

## CHAPTER 10

# Figures

These figures are from

*Understanding the properties of matter*

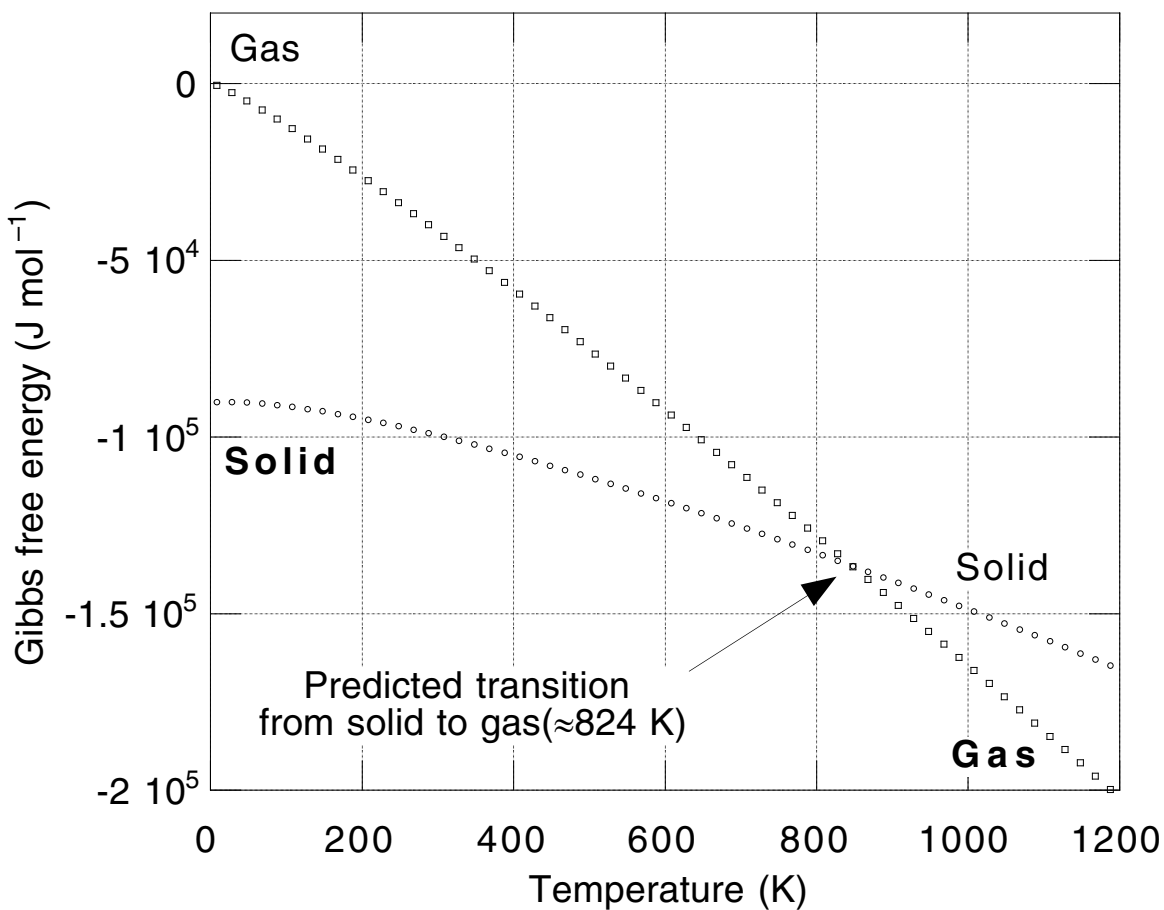
by Michael de Podesta.

The copyright of these figures resides with the publishers, *Taylor and Francis*.

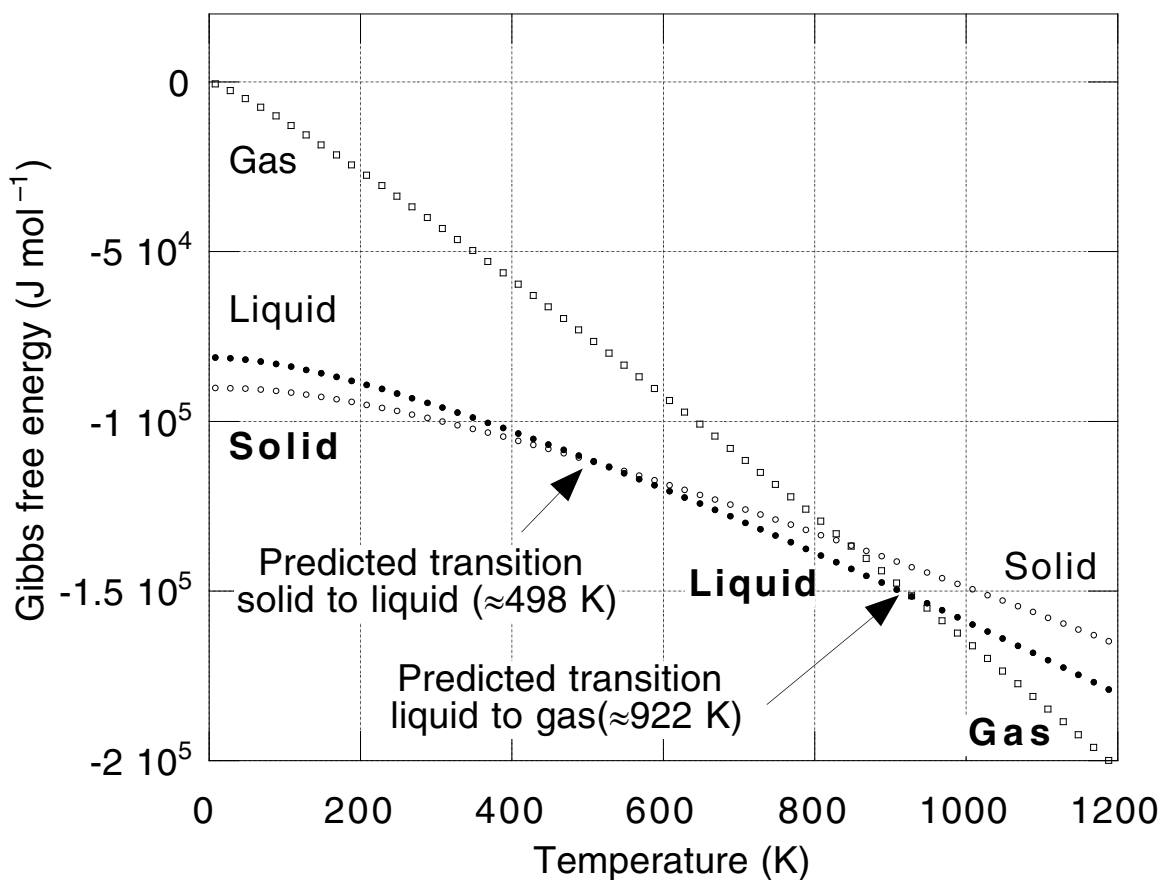
The figures may be used freely for educational purposes, but their source must be acknowledged.

For more details see [www.physicsofmatter.com](http://www.physicsofmatter.com)

