

CHAPTER 11

Figures

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Figure 11.1 A generic PT phase diagram

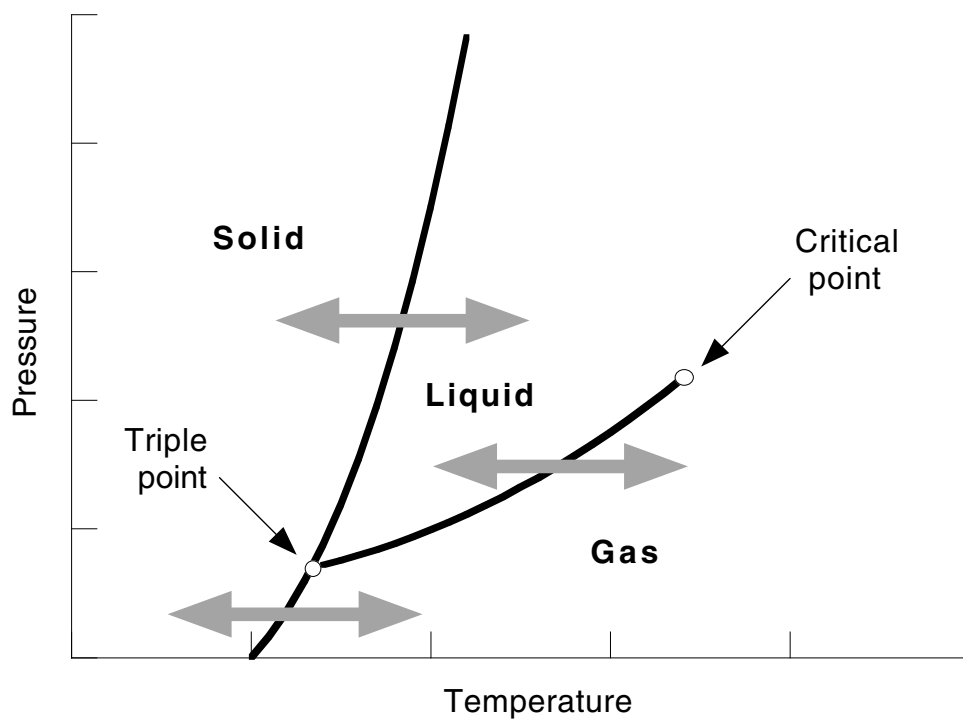


Figure 11.2 The five pictures illustrate the effect of application of heat energy to a substance in the solid state at the melting temperature. The heat serves only to transform more solid into liquid, but does not raise the temperature of the mixture. Notice that the solid phase is usually more dense than the liquid and sinks in the mixture. This is not always the case: water, silicon, germanium gallium and bismuth are examples where the liquid phase is denser than the solid phase. (See Tables 9.1 and 9.2.)

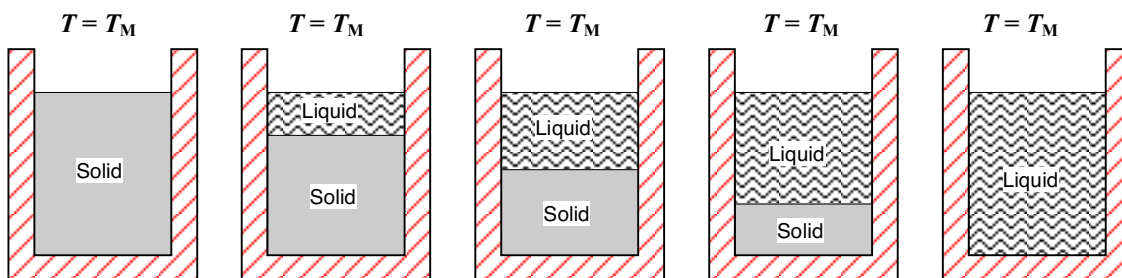


Figure 11.3 The melting temperatures of the elements plotted as function of atomic number. Notice that the pattern has similarities to several other patterns such as those seen in Figures 7.1 and Figures 11.4.

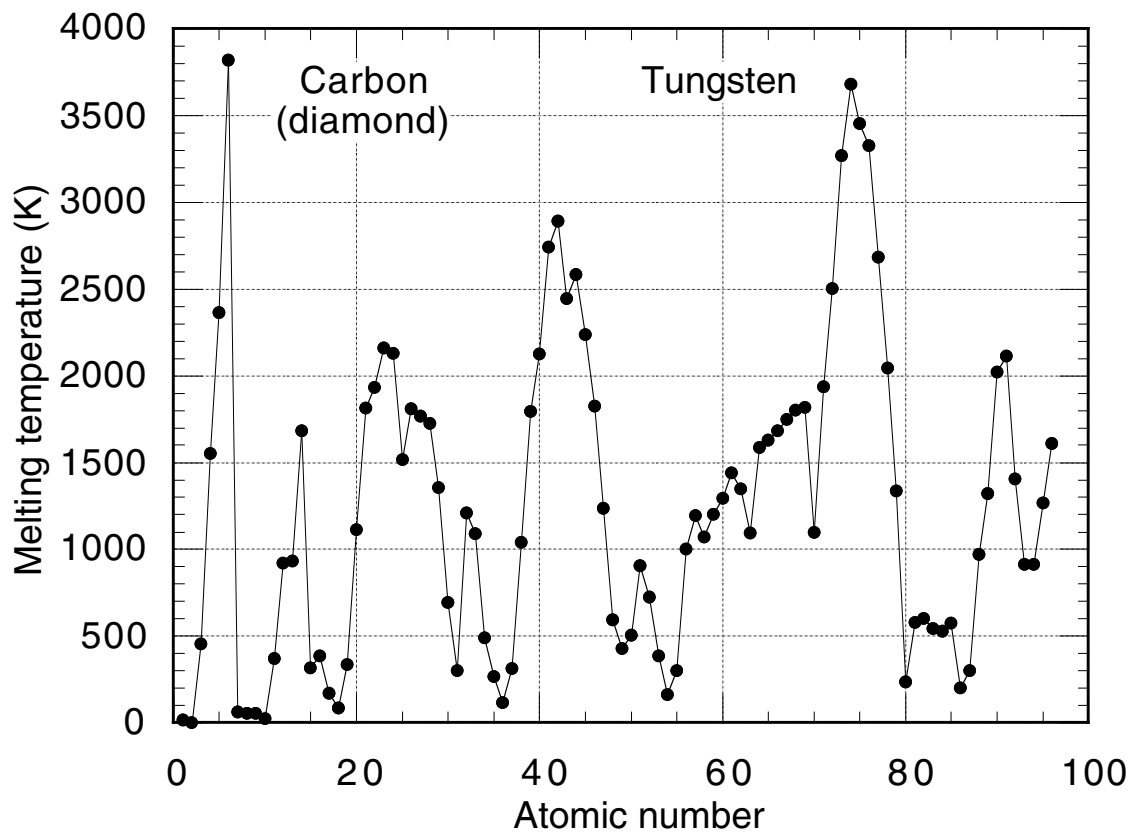
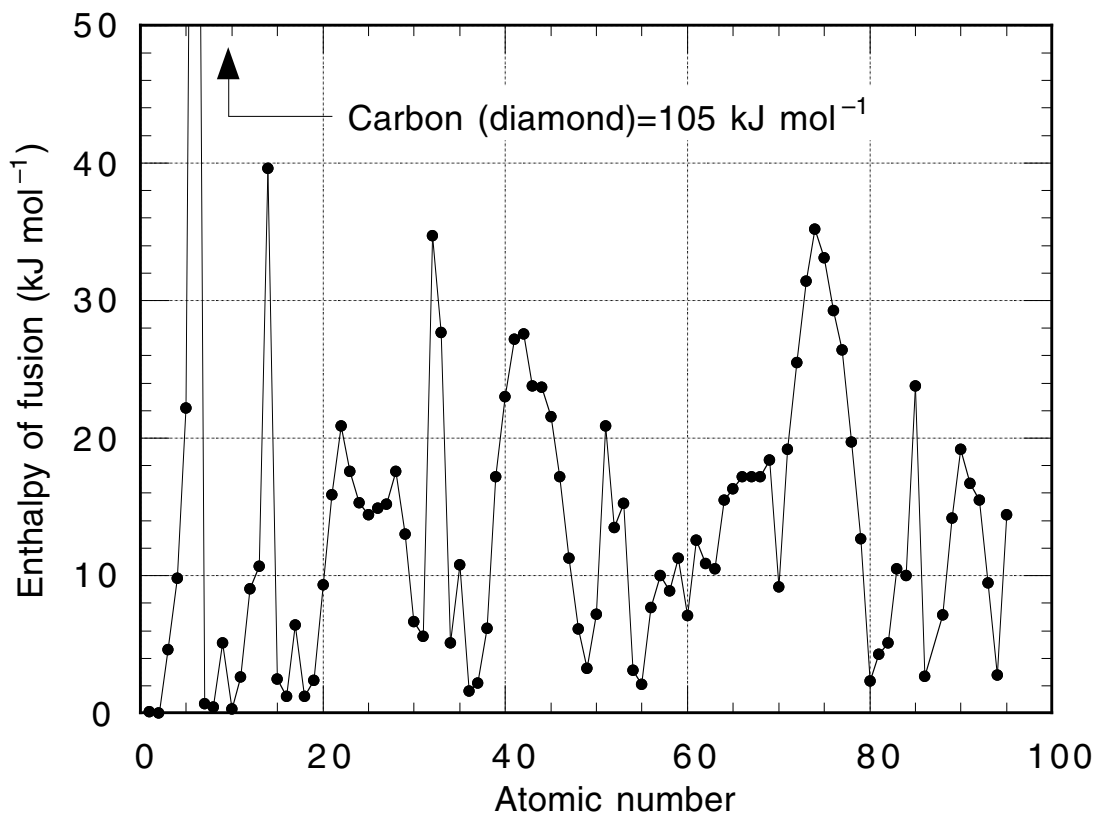


Figure 11.4 The molar enthalpy change of fusion of the elements plotted as function of atomic number. The datum for diamond has not been plotted so as to allow detail on the rest of the graph to be seen.



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Figure 11.5 The elevation of the melting temperature of silver and gold as a function of applied pressure. Notice that the pressures are extremely large, 1 kBar is 1000 times atmospheric pressure and the pressure scale shown extends up to 200 kBar.

