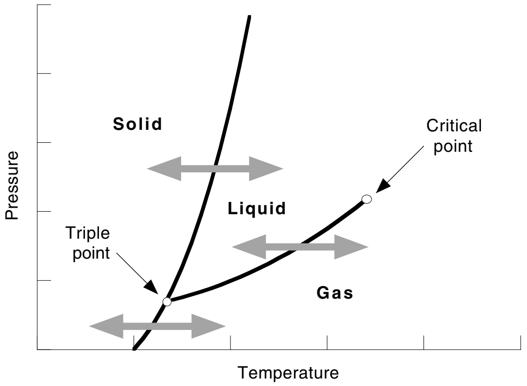
CHAPTER11

Changes of phase: comparison with experiment

11.1 Introduction

In the Chapter 10 we established that changes of phase can be described with the aid of a phase diagram. We spent some time establishing the general form of a phase diagram for a 'typical substance' and arrived at something like Figure 11.1. The three transitions between the phases that occur as a result of temperature changes at constant pressure are shown as double-ended arrows. In this chapter we would like to examine experimental data on all aspects of this diagram: the slopes of the phase boundaries and their points of intersection. In practice the amount of data involved is amazingly large so we restrict ourselves to data on the elements and a small range of relatively simple substances (§11.2).

Figure 11.1 A generic *PT* phase diagram



§11.3, §11.4 The solid ⇔ liquid and **liquid ⇔ gas transitions:** Although we refer to these transitions in the same manner, and they are both represented by the crossing of a single line in Figure 11.1, they are physically very different processes. We will find that we need to develop quite different microscopic models to understand each type of transition.

§11.5, §11.8 The critical point and **triple point:** Examining the data on these points reveals that they occur at similar relative positions on the phase diagrams of quite different substances.

§11.6 **Scaling: laws of corresponding states:** Throughout this book, we have discovered correlations between the physical properties of different substances. This raises the hope that we might be able to use *some* properties of a substance to predict an unknown property, either of that substance or another one. We will find that sometimes we can do this and sometimes we can not. But what is the origin of these partial correlations?

§11.7 **The solid ⇔ gas transitions:** Compared with the phase transitions considered in §11.3 and §11.4 the solid ⇔ gas transition is relatively understudied. We will find it is relatively easy to understand the process using a surprising extension of the cell model of a liquid.

§11.9 **Other types of phase transitions:** We mentioned in Chapter 10 that there is the concept of a phase transition could be applied more widely than to changes between solids in liquids and gas. In this section we look at what these transitions are and how they can be studied .

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

11.2 Data on the solid ⇔ liquid and liquid ⇔ gas transitions

This section consists of just two tables, which contain data that will be referred to in several of the following sections. Table 11.1 contains data relevant to the solid ⇔ liquid and liquid ⇔ gas transitions in the elements, and Table 11.2 contains the equivalent data for various substances.

Table 11.1 Thermal data for the elements: the melting and boiling temperatures in kelvin, and the enthalpies of fusion (melting) and vaporisation. The data refer to standard atmospheric pressure unless otherwise stated. Two elements – arsenic and carbon – which sublime when heated at atmospheric pressure. These are discussed in §11.7 on the solid ⇒ gas transition, and their the enthalpies of fusion and vaporisation are estimated from studies at high pressure.

Z	Name	Atomic weight	Density ($kg\ m^{-3}$)	Melting point (K)	Boiling point (K)	Enthalpy of fusion ($kJ\ mol^{-1}$)	Enthalpy of vaporisation ($kJ\ mol^{-1}$)
1	Hydrogen	1.008	89	14.01	20.28	0.12	0.46
2	Helium	4.003	120	0.95	4.216	0.021	0.082
3	Lithium	6.941	533	453.7	1620	4.6	134.7
4	Beryllium	9.012	1846	1551	3243	9.8	308.8
5	Boron	10.81	2466	2365	3931	22.2	538.9
6	Carbon	12.01	2266	Sublimes at ≈ 3700		105	710.9
7	Nitrogen	14.01	1035	63.15	77.4	0.72	5.577
8	Oxygen	16	1460	54.36	90.188	0.444	6.82
9	Fluorine	19	1140	53.48	85.01	5.1	6.548
10	Neon	20.18	1442	24.56	27.1	0.324	1.1736
11	Sodium	22.99	966	371	1156.1	2.64	89.04
12	Magnesium	24.31	1738	922	1363	9.04	128.7
13	Aluminium	26.98	2698	933.5	2740	10.67	293.72
14	Silicon	28.09	2329	1683	2628	39.6	383.3
15	Phosphorous	30.97	1820	317.3	553	2.51	51.9
16	Sulphur	32.06	2086	386	717.82	1.23	9.62
17	Chlorine	35.45	2030	172	239.18	6.41	20.403
18	Argon	39.95	1656	83.8	87.29	1.21	6.53
19	Potassium	39.1	862	336.8	1047	2.4	77.53
20	Calcium	40.08	1530	1112	1757	9.33	149.95
21	Scandium	44.96	2992	1814	3104	15.9	304.8
22	Titanium	47.9	4508	1933	3560	20.9	428.9
23	Vanadium	50.94	6090	2160	3650	17.6	458.6
24	Chromium	52	7194	2130	2945	15.3	348.78
25	Manganese	54.94	7473	1517	2235	14.4	219.7
26	Iron	55.85	7873	1808	3023	14.9	351
27	Cobalt	58.93	8800	1768	3143	15.2	382.4
28	Nickel	58.7	8907	1726	3005	17.6	371.8
29	Copper	63.55	8933	1356.6	2840	13	304.6
30	Zinc	65.38	7135	692.73	1180	6.67	115.3
31	Gallium	69.72	5905	302.93	3676	5.59	256.1
32	Germanium	72.59	5323	1210.6	3103	34.7	334.3
33	Arsenic	74.92	5776	Sublimes at 886		27.7	31.9
34	Selenium	78.96	4808	490	958.1	5.1	26.32
35	Bromine	79.9	3120	265.9	331.93	10.8	30
36	Krypton	83.8	3000	116.6	120.85	1.64	9.05
37	Rubidium	85.47	1533	312.2	961	2.2	69.2
38	Strontium	87.62	2583	1042	1657	6.16	138.91
39	Yttrium	88.91	4475	1795	3611	17.2	393.3

Z	Name	Atomic weight	Density (kg m^{-3})	Melting point (K)	Boiling point (K)	Enthalpy of fusion (kJ mol^{-1})	Enthalpy of vaporisation (kJ mol^{-1})
40	Zirconium	91.22	6507	2125	4650	23	581.6
41	Niobium	92.91	8578	2741	5015	27.2	696.6
42	Molybdenum	95.94	10222	2890	4885	27.6	594.1
43	Technetium	97	11496	2445	5150	23.81	585.22
44	Ruthenium	101.1	12360	2583	4173	23.7	567.8
45	Rhodium	102.9	12420	2239	4000	21.55	495.4
46	Palladium	106.4	11995	1825	3413	17.2	393.3
47	Silver	107.9	10500	1235.1	2485	11.3	255.1
48	Cadmium	112.4	8647	594.1	1038	6.11	99.87
49	Indium	114.8	7290	429.32	2353	3.27	226.4
50	Tin	118.7	7285	505.12	2543	7.2	290.4
51	Antimony	121.7	6692	903.9	1908	20.9	67.91
52	Tellurium	127.6	6247	722.7	1263	13.5	50.63
53	Iodine	126.9	4953	386.7	457.5	15.27	41.67
54	Xenon	131.3	3560	161.3	166.1	3.1	12.65
55	Caesium	132.9	1900	301.6	951.6	2.09	65.9
56	Barium	137.3	3594	1002	1910	7.66	150.9
57	Lanthanum	138.9	6174	1194	3730	10.04	399.6
58	Cerium	140.1	6711	1072	3699	8.87	313.8
59	Praseodymium	140.9	6779	1204	3785	11.3	332.6
60	Neodymium	144.2	7000	1294	3341	7.113	283.7
61	Promethium	145	7220	1441	3000	12.6	—
62	Samarium	150.4	7536	1350	2064	10.9	191.6
63	Europium	152	5248	1095	1870	10.5	175.7
64	Gadolinium	157.2	7870	1586	3539	15.5	311.7
65	Terbium	158.9	8267	1629	3396	16.3	391
66	Dysprosium	162.5	8531	1685	2835	17.2	293
67	Holmium	164.9	8797	1747	2968	17.2	251
68	Erbium	167.3	9044	1802	3136	17.2	292.9
69	Thulium	168.9	9325	1818	2220	18.4	247
70	Ytterbium	173	6966	1097	1466	9.2	159
71	Lutetium	175	9842	1936	3668	19.2	428
72	Hafnium	178.5	13276	2503	5470	25.5	661.1
73	Tantalum	180.9	16670	3269	5698	31.4	753.1
74	Tungsten	183.9	19254	3680	5930	35.2	799.1
75	Rhenium	186.2	21023	3453	5900	33.1	707.1
76	Osmium	190.2	22580	3327	5300	29.3	627.6
77	Iridium	192.2	22550	2683	4403	26.4	563.6
78	Platinum	195.1	21450	2045	4100	19.7	510.5
79	Gold	197	19281	1337.6	3080	12.7	324.4
80	Mercury	200.6	13546	234.28	629.73	2.331	59.15
81	Thallium	204.4	11871	576.6	1730	4.31	162.1
82	Lead	207.2	11343	600.65	2013	5.121	179.4
83	Bismuth	209	9803	544.5	1833	10.48	179.1
84	Polonium	209	9400	527	1235	10	100.8
85	Astatine	210	—	575	610	23.8	—
86	Radon	222	4400	202	211.4	2.7	19.1
87	Francium	223	—	300	950	—	—
88	Radium	226	5000	973	1413	7.15	136.8
89	Actinium	227	10060	1320	3470	14.2	293

Z	Name	Atomic weight	Density (kg m^{-3})	Melting point (K)	Boiling point (K)	Enthalpy of fusion (kJ mol^{-1})	Enthalpy of vaporisation (kJ mol^{-1})
90	Thorium	232	11725	2023	5060	19.2	543.9
91	Protactinium	231	15370	2113	4300	16.7	481
92	Uranium	238	19050	1405	4018	15.5	422.6
93	Neptunium	237	20250	913	4175	9.46	336.6
94	Plutonium	244	19840	914	3505	2.8	343.5
95	Americium	243	13670	1267	2880	14.4	238.5

Table 11.2 Thermal data for the various substances: the melting and boiling temperatures in kelvin, and the enthalpies of fusion (melting) and vaporisation. The data refer to standard atmospheric pressure unless otherwise stated and (s) indicates that the substance sublimes rather than boils and the melting temperature is obtained under pressure. (*) indicates a large discrepancy of ± 20 K amongst data from different sources.

Substance		MW	Density (kg m^{-3})	Melting point (K)	Boiling point (K)	Enthalpy of fusion (kJ mol^{-1})	Enthalpy of vaporisation (kJ mol^{-1})
Acetic acid	CH_3COOH	60	1049	289.75	391.1	11.535	—
Acetone	CH_3COCH_3	58	787	177.8	329.3	5.691	—
Aniline	C_6H_7N	93	1026	266.85	457.6	10.555	—
Benzene	C_6H_6	78	877	278.65	353.2	9.951	—
Chloroform	$CHCl_3$	119	—	209.55	334.4	8.800	—
Cyclohexane	C_6H_{10}	82	779	279.65	353.8	2.630	—
Ethyl acetate	$C_4H_8O_2$	88	—	189.55	350.2	10.481	—
Methanol	CH_3OH	32	791	179.25	337.7	3.177	—
Ethanol	C_2H_5OH	46	789	155.85	351.5	5.021	—
Propan-1-ol	C_3H_7OH	60	804	146.65	370.3	5.195	—
Propan-2-ol	C_3H_7OH	60	786	—	—	—	—
Butan-1-ol	C_4H_9OH	74	810	183.65	390.35	9.282	—
Butan-2-ol	C_4H_9OH	74	808	298.55	372.65	6.786	—
Toluene	C_7H_8	92	867	178.15	383.8	6.851	—
Lithium fluoride	LiF	25.9	2635	1118	1949	—	—
Lithium chloride	$LiCl$	42.39	2068	878	1620(*)	—	—
Lithium bromide	$LiBr$	86.9	3464	823	1538	—	—
Sodium chloride	NaF	42.0	2558	1266	1968	—	—
Sodium fluoride	$NaCl$	58.4	2165	1074	1686	—	—
Sodium bromide	$NaBr$	102.9	3203	1020	1663	—	—
Potassium fluoride	KF	58.1	2480	1131	1778	—	—
Potassium chloride	KCl	74.6	1984	1043	1273(s)	—	—
Potassium bromide	KBr	119.0	2750	1007	1708	—	—
Carbon dioxide	CO_2	44	—	216.55	194.7	—	—
Carbontetrachloride	CCl_4	154	1632	—	—	—	—
Carbon disulphide	CS_2	76	1293	162.35	319.6	4.395	—
Carbon monoxide	CO	28	—	74.15	81.7	—	—
Water	H_2O	18	998	273.15	373.15	5.994	40.608

Example 11.1

Calculate the amount of energy required to complete the following processes:

(a) Melt 1 mole of ice at its melting temperature.
(b) Heat 1 mole of liquid (water) from 0°C to 100°C.
(c) Melt 1 mole of copper at its melting temperature.

The data required to answer these questions is given in Tables 11.2, 9.11 and 11.1 respectively.