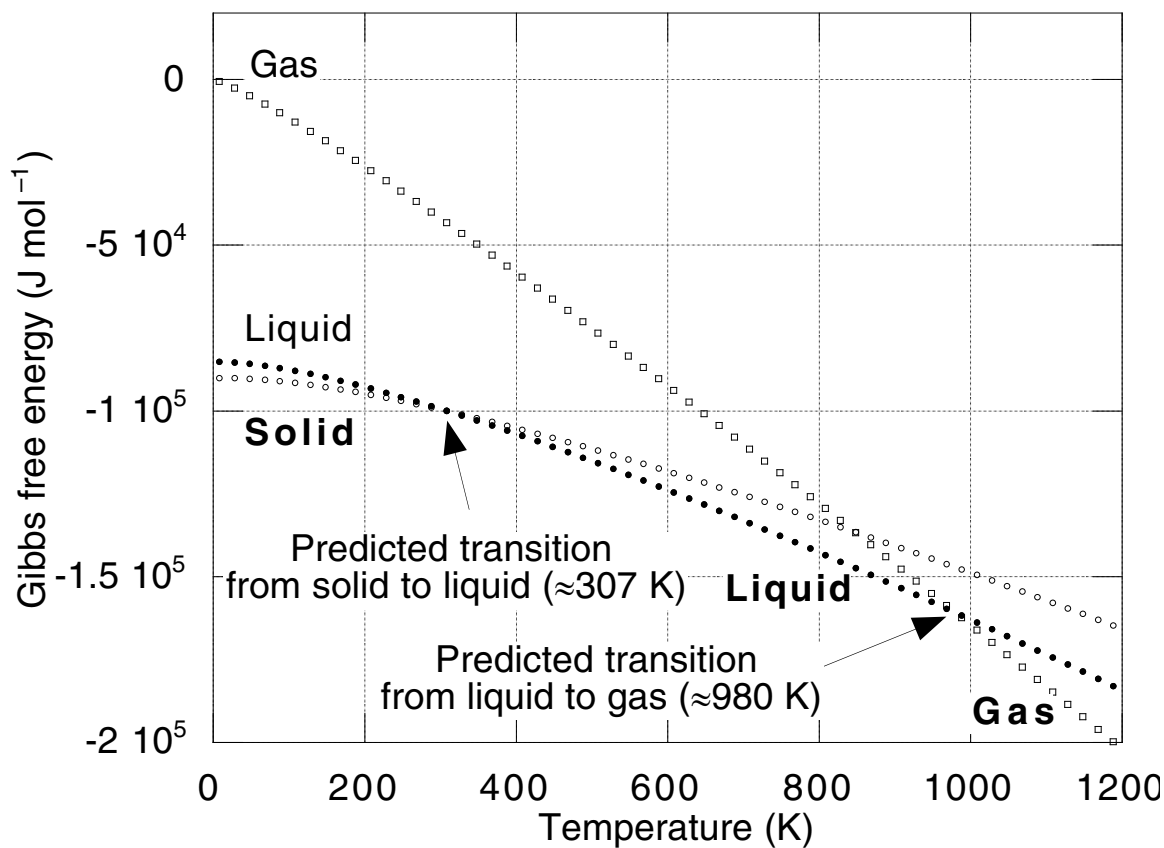
**Figure 10.1** The result of a calculation of the Gibbs free energy  $G$  for potassium in its solid and gaseous states. The simplest assumptions possible have been made about the behaviour of  $U$ ,  $S$  and  $V$  in this temperature range. Notice that at zero temperature  $G_{\text{gas}}$  is zero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



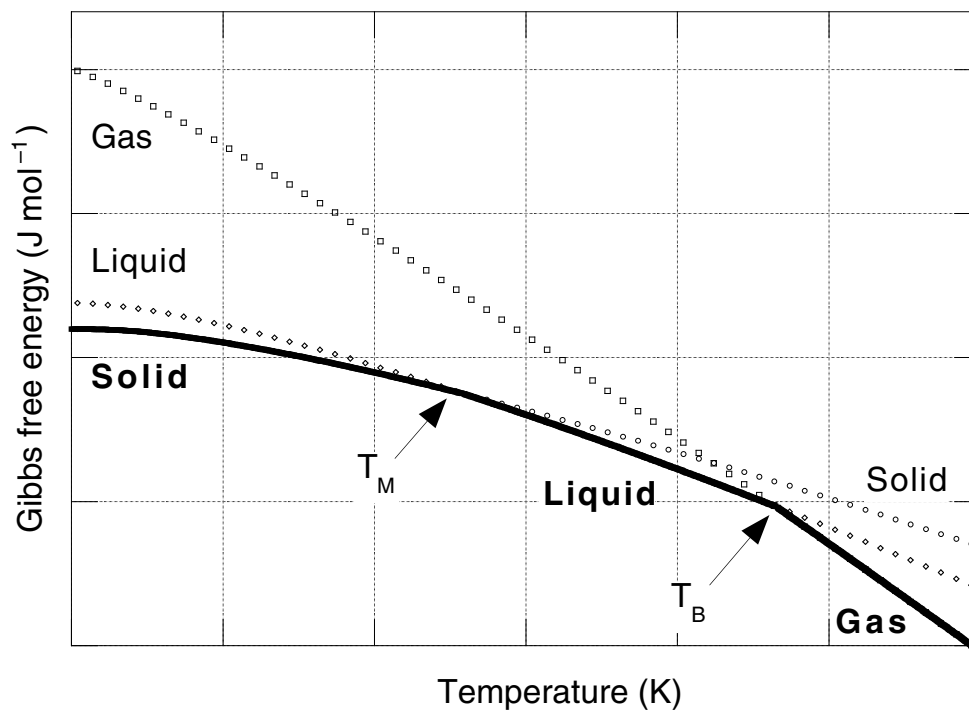
**Figure 10.2** The result of a calculation of the Gibbs free energy  $G$  for potassium in its solid, liquid and gaseous phases. See also Figure 10.1. Notice that at zero temperature  $G_{\text{liquid}}$  is just a little above  $G_{\text{solid}}$ . As we have seen, the heat capacities of liquids are 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.



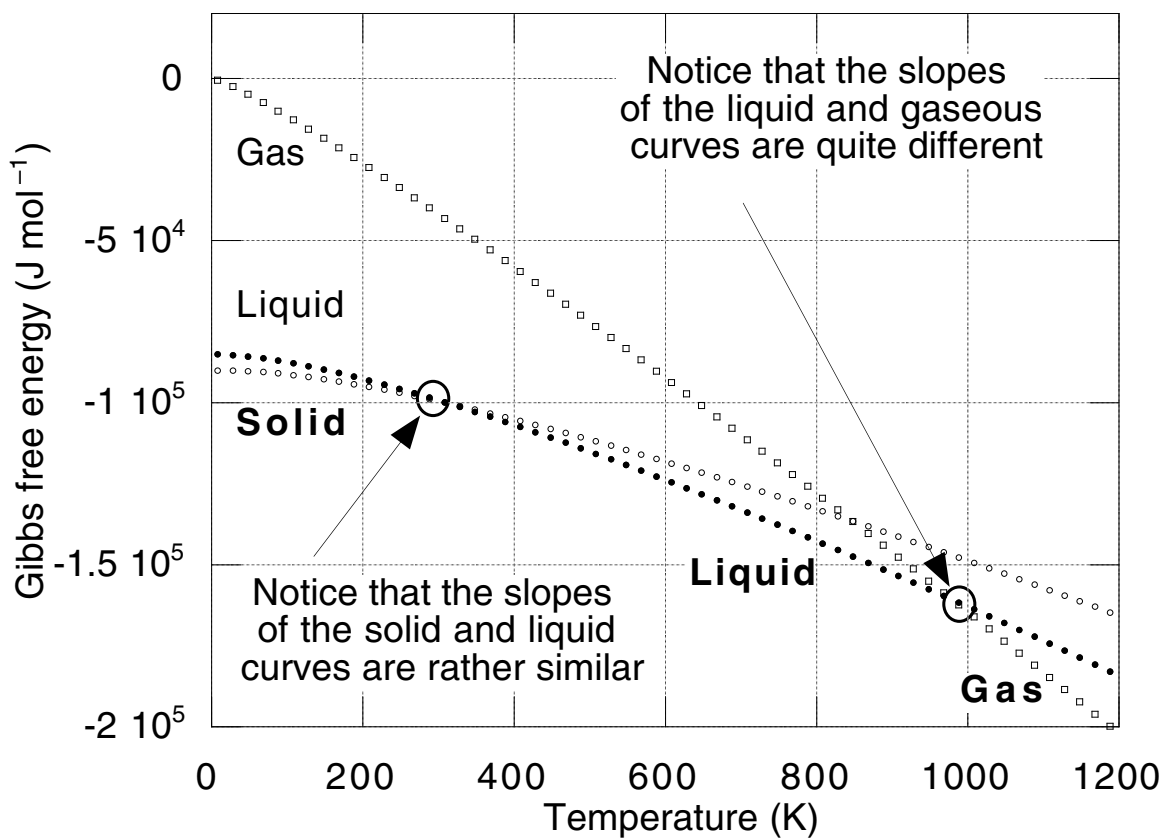
**Figure 10.3** The result of a calculation of the Gibbs free energy  $G$  for potassium in its solid, liquid and gaseous phases. See also Figure 10.2 above. In this figure we have assumed a cohesive energy in the liquid state of 95% of the solid value rather than 90% as assumed in Figure 10.2. The resulting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