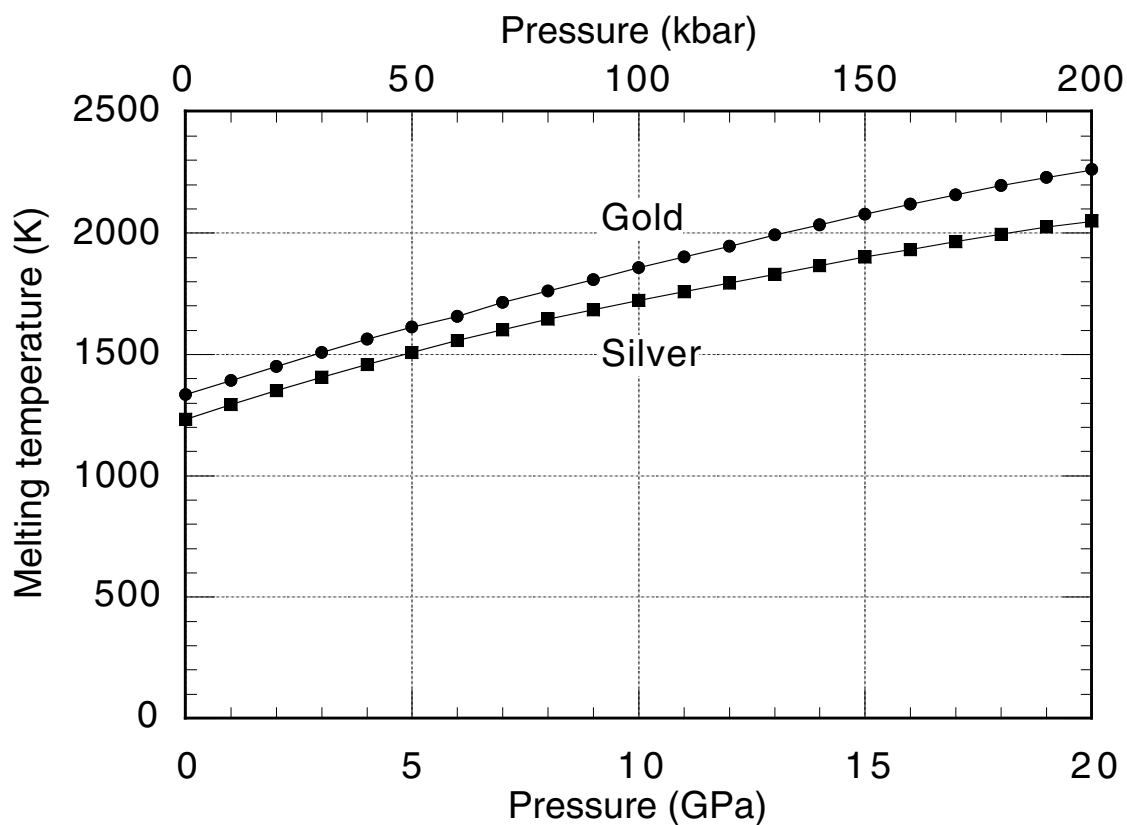


Figure 11.6 The melting and Debye temperatures of the elements plotted as function of atomic number. The temperatures are plotted on a logarithmic vertical axis. Notice the correlations between the two data-sets. The data points are connected by straight lines in order to highlight trends in the data. Since data on the Debye temperature is not available for all the elements, some straight lines appear to indicate a Debye temperature higher than the melting temperature (e.g. elements 7 to 10): This is an artefact of the plotting procedure.

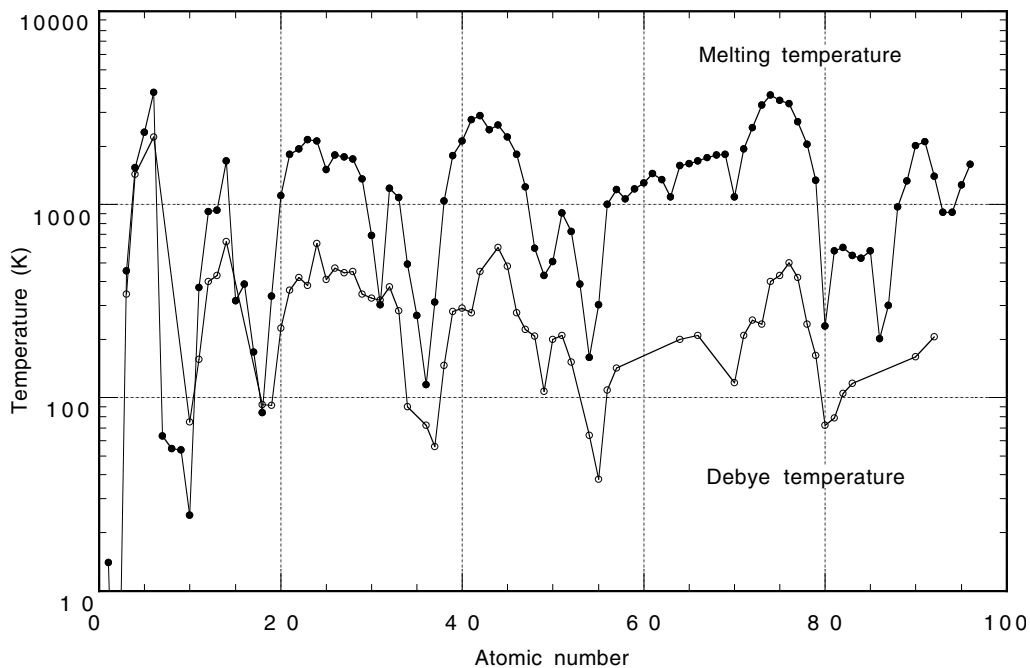


Figure 11.7 To test the Lindemann hypothesis we assume that each atom vibrates in a simple harmonic potential with amplitude A , which is some fraction f of the interatomic spacing a . According to the equipartition theorem (§2.5) the mean energy of vibration \bar{E}_x for vibration in one direction has the value $k_B T$. This is also equal to the potential energy of vibration at an extremum of vibration $\frac{1}{2}KA^2$.

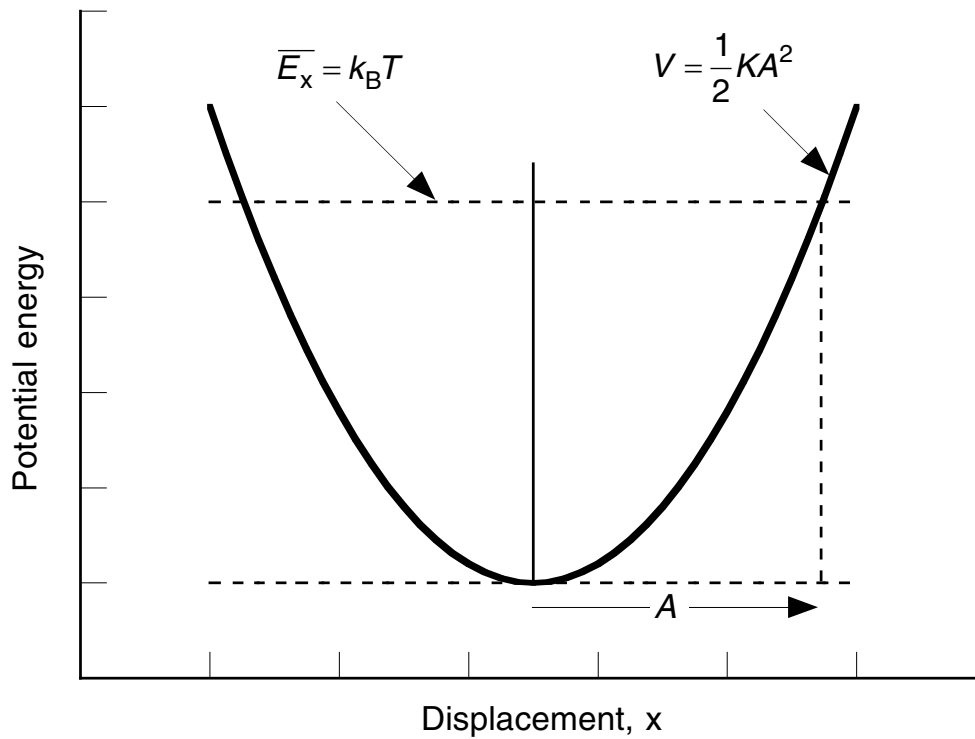


Figure 11.8 The Lindemann Fraction f calculated according Equation 11.7 for the elements. Notice that the fraction is around one twentieth of a lattice spacing and the data in the graph have a mean value of 0.052 ± 0.014 at one standard deviation. By comparison with Figure 11.2 this variability is extremely small.

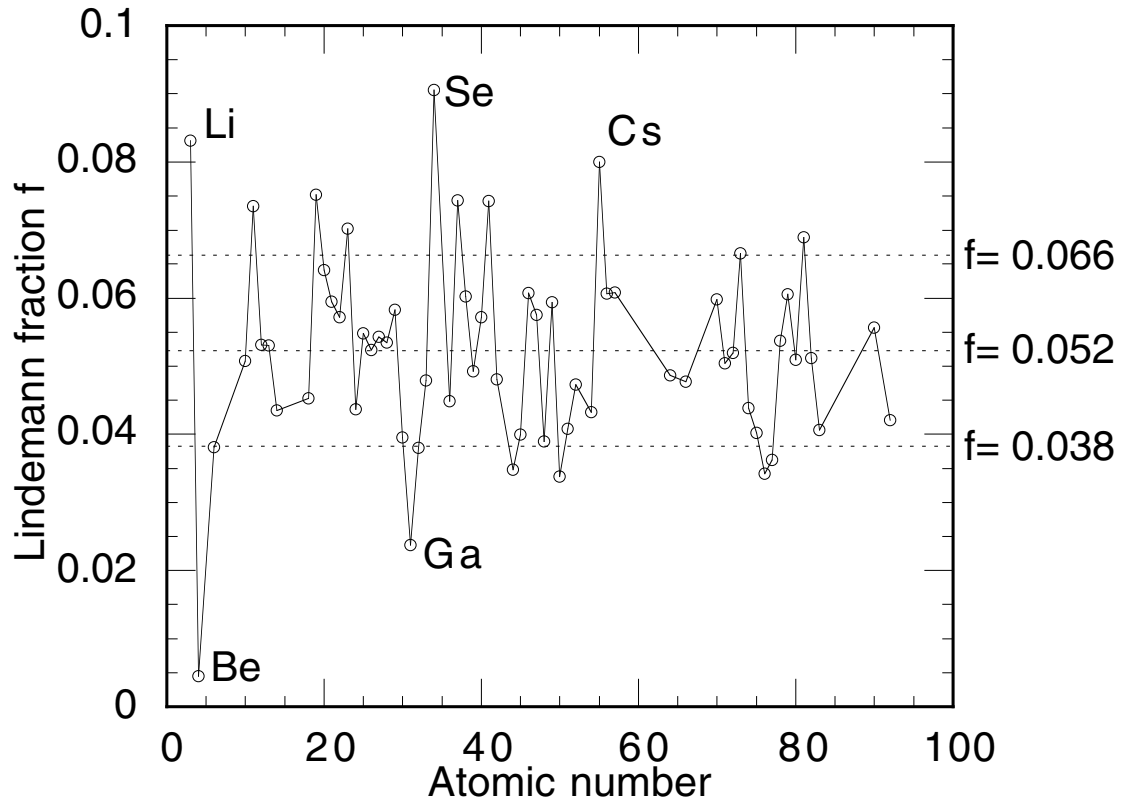
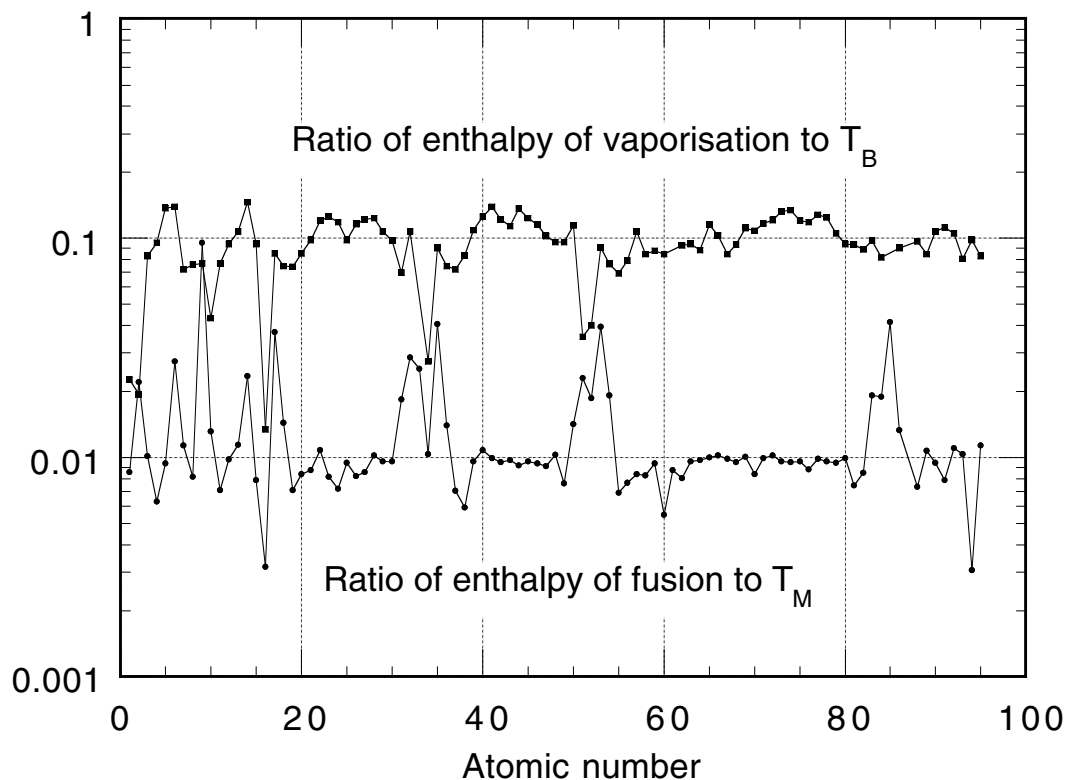


Figure 11.9 The relationship amongst the elements between the enthalpy of transformation (fusion or vaporisation) and the temperature at which a transformation takes place. The figure shows:

- the ratio of the enthalpy of fusion to the melting temperature has a relatively constant value of around 0.01 in the units chosen
- the ratio of the enthalpy of transformation to the boiling temperature has a relatively constant value of around 0.1 in the units chosen.

