a rough estimate of the temperature and pressure at which the gas volume becomes equal to the liquid volume. We will then refine our estimates to take account of the factors that the ideal gas equation has neglected.

### Ideal gas estimate

The molar volume of liquid water at around 373 K is $18.8 \times 10^{-6}$ m$^3$ (Table 9.2). Ignoring any thermal expansion of the liquid, we use the ideal gas equation to predict a range of pressures and temperatures at which the volume *of the gas* is $18.8 \times 10^{-6}$ m$^3$:

$$P = \frac{RT}{18.8 \times 10^{-6}} \qquad (10.54)$$

Equation 10.54 is satisfied for a range of temperatures and pressures. Plotting the points that satisfy this equation on the same graph as the vapour pressure, Equation 10.52, yields a rough estimate of the point at which the gas and liquid densities at the phase boundary are equal (Figure 10.14). This predicts that the critical temperature of water is greater than 1000 K and the critical pressure is around $4.5 \times 10^8$ Pa.

### Including the effect of molecular volume

However, this estimate is certainly an overestimate of the critical temperature and pressure because of our neglect of the volume of the molecules (§4.4.1). If we re-evaluate the pressure required to contain a gas in a given volume, using the *experimentally determined* critical volume for water (Table 11.4) of $59.1 \times 10^{-6}$ m$^3$ then we obtain an estimate of the critical temperature and pressure of 803 K and $1.13 \times 10^8$ Pa.

### Including the effect of molecular interactions

However, even this is an overestimate of the critical temperature because we have assumed the latent heat $Q_B$ would not vary with temperature. Clearly this cannot be quite right since at the critical point the liquid and gas phases are indistinguishable. So at that point there can be no latent heat associated with the transition. Thus somewhere between the boiling temperature and the critical temperature, the latent heat must fall to zero. This is due to changes in the structure of the liquid. In general, the way in which this happens is rather complicated, and much of the change is close to the critical point itself. However, we can see qualitatively what the effect of this is. Equation 10.52 predicts that the vapour pressure is:

$$P_B = P_o \exp\left[\frac{-Q_B}{RT_B}\right] \qquad (10.52^*)$$

If $Q_B$ becomes smaller, the vapour pressure will increase, all other factors being equal. This will lower the point of intersection of the lines on Figure 10.14. Thus, through these relatively crude approximations, we can begin to approach an understanding of how, and under what conditions, the critical point of a substance is approached. Roughly speaking it occurs in the region of the intersection of:

- the vapour pressure curve of a gas above a liquid
- the pressure required to keep a gas constrained to a volume a little greater than that occupied by liquid at STP.

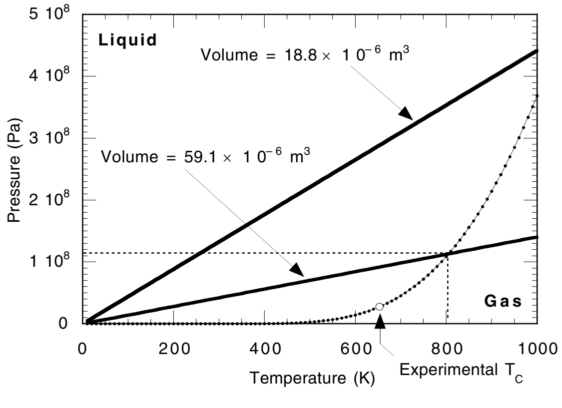


**Figure 10.14** The curved line is the calculated coexistence curve for water shown in Figure 10.12. The upper straight line represents an estimate of the pressure required to keep water vapour confined to a volume equal to the volume of liquid water at around 373 K. The lower straight line represents an estimate of the pressure required to keep water vapour confined to a volume equal to experimentally determined critical volume of water: $59.1 \times 10^{-6}$ m$^3$. The intersection of the curves represents a crude estimate of the critical temperature and pressure. The circle on the graph at ≈ 650 K represents the experimental value. Atmospheric pressure ≈ $10^5$ Pa is very close to the *x*-axis on this graph.