- From Table 11.2 the enthalpy of fusion of water is 5.994×10^3 J mol^{-1}. Thus to melt 1 mole (0.018 kg) of ice requires $1 \times 5.994 \times 10^3 = 5994$ J.
- From Table 9.13 the heat capacity of water is given as 75.9 J K^{-1} mol^{-1}. Thus to raise 1 mole (0.018 kg) of water from 0°C to 100°C requires $1 \times 75.9 \times 100 = 7590$ J, i.e. about 25% more energy than that required to melt the same amount of water.
- From Table 11.2 the enthalpy of fusion of copper is 13×10^3 J mol^{-1}. Thus to melt 1 mole (0.0635 kg) of copper requires $1 \times 13 \times 10^3 = 13000$ J. This amounts to about twice that required to melt 1 mole of water.

Example 11.2

Calculate the amount of energy required to complete the following processes:

(a) Boil 1 mole of water at its boiling temperature.
(b) Heat 1 mole of liquid (water) from 0°C to 100°C.
(c) Boil 1 mole of copper at its melting temperature.

The data required to answer these questions is given in Tables 11.2, 9.11 and 11.1 respectively.

(a) From Table 11.2 the enthalpy of vaporisation of water is 40.608×10^3 J mol^{-1}. Thus to boil 1 mole (0.018 kg) of water requires $1 \times 40.608 \times 10^{-3} = 40608$ J, i.e. about 7 times as much energy as is required to melt the same amount of water.
(b) From Table 9.13 the heat capacity of water is given as 75.9 J K^{-1} mol^{-1}. Thus to raise 1 mole (0.018 kg) of water from 0°C to 100°C requires $1 \times 75.9 \times 100 = 7590$ J, i.e. about 80% *less* energy than that required to boil the same amount of water.
(c) From Table 11.2 the enthalpy of vaporisation of copper is 304.6×10^3 J mol^{-1}. Thus to boil 1 mole (0.0635 kg) of copper requires $1 \times 304.6 \times 10^3 = 304600$ J. This amounts to about 23 times as much energy as required to melt the same quantity of copper, and about 8 times as much energy as required to boil 1 mole of water.

11.3 The solid ⇔ liquid transition: melting and freezing

11.3.1 Introduction

For most substances, the transition from the solid to the liquid state occurs gradually, over a range of temperature. However for *pure substances*, melting takes place at a well-defined temperature known as the *melting temperature*, T_M, or *melting point*. Defining what we mean by a pure substance is not as easy as it might at first appear. A working definition is:

- A pure substance is one composed of a single type of atom or molecule.

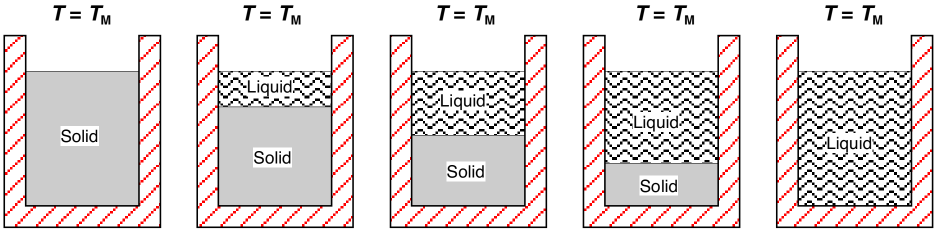
This definition requires occasional qualification, but it will serve for now.

At the melting temperature, a substance can be either a solid or a liquid. As illustrated in Figure 11.2, if a sample is 50% solid and 50% liquid it will stay that way until further heat is added to, or removed from, the substance. Heat input at the melting temperature does not raise the temperature of the solid/liquid mixture: it serves to transform more solid into liquid. The energy required to transform one mole of substance from solid to liquid at constant pressure is known by several equivalent terms: the molar *enthalpy change on fusion*; the molar *enthalpy of fusion*; the molar *latent heat of fusion*. The preferred form is the *enthalpy change on fusion,* the term *fusion* being an old term for melting.

11.3.2 Further data

The melting temperature T_M and molar enthalpy of fusion of the elements are recorded in Table 11.1 above, and plotted as a function of atomic number for the elements in Figures 11.3 and 11.4 respec-

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.)



tively. The figures show a qualitative similarity to one another, indicating that elements with a high melting temperature tend to have a high enthalpy of fusion. Furthermore, the structure in the data shows similar patterns to those seen in Figure 7.1 showing the density of elements.

Note that the temperature of the transition from the solid to the liquid phase is dependent on the pressure to which the liquid/solid is subjected. In general, higher pressures tend to increase the temperature at which solid ⇔ liquid transitions take place. Interestingly, in substances which contract on melting, higher pressures tend to *lower* the temperature at which solid ⇔ liquid take place. Figure 11.4 shows data for the elements silver and gold, and the depression of the melting temperature for water is discussed in §11.3.4.

The main questions raised by our preliminary examination of the experimental data on the solid ⇔ liquid transition in the elements are:

- Why do elements with a high T_M tend to have a high enthalpy of fusion?
- Why does the variation of T_M of the elements with atomic number show a pattern similar to that seen in the density of elements?
- Why does T_M of most substances increase with pressure, but decrease for substances which contract on melting?

These questions will be considered in §11.3.4, after we have examined the Lindemann theory of melting.

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.

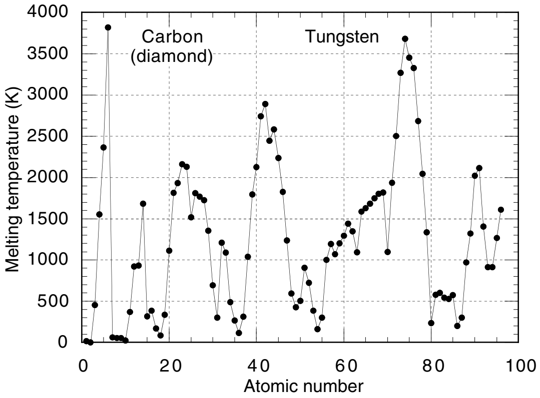


Figure 11.4 The molar enthalpy change of fusion of the elements plotted as function of atomic number. The datum for diamond has not been plotted so as to allow detail on the rest of the graph to be seen.

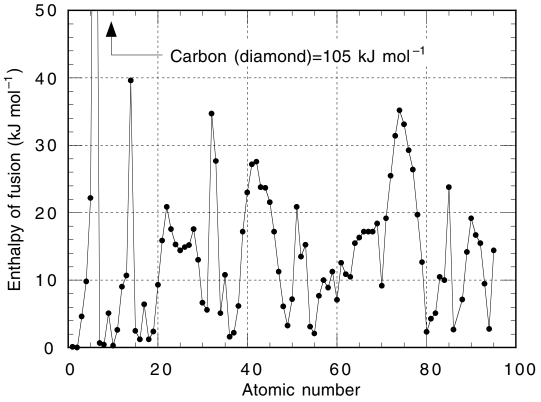
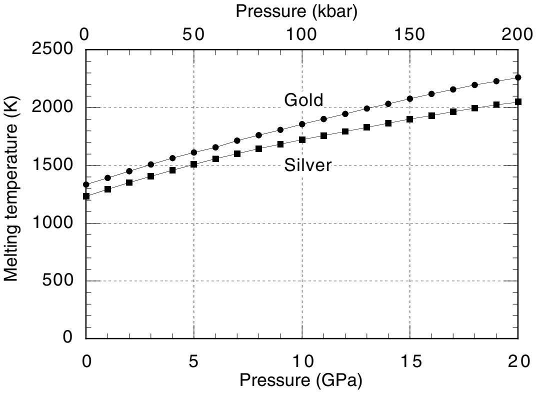


Figure 11.5 The elevation of the melting temperature of silver and gold as a function of applied pressure. Notice that the pressures are extremely large, 1 kBar is 1000 times atmospheric pressure and the pressure scale shown extends up to 200 kBar.



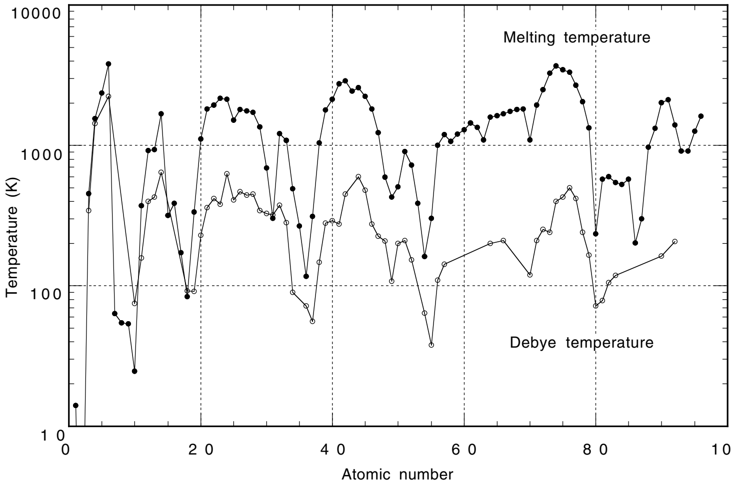
11.3.3 Lindemann theory of melting

The solid ⇒ liquid transition – melting – is a considerably more complex process than the liquid ⇒ gas transition – boiling. In the liquid ⇒ gas transition, essentially all interactions between molecules are eliminated after the phase change. Thus we can understand the transition in terms of the dramatic change in the environment of each molecule. However, from our discussion of the nature of liquids in Chapters 8 and 9, we see that in the solid ⇒ liquid transition the interactions and separations between molecules change by only a few per cent. Thus understanding what causes melting in anything more than a general sense is rather difficult. We can however still make a little headway into the problem.

First we can consider the process of melting in elemental substances only. Substances with more than one type of interatomic bond add an extra degree of complexity without adding more insight into the problem. Following the ideas of *Lindemann*, we hypothesise that melting is related to the amplitude of vibration of the atoms within the solid. Thus for small amplitude vibrations the solid state would be stable, but for larger amplitude vibrations the structure of the substance would lose rigidity and 'collapse' into the liquid state.

Support for this idea may be gleaned by considering Figure 11.6, which shows the way in which melting temperature and Debye temperature vary amongst the elements. In §7.6, we saw that the Debye temperature of a substance, Θ_D, is (roughly) the temperature at which the atoms gain access to all their degrees of freedom. Above this temperature, they begin to vibrate essentially independently of their neighbours. The correlation seen in Figure 11.6 represents strong evidence that, not surprisingly, there is a relationship between the melting temperature and level of atomic vibration.

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 datasets. 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.



The Lindemann hypothesis

Lindemann hypothesised that melting occurred when the amplitude of vibration A reached a certain fraction f of the interatomic spacing a. This idea seems reasonable, and we can test it fairly straightforwardly.

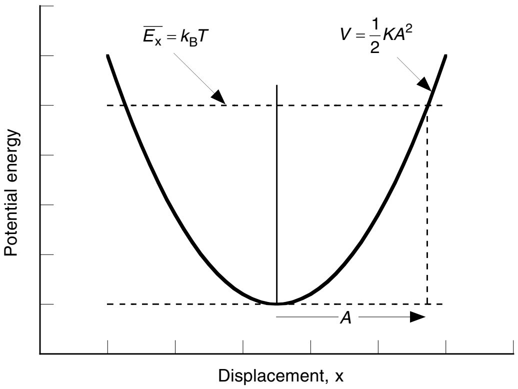
We suppose that the atomic vibration is simple harmonic – so we neglect the asymmetry of the interatomic potential energy (Figure 7.7). The average energy of vibration of an atom in such a potential is $\overline{E_x} = k_B T$ for each direction of vibration: $\frac{1}{2} k_B T$ for the degree of freedom associated with *kinetic energy* of vibration in the x-direction and $\frac{1}{2} k_B T$ for the degree of freedom associated with *potential energy* of vibration in the x-direction (See §2.5). This average energy is also related to the potential energy of vibration at the extreme point of the oscillation, i.e. at $x = A$, the amplitude of vibration. We thus write:

$$\begin{aligned} \overline{E_x} &= k_B T \\ &= \tfrac{1}{2} K A^2 \end{aligned} \qquad (11.1)$$

where K is the 'spring constant' of the harmonic potential. The Lindemann hypothesis is that melting occurs when the amplitude of vibration A is equal to a fraction f of the interatomic spacing a. Our task is to estimate this fraction f and see if it is similar for different elements. If it is, then we should find that:

$$k_B T_M = \tfrac{1}{2} K A^2 \qquad (11.2)$$

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 $\overline{E_x}$ 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 $\frac{1}{2} K A^2$.



Substituting $A = fa$ and re-arranging we have:

$$f^2 = \frac{2 k_B T_M}{K a^2} \qquad (11.3)$$

Before we can estimate f we need to find expressions for K and a which we do as follows.

Estimating *K*

Firstly, we recall that the frequency of vibration ω of an atom in a simple harmonic oscillator potential is given by:

$$\omega = \sqrt{\frac{K}{m}} \qquad (11.4)$$

where m is the mass of an atom. Hence we can write $K = m\omega^2$. Further we note the Debye temperature Θ_D is the temperature at which the thermal energy of vibration $k_B \Theta_D$ is roughly equal to the energy separation between quantum states ($\hbar\omega$) of the simple harmonic oscillator potential. This is equivalent to using an Einstein approximation (§7.6) and then estimating the Einstein temperature Θ_E as Θ_D. This likely to be accurate at around the 50% level. So at this level of approximation we write:

$$\begin{aligned} K &= m\omega^2 \\ &= m\left[\frac{k_B \Theta_D}{\hbar}\right]^2 \end{aligned} \qquad (11.5)$$

Estimating *a*

Secondly we can make a rough estimate of a for the elements by imagining each atom of mass m to occupy a volume a^3, and thus to have a density $\rho = m/a^3$. We can thus use the density data of Table 7.1 to estimate a from:

$$a = \left[\frac{m}{\rho}\right]^{1/3} \qquad (11.6)$$

Estimating *f*

Substituting Equations 11.5 and 11.6 into Equation 11.3 we arrive at:

$$f^2 = \frac{2k_B T_M}{Ka^2} = \frac{2k_B T_M}{m\left[\frac{k_B \Theta_D}{\hbar}\right]^2 \left[\frac{m}{\rho}\right]^{2/3}} \qquad (11.7)$$

We can use Equation 11.7 to evaluate the fraction *f* for all the elements for which we have Debye Temperature data (Table 7.12). The results of this calculation are graphed in Figure 11.8.