The 0.01 and 0.1 figures have no absolute significance and are only the result of felicitous choice of units.



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Figure 11.10 Analysis of the correlation between melting temperature and enthalpy change on transformation (ΔQ_{LS}). U_0 represents the cohesive energy of either the solid or liquid states at 0 kelvin. The figures represent the variation of the Gibbs free energy of a substance with cohesive energy which is (a) small and (b) large. The general effect of the large U_0 is to give rise to a large difference between $U_0(\text{liquid})$ and $U_0(\text{solid})$. So a high T_M and a large ΔQ_{LS} are correlated with each other, because they are both correlated with a large U_0 .

(a) Small cohesive energy

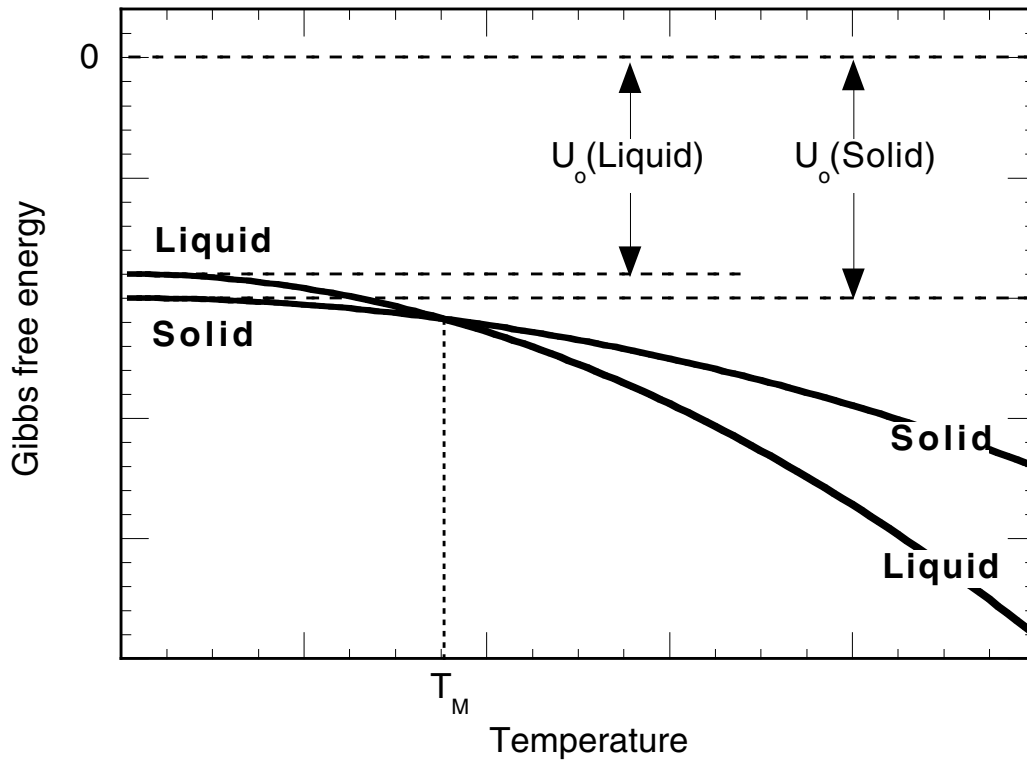


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(b) Large cohesive energy

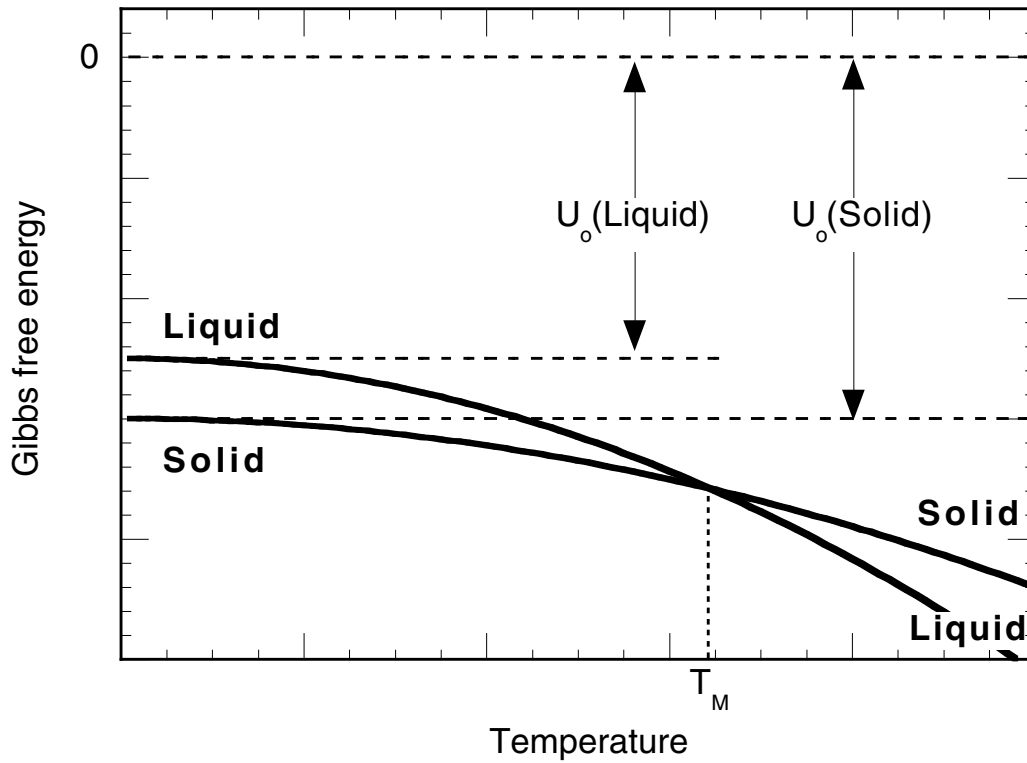


Figure 11.11 Analysis of the correlation between boiling temperature and enthalpy change on vaporisation (ΔQ_{LG}). U_0 represents the cohesive energy of the liquid state at 0 kelvin. The figures represent the variation of the Gibbs free energy of a substance with cohesive energy which is (a) small and (b) large. The general effect of the large U_0 is to give rise to a large difference between $U_0(\text{gas})$ and $U_0(\text{liquid})$. So a high T_B and a large ΔQ_{LG} are correlated with each other, because they are both correlated with a large U_0 .

(a) Small cohesive energy

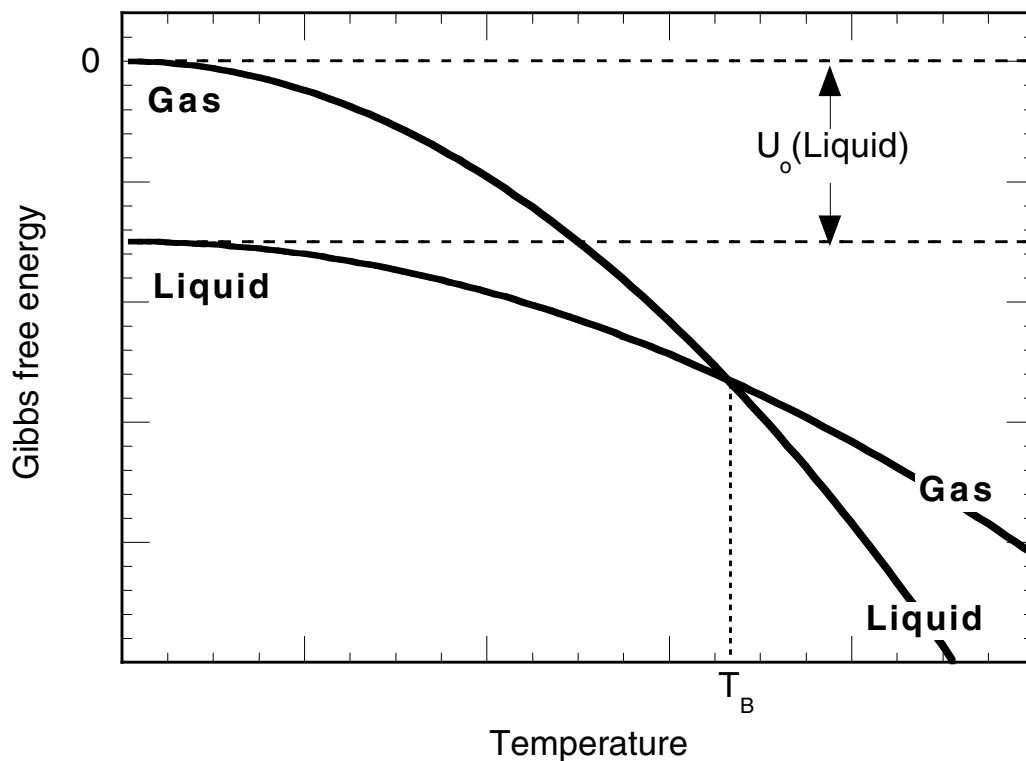


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(b) Large cohesive energy

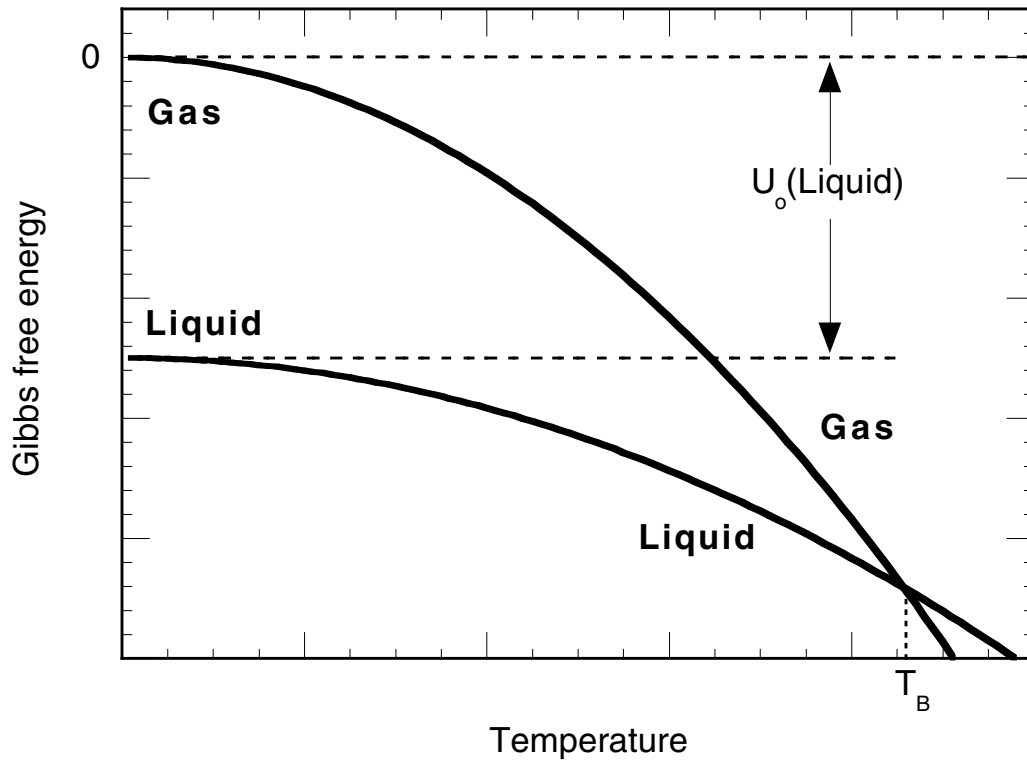


Figure 11.12 Change in viscosity of (a) various liquids and (b) water under applied pressure. Notice the very large pressures involved in these measurements: 100MPa is approximately 1000 times atmospheric pressure.