### 10.7.3 The triple point

The triple point, like the critical point discussed in §10.7.2, is another special point on a phase diagram. It marks the pressure and temperature at which the line representing the solid ⇔ liquid phase transition intersects with the line representing the liquid ⇔ gas transition. In order to determine where this intersection takes place, we will use the Clausius–Clapeyron equation (Equation 10.43). This will allow us to analyse the solid ⇔ liquid transition in the same way that we analysed the liquid ⇔ gas transition in §10.6.1 on the critical point.

**The solid ⇔ liquid co-existence curve**

We start once again with the Clausius–Clapeyron equation:

$$\frac{dP}{dT} = \frac{\Delta Q_T}{T_T\left(V_1 - V_2\right)} \qquad (10.44^*)$$

where phase 1 is the liquid phase and phase 2 is the solid phase. In this case, $\Delta Q_T$ is the enthalpy change on fusion $\Delta Q_M$, and $T_T$ is the melting temperature $T_M$. So Equation 10.44 becomes:

$$\frac{dP_M}{dT_M} = \frac{\Delta Q_M}{T_M\left(V_L - V_S\right)} \qquad (10.55)$$

We first of all notice the effect of the volume change $\Delta V_{LS}$ between the liquid and the solid.

For most substances $\Delta V_{LS}$ is positive – the liquid is less dense than the solid – and amounts to around 10 % of the volume of the solid (Figure 9.1). This volume change is dramatically smaller than the volume change between liquid and gas, perhaps by a factor 1000 or so. So the slope of the melting curve (where solid and liquid co-exist) is typically much steeper than the slope of the vaporisation curve (where liquid and gas co-exist).

For a few substances $\Delta V_{LS}$ is negative – the liquid is more dense than the solid – and again amounts to around 10% of the volume of the solid (Figure 9.1). For these substances, the slope of the melting curve will still be just as steep as it is for normal substances, but the slope will be negative (Figure 10.15).

### Example 10.8

**At atmospheric pressure ice melts at 273.15 K and undergoes a density change from around 920 kg m$^{-3}$ (Table 7.1, Figure 9.1) to 999.84 kg m$^{-3}$ (Table 8.1). The latent heat required to melt 1 mole of ice is 5994 Jmol$^{-1}$. What is the melting temperature at a pressure (a) twice atmospheric pressure, and (b) 1000 times atmospheric pressure?**

We use the Clausius–Clapeyron Equation (10.43)

$$\frac{dP_M}{dT_M} = \frac{\Delta Q_F}{T_F\left(V_L - V_S\right)}$$

First we evaluate $\Delta V_{LS}$, the volume change between liquid and solid. Considering one mole of water substance i.e. 18 × 10$^{-3}$ kg, we have:

$$V_L = \frac{18\times10^{-3}}{999.84} = 18.00\times10^{-6}\ \text{m}^3\ \left(=18.00\ \text{cm}^3\right)$$

and:

$$V_S = \frac{18\times10^{-3}}{920} = 19.57\times10^{-6}\ \text{m}^3\ \left(=19.57\ \text{cm}^3\right)$$

so that :

$$\begin{aligned} V_{LS} &= 18.00\times10^{-6} - 19.57\times10^{-6} \\ &= -1.57\times10^{-6}\ \text{m}^3 \end{aligned}$$

Substituting $\Delta Q_F$ = 5994 J mol$^{-1}$ and $T_M$ = 273.15 K we find:

$$\begin{aligned} \frac{dP_M}{dT_M} &= \frac{5994}{273.15\times\left(-1.57\times10^{-6}\right)} \\ &= -13.98\times10^{6}\ \text{Pa}\,\text{K}^{-1} \end{aligned}$$

This indicates that to *lower* the melting temperature by 1K, we need to apply a pressure of around 10$^7$ Pa, which is roughly 100 times atmospheric pressure.

We can estimate the change in melting temperature $\Delta T_M$ due to a change in pressure $\Delta P_M$ using:

$$\frac{\Delta P_M}{\Delta T_M} \approx \frac{dP_M}{dT_M} = -13.98\times10^{6}\ \text{Pa}\,\text{K}^{-1}$$

and hence:

$$\Delta T_M \approx \frac{\Delta P_M}{-13.98\times10^{6}} = -7.15\times10^{-8}\ \text{Pa}^{-1}$$

(a) For a pressure of twice atmospheric pressure $\Delta P_M$ = 1.013 × 10$^5$, $\Delta T_M$ evaluates to –7.25 × 10$^{-3}$ K, i.e. a doubling of the pressure results in a *lowering* of melting temperature of only 7.25 mK.