**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  $T_B$ .

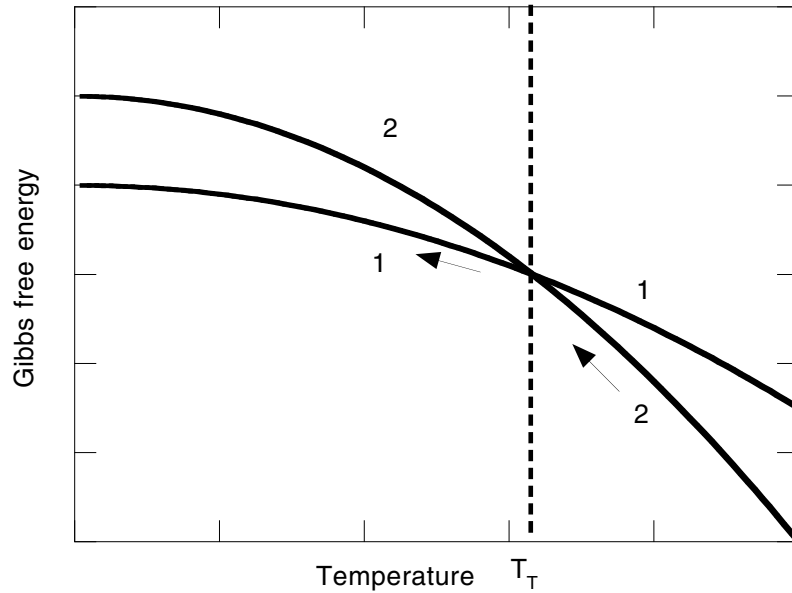


**Figure 10.5** According to the considerations of sections 10.1 and 10.2, a general feature of the enthalpy changes on transformation is that the enthalpy change on fusion (melting) is less than the enthalpy change on vaporisation (boiling). On the  $G(T)$  graph, the enthalpy changes are related to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

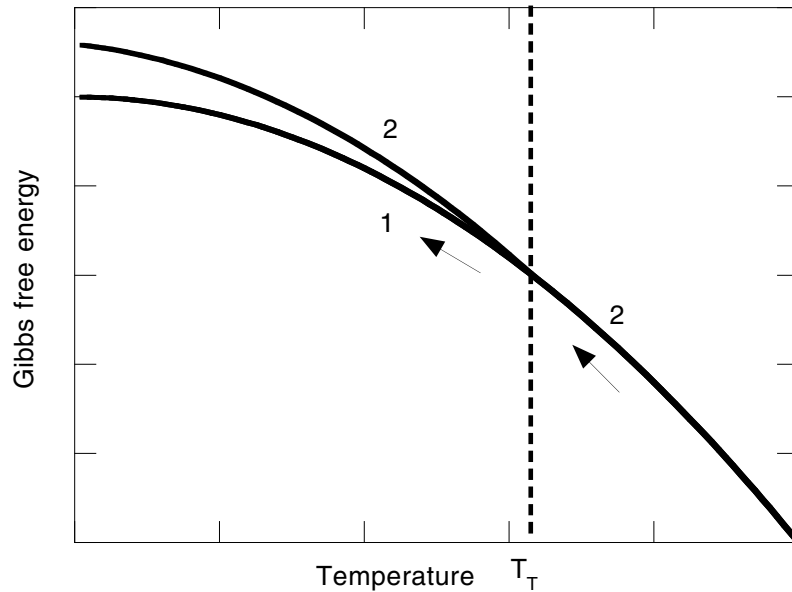


**Figure 10.6** Schematic illustration of the changes in the Gibbs free energy  $G$  at (a) a first-order and (b) a second-order phase transition at temperature  $T_T$ . In a first-order transition, entropy (and hence heat energy) equal to the difference in gradients must be supplied. In a second-order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

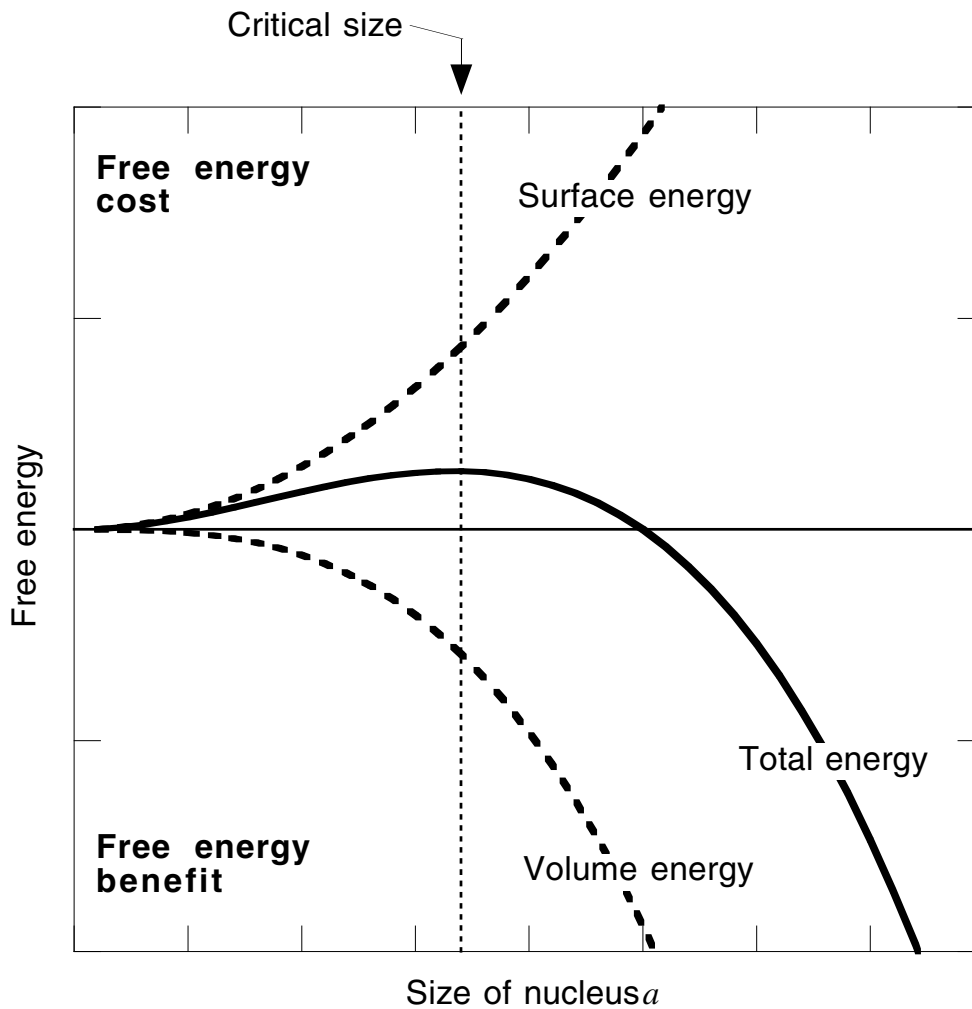
(a)



(b)

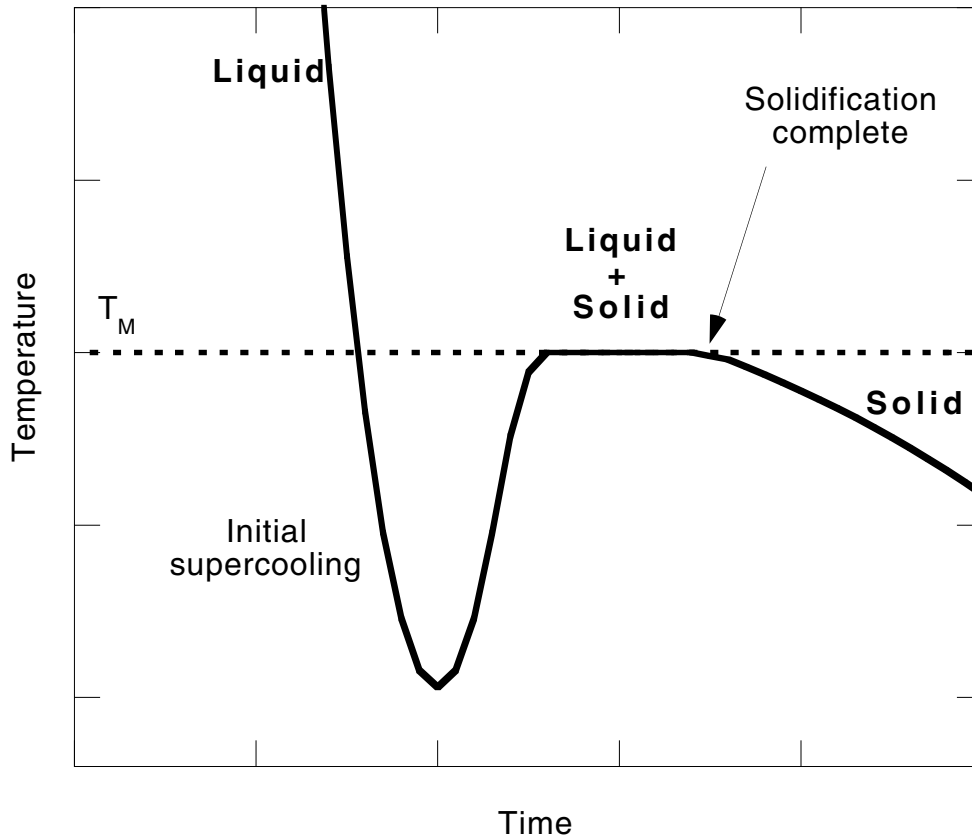


**Figure 10.7** The origin of the phenomena of supercooling. Nuclei of the solid state within the liquid state will not grow unless doing so lowers the free energy. This leads to the phenomenon of a critical size of nucleus. As the temperature falls below the melting temperature (at which the free energies 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.