The Lindemann fraction *f* has a value of around one twentieth of an interatomic spacing for a wide variety of different elements. The 25 % variability in the data (*f* = 0.052 ± 0.014 to 1 standard deviation) is extremely small when we consider that it describes substances as different as argon and tungsten!

	T_M (K)	*f*
Argon	83.8	0.045
Tungsten	3680	0.044

Since we have completely ignored the crystal structure of the substances, small approximations such as $\Theta_E \approx \Theta_D$ in Equation 11.5 are relatively small contributors to the overall uncertainty in the estimate for *f*. From our perspective, it is the *constancy* of *f* which gives support to the Lindemann hypothesis. Thus melting occurs when the amplitude of atomic vibration reaches a fraction of roughly one twentieth of a lattice spacing. It is surprising – to me at least – that vibrations with this small amplitude are sufficient to destabilise a crystal structure to the extent that it melts.

Example 11.3

Calculate the Lindemann fraction *f* for copper.

We have:

$k_B = 1.38 \times 10^{-23}$ J K^{-1}, $\hbar = 1.034 \times 10^{-34}$ J s,
$N_A = 6.02 \times 10^{23}$ mol^{-1}

and

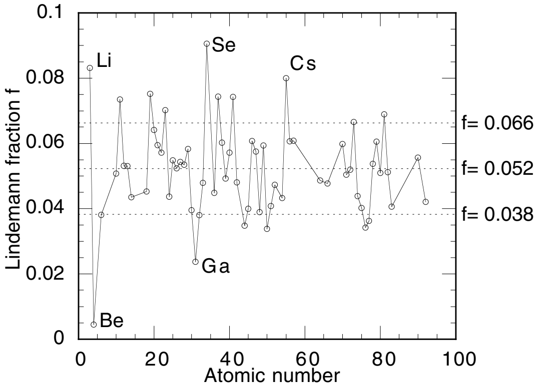
$T_M = 1356.6$ K (Table 11.1)
$m = 63.55 \times 10^{-3}$ kg/N_A (Table 7.2)
$= 1.056 \times 10^{-25}$ kg
$\rho = 8933$ kg m^{-3} (Table 7.2)
$\Theta_D = 343$ K (Table 7.12)

We thus estimate *f* as:

$$f^2 = \frac{2\times1.38\times10^{-23}\times1356.6}{1.056\times10^{-25}\left[\frac{1.38\times10^{-23}\times343}{1.054\times10^{-34}}\right]^2\left[\frac{1.056\times10^{-25}}{8933}\right]^{2/3}}$$

which evaluates to $f^2 = 3.388 \times 10^{-3}$ and $f = 0.0582$. This lies within the upper one standard deviation limit about the average value indicated in Figure 11.7

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.



11.3.4 Understanding the solid ⇔ liquid transition

Having established in general microscopic terms what happens when a substance melts, let us return to the questions raised by the data in §11.3.1 on the solid ⇔ liquid transition. These questions are considered in turn below.

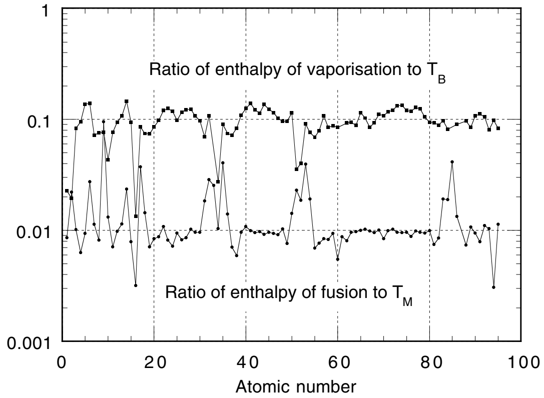
Why do elements with a high melting temperature tend to have a high enthalpy of fusion?

This question is similar to the first question in the next section §11.4.1 on the liquid ⇔ gas transition: Why do elements with high boiling temperatures tend to have high enthalpies of fusion? We will proceed by first reviewing the data for the

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.



elements, and then consider both of these questions together, first in a simple way, and then using the more sophisticated Gibbs free energy analysis.

Simple analysis

Figure 11.9 combines data from different columns in Table 11.1 and shows that roughly speaking – and with some striking exceptions – that:

- the melting temperature in kelvin is around 1% of the enthalpy change on melting in kJ mol^{-1}
- the boiling temperature in kelvin is around 10% of the enthalpy change on vaporisation in kJ mol^{-1}.

First, we can then say that these correlations are exactly what we would expect. Using Lindemann theory (§11.3.3) we saw that melting occurs when the amplitude of vibration of atoms reaches around a twentieth of an interatomic spacing. If the bonds between atoms are very strong, then (a) it will (by definition) require a great deal of energy to break them, and (b) it will generally require a great deal of energy to *stretch* or *bend* them. These two facts lead directly to correlations between enthalpy change on melting and – through the Lindemann criterion – the melting temperature.

Similarly with boiling: if the bonds between atoms are very strong, then (a) it will (by definition) require a great deal of energy to break them, and (b) the temperature at which atoms have sufficient energy ($\approx \frac{1}{2}k_BT$ per degree of freedom) to break the bonds will be very high. These two facts lead again to correlations between enthalpy change on vaporisation and the boiling temperature.

Gibbs free energy analysis

We can examine the matter further by considering the general form of the variation of the Gibbs free energy G of a substance with temperature T. There is no simple approximation to the form of the free energy curves, but as outlined in §10.2 and Figure 10.4, the solid and liquid free energy curves both have negative slopes and negative curvatures (i.e. they curve downwards).

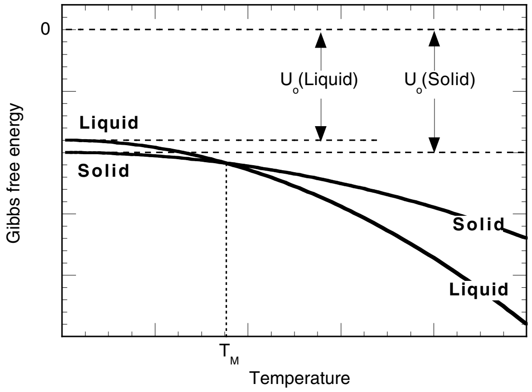
The general effect of a large cohesive energy U_o is to give rise to large *difference* between the cohesive energy of the liquid and solid states at $T = 0\ \text{K}$. Recall (Figure 11.10) this difference is typically a fraction (≈ 5%) of the total cohesive energy of the solid. There are two important consequences of a large difference between the cohesive energies of the solid and liquid states:

- First, the point at which the liquid and solid free energies become equal – by definition, the melting temperature – is displaced to a higher temperature.
- Second, *at the transition temperature*, the difference in slopes of the free energy curves is the *entropy* change on transformation. If this entropy (Q_M / T_M) is supplied at higher temperatures, then the heat supplied Q_M – the enthalpy change on melting – must also be greater.

Thus, a high melting temperature and a large latent heat of melting are both correlated with a large cohesive energy. Similar arguments lead to correlations between the cohesive energy, the boiling temperature and the latent heat of vaporisation (Figure 11.11)

Figure 11.10 Analysis of the correlation between melting temperature and enthalpy change on transformation (ΔQ_{LS}). U_o 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_O is to give rise to a large difference between U_O(liquid) and U_O(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_O.

(a) Small cohesive energy



(b) Large cohesive energy

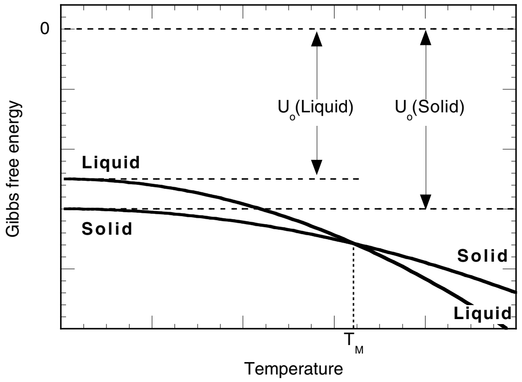
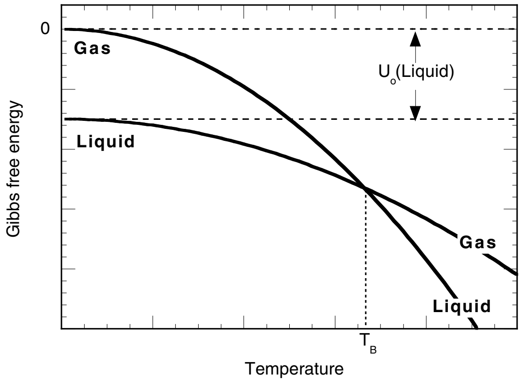
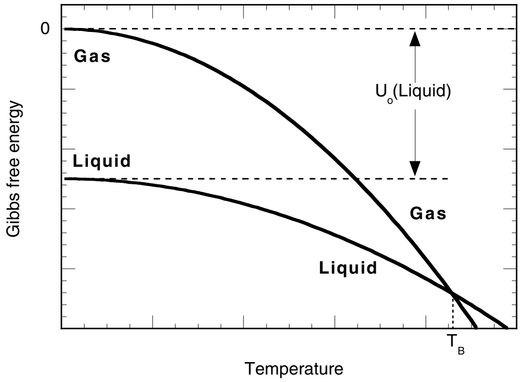


Figure 11.11 Analysis of the correlation between boiling temperature and enthalpy change on vaporisation (ΔQ_{LG}). U_o represents the cohesive energy of the liquid state at 0 kelvin. The figures represent the variation of the Gibbs free energy of a substance with cohesive energy which is (a) small and (b) large. The general effect of the large U_o is to give rise to a large difference between U_O(gas) and U_O (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_O.

(a) Small cohesive energy



(b) Large cohesive energy



The variation of melting temperature with atomic number

The second question raised by our analysis of the solid ⇔ liquid transition is why the variation of the melting temperature of the elements with atomic number, shows patterns similar to that seen in the density of elements (Figure 7.1). The origin of this correlation, as with that between melting temperature and enthalpy of fusion, has its root in the cohesive energy of the substance. This implies, not wholly surprisingly, that substances with a high cohesive energy tend to be particularly dense. This matter is considered further in §11.6.

Dependence of melting temperature on pressure

Finally, we come to the question of why the melting temperature of most substances increases with pressure, but decreases for substances which contract on melting. We will approach this question qualitatively, and then see how our considerations can be made more rigorous. In §9.2 we explained the origin of the expansion on melting, as being due to the inefficiency with which molecules are packed together in the liquid state. The extra ‘empty space’ inside a liquid enabled us to understand why the liquid state was typically 33% easier to compress than the solid state (§9.4 on speed of sound in liquids). We assumed that the empty space within the liquid was relatively easy to ‘reclaim’ when pressure was applied.

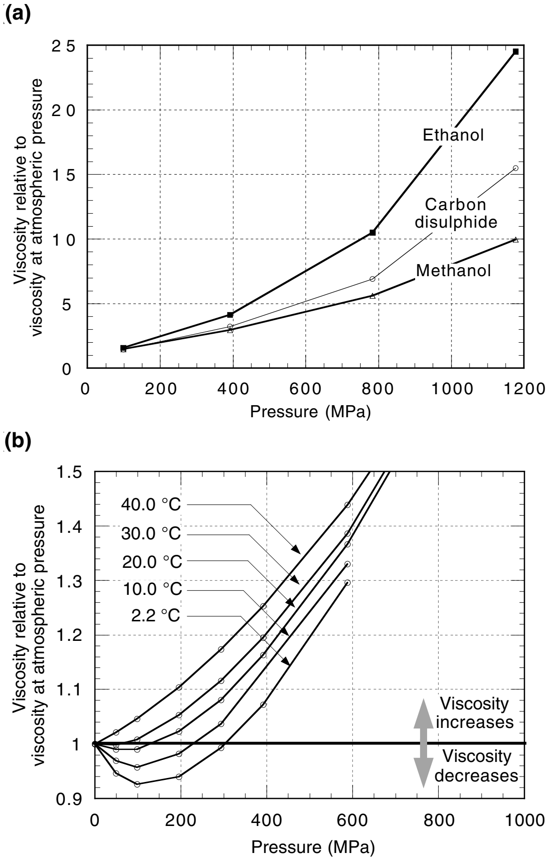
If this idea is correct, then reclaiming the ‘empty space’ within a liquid must necessarily make the liquid more solid-like. In particular, it must reduce the ease with which a molecule may ‘hop’ from one ‘cell’ within the liquid to another. So we will attempt to understand the pressure dependence of the melting temperature by suggesting that (in general) the application of pressure at a fixed temperature makes a liquid more solid-like. If we imagine applying pressure at a temperature just above the melting temperature, then making the liquid more like a solid will tend to stabilise the solid phase. If the solid phase is stabilised at a temperature at which the liquid phase used to be stable, then we have (by definition) raised the melting temperature.