(b) For a pressure of 1000 times atmospheric pressure $\Delta P_M$ = 1.013 × 10$^8$, $\Delta T_M$ evaluates evaluates to –7.25 K. Although much larger than the shift in (a) this large pressure only shifts the melting temperature by around 7 K in 273 K, i.e. a shift of only 3%.

### Predicting the melting curve

If we plot the melting line on the same diagram on which we plotted the vapour pressure curve, then their intersection will provide an estimate of the location of the triple point. Starting with the Clausius–Clapeyron equation we equation we write:

$$\frac{\mathrm{d}P_{\mathrm{M}}}{\mathrm{d}T_{\mathrm{M}}} = \frac{\Delta Q_{\mathrm{M}}}{T_{\mathrm{M}}(V_{\mathrm{L}} - V_{\mathrm{S}})} \qquad (10.56)$$

In order to estimate the order of magnitude of the quantities involved, we make two assumptions. First, we assume that the latent heat of fusion $\Delta Q_{\mathrm{M}}$ does not vary with pressure or temperature. And second, we assume that the volume difference between the liquid and solid phase $V_{\mathrm{L}} - V_{\mathrm{S}}$ does not vary with pressure or temperature. In fact, both quantities do vary with pressure and temperature, but usually only rather slowly. This affects the detailed shape of the melting curve, but not its qualitative form. With these assumptions we write:

$$\mathrm{d}P_{\mathrm{M}} = \frac{\Delta Q_{\mathrm{M}}}{\Delta V_{\mathrm{LS}}} \frac{\mathrm{d}T_{\mathrm{M}}}{T_{\mathrm{M}}} \qquad (10.57)$$

Integrating this from zero pressure yields:

$$\int_{\mathrm{P_M=0}}^{\mathrm{P_M}} \mathrm{d}P_{\mathrm{M}} = \frac{\Delta Q_{\mathrm{M}}}{\Delta V_{\mathrm{LS}}} \int_{\mathrm{T_M(P_M=0)}}^{\mathrm{T_M(P_M)}} \frac{\mathrm{d}T_{\mathrm{M}}}{T_{\mathrm{M}}} \qquad (10.58)$$

Remembering that $\int \mathrm{d}x/x = \ln(x)$ this becomes:

$$P_M = \frac{\Delta Q_{\mathrm{M}}}{\Delta V_{\mathrm{LS}}} \left[\ln(T_{\mathrm{M}}(P_{\mathrm{M}} = 0)) - \ln(T_{\mathrm{M}}(P_{\mathrm{M}}))\right] (10.59)$$

Re-writing this we find:

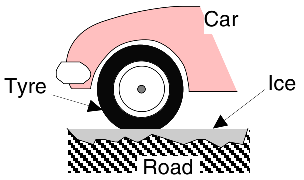
$$P_{\mathrm{M}} = \frac{\Delta Q_{\mathrm{M}}}{\Delta V_{\mathrm{LS}}} \ln\left[\frac{T_{\mathrm{M}}(P_{\mathrm{M}} = 0)}{T_{\mathrm{M}}(P_{\mathrm{M}})}\right] \qquad (10.60)$$

This equation allows us to predict the pressure required to cause a liquid to solidify, in terms of the melting *temperature* of the substance at zero pressure $T_{\mathrm{M}}(P_{\mathrm{M}} = 0)$. In fact at zero pressure a substance does not melt but sublimes; ignoring this for the moment, we choose a value for $T_{\mathrm{M}}(P_{\mathrm{M}} = 0)$ to agree with the experimental melting temperature of 273.15 K for ice at $P_{\mathrm{M}} = 1.013 \times 10^5$ Pa. The resulting curve is plotted

## Example 10.9

**Why is ice so slippery?**

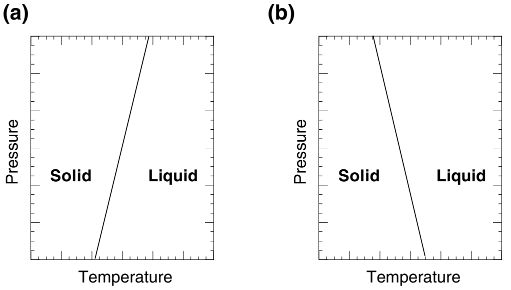
One theory commonly propounded is that when pressurised, ice melts because its melting temperature has been lowered. Does this make sense? Consider a car with a mass of around 1000 kg distributed equally across four wheels.