In (a) the data are taken at 30°C and show the change in viscosity of each substance relative to the viscosity of the same substance at zero pressure. In (b) the data are taken at various temperatures and show the change in viscosity of water relative to the viscosity at the same temperature and zero pressure. Notice that for temperatures below $\approx 30^\circ\text{C}$ the effect of pressure is first to cause a *decrease* in viscosity in contrast with the behaviours of ‘normal’ liquids shown in (a).

(a)

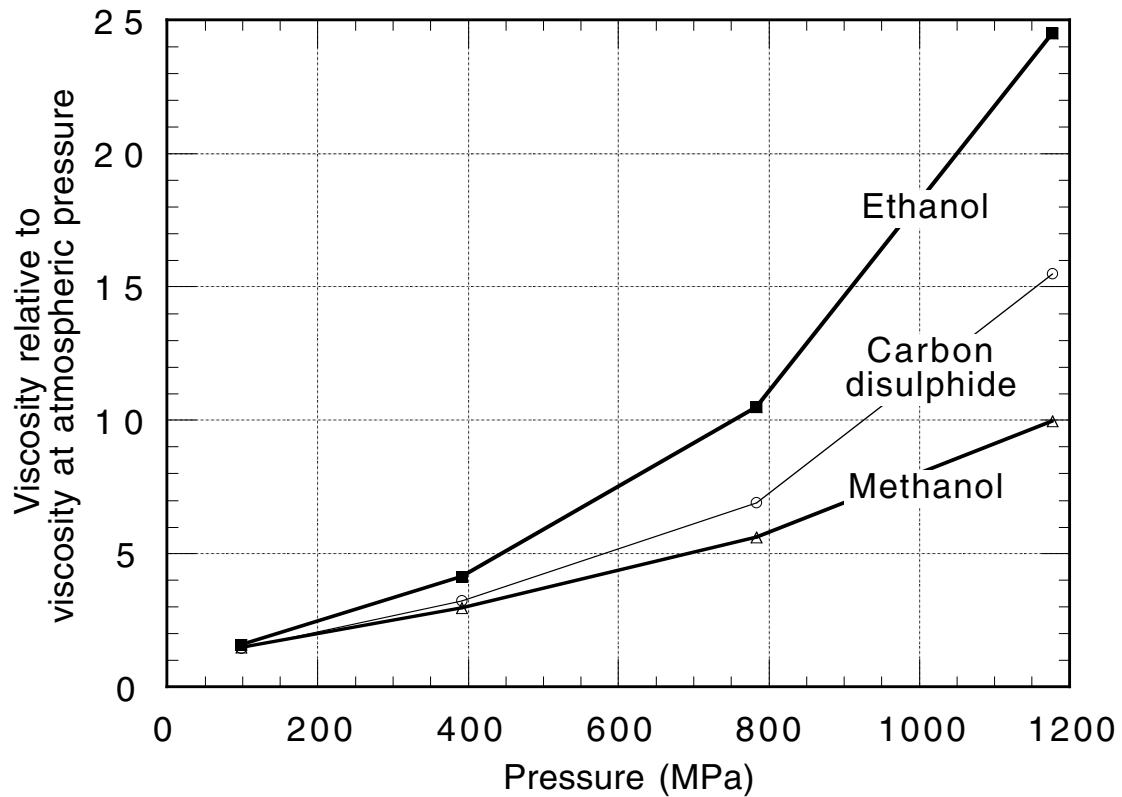


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(b)

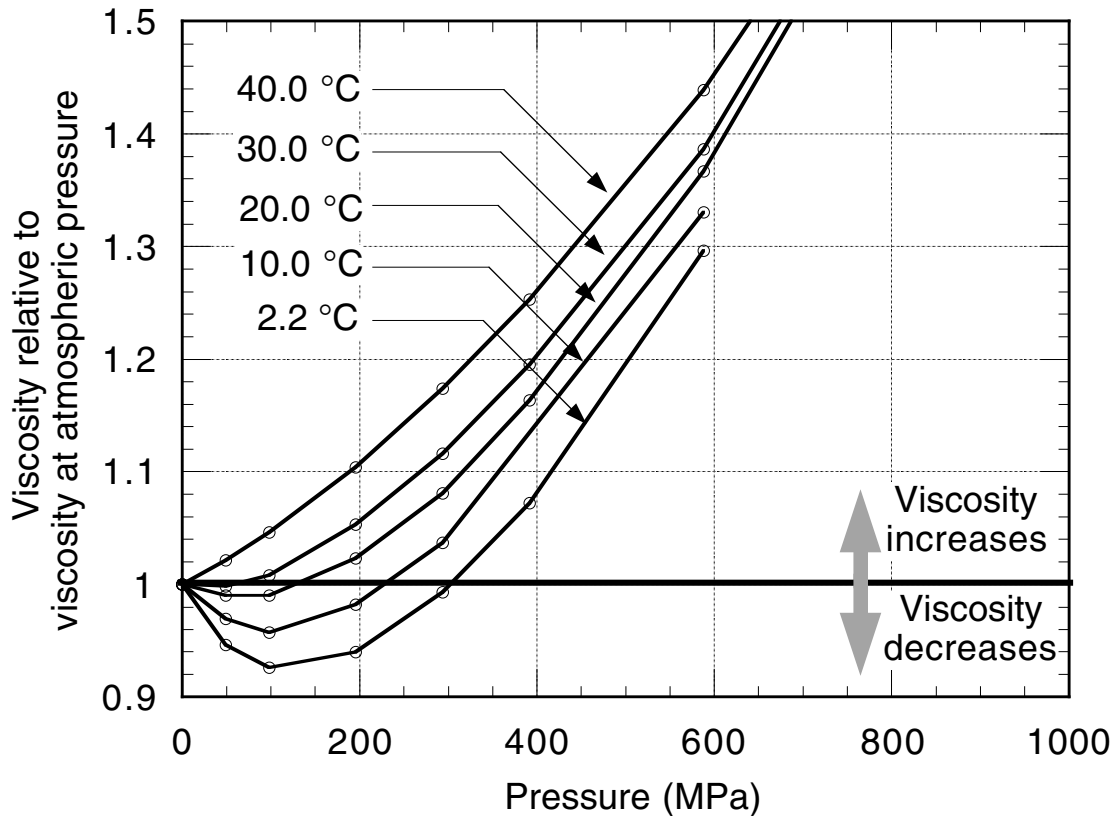


Figure 11.13 What happens when a liquid boils? Temperature fluctuations within the liquid cause small bubbles to form. Initially these are only a few atomic diameters in size. Whether the bubble grows or shrinks depends on the balance between the pressure of the liquid around the bubble, and the vapour pressure within the bubble. If the temperature is such that the vapour pressure exceeds the external pressure then bubbles will form in the liquid and grow. Because of the density difference between the gas and the liquid, the bubbles rise within the liquid and ‘burst’ when they reach the surface. Changes in the external pressure therefore cause changes in the boiling temperature of the liquid.

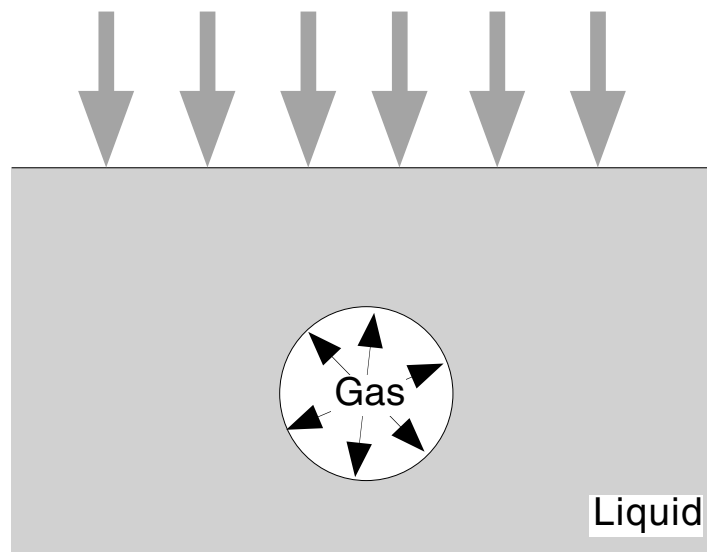


Figure 11.14 The boiling temperatures of the elements plotted as function of atomic number.