This is an idea we may test fairly straightforwardly: if it is more difficult for a molecule to ‘hop’ from ‘cell’ to ‘cell’, then a liquid should become more viscous as pressure is applied. Data on the change in viscosity of a liquid under pressure are shown in Figure 11.12. They indicate that for normal liquids, the viscosity increases under applied pressure as expected. However, for water – one of the few liquids which is more dense than its corresponding solid – the reverse process can happen. For water at a temperature just above its melting temperature, pressure first *decreases* the viscosity. Thus pressure makes a normal liquids more viscous (more solid-like), but makes water just above 0 °C less viscous (more liquid-like).

We understood the normal liquid by assuming that there is ‘free space’ in the liquid which is removed by pressure. For water – and other substances which contract on melting – it is the solid state which has the ‘free space’ due to the open hydrogen-bonded crystal structure. We can understand the pressure data by supposing that there is already too much ‘free space’ in the liquid state, and pressure has the effect of increasing the forces which allow molecules to move past one another.

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 ≈ 30 °C the effect of pressure is first to cause a *decrease* in viscosity in contrast with the behaviours of ‘normal’ liquids shown in (a).



Thus pressure makes most liquids more the solid-like, but makes liquids which contract on melting more liquid-like. Thus it is not surprising that the effect of pressure is to raise the melting temperature, but for liquids which contract on melting the effect is to lower the melting temperature.

11.4 The liquid ⇔ gas transition: boiling and condensing

11.4.1 Introduction

Although the *boiling temperature* of a pure liquid substance is a well-defined temperature, *the process of transformation from liquid to gas occurs at all temperatures.* At any temperature, a liquid attempts to sustain above its surface a characteristic pressure of its vapour: the *vapour pressure.* We developed a theory for the equilibrium vapour pressure above a liquid based on the cell model of liquid in §9.8. We also developed a prediction based on more general grounds (the *Clausius-Clapeyron* equation) in §10.43. In both analyses, we predicted that (in agreement with experiment) the vapour pressure should increase exponentially with increasing temperature.

Since the liquid and gas phases of a substance coexist at all temperatures at which the liquid is stable, a sensible choice is made as to the pressure of vapour which defines the transition to the gaseous phase. We define the transition temperature as the temperature at which the vapour pressure of liquid reaches standard atmospheric pressure (1.0135×10^5 Pa). This choice may be sensible, but it is important to realise that it is also arbitrary: another defining pressure could have been chosen. If for example we had evolved on a planet with a much lower atmospheric pressure, our table of the boiling temperatures of substances would all be considerably lower. (It is interesting to note that this is not the case for a solid⇔liquid phase change. This is because the melting curve is much steeper than the vaporisation curve (§10.7) and so the melting temperatures of substances do not depend strongly on atmospheric pressure.)

The phenomenon of 'boiling' in which bubbles form at the transition temperature from liquid to vapour is one with which we are familiar from observations of water. However, bubble formation (Figure 11.13) at the liquid⇒vapour transition is not really a fundamental feature of the transition. In liquid helium, normal boiling occurs at 4.2 K, but on cooling below 2.17 K, the bubbling associated with boiling ceases. However, despite this, evaporation of molecules from the liquid surface

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.

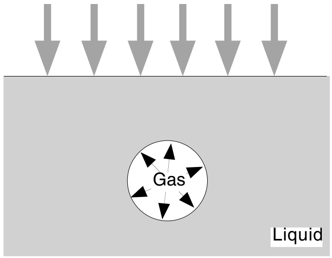


Figure 11.14 The boiling temperatures of the elements plotted as function of atomic number.

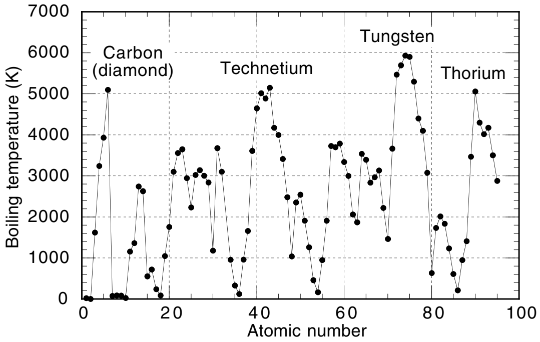
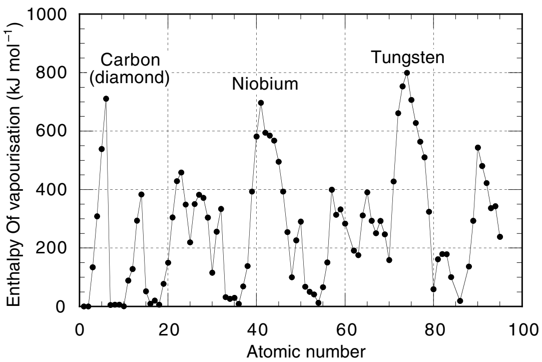


Figure 11.15 The enthalpy change on vaporisation of the elements plotted as function of atomic number.



continues uninterrupted. What has happened is that at this temperature helium undergoes a transition to a new liquid structure with a thermal conductivity hundreds of times greater than in its ‘normal’ state. The excellent thermal conduction reduces the magnitude of thermal gradients and fluctuations within the liquid below the level sufficient to cause bubble formation. Helium is an unusual liquid (to be sure!), but it highlights an important insight about ‘boiling’. The phenomenon is related to the magnitude of temperature gradients and fluctuations within the liquid, rather than being intrinsic to the liquid⇒vapour transition *per se*.

11.4.2 Data on the liquid⇒gas transition

The boiling temperatures of the elements and other substances are recorded in Tables 11.1 and 11.2 and graphed as a function of atomic number in Figures 11.14 and 11.15. These figures show that there are correlations between the boiling temperatures and enthalpy changes on vaporisation of the elements.

The main questions raised by our preliminary examination of the experimental data on the liquid to gas transition are:

- Why do elements with a high boiling temperature tend to have a high enthalpy of vaporisation?
- Why does the variation of the boiling temperature of the elements with atomic number show a pattern similar to that seen in the density of elements?
- Why does the vapour pressure of a substance increase strongly with temperature?

In fact we have already answered all three of these questions. The first two questions have already been addressed in §11.3.4 where they are considered along with similar questions from the solid ⇔ liquid transition. The final question was addressed in §9.8, where we developed a theory of the vapour pressure of a liquid. However we are now in a position to extend the cell model theory so that one of its key parameters can be compared directly with experiment.

11.4.3 Understanding the value of the latent heat: the cell model re-visited

In §8.4 we saw that ΔE_e was the cell model parameter that characterised the energy required to remove an individual molecule from the liquid and move it into the vapour. In §9.10 we looked at values of ΔE_e deduced from the slopes of vapour pressure versus temperature graphs and compared them with other cell model parameters. We saw that, broadly speaking, we could understand the *relative* values of ΔE_e, ΔE_h, and ΔE_s. Now however we are in a position to relate the absolute value of ΔE_e to the latent heat of the liquid.

The theory is shockingly simple. If ΔE_e represents the energy required to remove a single molecule of a substance from the liquid, then $N_A\Delta E_e$ represents the energy required to remove N_A molecules of a substance from the liquid. This is nothing more than the latent heat of vaporisation of a mole of the liquid. In other words ΔE_e is effectively the ‘latent heat per molecule’. We thus expect to find:

$$L = N_A \Delta E_e \qquad (11.8)$$

Based on Equation 11.8, we can predict a value for the latent heat of vaporisation for any liquid for which have a value of ΔE_e. The data for ΔE_e from Table 9.12 is reanalysed in Table 11.3 and compared with the experimental value of the latent heat from Table 11.1. We see to within about 10%, we can predict the latent heat of vaporisation

Table 11.3 Comparison of $N_A\Delta E_e$ with the experimental value of the latent heat of vaporisation L. The final column shows the ratio of these two quantities $N_A\Delta E_e/L$. The values of ΔE_e are drawn from Table 9.12.

Substance	**ΔE_e(J) × 10^{-21}**	**$N_A\Delta E_e$ (kJ mol^{-1})**	**L (kJ mol^{-1})**	**$N_A\Delta E_e/L$**
Copper	486	292.7	300.5	0.97
Silver	403	242.7	255.06	0.95
Gold	516	310.7	324.43	0.96
Aluminium	447	269.2	290.8	0.92
Tin	436	262.6	290.37	0.90
Helium	0.13	0.078	0.08	0.98
Neon	3.23	1.95	1.77	1.10
Argon	10.8	6.50	6.52	0.99
Krypton	17.2	10.36	9.03	1.15
Xenon	24.4	14.69	12.64	1.16

of substances with greatly different boiling temperatures. This prediction is deduced from the temperature-dependence of the vapour pressure. This level of agreement gives us confidence that the cell model we developed in Chapter 9 is applicable to real liquids, and that ΔE_e has been realistically estimated.

11.5 The critical point

11.5.1 Introduction

The fact that the liquid and gaseous phases of a substance co-exist over a wide range of temperatures is a clue to the close relationship between the phases. Evidence for this is strengthened by the fact, above a certain temperature, known as the *critical temperature* T_C, there is no distinct transition from liquid to gas. Since there is no distinct transition, then we do not know whether to describe the state of the substance as a liquid or a gas. The correct designation is to describe a substance above its critical temperature as being a *supercritical fluid*. This is a state can be reached smoothly without a phase transition from *either* the liquid *or* the gas phase.

A *critical pressure* and *critical volume* can also be defined as the pressure and volume at which the densities of the *co-existing* gas and liquid phases are equal.

11.5.2 Further data

The critical parameters of various substances discussed are listed in Table 11.5.

Figure 11.17 represents an attempt to find structure in the critical parameter data from Table 11.5. The data are plotted on a logarithmic scale and so a good deal of the variation amongst the data is not clearly shown. However, it is clear that, apart from the smallest molecular masses, the critical parameters are roughly independent of molecular mass. We can notice that there are, not surprisingly, significant correlations between the critical temperature pressure and volume for a particular substance.

Roughly speaking we find ballpark values of critical parameters in Table 11.5 are:

$T_C \approx 500\ \text{K} \approx 200\ °\text{C}$

$P_C \approx 5\ \text{MPa} \approx 50$ atmospheres

$V_C \approx 200 \times 10^{-6}\ \text{m}^3\ \text{mol}^{-1} \approx$ a sphere about 7 cm in diameter per mole

Table 11.5 also indicates that the density of most substances at the critical point is close to one-third their density at normal pressures and temperatures. Such figures indicate that in the critical condition there is little 'free space' around each molecule as compared to a gas. However, the density ratio indicates that at the critical point roughly two-thirds of the volume of the substance is free space (at least as compared with the liquid state).

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 pressure 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.

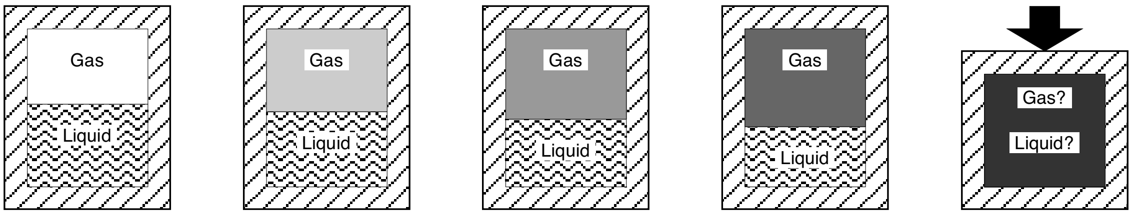


Table 11.4 The critical parameters of various substances discussed in Chapter 6 and Chapter 8. P_C, V_C and T_C are the critical pressure, molar volume and temperature. Z_C is the *compression factor* which is discussed in §11.5.3. The next column gives the density at the critical point, calculated from the molecular mass and V_C. This may be compared with the density of the substance in the liquid state well away from T_C. For the inorganic substances where the liquid density data is not available, the solid density has been used instead The final column gives the ratio of the density at the critical point to that at a temperature well below the critical point.