The weight of the car is supported on a relatively small area of contact on each tyre. Recalling that the tread of the tyre reduces the area of rubber in contact with the road by around 30%, we estimate this contact area as 70% of 15cm × 15 cm = $15.75 \times 10^{-3}$ m$^2$ per tyre. The force supported over this area is the mass of the car times the acceleration due to gravity, which we take as 10 m s$^{-2}$. The force per tyre is therefore 1000 × 10/4 = 2500 N. The force per unit area under each tyre i.e. the pressure each tyre exerts is therefore approximately $2500/(15.75 \times 10^{-3}) = 1.6 \times 10^5$ Pa or an excess pressure of around 1.6 atmospheres. Taking into account the uncertainties in our estimates, and allowing for the excess pressure that may be generated if the car is motion, we might estimate that the maximum pressure under the tyres of a car is around $10^6$ Pa.

Using Example 10.8 as a guide, $10^6$ Pa will lower the melting temperature by around 0.1 K. Thus a car travelling over an iced surface will indeed increase the pressure on the ice such that the ice is taken to its melting temperature *if* the ice is already with approximately 0.1 K of its melting temperature. Do you think this is why ice is slippery?

**Figure 10.15** Illustration of the difference between the melting curves of (a) normal substances and (b) substances whose liquid phase is more dense than their solid phase.



alongside the vaporisation curve (from Figure 10.12) in Figure 10.16 (a) and (b).

If we consider now what happens at low pressures, we see that the triple point marks the point below which the liquid phase disappears. As we shall see in §11.7, solids support a vapour pressure above their surface in much the same way as liquids do, and so the melting curve disappears. The vaporisation curve continues below the triple point in approximately the same way as it 'would have done' for the liquid $\Leftrightarrow$ gas transition. Experimental data on the differences between the liquid $\Leftrightarrow$ gas and solid $\Leftrightarrow$ gas phase transitions is given in §11.7.

## 10.7.3 Constructing a phase diagram

### Water

By combining the co-existence curves for liquid–gas, solid–gas and solid–vapour phases, we can construct a phase diagram for water substance. The result is shown in Figure 10.16 with the pressure plotted on both linear and logarithmic scales.

In fact, the phase diagram of water is not so simple as indicated in Figure 10.16(c). In different regimes of temperature and pressure there are at least ten known crystal structures of the solid phase of water (ice). The common crystal structure (known as ice Ih) collapses under the application of pressure ($\approx 2 \times 10^8$ Pa at – 40 °C) to form ice II, which is denser than liquid water at that pressure. This changes the slope of solid–liquid coexistence curve from its initial negative slope to the more common positive slope. The experimental phase diagram is shown in Question 28 in Chapter 12.

### Potassium

Let us look at a second example of a phase diagram, this time for the metal potassium discussed in §10.2. The procedure for constructing the phase diagram is exactly that discussed above for water.

We can predict the vaporisation curve using Equation 10.52:

**Figure 10.16** The phase diagram for water (a) The curve of the melting pressure versus temperature. Also shown is the vaporisation curve for water from Figure 10.12. (b) The same graph as (a) but with the data plotted on a logarithmic scale. This shows the low-pressure behaviour more clearly and allows us to identify the triple point at the intersection of the vaporisation and melting curves. (c) The same as (b) but with the low-pressure end of the melting curve removed. This is the phase diagram for water substance.