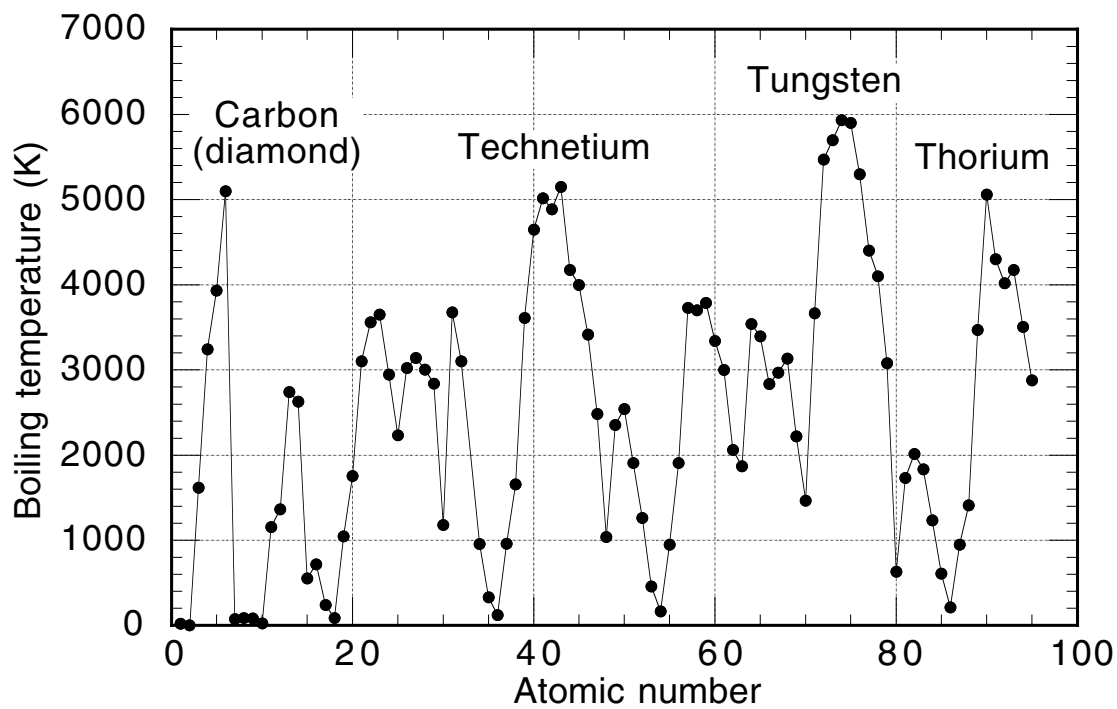
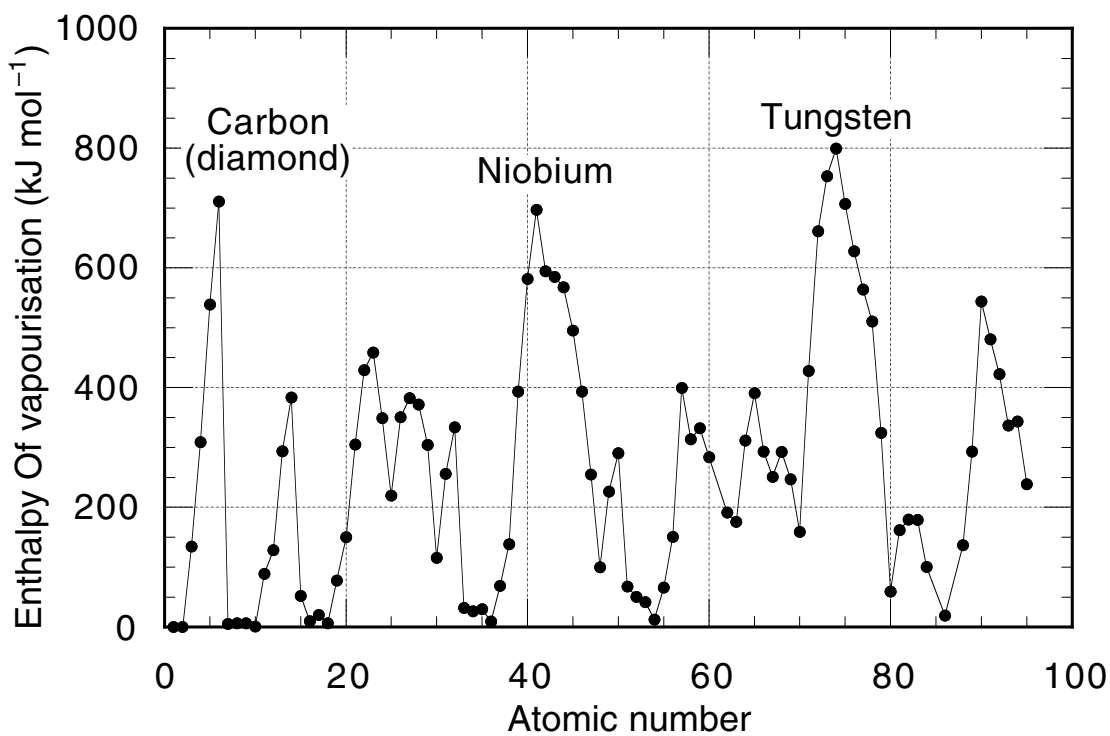


Figure 11.15 The enthalpy change on vaporisation of the elements plotted as function of atomic number.



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Figure 11.16 The approach to the critical point. The five pictures illustrate the effect of application of heat energy to a substance in the liquid state in a closed container. As the temperature rises the density of the vapour increases exponentially with temperature. When the density of the vapour approaches that of the liquid state, a reduction in volume may take the system to a situation where the density of the vapour and the liquid are equal – a situation known as the critical point.

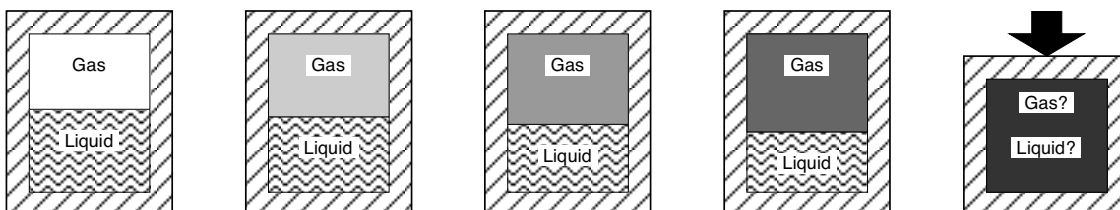


Figure 11.17 The critical parameters (Table 11.5) of various substances discussed in Chapter 6 and Chapter 8 plotted as a function of their relative molecular mass. Note that the vertical axis is logarithmic, which compresses much of the actual variation amongst the data.

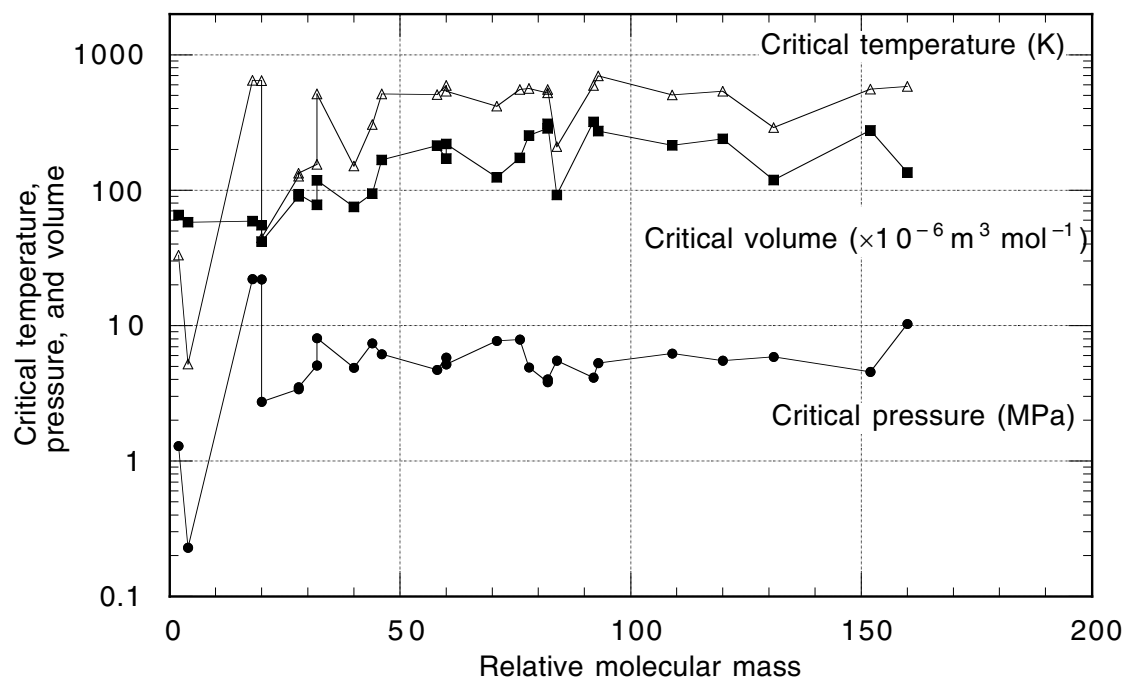


Figure 11.18 Qualitative indication of the radial density function of a solid, a normal liquid and a liquid in the critical condition. In the solid state the peaks correspond to nearest neighbours, next-nearest neighbours etc. In the liquid state, the peaks are maintained but they are smoothed by the increased disorder of the liquid state. In the critical state the peaks are weaker still, and the overall density is much reduced in comparison with either the liquid or solid states.

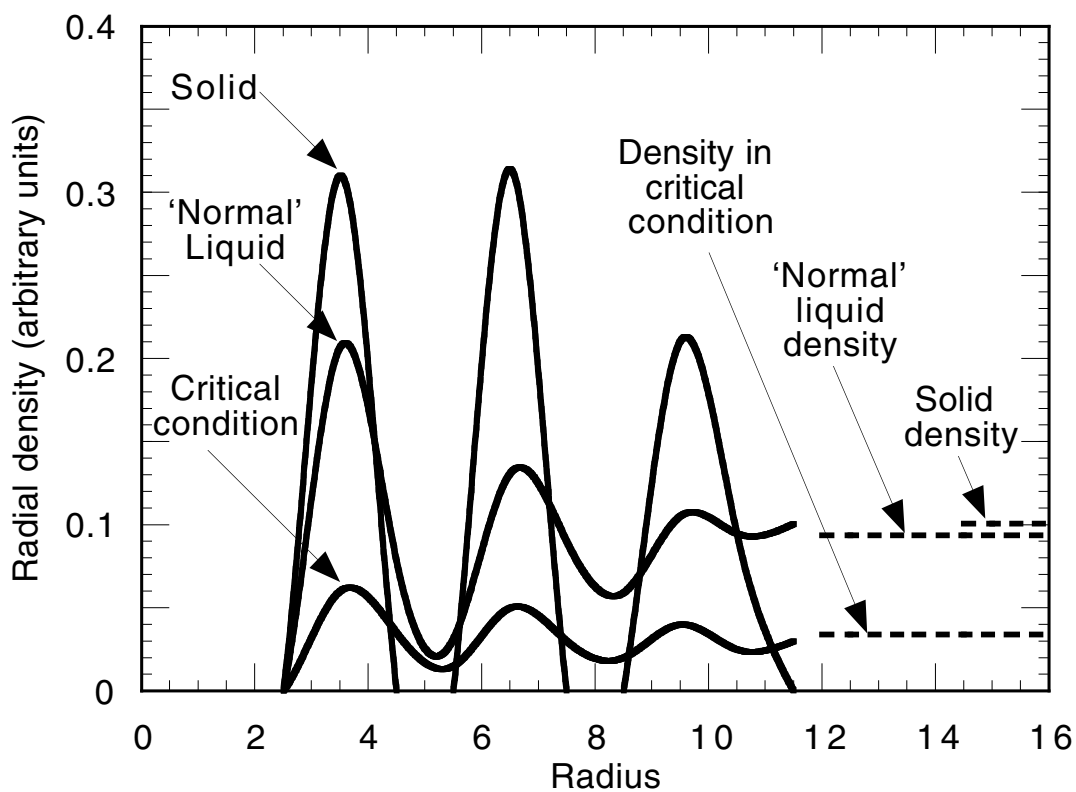


Figure 11.19 Data on the surface tension of water from Figure 9.21 re-plotted on a large scale. The linear extrapolation is based on a linear least squares fit to the data between 0 °C and 100 °C. The data imply that the surface tension will reach zero at a temperature just greater than the actual critical temperature. ($T_C = 647$ K)