Substance	**P_C (MPa)**	**V_C ($\times 10^{-6}$ m^3 mol^{-1})**	**T_C (K)**	**$Z_C = P_C V_C / RT_C$**	**Critical Density (kg m^{-3})**	**Liquid Density (kgm^{-3})**	**Density Ratio**
Methanol, CH_3OH	8.09	118	512.6	0.224	271	791	0.343
Ethanol, C_2H_5OH	6.14	167	513.9	0.240	275	789	0.349
Propan-1-ol , C_3H_7OH	5.17	219	536.8	0.254	274	804	0.340
Acetic acid, $C_2H_4O_2$	5.79	171	594.5	0.200	351	1049	0.334
Acetone, C_3H_6O	4.7	213	508.1	0.237	272	787	0.346
Aniline, C_6H_7N	5.3	274	698.9	0.250	339	1026	0.330
Benzene, C_6H_6	4.9	254	562.2	0.266	307	879	0.349
Bromoethane, C_2H_5Br	6.23	215	503.8	0.320	507	1456	0.348
Chloroform, $CHCl_3$	5.5	240	536.4	0.296	500	1498	0.333
Cyclohexane, C_6H_{10}	4.02	308	553.4	0.269	266	941.6	0.282
Ethyl acetate, $C_4H_8O_2$	3.83	286	523.2	0.252	287	900.6	0.319
Toluene, C_7H_8	4.11	320	591.8	0.267	288	868.8	0.331
Carbon monoxide, CO	3.50	93.1	133	0.295	300.75	—	—
Carbon dioxide, CO_2	7.38	94.0	304.2	0.274	468.09	—	—
Carbon disulphide, CS_2	7.9	173	552	0.298	439.31	1263	0.348
Carbon tetrachloride, CCl_4	4.56	276	556.4	0.272	550.72	1604	0.343
Hydrogen, H_2	1.294	65.5	32.99	0.309	30.534	89	0.343
Nitrogen, N_2	3.39	90.1	126.2	0.291	310.77	1035	0.300
Oxygen, O_2	5.08	78	154.8	0.308	410.26	1460	0.281
Chlorine, Cl_2	7.71	124	417	0.276	572.58	2030	0.282
Bromine, Br_2	10.3	135	584	0.287	1185.2	3120	0.380
Helium, He	0.229	58	5.2	0.307	68.966	120	0.575
Neon, Ne	2.73	41.7	44.4	0.309	479.62	1442	0.333
Argon, Ar	4.86	75.2	150.7	0.292	531.91	1656	0.321
Krypton, Kr	5.50	92.3	209.4	0.292	910.08	3000	0.303
Xenon, Xe	5.88	119	289.7	0.291	1100.8	3560	0.309
Radon, Rn	6.3	—	377		—	4400	
Water, H_2O	22.12	59.1	647.3	0.243	304.57	1000	0.305
Heavy water, D_2O	21.88	54.9	644.2	0.224	364.30	1100	0.331

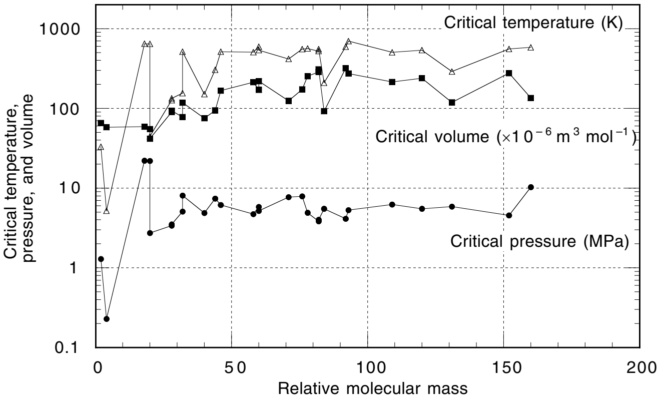


Figure 11.17 The critical parameters (Table 11.5) of various substances discussed in Chapter 6 and Chapter 8 plotted as a function of their relative molecular mass. Note that the vertical axis is logarithmic, which compresses much of the actual variation amongst the data.

The main questions raised by our preliminary examination of the experimental data on the critical temperature of substances are:

- Why do the critical temperatures, volumes and pressures have broadly similar values for substances with a wide range of molecular masses?
- Why is the density at the critical point roughly one-third of the density at normal pressure and temperature?

11.5.3 Understanding the data on the critical temperature

To understand what is happening as a substance approaches its critical condition we may chart the development of the *radial density function* (§8.2.2). This is illustrated qualitatively in Figure 11.18, which is itself adapted from Figure 8.6. Figure 11.18 illustrates the continuous evolution of the liquid state:

- Just above the melting temperature, a great deal of the short-range order of the solid still remains.
- As the temperature is raised, the density of the liquid state falls continuously (Figures 9.3 and 9.4) the short-range order is systematically weakened.
- At the critical condition, the overall density of the liquid state is around 34% of its 'normal' value, and little of the short-range order remains.

We have already seen evidence of this evolution of the liquid state in Figure 9.21, where we looked at data on the surface tension of liquids. There we saw that the surface tension of all liquids declines roughly linearly with temperature. In Figure 11.19 we re-examine the data on water shown in Figure 9.18. We see clearly that the data, when extrapolated, indicate that water substance will have zero surface tension (i.e. be indistinguishable from a dense gas) at a temperature just above the critical temperature. Given the crude extrapolation, and the unusual properties of water, we see that even between 0 °C and 100 °C, the structure of water is already evolving in a way destined for 'completion' at T_C.

Example 11.4

Work out the volume occupied per molecule when ethanol is in its critical state.

Considering ethanol in Table 11.4 we see that it has a critical volume of 167×10^{-6} m^3 mol^{-1}. i.e. this volume contains the Avogadro number of molecules. Thus the volume per molecule in the critical state is:

$$\begin{aligned}\text{Volume per molecule} &= \frac{167\times10^{-6}}{6.02\times10^{23}}\\ &= 2.77\times10^{-28}\ \text{m}^3\end{aligned}$$

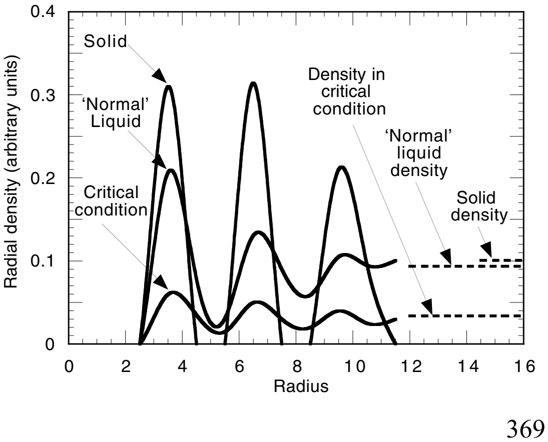
If we imagine each molecule confined to a cube of volume $a \times a \times a$ then the cube would have side:

$$\begin{aligned}a &= \sqrt[3]{2.77\times10^{-28}}\\ &= 6.5\times10^{-10}\ \text{m}\end{aligned}$$

This volume would contain one ethanol molecule C_2H_5OH, i.e. two carbon atoms, six hydrogen atoms and one oxygen atom. Considering that a typical atom has a diameter of a *few* × 10^{-10} m and that the bonds between atoms are separated by similar amount, this leaves little free space in between molecules.

Returning to direct consideration of the questions raised in the previous section, we see that the key linking feature of the critical point data is that the density at the critical point is around one-third of the normal liquid density. Thus we can understand

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.



the relative uniformity of critical molar volumes merely by noting that the *normal* liquid densities of the substances in Table 11.4 only vary by a factor ≈ 3, which is considerably compressed on the logarithmic scale of Figure 11.17.

The virial approach to the critical condition

Let us consider approaching the critical temperature and pressure in two stages, as indicated on Figure 11.20. We start with a gas at around STP and then in stage 1 we heat the gas to the critical temperature, T_C. In stage 2 we then compress it until we arrive at the critical pressure P_C.

At around STP we know that the gas is 'well described' by the ideal gas equation, and in general, this will also be the case when the gas is heated to T_C. Let me say more precisely what I mean by 'well described'. In §4.4, we saw that the *compression factor* Z was defined by:

$$Z = \frac{PV_m}{RT} \qquad (4.50^* \text{ and } 11.9)$$

where V_m is the molar volume. We noted that the deviations from ideal gas behaviour could be described by a so-called *virial* expansion:

$$Z = 1 + \frac{B(T)}{V_m} + \frac{C(T)}{V_m^2} + \ldots (4.50^* \text{ and } 11.10)$$

Recall that in §4.4, I stated that the second virial coefficient $B(T)$ depended on strength of interactions between *pairs* of molecules, while the third virial coefficient $C(T)$ depended on strength of interactions between *clusters of three* molecules. Importantly, the virial coefficients depend *only* on temperature. The second and third virial terms amount to only a fraction of a per cent for gases at modest pressures and temperatures. So by 'well described', I mean that the compression factor for the substance is close to unity.

Now for a gas at around atmospheric pressure and the critical temperature, the terms $B(T)/V_m$ and $C(T)/V_m^2$ are small. In Stage 1 of our approach to the critical point, we increase the temperature and constant pressure. This can result in increases or decreases of the virial coefficients, but in general the terms in the virial series remain small. However, as we increase the pressure in Stage 2, the terms in the virial expansion become larger. This is because, although the virial coefficients do not depend on pressure, the molar volume (which occurs in the denominator of all the terms) is decreased. Now the critical molar volume is typically of the order of $V_C \approx 200 \times 10^{-6}\ \mathrm{m^3\,mol^{-1}}$

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)

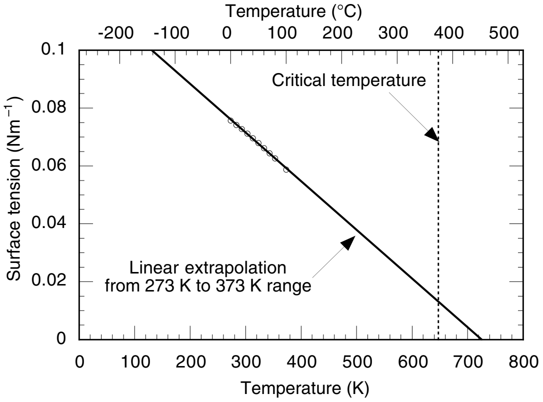
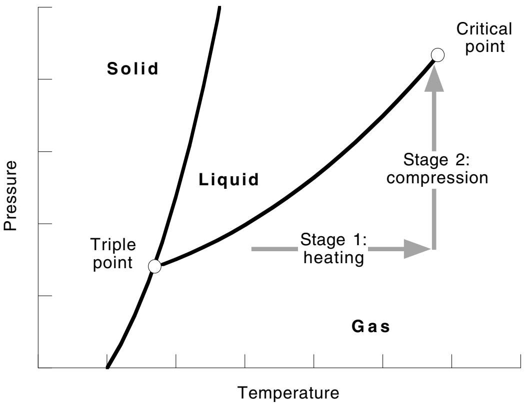


Figure 11.20 The virial approach to critical condition. Starting with a low-pressure gas we can approach the critical condition in two stages. In Stage 1, the gas is heated at constant pressure causing it to expand considerably. In Stage 2 the gas is compressed at constant temperature. In this stage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



compared with 22.4 litres ($V_C \approx 22400\times 10^{-6}$ m^3 mol^{-1}) at STP. So, we see that at the critical point, the second term in the virial expansion is around 100 times larger than at STP, the third term is around $100^2 = 10^4$ larger, and subsequent terms larger still. Physically we can see the growth of the higher-order terms results from the increasing significance of ever larger clusters of molecules as the pressure approaches the critical value. As Table 11.5 makes clear, the compression factor *at* the critical point for many substances has a value of $Z_C = P_CV_C/RT_C$ in the range 0.2 to 0.3. This may be compared with a value very close to unity in the gas phase, well away from the critical point.

The question remains of *why* the density at the critical is point is roughly one-third the normal liquid density. The value of one-third is just what it turns out to be! We can see that the value does indeed correspond to an extremely dense gas as one would expect. The question of why the value – whatever might have turned out to be – is 'universal', is a question which is considered in the following section (§11.6) on laws of 'corresponding states'.

11.6 Scaling: laws of corresponding states

11.6.1 Introduction

Consider the following:

- In §11.3, we noted that substances with high boiling temperatures also tend to have high melting temperatures.
- In §11.3.3, Figure 11.9, we noted that the ratio of the enthalpy of fusion of an element to its melting temperature has a relatively constant value of around 0.01 J K^{-1} mol^{-1} . Also we saw that the ratio of the enthalpy of vaporisation of an element to its boiling temperature has a relatively constant value of around 0.1 J K^{-1} mol^{-1}.
- In §11.3.3.1 we noted that the Lindemann fraction for the elements had a common value of around $\frac{1}{20}$.
- In §11.5.2, Table 11.4 we noted that the densities of substances at their critical point were all roughly one-third of their value in the liquid phase.
- In §11.4.2 Equation 11.8 we noted that the value of P_CV_C / RT_C has value of around 0.25 for a wide range of substances.
- In §9.9 we concluded that the *cell model* could plausibly describe the dynamic properties of a wide variety of liquids with just four 'free parameters'.

The observations above, and many others that you can find throughout the book, raise the hope that it might be possible to find a model of an 'ideal substance' analogous to our model of an 'ideal gas'. In fact, the properties of substances, particularly solids are too diverse to make this a worthwhile endeavour.

However, many of the correlations between substances are particularly striking: Example 11.5 predicts the critical temperature of water based only on its boiling temperature, and the properties of liquid krypton! It is clear that there must be something physically significant underlying the observed universality. Such correlations offer the tantalising possibility that if we could understand them, then surely we must be on the verge of understanding at least 'something about everything'. In practice, what we arrive at are a great many 'rules of thumb', each applicable in most cases but with several exceptions. These rules tell us something approximately true about several substances, but nothing definite about any particular substance.

For instance, in Example 11.5 we also consider potassium and water. We notice that for these substances the melting temperature is poorly predicted from the boiling temperature. In the following sections we examine the data to see to what extent we may trust a simple scaling approach to all substances.

11.6.2 Further data on melting, boiling, and critical temperatures

In Figure 11.21 we compare the critical temperature T_C and melting temperature T_M with the boiling temperatures of various substances. As expected from Example 11.5, the figure shows that the critical temperature is strongly correlated with the boiling temperature of the liquid, and is typically a factor of roughly 1.6 higher. Recall from Example 11.5 that T_C for argon was a factor 1.73 higher than T_B.

So the main question raised by this preliminary examination of the experimental data on the melting, boiling, and critical temperatures of substances is simply:

- What is the origin of the common relationship between T_M, T_B and T_C observed in a variety of substances?

11.6.3 Understanding the origin of corresponding states

At high temperatures all substances enter the gaseous phase and, as we have seen, obey the perfect gas equation reasonably well, at least at low density. The reason for this is that the approximations underlying the derivation of $PV = zRT$ are well satisfied by real gases.

As a substance is cooled in the gas phase its density increase and eventually it reaches the point at which further cooling will cause it to enter one of the condensed states. The temperature and density at which this occurs depends on the strength of interaction between the molecules of the gas.

Recall that all molecules are naturally 'sticky': when molecules collide they stick together unless the kinetic energy of the molecules is high enough to prevent it. As we saw in §4.3, the average speed of the Maxwell distribution of molecular speeds falls as the temperature falls. Eventually, for any substance the average kinetic energy of the molecules is such that, on collision, the molecules stick together.