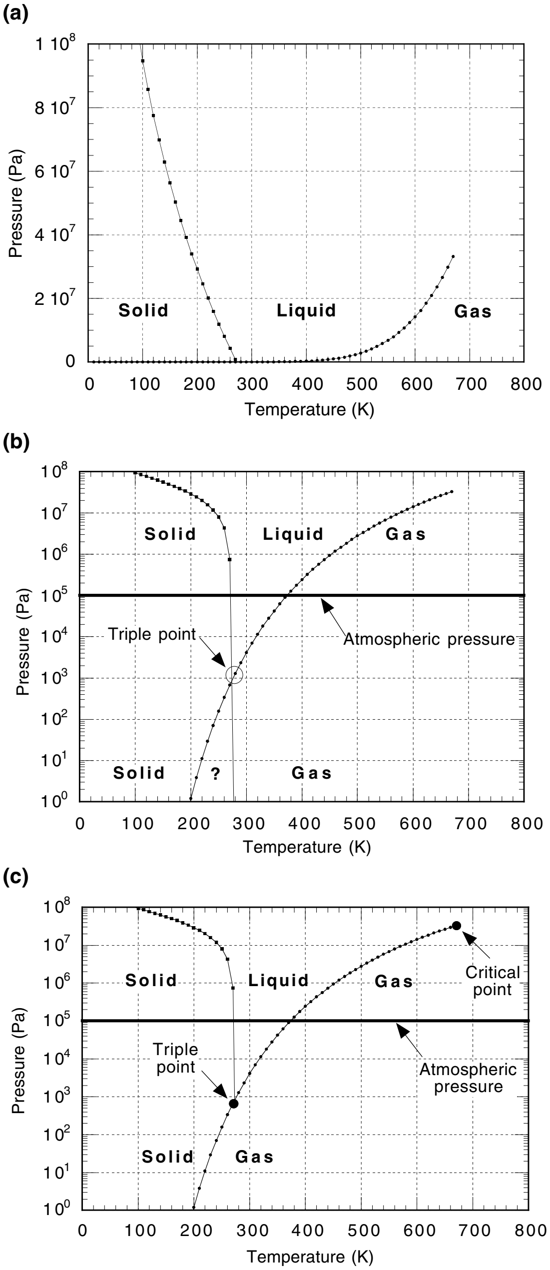
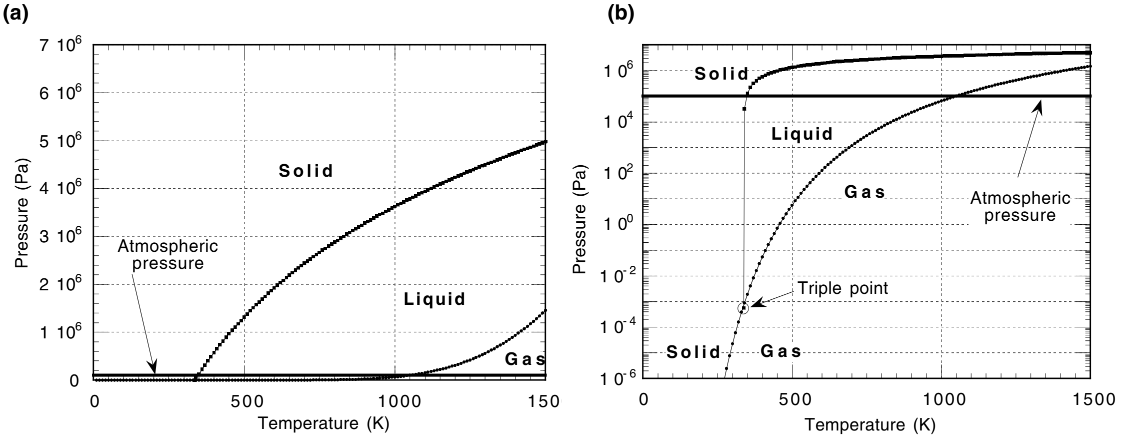


**Figure 10.17** The phase diagram for potassium (a) with pressure shown on a linear scale and (b) with pressure shown on a logarithmic scale. The curves are predicted according to Equations 10.62 and 10.63 using data from Table 11.1 and Table 9.2: molar mass = 39.1 × $10^{-3}$ kg; solid density = 862 kg $m^{-3}$; liquid density = 824 kg $m^{-3}$; $T_M$ = 336.8 K; $T_B$ = 1047 K; $Q_{LS}$ = 2.4 kJ $mol^{-1}$; $Q_{LG}$ = 77.53 kJ $mol^{-1}$. Comparing this with Figure 10.16 (c), the vaporisation curve is much lower in pressure than that for water at the same temperature, and the slope of the melting curve is positive. The critical point has not been marked on the liquid ⇔_gas phase boundary.



$$P_B = P_o \exp\left[\frac{-Q_B}{RT_B}\right] \quad \text{(10.52* and 10.61)}$$

with $P_o$ adjusted to yield a vapour pressure of one atmosphere at 1047 K in agreement with the boiling temperature of potassium (Table 11.1).