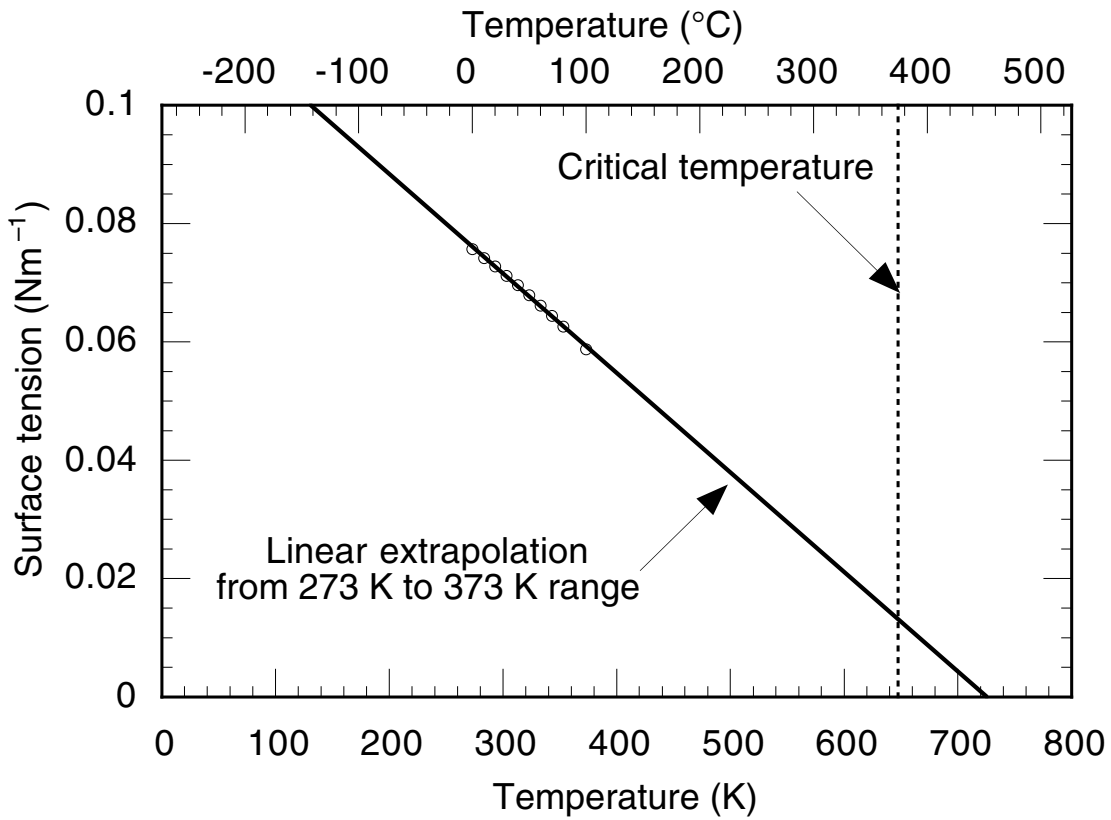


Figure 11.20 The virial approach to critical condition. Starting with a low-pressure gas we can approach the critical condition in two stages. In Stage 1, the gas is heated at constant pressure causing it to expand considerably. In Stage 2 the gas is compressed at constant temperature. In this stage the volume is reduced, increasing the importance of molecular interactions.

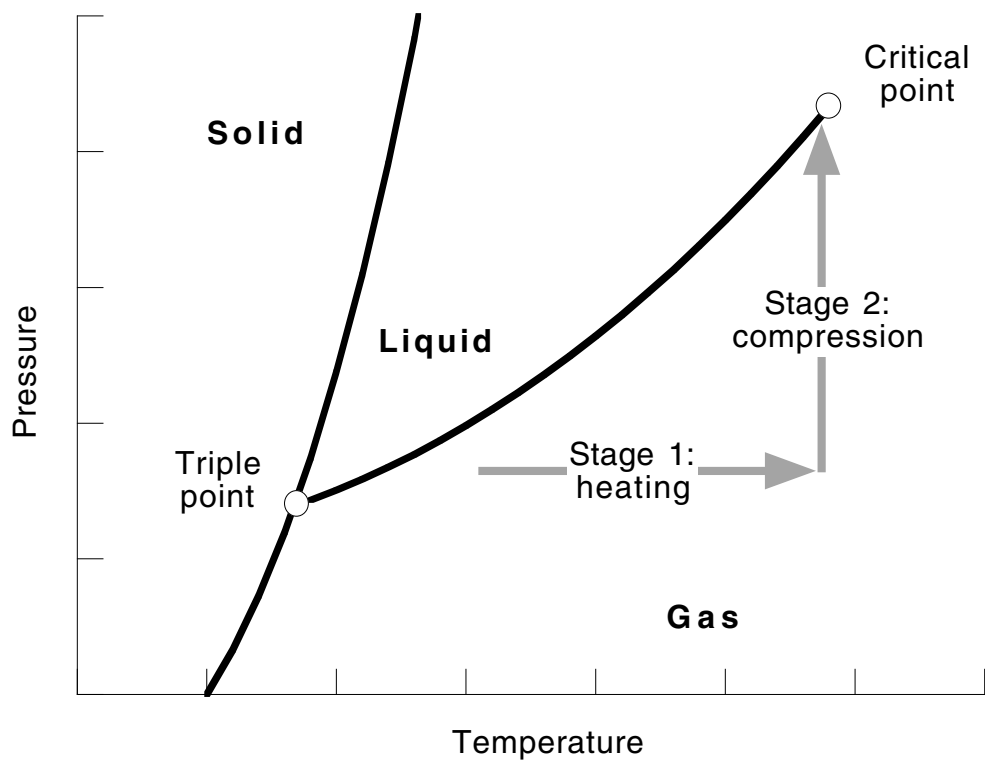


Figure 11.21 The critical temperature (Table 11.4) and melting temperature (Table 11.1) plotted as function of boiling temperature for various liquids. The boiling temperature line is a line of slope = 1. The vertical separation between the melting point datum and the boiling temperature line is an indication of the temperature range over which the substance exists as a liquid. The cluster of substances with boiling temperatures between 300 K and 400K are all organic substances.

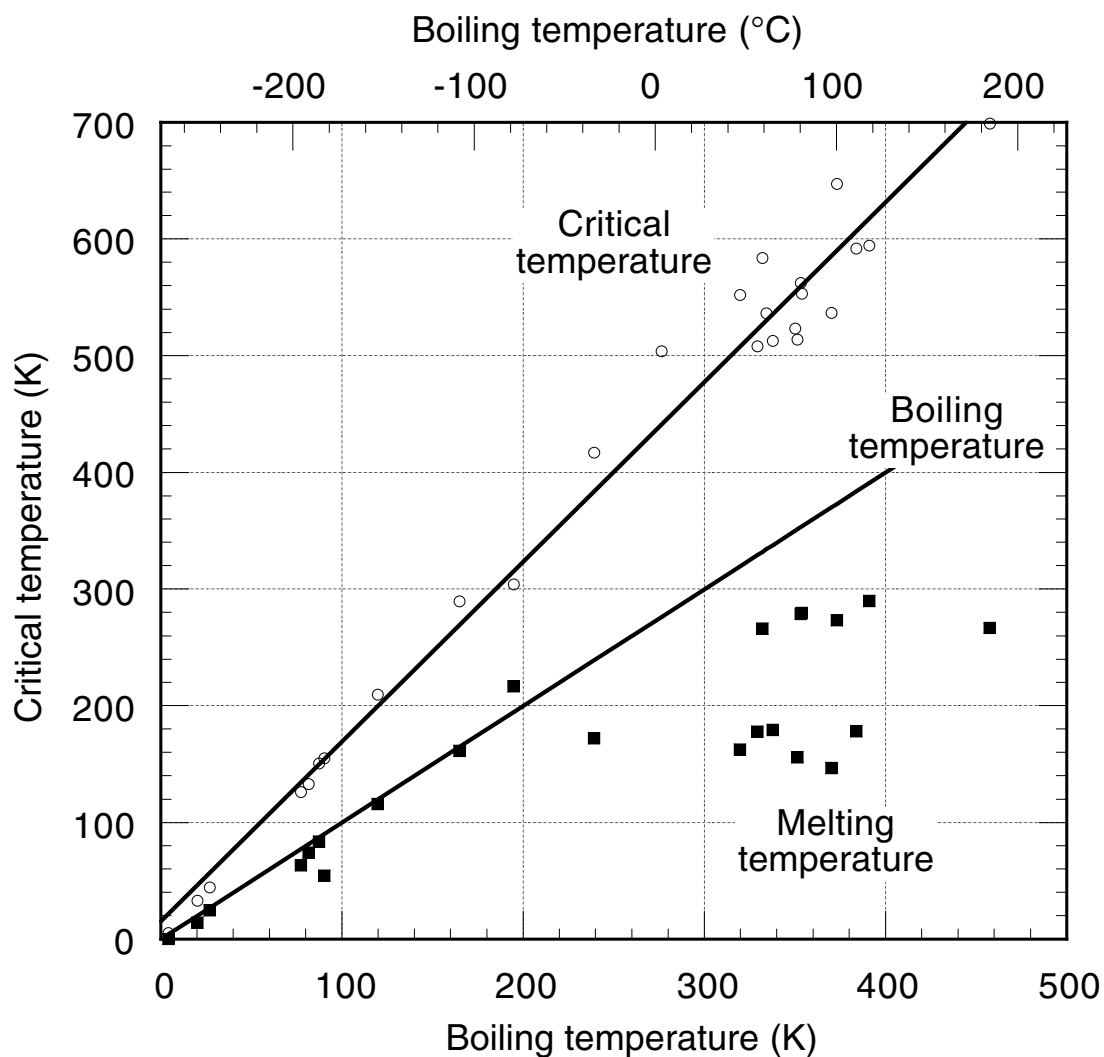


Figure 11.22 The melting temperature of the elemental metals plotted as a function of their boiling temperature. The vertical separation between the melting point datum and the boiling temperature line is an indication of the temperature range over which the substance exists as a liquid. Roughly, the melting temperatures are around two-thirds the boiling temperature, but there is a good deal of fluctuation around this figure. Some metals appear to have an anomalously large range of existence in the liquid phase. Gallium for example melts at only 302.9 K, but does not boil until 3676 K, a factor of 10 difference.

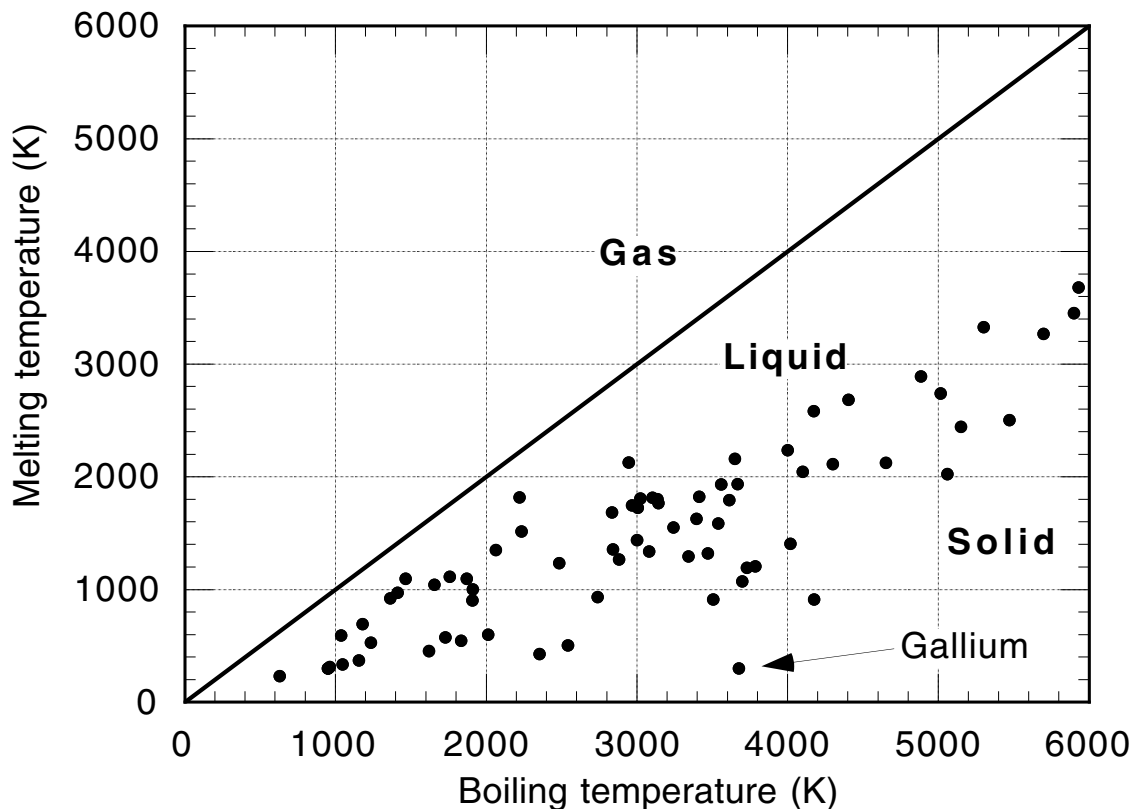


Figure 11.23 The boiling temperatures of the elements plotted as function of their cohesive energy (Table 11.5). It is clear that the data show a broad trend – with exceptions – indicating that substances with higher cohesive energies tend to have higher boiling temperatures. The solid line in the figure is the predicted melting temperature according to $T_B = (U_o/xR)$ with $x = 10$.