The temperature at which this happens will be related to the stickiness (binding energy) of the molecules. Thus the boiling temperature is related directly to the binding energy of molecules – and hence to the *cohesive energy* of the substance. It is this phenomenon which links the characteristic temperatures for a substance, to the binding energy per molecule. Ignoring factors of the order of 'a few', we write:

$$u_o \approx k_B T_B \qquad (11.11)$$

Example 11.5

The table below shows the critical, boiling and melting temperatures for krypton.

T_C(K)	**T_B(K)**	**T_M(K)**
209.4	**120.85**	**116.6**

Does knowing these figures for krypton allow us to predict the equivalent quantities for the other solids knowing only their boiling temperature?

First let us normalise the data to the boiling temperature of the substance. The above table now looks like:

	T_C	T_B	T_M
Krypton	1.73	1.00	0.965

If the simplest form of scaling theory is correct then given the boiling temperature of other substances we should find that their melting temperature is around 96% of T_B and their critical temperature is around 73% higher than T_B. Let us see if it works:

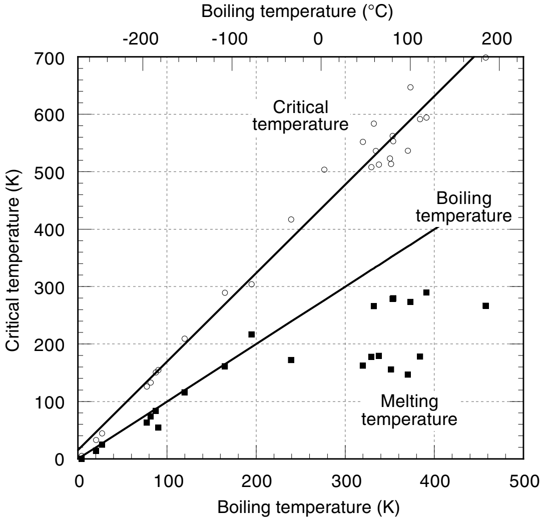
	T_C(K)	T_B(K)	T_M(K)
Expectation for argon	151.0	87.3	84.2
Data for argon	150.7	87.3	83.8
Expectation for neon	46.9	27.1	26.1
Data for neon	44.4	27.1	24.6

The agreement for argon is rather good, while that for neon is not so good. But before we accept the scaling idea wholesale let us try it on a couple of other rather different substances.

	T_C(K)	T_B(K)	T_M(K)
Expectation for water	645.6	373.2	360.1
Data for water	647.3	373.2	273.2
Expectation for potassium	–	1047	1010
Data for potassium	–	1047	337

We see that the results are rather more mixed. The theory predicts the critical temperature of water astonishingly well, but predicts the melting temperature very poorly. Similarly, the melting temperature of potassium is very poorly predicted.

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.



or using cohesive energies per mole:

$$U_o \approx x N_A k_B T_B \approx x R T_B \tag{11.12}$$

where x is the number of bonds (roughly speaking, the number of nearest neighbours) with which a molecule interacts in the condensed state. Of course there are many other factors to be taken into account, for example, the shape of complex molecules. However for reasons of simplicity we stick with our Equation 11.12. Table 11.5 contains calculated data for the cohesive energies of the elements. These are the results both of complex calculations similar to those we embarked upon in Chapter 6, and analysis of experimental results. It is worthwhile recalling that this energy is *electrostatic in origin* (as mediated by the laws of quantum mechanics) and arises from the bonding mechanisms outlined in Chapter 6.

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.

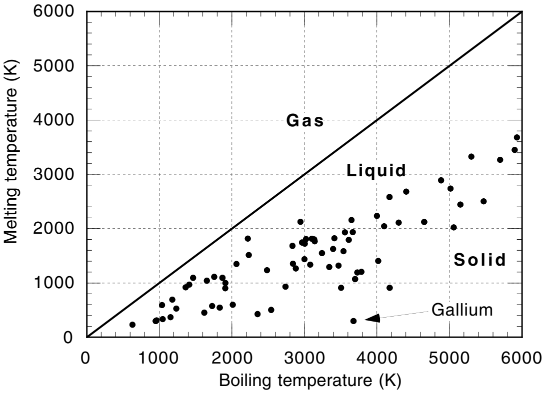
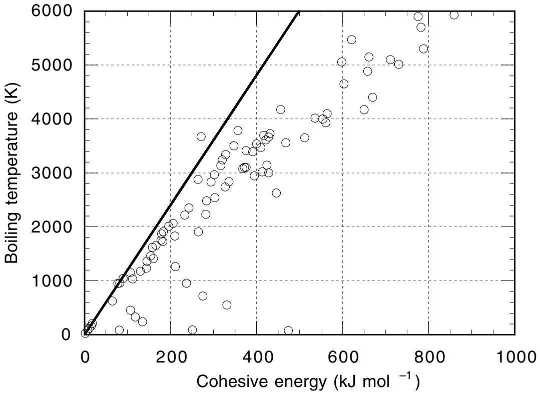


Figure 11.23 The boiling temperatures of the elements plotted as function of their cohesive energy (Table 11.5). It is clear that the data show a broad trend – with exceptions – indicating that substances with higher cohesive energies tend to have higher boiling temperatures. The solid line in the figure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



Cohesive energy and boiling temperature

Given the value of U_o, the boiling temperature may be predicted according to Equation 11.20. The function $T_B \approx U_o / xR$ is graphed in Figure 11.27, along with the actual boiling temperature. We have assumed ten nearest neighbours as a

Table 11.5 The cohesive energies U_o of the elements in units of kJ mol^{-1}. U_o is the energy required to separate the atoms of a solid at $T = 0$ K into isolated neutral atoms.

Z	*Element*	U_o (kJ mol^{-1})	*Z*	*Element*	U_o (kJ mol^{-1})	*Z*	*Element*	U_o (kJ mol^{-1})
1	Hydrogen	—	32	Germanium	372	63	Europium	179
2	Helium	—	33	Arsenic	285.3	64	Gadolinium	400
3	Lithium	158	34	Selenium	237	65	Terbium	391
4	Beryllium	320	35	Bromine	118	66	Dysprosium	294
5	Boron	561	36	Krypton	11.2	67	Holmium	302
6	Carbon	711	37	Rubidium	82.2	68	Erbium	317
7	Nitrogen	474	38	Strontium	166	69	Thulium	233
8	Oxygen	251	39	Yttrium	422	70	Ytterbium	154
9	Fluorine	81	40	Zirconium	603	71	Lutetium	428
10	Neon	1.92	41	Niobium	730	72	Hafnium	621
11	Sodium	107	42	Molybdenum	658	73	Tantalum	782
12	Magnesium	145	43	Technetium	661	74	Tungsten	859
13	Aluminium	327	44	Ruthenium	650	75	Rhenium	775
14	Silicon	446	45	Rhodium	554	76	Osmium	788
15	Phosphorous	331	46	Palladium	376	77	Iridium	670
16	Sulphur	275	47	Silver	284	78	Platinum	564
17	Chlorine	135	48	Cadmium	112	79	Gold	368
18	Argon	7.74	49	Indium	243	80	Mercury	65
19	Potassium	90.1	50	Tin	303	81	Thallium	182
20	Calcium	178	51	Antimony	265	82	Lead	196
21	Scandium	376	52	Tellurium	211	83	Bismuth	210
22	Titanium	468	53	Iodine	107	84	Polonium	144
23	Vanadium	512	54	Xenon	15.9	85	Astatine	—
24	Chromium	395	55	Caesium	77.6	86	Radon	18.5
25	Manganese	282	56	Barium	183	87	Francium	—
26	Iron	413	57	Lanthanum	431	88	Radium	160
27	Cobalt	424	58	Cerium	417	89	Actinium	410
28	Nickel	428	59	Praseodymium	357	90	Thorium	598
29	Copper	336	60	Neodymium	328	91	Protactinium	—
30	Zinc	130	61	Promethium	—	92	Uranium	536
31	Gallium	271	62	Samarium	206			

rough estimate of the number of interacting pairs of molecules and we see that the prediction is of the correct order of magnitude and broadly captures the trend of the data

Having seen that condensation/boiling temperature is related to the cohesive energy, it is fairly straightforward to conceive how the melting temperature can be related to the boiling temperature using extensions of the arguments leading to the concept of the Lindemann fraction. Similarly the link with the Debye temperature follows plausibly. Further, as outlined in §11.3.4, the cohesive energy of a substance is linked directly to the enthalpy changes on fusion and vaporisation. If we plot the calculated cohesive energy as a function of atomic number (Figure 11.24) we see the periodic variation with temperature that we have observed in many properties of the elements. It is the cohesive energy – modified differently in each case – which underlies all of the periodic variations of elemental properties that we have observed in:

- the density: Figure 7.1
- the Debye temperature: Figure 11.6
- the melting temperature: Figure 11.3
- the boiling temperature: Figure 11.14
- the enthalpy change on fusion: Figure 11.4
- the enthalpy change on vaporisation: Figure 11.15

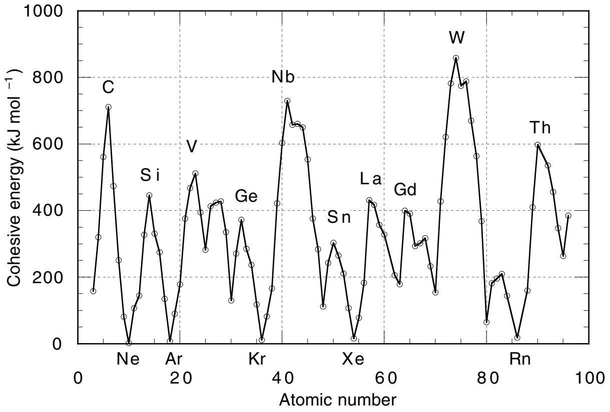


Figure 11.24 The cohesive energy of the elements (Table 11.5) plotted as a function of atomic number. It is clear that the data show periodic increases and decreases which reflect the effect of the filling of electron shells and the type of bonding possible. It is this graph which is at the heart of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

Thus, despite the bewildering variety of properties displayed by matter, on a course scale we can conceive as matter in a very simplistic way. We imagine each molecule to be just a 'blob' of mass *m* interacting with a cohesive energy somewhere in the range 0.1 eV per atom to 10 eV per atom. The universal behaviour arises because, roughly speaking, *all* matter can be described in this rather general way.

11.7 The solid ⇔ gas transition: sublimation

11.7.1 Introduction

The sections above have described a familiar story: solids melt into liquids, which evaporate to become gases. However, some substances transform straight from the solid state to the gaseous state in a process known as *sublimation*. The unfamiliarity of this transformation deserves some comment.

The vapour pressure above a solid

The transformation from solid to gas – like the transformation to liquid to gas – is a continuous process: solid and gas co-exist at all temperatures. However, the *vapour* pressure of many solids, such as iron, is exceedingly small at around room temperature. Figure 9.24 shows the vapour pressure of several metals and in Exercise 11.24 you can see just how small the vapour pressure is above a solid. However, even these substances are regularly evaporated, but they must first be heated to high temperatures often, but not always, melting in the process. This is the technique by which thin aluminium coatings are placed on, for example, compact discs.

However, for many solids the vapour pressure *is* appreciable even at around room temperature. The vapour pressure of water substance in both its liquid and solid phases is shown in Figures 11.25.

Notice that when water freezes, the vapour pressure does not suddenly fall to zero, but maintains a continuous curve. The figure shows the vapour pressure above the solid, and above supercooled liquid. It is clear from Table 11.6 and Figure 11.25, that the vapour pressure above the surface of liquid water is similar to (but slightly higher than) the vapour pressure above solid ice at the same temperature.

Similar behaviour is also seen in Figure 9.23 showing the vapour pressure above the solid noble 'gases': neon, argon, krypton, and xenon. Over most of the temperature range shown the substances (except helium) are solid – their liquid phase exists for only a few kelvin below their boiling temperature. However there is no striking discontinuity between the vapour pressure above their solid and liquid phases.

Sublimation

We may define a *sublimation temperature* for a solid – by analogy with the definition of the boiling temperature – as the temperature at which the vapour pressure above a solid reaches atmospheric pressure. By this definition, only two elements, carbon and arsenic, sublime.

We have noted previously that the application of pressure tends to increase the temperature of liquid ⇒ gas transition and the same is true of the solid ⇒ gas transition. Thus the temperature of the complete transition to the gaseous state can be moved to a higher temperature by the application of pressure. We also noted in §11.2 that the temperature of a solid ⇒ liquid transition is also in general increased by application of pressure.

Consider a liquid at atmospheric pressure just above its melting temperature: application of pressure will raise the melting temperature and return the substance to the solid state. Similarly, application of pressure to a gas just above its boiling temperature may cause condensation of the substance into the liquid state. Thus in each case the application of pressure favours the more condensed of the phases available to the substance.

Similarly, application of pressure to a substance which sublimes may sometimes cause a stabilisation of the liquid phase, which allows the solid ⇔ liquid and liquid ⇔ gas transitions to be investigated. For example, arsenic is recorded in Table 11.2 as subliming at 886 K. However, under application of a pressure of 28 atmospheres (≈ 2.8 MPa) arsenic first melts at 1090 K, and then evaporates, allowing investigation of the enthalpies of fusion and vaporisation. Note that the boiling temperature conventionally refers to normal atmospheric pressure and so the boiling temperature 'under pressure' is not usually recorded.

The main questions raised by our preliminary examination of the experimental data on the solid to gas transition:

- Why does sublimation occur at all?
- Why is sublimation relatively so rare?

Table 11.6 The equilibrium vapour pressure (Pa) of water substance above the solid or liquid surface as a function of temperature. The shaded data on the liquid corresponds to data taken on supercooled water.