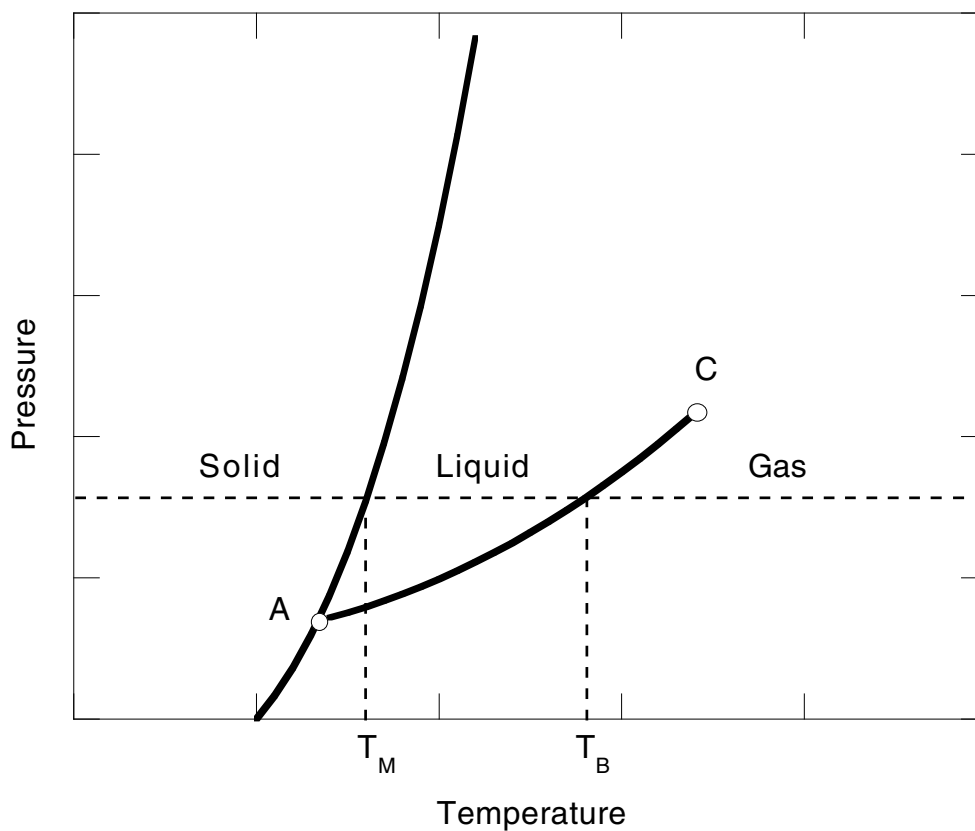




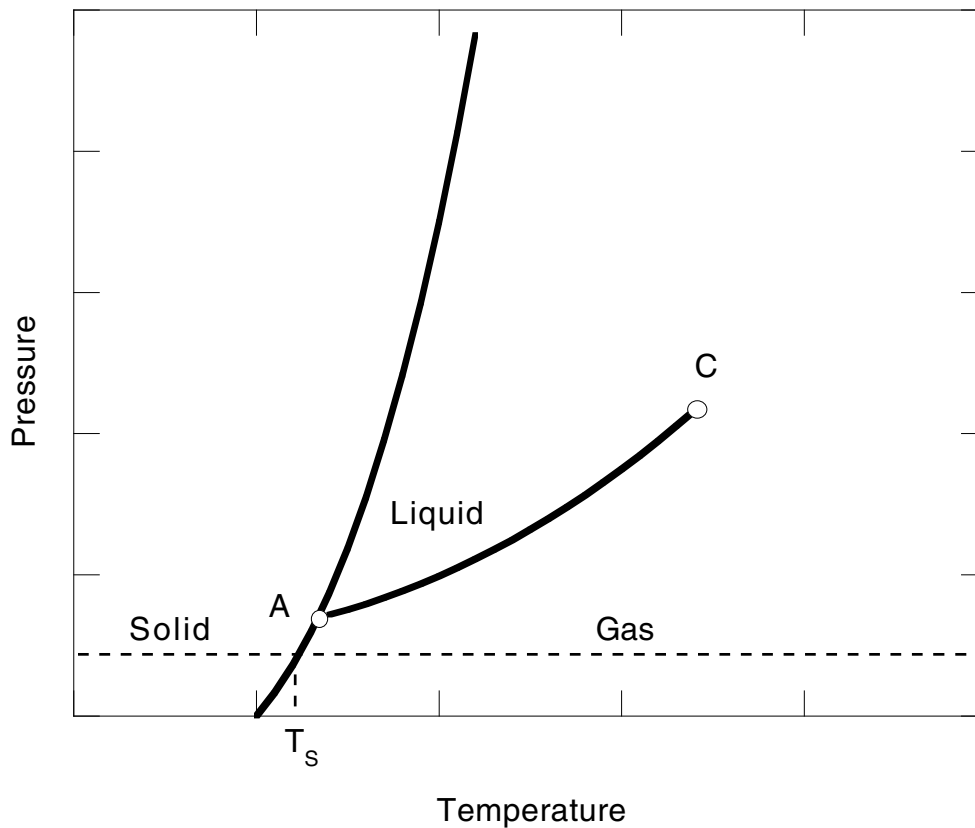
**Figure 10.8** Schematic illustration of the variation of temperature with time during the slow cooling of a pure substance through its equilibrium melting temperature. As discussed in the text, the liquid always supercools to some extent. This continues until the critical radius reduces to the same 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.



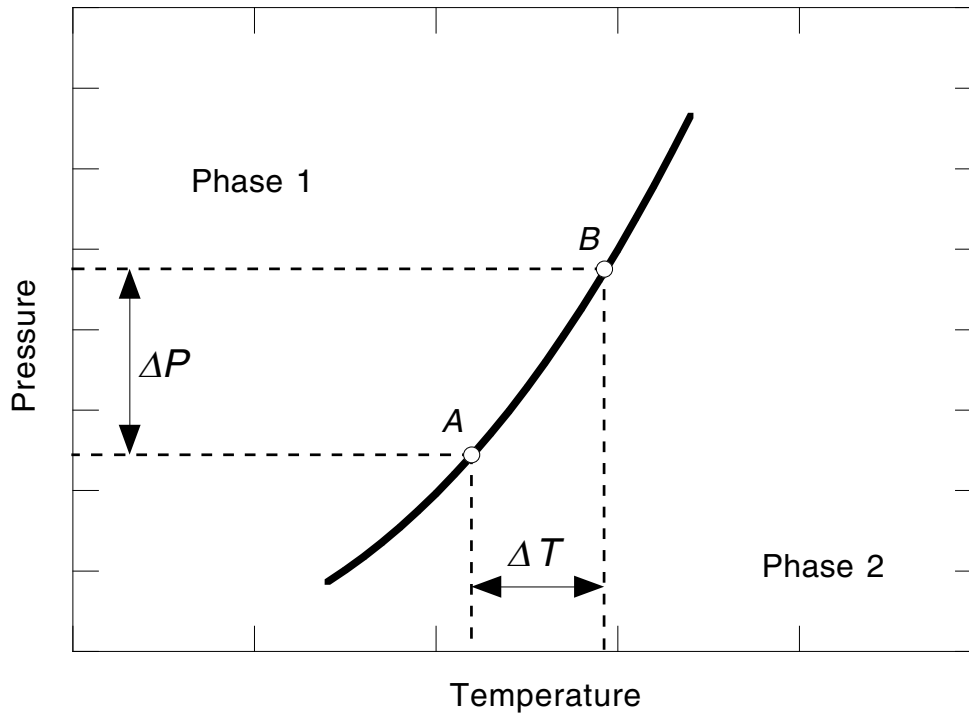
**Figure 10.9** Schematic phase diagram of a typical substance on the  $PT$  plane. Note: The drawing is not to scale. This type of diagram refers to the state of a fixed amount of a substance, usually one mole. The volume of the substance is free to take any value and is not recorded on this type of 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).