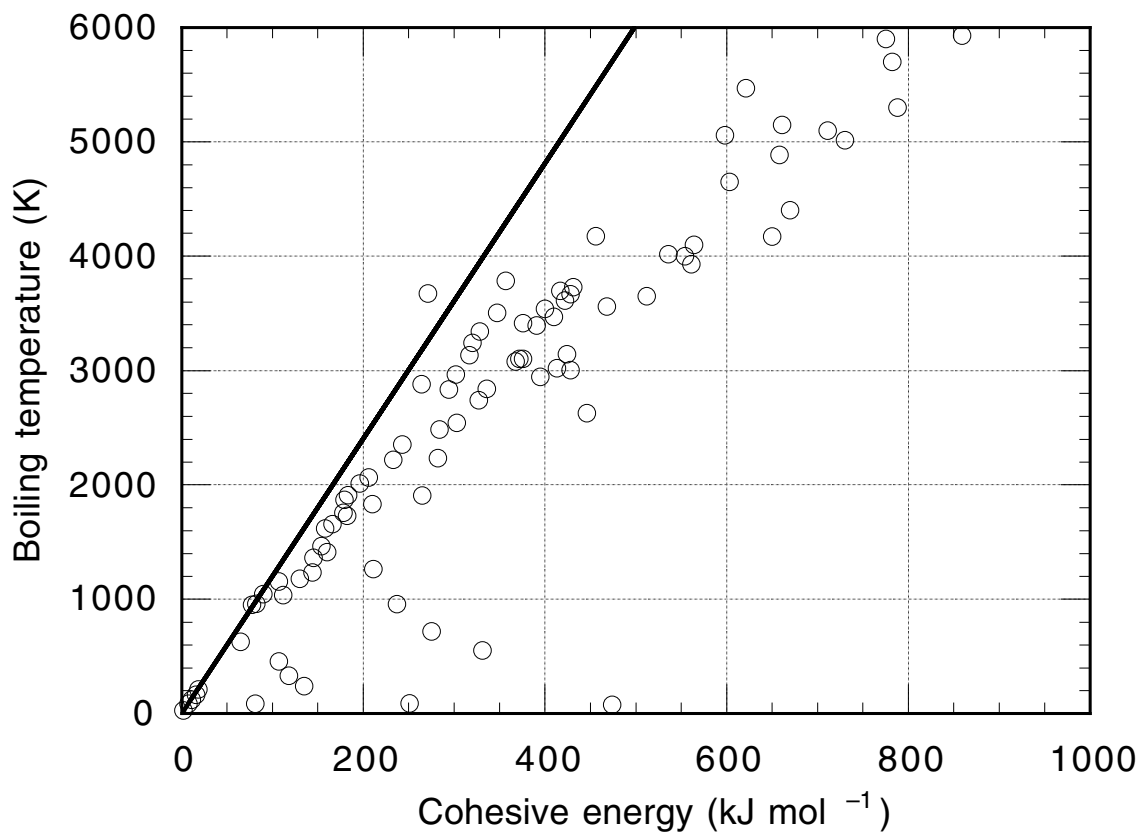


Figure 11.24 The cohesive energy of the elements (Table 11.5) plotted as a function of atomic number. It is clear that the data show periodic increases and decreases which reflect the effect of the filling of electron shells and the type of bonding possible. It is this graph which is at the heart of the periodic variations observed amongst elemental density; melting, boiling and Debye temperatures; and the enthalpies of fusion and vaporisation.

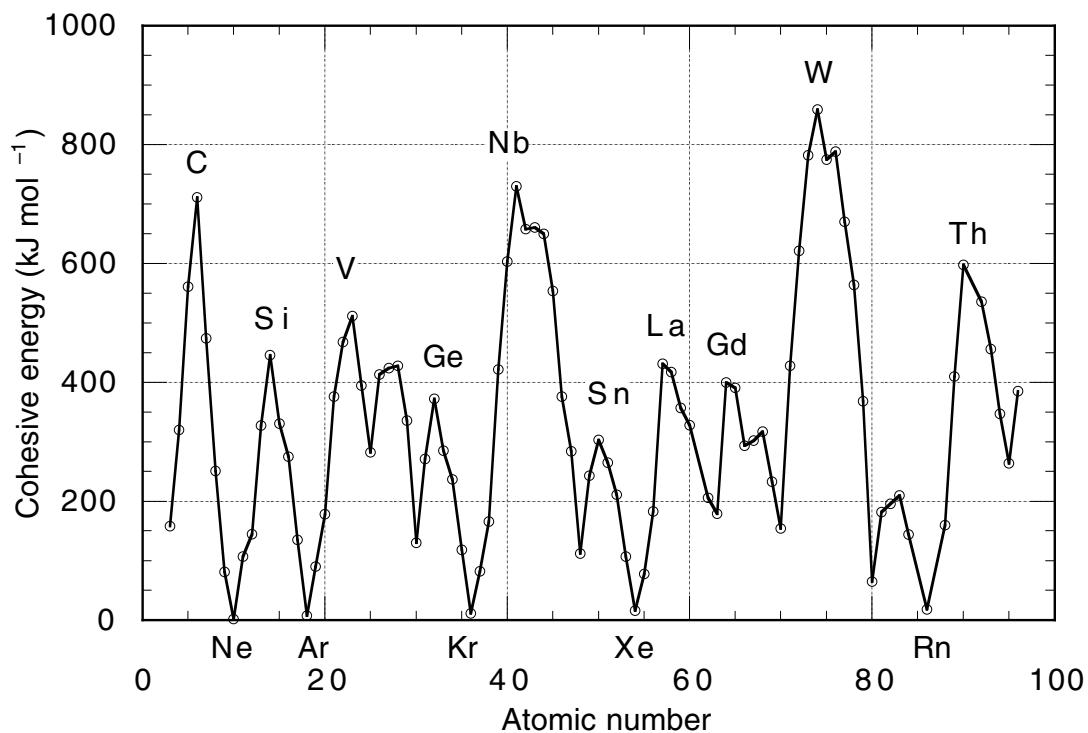


Figure 11.25 The vapour pressure of water and ice as function of temperature (Table 11.6) Plotted on (a) a logarithmic and (b) a linear vertical scale. Note the vapour pressure data is plotted logarithmic scale. The figure shows data for liquid water which has been supercooled below its freezing temperature, and for ice. Notice that at 0°C the vapour pressures of ice and water are extremely close, but that below this temperature the vapour pressure of the liquid is slightly greater than the vapour pressure of the solid.

(a)

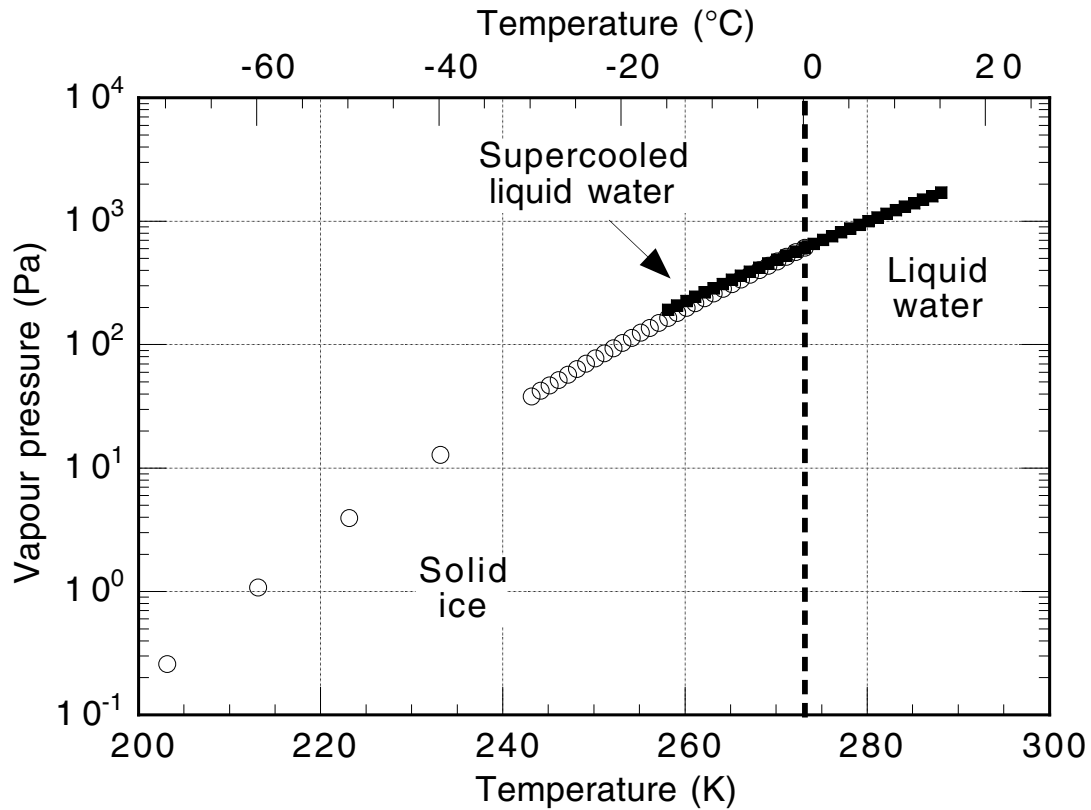


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(b)