T (°C)	Solid	Liquid	*T* (°C)	Solid	Liquid
–90	0.009	—	–15	165.5	191.50
–80	0.053	—	–14	181.5	208.03
–70	0.258	—	–13	198.7	225.50
–60	1.077	—	–12	217.6	244.57
–50	3.940	—	–11	238.0	264.98
–40	12.88	—	–10	260.0	286.58
–30	38.12	—	–9	284.2	310.18
–29	42.27	—	–8	310.2	335.26
–28	46.80	—	–7	338.3	362.06
–27	51.87	—	–6	368.7	390.86
–26	57.34	—	–5	401.8	421.80
–25	63.47	—	–4	437.4	454.74
–24	70.14	—	–3	475.8	489.81
–23	77.34	—	–2	517.4	527.55
–22	85.34	—	–1	562.4	567.83
–21	94.01	—	0	610.6	610.6
–20	103.4	—	1	—	656.9
–19	113.8	—	2	—	706.0
–18	125.2	—	3	—	758.1
–17	137.5	—	4	—	813.6
–16	151.0	—	5	—	872.5
			6	—	935.2
			7	—	1002
			8	—	1073
			9	—	1148
			10	—	1228.1
			11	—	1312.7
			12	—	1402.6
			13	—	1497.7
			14	—	1598.5
			15	—	1705.3

11.7.2 The solid ⇔ gas transition

From the data referred to §11.7.1, we first note that the vapour pressure above a solid is broadly similar to that above a liquid. From this we conclude that, broadly speaking, the process of sublimation is equivalent to 'boiling from the solid' in contrast with the more usual 'boiling from the liquid'. Normally when the temperature is high enough for a substance to have a significant vapour pressure the substance has already melted. However arsenic, for example, does not melt until a temperature which is higher than the temperature at which the vapour pressure is one atmosphere.

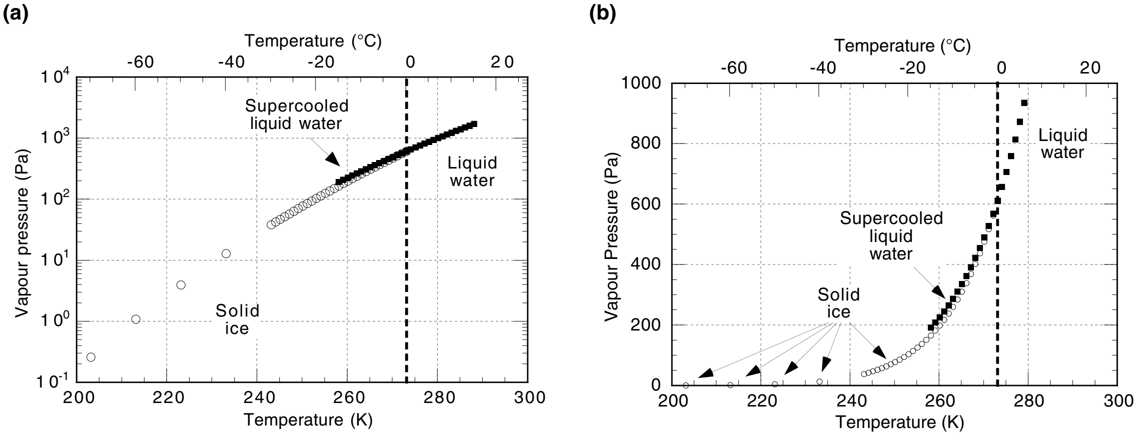


Figure 11.25 The vapour pressure of water and ice as function of temperature (Table 11.6) Plotted on (a) a logarithmic and (b) a linear vertical scale. Note the vapour pressure data is plotted logarithmic scale. The figure shows data for liquid water which has been supercooled below its freezing temperature, 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.

We will consider sublimation in two different ways: first microscopically, and then in terms of the Gibbs free energies of the phases.

Microscopic considerations

Let us use the cell model of liquid dynamics outlined in §8.4, to try to understand the situation of arsenic in its liquid state.

Figure 11.26, is intended as schematic illustration and is not to be considered quantitatively, but indicates plausibly the situation of arsenic. It shows a situation in which ΔE_h is greater than ΔE_e. In other words, the activation energy for the ‘hopping’ process is greater than the energy ΔE_e for escape from the substance altogether. Recall that ΔE_h is the activation energy involved when a liquid flows. Thus Figure 11.26 illustrates a substance which evaporates before it flows. We now need to understand how this could situation could arise.

Arsenic

For arsenic the situation is mainly due to anomalously weak and directional bonds between the atoms. Consider the data from Table 11.1 on the enthalpy of fusion of the elements around arsenic:

We see that the enthalpy of vaporisation for arsenic is anomalously low in comparison to its enthalpy of fusion. This indicates, as we supposed, that evaporation is relatively easy in comparison with melting. The high energy involved in forming the liquid state is likely to arise because of a high degree of directional covalent bonding between atoms. The weakness of the bonding is likely to arise because of the difficulty of fully bonding its

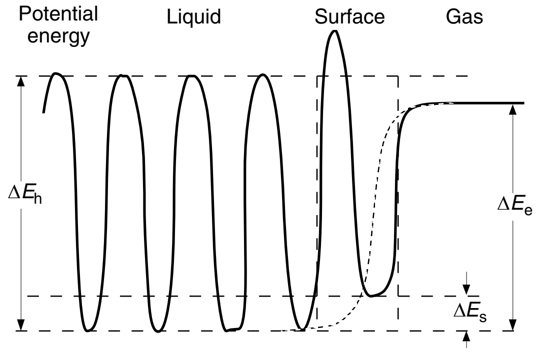


Figure 11.26 An illustration of the cell model with parameters appropriate to arsenic. Ignoring the situation at the surface of the liquid, we notice immediately that ΔE_h is greater than ΔE_e. In other words the activation energy for the ‘hopping’ process is less than the energy ΔE_e for escape from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

Extract from Table 11.1

Z	Name	Density ($kg\ m^{-3}$)	Melting point (K)	Boiling point (K)	Enthalpy of fusion ($kJ\ mol^{-1}$)	Enthalpy of vaporisation ($kJ\ mol^{-1}$)
31	Gallium	5905	302.93	3676	5.59	256.1
32	Germanium	5323	1210.6	3103	34.7	334.3
33	Arsenic	5776	Sublimes at 886		27.7	31.9
34	Selenium	4808	490	958.1	5.1	26.32

five valence electrons. The crystal structure adopted by arsenic in trying to do this is complex and changes with temperature. In the structure adopted just below the sublimation temperature, the arsenic atoms first form strongly bonded tetrahedra, which are then relatively weakly bonded to each other.

Carbon

For carbon we can understand the reluctance to form a liquid state in terms of the exceptional strength and directionality of the C–C covalent bond. This makes the 'hopping' processes required for liquid behaviour extremely energetically costly.

Gibbs free energy considerations

In §10.2, we considered the transformation from solid to liquid by examining schematic Gibbs free energy diagrams. We noted that the *free energies* of the solid and liquid states were particularly sensitive to the difference in their *cohesive energy* at $T = 0$ K. In Figures 10.2 and 10.3, we saw the effect on potassium of increasing the energy of the liquid state by 5 % of the cohesive energy of the solid. This caused the predicted melting temperature to increase by 62 %, from 307 K to 498 K. So if the cohesive energy of the liquid state $|U_{\text{liquid}}|$ is particularly small, then it seems quite plausible that this could shift the melting transition to considerably higher temperatures. In this case it appears that T_M is shifted even above T_B. The reason that the cohesive energy of the liquid state is high is due to the difficulty of optimally bonding to other atoms in the disordered liquid state,

In the case of arsenic matters are complicated by the complex crystal structure, and the structural transformation from one crystal structure to another at around 500 K. In order to represent this we would need to draw a fourth line on Figure 10.3 representing the Gibbs free energy of gas, liquid and the two solid phases. This situation is too complex for further consideration at this level.

11.8 The triple point

11.8.1 Data on the triple point

In the previous sections, we examined data on the transitions between the states of matter discussed earlier: solid ⇔ liquid, solid ⇔ gas and liquid ⇔ gas. These transitions take place over a range of temperatures depending on the pressure at which the substance is investigated. However, there is a temperature at which all three phases of matter can co-exist in equilibrium. This is called the *triple–point temperature* and is a characteristic temperature for each pure substance. Table 11.7 shows that the triple point occurs at a temperature just a little above the melting temperature.

So the main question raised by our preliminary examination of the experimental data on the triple points of substances is:

- Why is the triple-point temperature T_{Tr} so close to the melting temperature T_M of a substance at atmospheric pressure?

11.8.2 Understanding the triple-point data

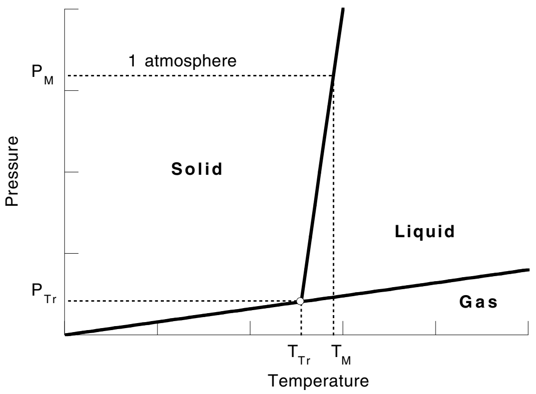
As we saw in §10.7, the triple point lies at the intersection of the solid ⇔ liquid phase boundary (the melting curve) and liquid ⇔ gas phase boundary (the vaporisation curve). We have men-

Table 11.7 The melting, boiling and triple-point temperatures of various substances. The T_{tr} values are often known extremely accurately. The T_M and T_B values are typically known to within ≈ 10 mK.

Substance	T_M (K)	T_{Tr} (K)	T_B (K)
Oxygen	54.35	54.3584	90.188
Nitrogen	63.15	63.150	77.352
Argon	83.75	83.8058	87.29
Water	273.15	273.16	373.15

tioned previously (Examples 10.6 and 10.7) that the slope of the melting curve was very much steeper than the slope of the vaporisation curve. We shall make a calculation in moment, but before we calculate anything, it is worth just noting that it is the extreme steepness of the melting curve which causes the triple point to lie close to the melting temperature at atmospheric pressure. As illustrated in Figure 11.27, changing the pressure on a substance by several orders of magnitude has relatively little effect on the melting temperature.

Figure 11.27 A schematic phase diagram illustrating the relative steepness of the solid ⇔ liquid phase boundary in comparison with the liquid ⇔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.



The slope of each of these phase boundaries may be predicted using the Clausius–Clapeyron equation. At the solid ⇔ liquid phase boundary:

$$\frac{dP_M}{dT_M} = \frac{(S_1 - S_2)}{(V_1 - V_2)} = \frac{\Delta Q_M}{T_M(V_L - V_S)} \qquad (10.55^* \text{ and } 11.13)$$

and at the liquid ⇔ gas phase boundary:

$$\frac{dP_B}{dT_B} = \frac{(S_1 - S_2)}{(V_1 - V_2)} = \frac{\Delta Q_B}{T_B(V_G - V_L)} \qquad (10.46^* \text{ and } 11.14)$$

From Figure 11.9 we notice that the ratio $\Delta Q_B / T_B$ to $\Delta Q_M / T_M$ is around 10 for many elements, and so we write that roughly:

$$\frac{dP_M}{dT_M} \approx \left[10 \times \frac{(V_G - V_L)}{(V_L - V_S)}\right] \frac{dP_B}{dT_B} \qquad (11.15)$$

Now the volume of a gas, though thoroughly variable, is around 1000 times the volume of the equivalent solid at around atmospheric pressure. The volume difference between a liquid and a solid (Figure 9.1) is typically ≈ 10% of the solid volume. Using these approximations we find that:

$$\frac{dP_M}{dT_M} \approx \left[10 \times \frac{1000 V_S}{0.1 V_S}\right] \frac{dP_B}{dT_B} \approx 10^5 \frac{dP_B}{dT_B} \qquad (11.16)$$

Equation 11.16 indicates that the slope of the melting curve is typically 10^5 times steeper than the slope of the vaporisation curve. This is also clear graphically in either of the examples in Figures 10.16 and 10.17. The consequence of this is that, in comparison with the vaporisation curve, the melting curve on a phase diagram is nearly vertical. So the *pressure* at which the vaporisation curve intersects the melting curve hardly makes any difference to the *temperature* at which the intersection takes place. Recall that:

- the *melting temperature* is the intersection of the melting curve with a horizontal line at $P = 1$ atmosphere
- the *triple–point temperature* is the intersection of the melting curve with the vaporisation curve, and occurs at a different pressure.

However the extreme steepness of the melting curve means that the temperature difference between these two intersections is small, frequently less than a kelvin.

11.9 Other types of phase change

11.9.1 Introduction

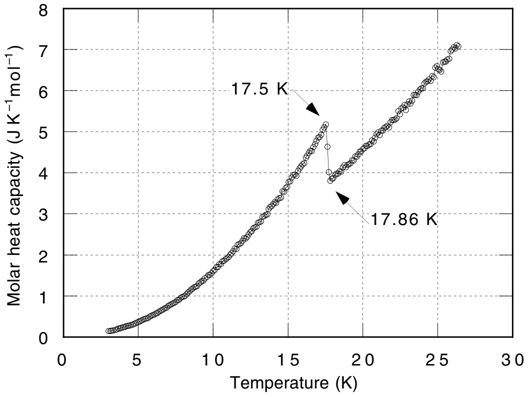
The transitions between the three phases of matter are manifest to us all. However, other transitions take place *within* all three phases of matter that also merit the title 'phase change'. These phase changes are often not apparent by merely looking at a substance. Let us look at some examples of phase changes, and then look to see what they have in common with melting, freezing, condensation, evaporation, and sublimation. Perhaps the main criterion that we consider when classifying a physical change as being due to a phase transition is that it should occur *suddenly*.