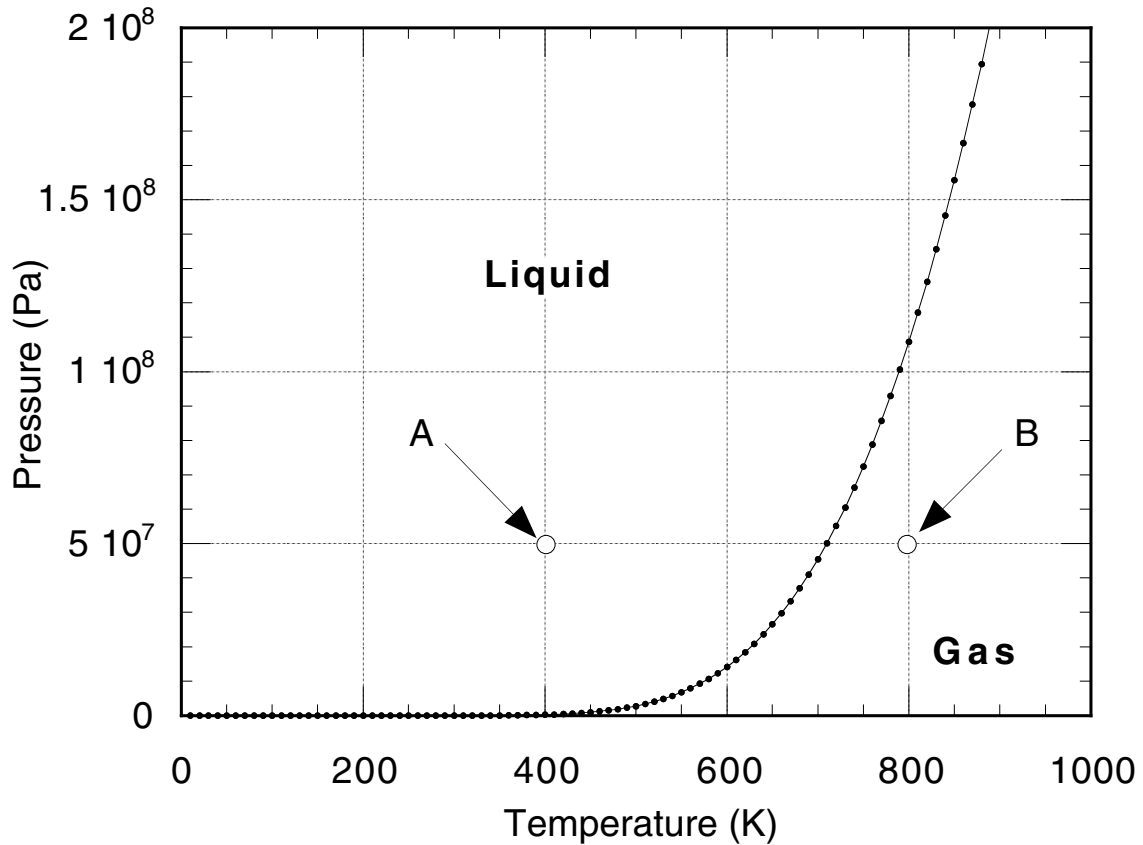
**Figure 10.10** Schematic phase diagram of a typical substance on the  $PT$  plane. Note: The drawing is not to scale. If a solid is heated at low pressure, i.e. the pressure is not allowed to rise on heating, then at ‘low enough pressure’ the solid always transforms directly into the gas phase. This 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).



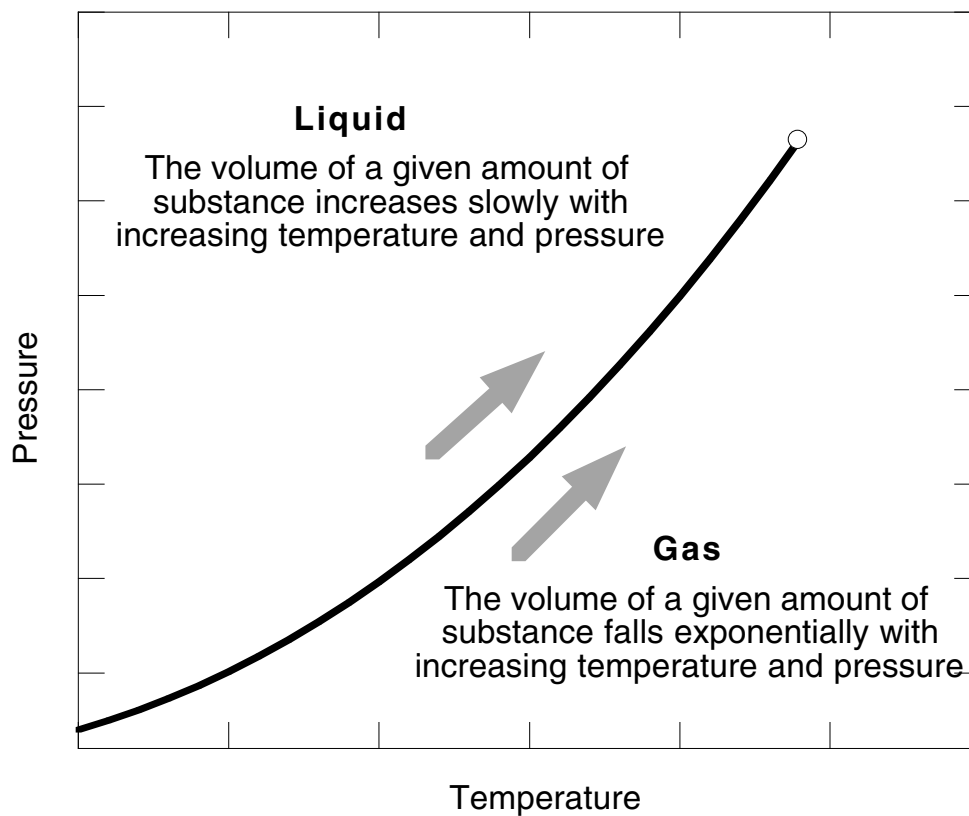
**Figure 10.11** A detailed view of the phase boundary between two phases 1 and 2 which might, for example, refer to a liquid $\leftrightarrow$ solid phase boundary. At each point along the phase boundary the Gibbs free energies of the phases on either side of the phase boundary are equal. At point *A* 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  $G_B$ .



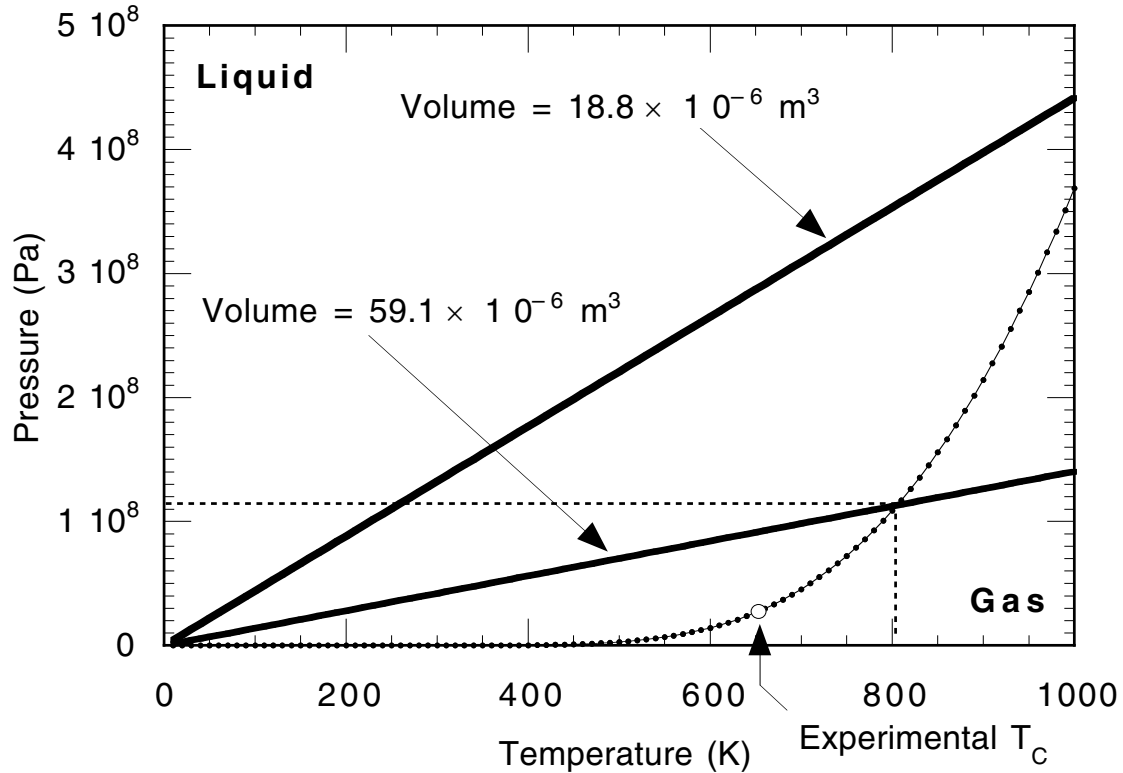
**Figure 10.12** The equilibrium vapour pressure above liquid water predicted according to Equation 10.52. Consider point *A* on the graph which refers to water at a pressure of  $5 \times 10^7$  Pa and a temperature of 400 K (127 °C). The graph tells us that the water would be in the liquid phase. At 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 ( $\approx 10^5$  Pa) is very close to the x-axis on this graph.