The melting curve is predicted from Equation 10.60:

$$P_M = \frac{\Delta Q_M}{\Delta V_{LS}} \ln\left[\frac{T_M(P_M = 0)}{T_M(P_M)}\right] \qquad (10.60^*)$$

with the melting temperature at zero pressure set to 336.8 K in rough agreement with the melting temperature at one atmosphere (Table 11.1).

The phase diagram constructed from these equations is shown in Figure 10.17.

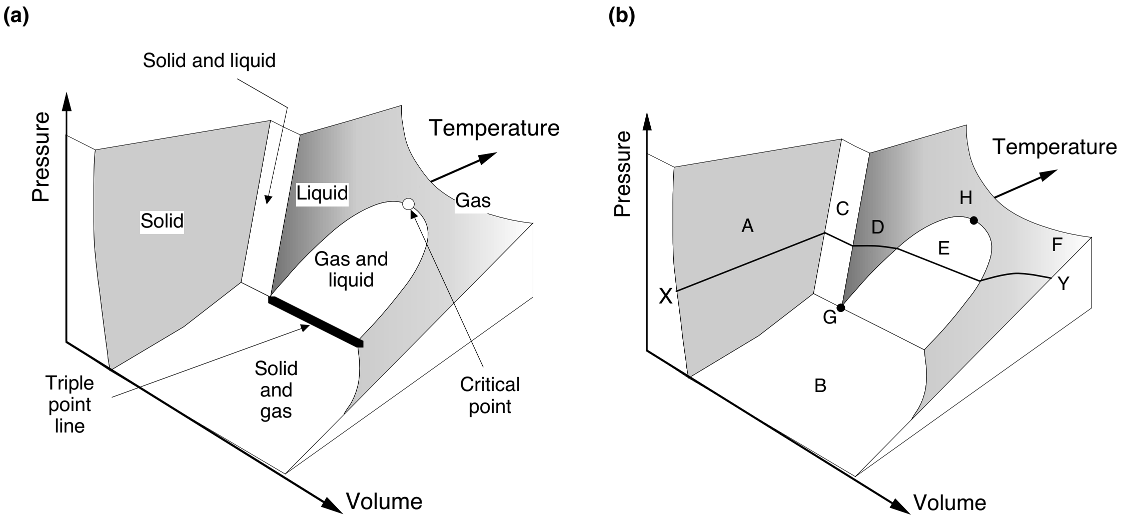
Notice that because latent heat of vaporisation is considerably greater for potassium than for water, the vaporisation curve is much lower in pressure than that for water (Figure 10.16) at the same temperature. Notice also that because the volume of potassium increases as it melts, the slope of the melting curve is positive, i.e. the application of pressure suppresses the melting transition.

### 10.7.4 The *PVT* surface

Phase diagrams such as those shown in §10.7.3 are an enormously useful way to present a great deal of information about a substance in summary form. As we mentioned before, phase diagrams refer to a given amount of a substance – usually one mole – and give information about what phase (liquid, solid or gas) a substance will adopt at any pressure or temperature. However, there is an unplotted variable on these phase diagrams: the volume which the given amount of substance adopts in each of these three phases.

The volume varies by many orders of magnitude across the different experimental conditions outlined in the phase diagrams, and its variation with pressure and temperature is different in each of the different phases. There is a construction, known as the *PVT* surface, which indicates the volume of a given amount of substance at different points on the phase diagram. A schematic illustration of such a surface is shown in Figure 10.18. I think it is important for you to realise that the concept of a *PVT* surface is pedagogical rather than practical. It is generally used to indicate schematically the phases that substances adopt, rather than as an aid to any particular calculation.