The superconducting transition.

As discussed in §7.7, below a temperature T_C, known as the *critical temperature*, the electrical resistivity of some substances falls suddenly to values indistinguishable from zero. Thus electric currents can flow without energy loss in these materials.

As determined by the electrical resistivity, the transition is extremely sharp. In pure unstrained materials the width of the transition may be only a few micro kelvin. The heat capacity of a superconducting compound Nb_3Sn (niobium-three-tin) (Figure 11.28) shows a large jump at T_C. It is quite clear that something has suddenly happened, or at least suddenly *started* to happen, when Nb_3Sn is cooled below T_C.

Figure 11.28 My own measurements of the heat capacity of Nb_3Sn. 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.



Superfluid

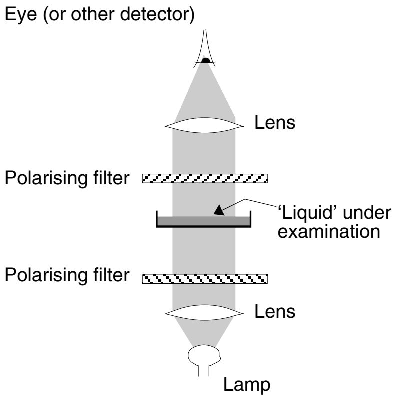
Helium, which behaved as a closely ideal gas in its gaseous phase, behaves as an *extremely* anomalous liquid when it condenses. The list of unusual properties is too long to enumerate here, but one of the most striking is that at atmospheric pressure the liquid does not solidify on cooling. Helium can be cooled as close to absolute zero as is achievable and still does not solidify. The origin of this phenomenon is the large value of the zero-point energy of helium (due to its low mass) when compared with weakness of its interatomic forces (due to its rigid electronic structure). The normal boiling temperature of the liquid is 4.2 K, but if the temperature is lowered below 2.172 K (precisely) the liquid begins to display so-called *superfluid* properties. These include the ability to flow with absolutely zero viscosity. The heat capacity in this range displays a large, very sharp peak deemed by early researchers to be shaped like the Greek letter λ (lambda) and hence known as the λ-transition. It is again clear that something has suddenly happened, or suddenly *started* to happen, when liquid helium is cooled below its λ-point.

Liquid crystal states

As we saw in Chapter 8, many organic substances may exist in a form intermediate between the liquid and solid states known as a *mesophase* or *liquid crystal state*. In these states the substances display unusual optical properties. If these, normally transparent, liquids are viewed in an arrangement similar to that shown in Figure 11.34, they display striking properties. The key feature of the apparatus is the two polarising filters on either side of the liquid under examination. Normal liquids do not significantly affect the polarisation of light passing through them.

Thus if the polarising filters are crossed no light is transmitted. However, above a certain transition

Figure 11.29 Apparatus for observing liquid crystal phases.



temperature these liquids strongly affect the polarisation of light passing through them. When viewed through a microscope as shown, the liquids look like a window on a frosty morning: crystals appear to have grown in from the edges of the container. However, crystals have not grown: the liquid is still a liquid in the sense that it will still flow, but something has certainly changed within the liquid. The onset of the effect is sudden, and the destruction of the effect above a second critical temperature is also sudden.

Ferromagnetic materials

As discussed in Chapter W2, in the absence of an applied magnetic field, the magnetic moment of a piece of iron at 771 °C is exactly zero. However, at 769 °C the magnetic moment becomes finite even in the absence of an applied magnetic field. The magnetic moment then increases in magnitude as the temperature is lowered below the *Curie temperature* of 770 °C. Similar behaviour is observed in all ferromagnetic materials, although Curie temperatures vary significantly. Figure 11.30 shows the heat capacity of the alloy CePt which becomes ferromagnetic at around 6 K. The Curie temperatures of the ferromagnetic elements are: iron: 760 °C; nickel: 358 °C; cobalt: 1115 °C; gadolinium: 16 °C. All ferromagnetic substances show similar heat capacity anomalies close to their Curie temperature, and the anomaly in gadolinium is responsible for the unusually high value of its heat capacity at 20 °C noted earlier in Table 7.1.

11.9.2 Discussion

What these changes have in common is that at a particular temperature, 'something happens' or 'something starts to happen'. That is, 'some property' of the substance changes rapidly as the environment of the substance is changed by just a small amount. The differences between the different types of phase transition may be considered to be 'merely' to do with the physical property that changes suddenly. Many of these transitions are accompanied by heat capacity anomalies which often look somewhat similar, even though the processes taking place are dramatically different.

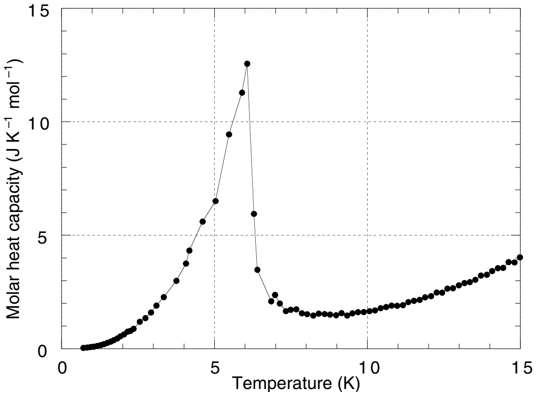
The main questions raised by our preliminary examination of the experimental data on different types of phase changes are:

- Why do phase changes occur suddenly at a well-defined temperature?
- Why do materials display similar anomalies in their heat capacity around these transitions?

That these questions are raised in the last section of the penultimate chapter of this book is perhaps something of a shame. Understanding and providing answers to these questions has been a triumph of twentieth-century mathematical physics. Indeed, as I write I have in front of me two books devoted entirely to answering these questions.

Perhaps the simplest way to consider these various transitions is to consider how they would look on a free energy diagram. In fact, for all the transi-

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



tions I have mentioned, the transitions are *continuous* rather *first-order*, in the sense used in Figure 10.6. What happens is that above the transition temperature, the substance fluctuates and 'discovers' that certain types of fluctuation have lower entropy, and lower energy. Recall the form of the Gibbs free energy:

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

and that the equilibrium phase of a substance is the phase which minimises G. Lower *energy* states tend to minimise G, but lower *entropy* states in which there is extra order of some kind increase G. However as the temperature is lowered, the TS term becomes less significant and fluctuations into the ordered states become more likely. The fluctuations begin to grow, both in their time-scale, and their length-scale. Eventually, a point is reached at which the time-scale for the fluctuations has grown perhaps from picoseconds originally to microseconds and eventually to seconds. Similarly the length scale of the fluctuations grows from nanometres to metres. Below a certain temperature, the new type of behaviour exists throughout a sample.

In the previous paragraph, I have not discussed the type of order (i.e. what has happened) that has become established. In general, this is not at all obvious from the heat capacity curves. The heat capacity curves reflect the generic shape of he underlying free energy curves, and this is the reason for similar behaviour in $C(T)$ in widely differing substances.

To determine what has happened at a phase transition, we need to measure a property more directly related to type of order that the substance has 'discovered'. Measuring the magnetisation, resistivity or polarisability generally gives a good idea of the nature of the phase change involved.

Finally I should mention that not all phase changes within the liquid or solid are continuous in nature. Many such transitions, particularly structural transitions, are first-order.

11.10 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

C1. From Table 11.1 find out which element has:
(a) the highest melting temperature?
(b) the fourth highest melting temperature?
(c) the highest latent heat of melting (fusion) per mole?
(d) the highest latent heat of vaporisation per mole?
(e) the highest ratio of latent heat of vaporisation per mole to the latent heat of melting (fusion) per mole? (You may need to use a spreadsheet for this last part.

P2. Which quantities in Table 11.1 are the best indicator of the cohesive energy of an element? Justify your answer. From Table 11.1, estimate which element has the highest cohesive energy per mole and compare your answer with the calculated results in Table 11.5.

P3. What is the boiling temperature of (a) methanol, (b) ethanol, and (c) acetone (Table 11.2)?

C4. The melting and boiling temperatures of the alkali halides are listed in Table 11.2. Do these temperatures show any systematic variation with the member of the halide family involved? Is the weak variation of melting temperature with components what you would have expected from the discussion of ionic and covalent bonding in §6.3?

P5. How much energy is required to melt 1 kg of (a) helium, (b) neon, (c) argon, (d) krypton? (Table 11.1)

P6. How much energy is required to melt 1 kg of (a) copper, (b) silver, (c) gold, (d) mercury? (Table 11.1)

P7. Based on Figures 11.3 and 11.4, indicate to what extent knowledge of the melting temperature and molar enthalpy of fusion of an element with atomic number Z are sufficient to predict the melting temperature and molar enthalpy of fusion of the element with atomic number $Z + 1$. Include a discussion of the relationship between the variation shown in Figures 11.3 and 11.4 and the periodic table (Figure 2.2)

P8. By how much does the melting temperature of gold (Table 11.1, Figure 11.5) change when atmospheric pressure changes from 1 to 1.1 atmospheres?

P9. Repeat the Lindemann melting theory calculation of Example 11.3 for gold. Does your answer lie within the one standard deviation limits drawn on Figure 11.8?

P10. How good are the rough estimates of the enthalpy of fusion and vaporisation of the elements indicated in Figure 11.9? Based on the rough figures in the legend to Figure 11.9, estimate the enthalpy of fusion and vaporisation for (a) an element with T_M = 1683 K and T_B = 2628 K, (b) an element with T_M = 1357 K and T_B = 2840 K, and (c) an element with T_M = 3680 K and T_B = 5930 K. Compare your results with the actual values in Table 11.1. Can you identify the elements?

P11. An unknown elemental metal has its melting temperature determined with an uncertainty of ±3 K. How well would this serve to uniquely identify the element? (Table 11.1 and Figure 11.3)

P12. How much energy is required to boil 1 kg of (a) helium, (b) neon, (c) argon, (d) krypton? (Table 11.1)

P13. How much energy is required to boil 1 kg of (a) copper, (b) silver, (c) gold, (d) mercury? (Table 11.1)

C14. The temperatures at which the vapour pressures of several organic substances reach 10^3, 10^4 and 1.013×10^5 Pa are listed below. Estimate their molar latent heat of vaporisation (kJ mol^{-1}) (Equations 9.16 & 11.8)

Substance	***T* (K) for *P* =10³ Pa**	***T* (K) for *P* =10³ Pa**	**T_B (K)**
Acetic acid,CH_3COOH	—	329	391.1
Acetone, CH_3COCH_3	237	349	329.3
Aniline, C_6H_7N	337	385	457.6
Benzene, C_6H_6	—	293	353.2
Chloroform, $CHCl_3$	240	278	334.4
Cyclohexane, C_6H_{10}	—	292	353.8
Ethyl acetate, $C_4H_8O_2$	255	294	350.2
Methanol, CH_3OH	253	288	337.7
Ethanol, C_2H_5OH	267	302	351.5
Propan-1-ol, C_3H_7OH	284	320	370.3
Propan-2-ol, C_3H_7OH	274	307	355.4
Butan-1-ol, C_4H_9OH	301	338	390.35
Butan-2-ol, C_4H_9OH	288	322	372.65
Toluene, C_7H_8	275	318	383.8

P15. What are the critical temperature, pressure and molar volume of (a) water (b) carbon dioxide and (c) ethanol? What is the density of each of these substances in the critical state, and roughly what fraction of the solid density does this correspond to? (Table 11.4)

P16. Calculate the volume per molecule of water in (a) its critical state and (b) its liquid state at 20 °C (Example 11.5, Figure 11.12)

C17. Based on the data in Table 11.1 estimate the average scaling law ratios between T_B, T_C and T_M for the elements. (Figures 11.22 and 11.23)

C18. Figure 11.6 indicates that there is a rough relationship between the Debye temperature of an element and its melting temperature. Use the data in Tables 7.12 and 11.1 to produce a rule of thumb relating θ_D and T_M

P19. Predict the Debye temperature of copper based on the melting temperatures of copper, silver and gold and the Debye temperatures of gold and silver (Tables 11.1 and 7.12). How good is your estimate?

P20. Identify the elements in Figure 11.23 which have anomalously low boiling points for their cohesive energy. Explain how these anomalies arise and why their existence does not invalidate the general correlation of boiling temperature and cohesive energy?

P21. What is the equilibrium vapour pressure above (a) ice and (b) water (if applicable) at a temperature of (i) 0 °C, (ii) –10 °C and (iii) –20 °C. (Table 11.6) Based on your answers to these questions discuss whether there are any conditions under which snow might evaporate directly without first melting.

P22. Suggest a reason why the equilibrium vapour pressure above ice is slightly less than that above water (Table 11.6 and Figure 11.25 (a) and (b)). How could you verify your suggestion?

P23. What is the triple point of (a) water and (b) argon (Table 11.7)

P24. In §9.8, the dependence of vapour pressure on temperature is discussed. Given the latent heat and the boiling temperature (Table 11.1) of the elements it is possible to estimate the vapour pressure at any temperature (Equation 9.35 and Table 11.3). Estimate the vapour pressure at 100 °C and 1000 °C of: (a) potassium, (b) copper, (c) iron and (d) tungsten

P25. A strong metal box containing water in its solid phase is heated from –20 °C to + 20 °C and the heat capacity of the combined object is measured continuously. If you had no *a priori* technique for separately accounting for heat supplied as latent heat and heat which raised the temperature of the box, then you would assume that there was 'anomaly' in the heat capacity of the box. Sketch the general form of the 'anomaly that you would observe. Discuss any similarities or difference between your graph and Figures 11.28 and 11.30.