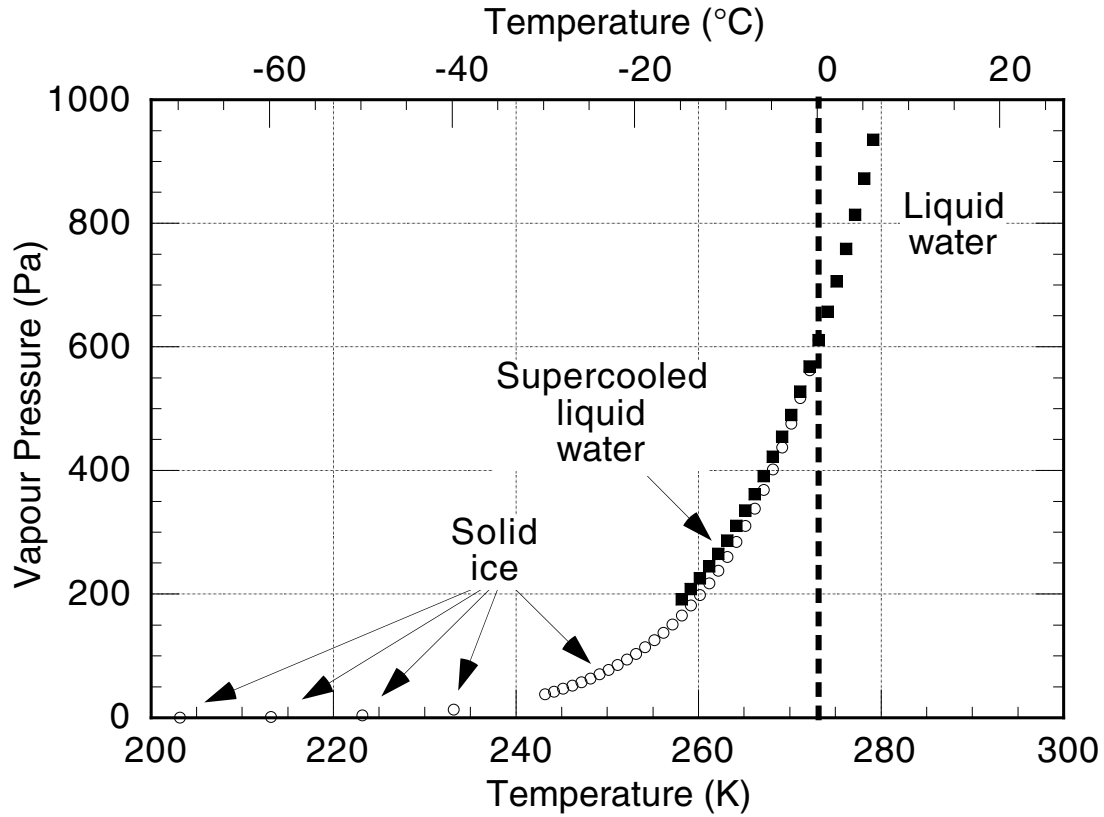


Figure 11.26 An illustration of the cell model with parameters appropriate to arsenic. Ignoring the situation at the surface of the liquid, we notice immediately that ΔE_h is greater than ΔE_e . In other words the activation energy for the 'hopping' process is less than the energy ΔE_e for escape from the substance altogether. Note: Be careful in interpreting ΔE_h . It is *not* a single-particle hopping process: see §8.4 for further details.

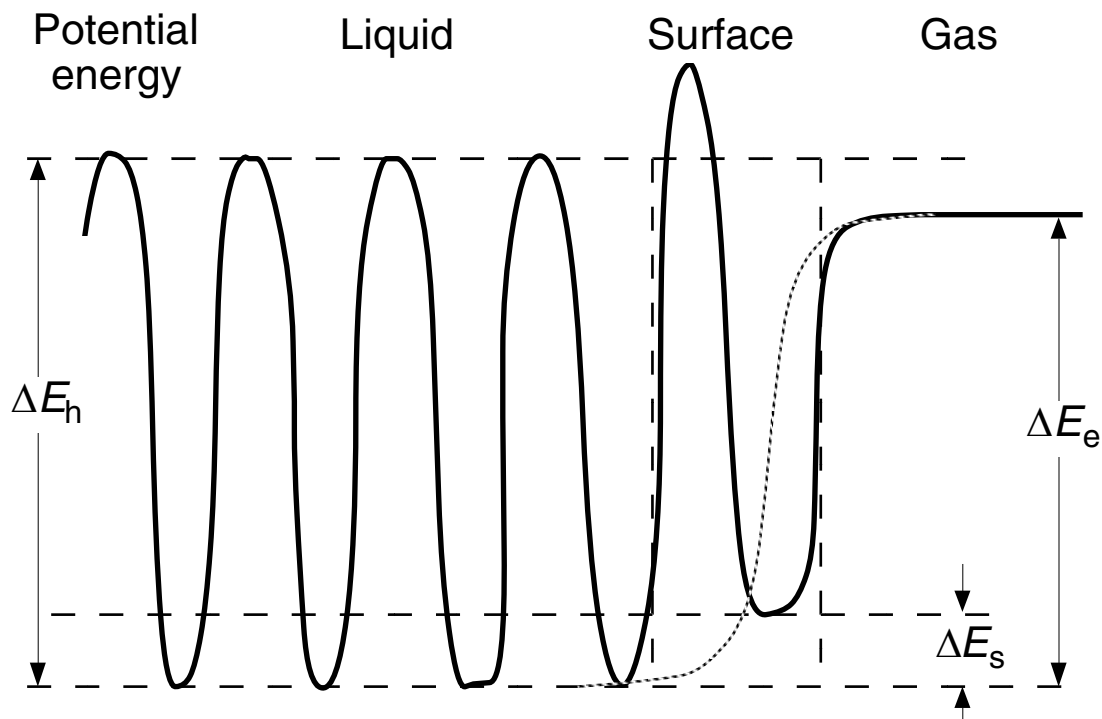


Figure 11.27 A schematic phase diagram illustrating the relative steepness of the solid \leftrightarrow liquid phase boundary in comparison with the liquid \leftrightarrow gas phase boundary. This means that points on the melting curve at different pressures – such as one atmosphere and the triple point pressure – occur at quite closely spaced temperatures.

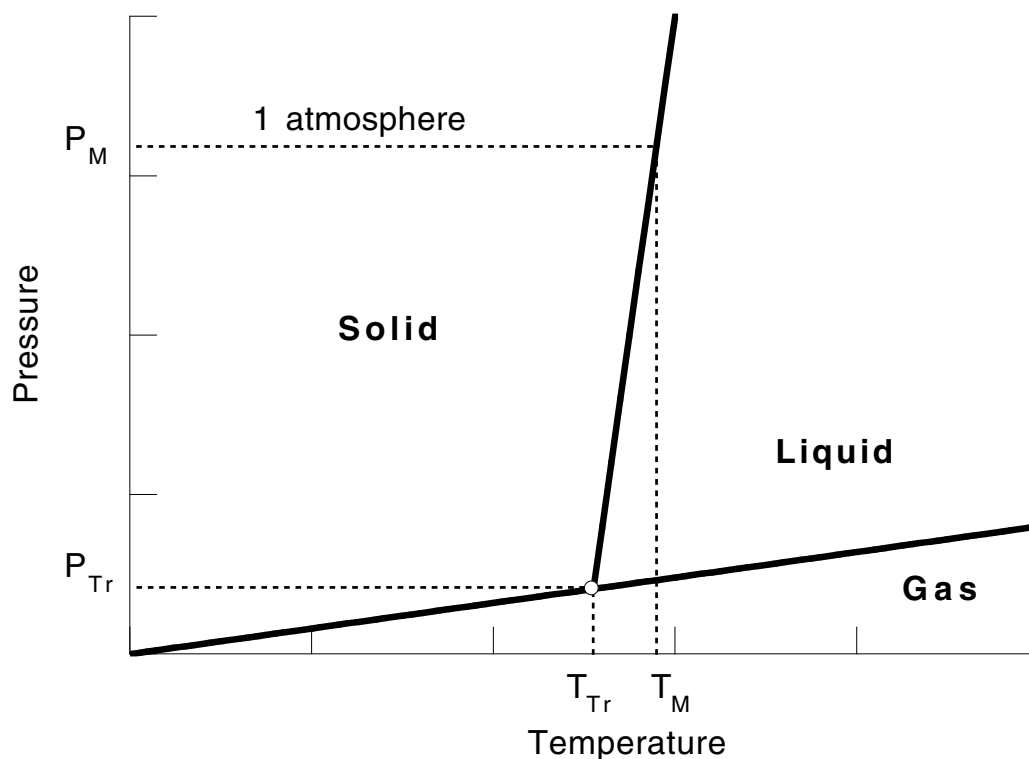


Figure 11.28 My own measurements of the heat capacity of Nb₃Sn. Notice the large jump in the heat capacity at the superconducting transition temperature T_C . The jump occurs on top of the heat capacity due to lattice vibrations discussed in §7.6.

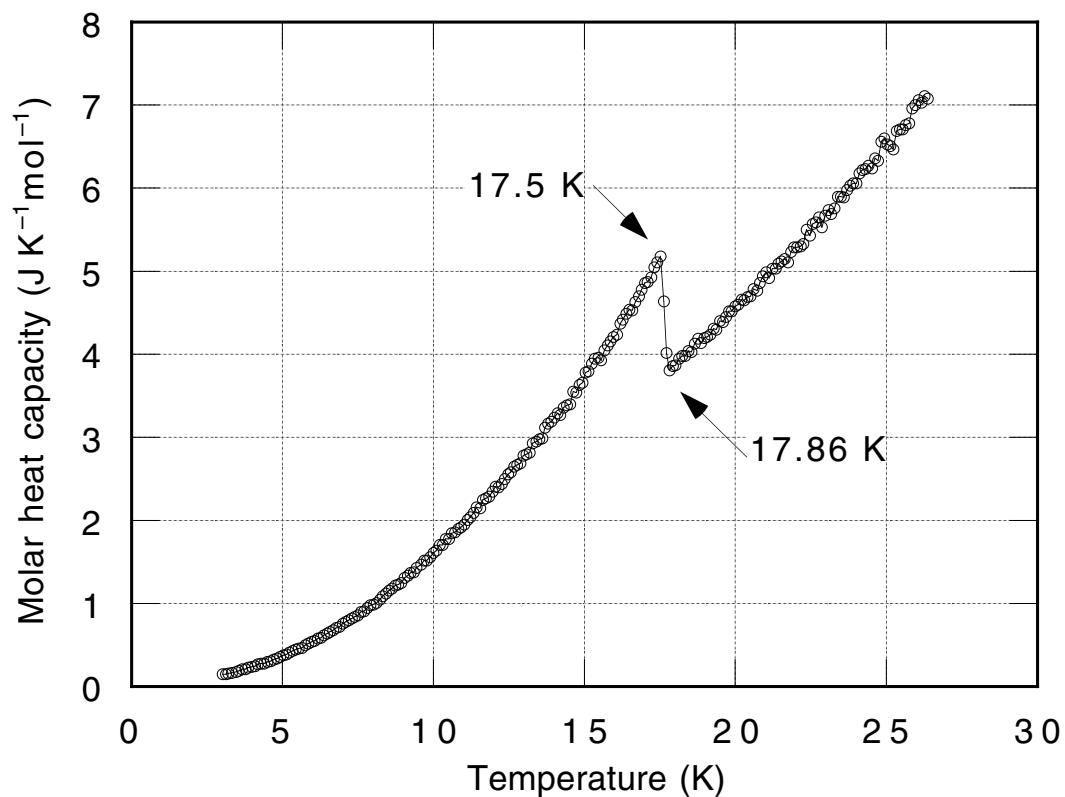


Figure 11.29 Apparatus for observing liquid crystal phases.

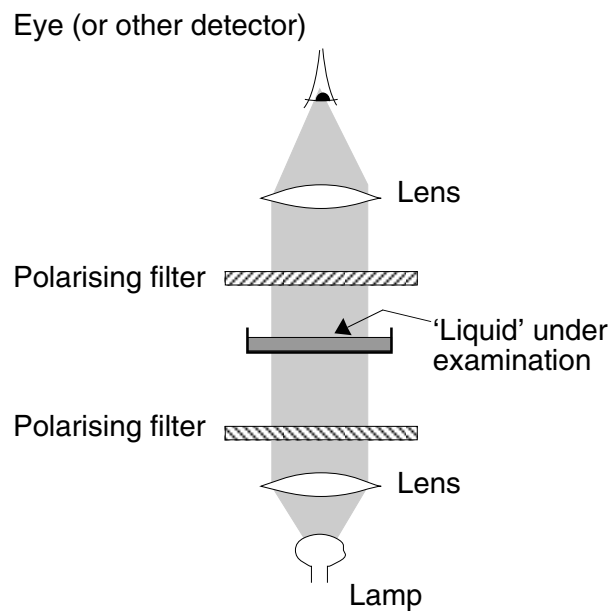


Figure 11.30 My own measurements of the heat capacity of CePt. This material becomes ferromagnetically ordered below ≈ 6 K.