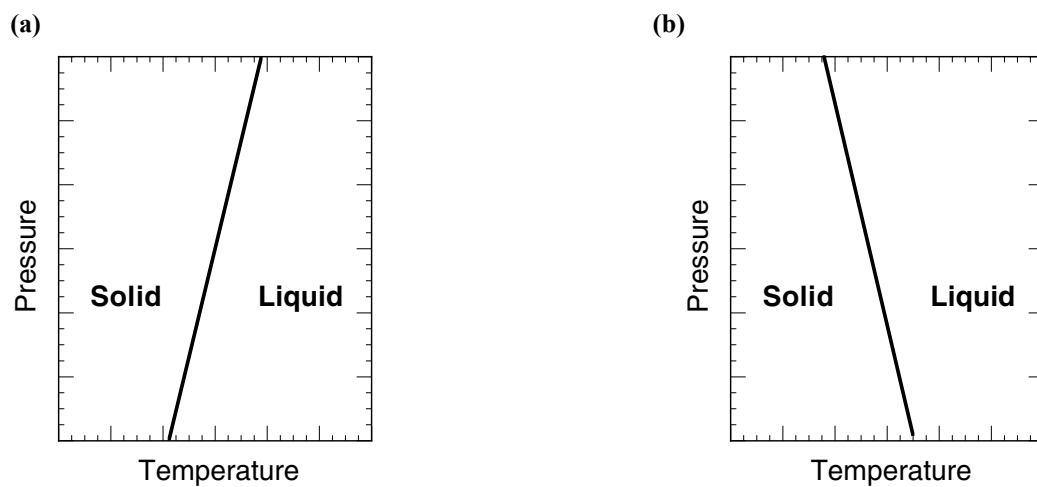
**Figure 10.13** At the critical point the volume of a substance is the same in either the 'liquid' or the 'gas' phase.



**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:  $59.1 \times 10^{-6} \text{ m}^3$ . The intersection of the curves represents a crude estimate of the critical temperature and pressure. The circle on the graph at  $\approx 650 \text{ K}$  represents the experimental value. Atmospheric pressure  $\approx 10^5 \text{ Pa}$  is very close to the x-axis on this graph.



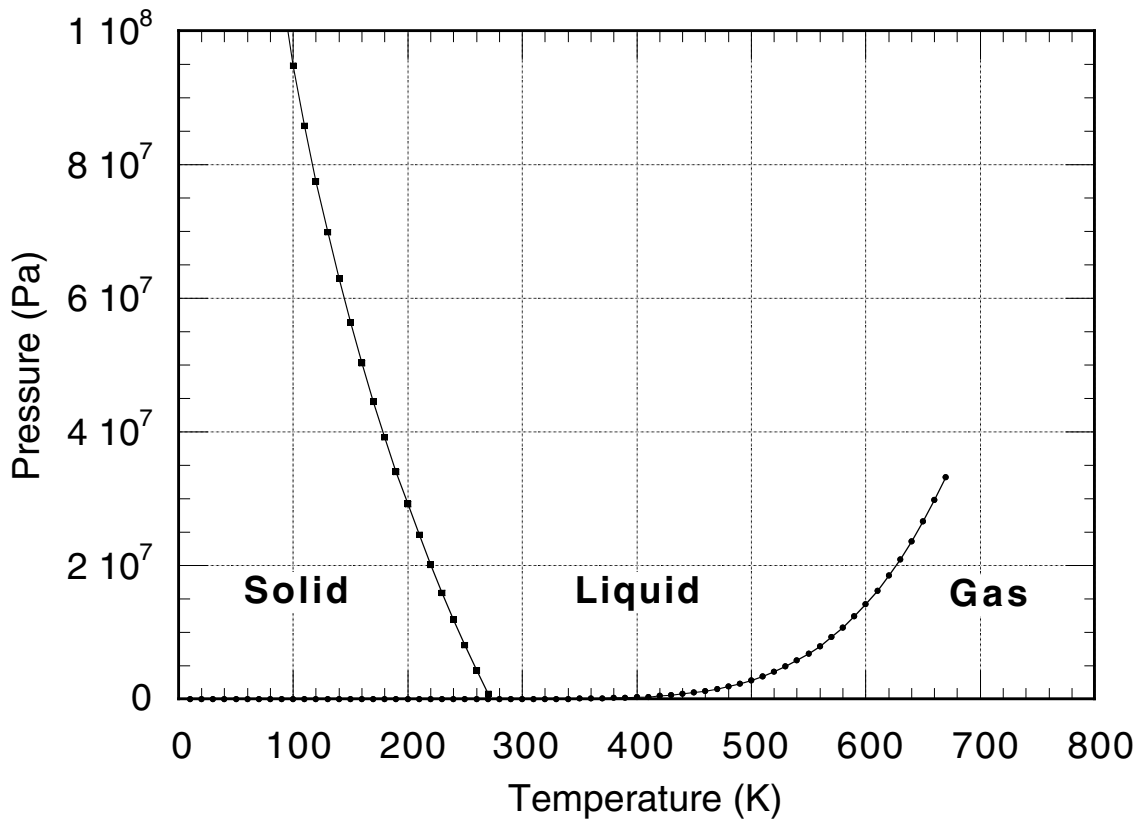
**Figure 10.15** Illustration of the difference between the melting curves of (a) normal substances and (b) substances whose liquid phase is more dense than their solid phase.





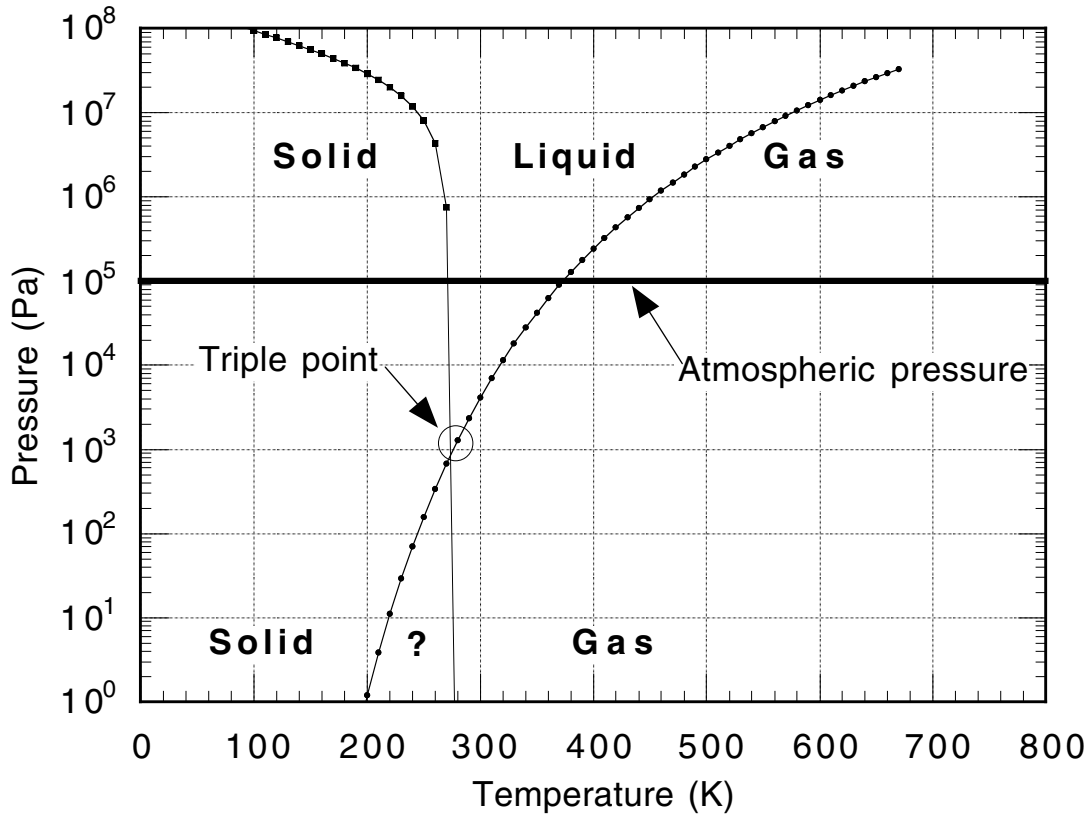
**Figure 10.16** The phase diagram for water (a) The curve of the melting pressure versus temperature. Also shown is the vaporisation curve for water from Figure 10.12. (b) The same graph as (a) but with the data plotted on a logarithmic scale. This shows the low-pressure behaviour more clearly and allows 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.