**Figure 10.18**. (a) The *PVT* surface of a hypothetical 'typical' substance. The specification of this surface for a substance describes the equilibrium behaviour of a substance. In general each part of the surface may be described by an equation state. (b) The line *XY* represents a process in which the substance is heated at constant pressure. In the solid state (*A*) the volume changes only a little with temperature. The substance then melts (*C* ) and expands at constant temperature until it is all transformed to the liquid state (*D*). There the thermal expansion is slightly larger than in the solid state. Eventually the substance reaches its boiling temperature and its volume increases dramatically as it vaporises (*E* ). Eventually all the substance is transformed to the gas phase.



## 10.8 Exercises

Exercises marked with a P prefix are 'normal' exercises. Those marked with a C prefix are best solved numerically by using a computer program or spreadsheet.. Exercises marked with an E prefix are in general rather more challenging that the P and C exercises. Answers to all the exercises are downloadable from www.physicsofmatter.com

**P1.** At temperatures less than 30K, the heat capacity of metal varies like $C \approx \gamma T + \alpha T^3$ J K$^{-1}$ mol$^{-1}$ where $\gamma = 10^{-4}$ J K$^{-2}$ mol$^{-1}$ and $\alpha = 10^{-5}$ J K$^{-4}$ mol$^{-1}$. Calculate the thermal contribution $U(T)$ to the internal energy of the solid at 1 K and 20 K. How does this compare with typical values of the internal energy due to electrostatic attraction $U_o$ (Table 11.5).

**P2.** Assuming that the heat capacity of a substance follows the Debye law (Figures 7.28 and 7.29) sketch the approximate form of $U(T)$. Indicate clearly the value of $U(T)$ at $T = 0$ K and the limiting slope at temperatures greater than the Debye temperature.

**P3.** One mole of an elemental solid substance has a cohesive energy $U_o = 100$ kJ mol$^{-1}$. By considering this energy to arise from atoms arranged in a simple cubic structure ($a \approx 0.3$ nm) with nearest neighbour interactions only, show that each atomic bond contributes approximately 1/3 eV to the cohesive energy of the substance.

By considering the energy required to split a cube of the substance in two (or otherwise), show that the energy required to a form a new surface of the substance is approximately $\Delta G_S \approx 0.3$ J m$^{-2}$.

**P4.** The substance considered in P3 has a melting temperature $T_M = 700$ K. Close to the melting temperature, the Gibbs free energy of the liquid phase has a slope $\partial G_L/\partial T = -400$ J K$^{-1}$ mol$^{-1}$ and the Gibbs free energy of the solid phase has slope $\partial G_S/\partial T = -395$ J K$^{-1}$ mol$^{-1}$. Use Equation 10.41 with a value of $\Delta G \approx 0.3$ J m$^{-2}$ to estimate the size of a critical embryo if the substance supercools by 0.7 K before commencing solidification. Note that before you can substitute into Equation 10.41 you must convert the Gibbs free energy difference $\Delta G_{LS}$

from J mol$^{-1}$ to J m$^{-3}$ . Do you think your estimate for the critical embryo size is plausible?

**P5.** Following Example 10.7, work out the rate at which the freezing temperature of ethanol would increase with applied pressure. If the maximum achievable laboratory pressure is around $10^5$ atmospheres, could a pressure be achieved at which the melting temperatures of ethanol and water were equal? (In fact the structure of ice changes at high pressure and slope of melting curve then becomes positive.)

**P6.** Following Examples 10.8 and 10.9, write a short report with calculations on whether the slipperiness of ice is evidence for the existence of a pre-melted surface (§10.5.1). As part of your report conduct informal experiments with ice cubes that are cooled as far below 0 °C as you can achieve (a three star domestic freezer will cool ice to –18°C). In particular, address the question of whether the slipperiness is connected with the temperature of the sliding object.

**P7.** Water substance is held in equilibrium at a series of temperatures and pressures (a) to (g). For each state (a) to (g) indicate the phase of the water substance according to Figure 10.16.

(a) 200 K, $10^5$ Pa (b) 200 K, $10^8$ Pa
(c) 400 K, $10^8$ Pa (d) 400 K, $10^5$ Pa
(e) 700 K, $10^5$ Pa (f) 700 K, $10^8$ Pa
(g) 273.15 K, 611 Pa