(a)



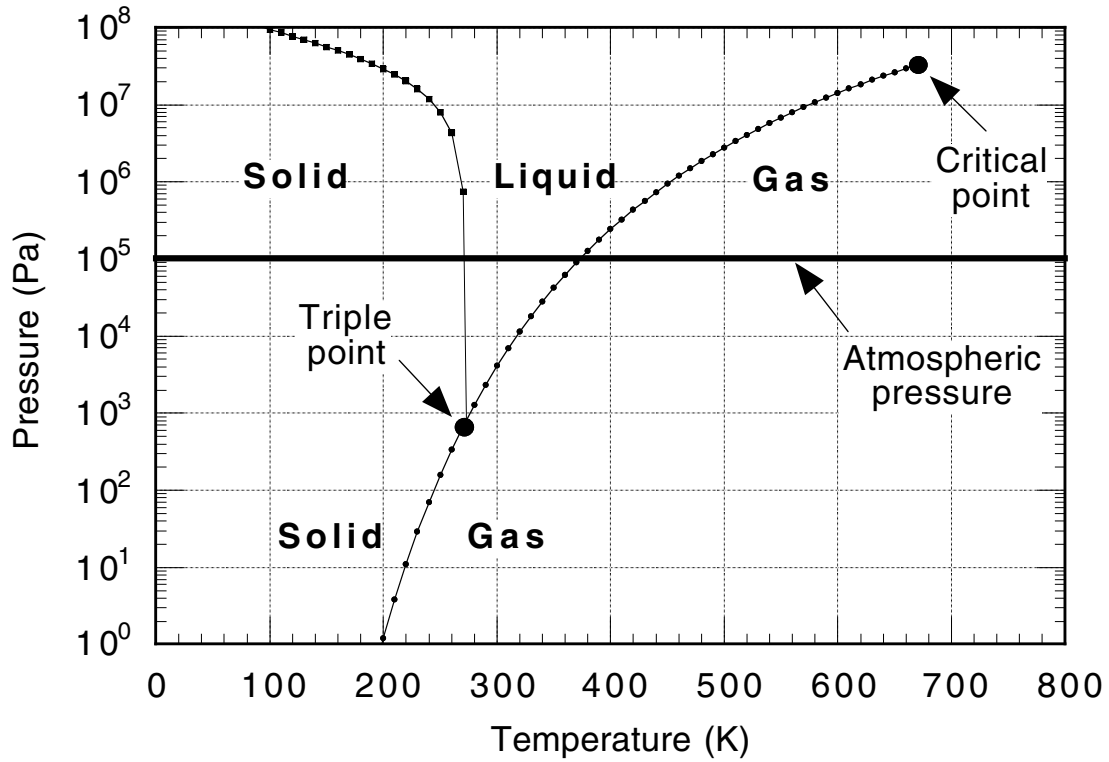
**Figure 10.16** The phase diagram for water (a) The curve of the melting pressure versus temperature. Also shown is the vaporisation curve for water from Figure 10.12. (b) The same graph as (a) but with the data plotted on a logarithmic scale. This shows the low-pressure behaviour more clearly and allows 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.

(b)



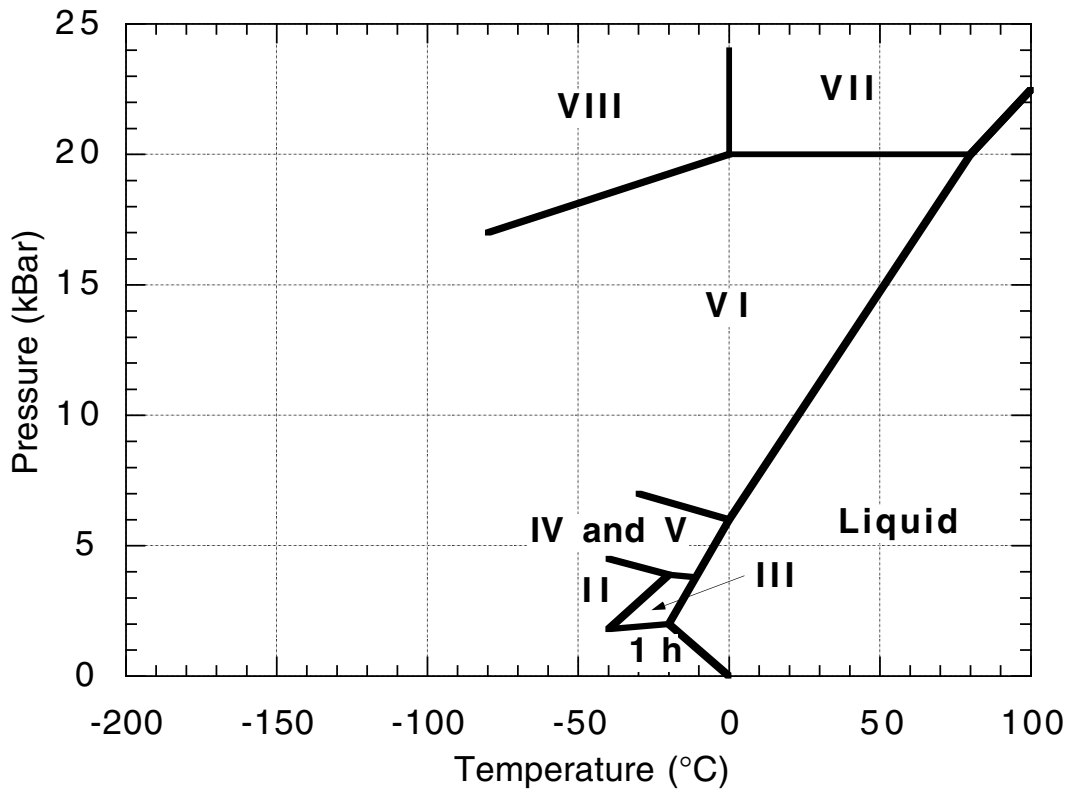
**Figure 10.16** The phase diagram for water (a) The curve of the melting pressure versus temperature. Also shown is the vaporisation curve for water from Figure 10.12. (b) The same graph as (a) but with the data plotted on a logarithmic scale. This shows the low-pressure behaviour more clearly and allows 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.

(c)



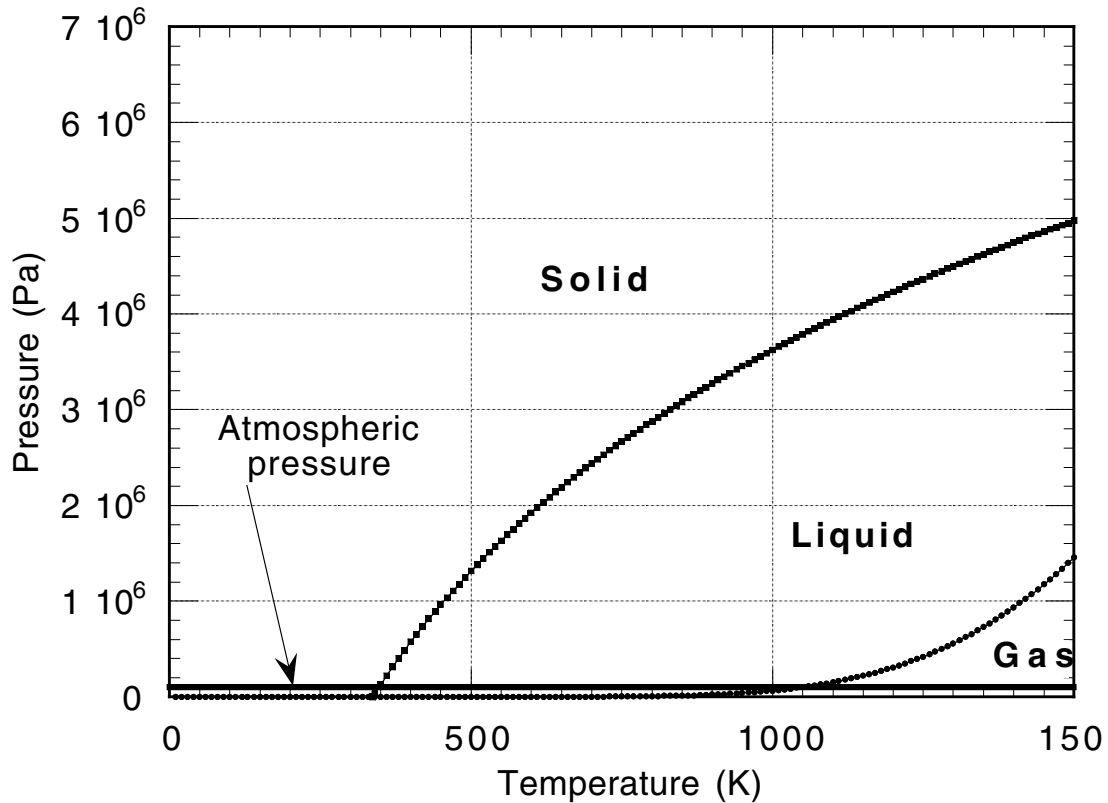
**From Question 28** page 400

Figure 10.16 shows a phase diagram for water substance constructed on the basis of extrapolation of the theoretical expressions for the melting and vaporisation curves. These expressions do not remain accurate at very high pressures because the normal ice structure, called Ice I (or Ice Ih where the h stands for *hexagonal*), collapses into a series of ever-denser structures. The experimentally determined phase diagram of ice is shown above. The roman numerals indicate regimes of temperature and pressure in which ice adopts one its ten different crystal structures. The *full* phase diagram is even more complicated than the one shown and includes a large number of metastable crystal structures.



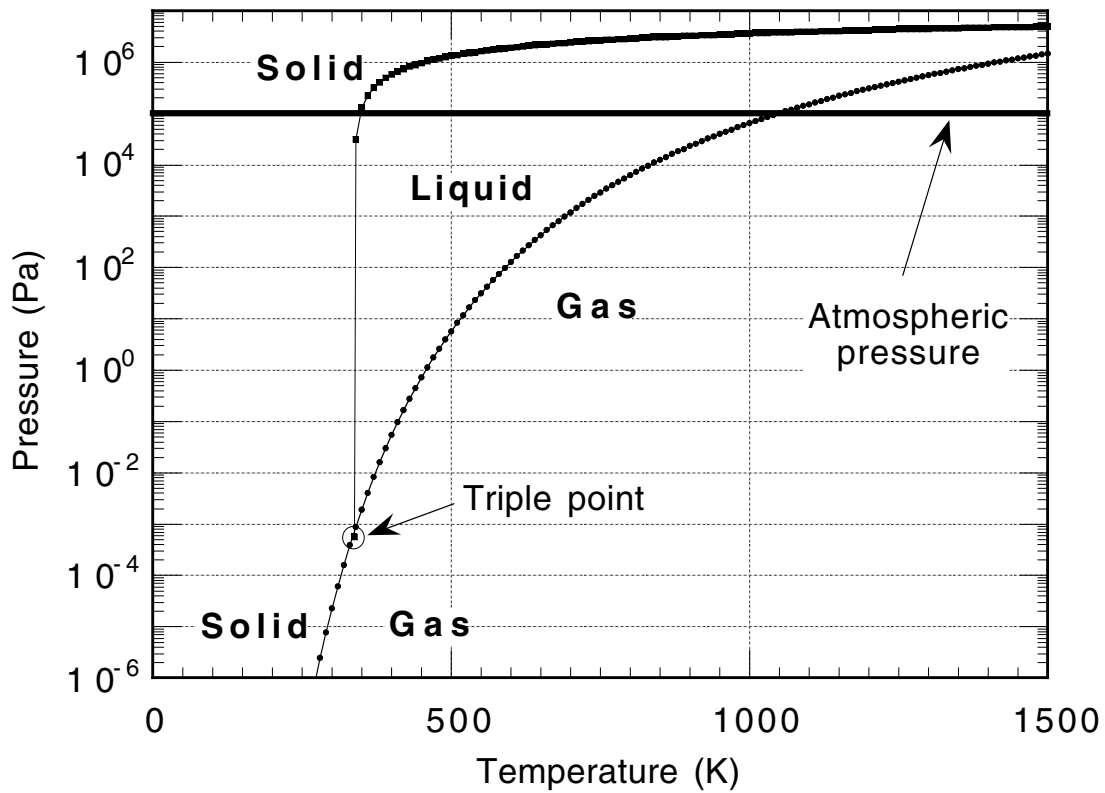
**Figure 10.17** The phase diagram for potassium (a) with pressure shown on a linear scale and (b) with pressure shown on a logarithmic scale. The curves are predicted according to Equations 10.62 and 10.63 using data from Table 11.1 and Table 9.2: molar mass =  $39.1 \times 10^{-3}$  kg; solid density =  $862 \text{ kg m}^{-3}$ ; liquid density =  $824 \text{ kg m}^{-3}$ ;  $T_M = 336.8 \text{ K}$ ;  $T_B = 1047 \text{ K}$ ;  $Q_{LS} = 2.4 \text{ kJ mol}^{-1}$ ;  $Q_{LG} = 77.53 \text{ kJ mol}^{-1}$ . 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  $\leftrightarrow$  gas phase boundary.

(a)



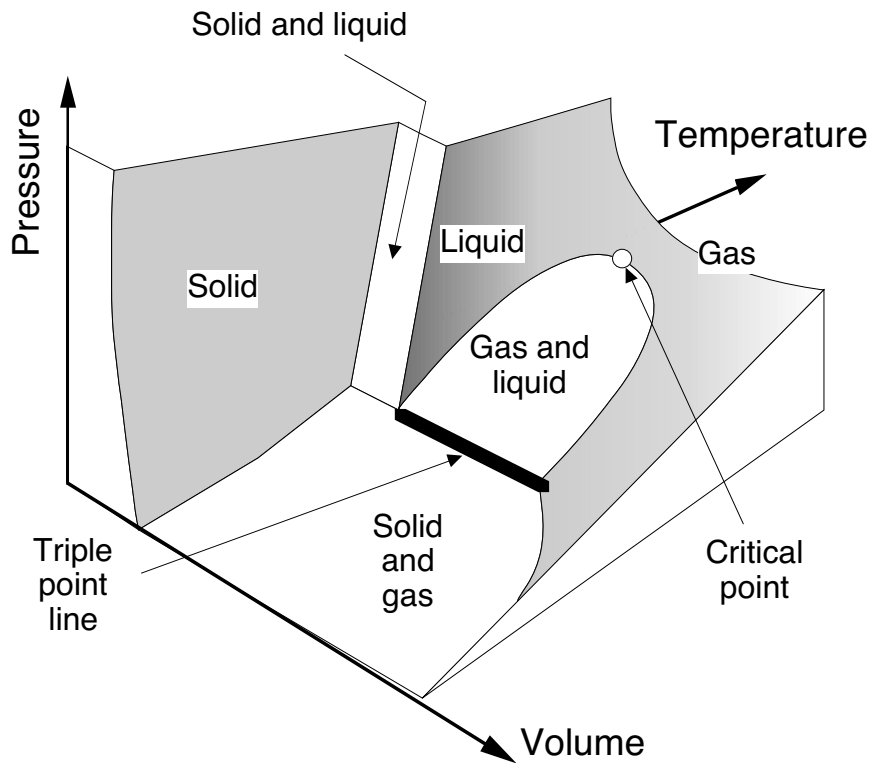
**Figure 10.17** The phase diagram for potassium (a) with pressure shown on a linear scale and (b) with pressure shown on a logarithmic scale. The curves are predicted according to Equations 10.62 and 10.63 using data from Table 11.1 and Table 9.2: molar mass =  $39.1 \times 10^{-3}$  kg; solid density =  $862 \text{ kg m}^{-3}$ ; liquid density =  $824 \text{ kg m}^{-3}$ ;  $T_M = 336.8 \text{ K}$ ;  $T_B = 1047 \text{ K}$ ;  $Q_{LS} = 2.4 \text{ kJ mol}^{-1}$ ;  $Q_{LG} = 77.53 \text{ kJ mol}^{-1}$ . Comparing this with Figure 10.16 (c), the vapourisation 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  $\leftrightarrow$  gas phase boundary.

(b)



**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 of 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.

(a)



**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 of 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.

(b)

