

## CHAPTER

# 8



## Phase equilibria

We now come to discuss systems consisting of two or more phases in equilibrium. A phase is a homogeneous part of a system bounded by surfaces across which the properties change discontinuously. In the most general situation each phase will contain several components i.e. it will contain several different species of molecules or ions. For example a gaseous phase might consist of a mixture of gases; a liquid phase might be a solution. To specify the properties of a phase we must then specify the concentrations of the various components in it. One then has the possibility of transfer of matter between different phases and also of chemical reactions (which change the amounts of different components). Except for a brief discussion of multi-component systems in section 12.5, we shall restrict ourselves to the discussion of systems containing one component only, since a thorough treatment of multi-component systems would take up too much space.\* A one-component system can of course still exist in different phases, corresponding to gaseous, liquid and different crystalline forms of matter.

The problem of the equilibrium between different phases is much harder than any we have studied so far. The atomic viewpoint does, of course, provide a qualitative understanding of the observed phenomena. For example, the increasing degree of molecular disorder of crystalline,

\* The reader will find good discussions in the books by Landau and Lifshitz,<sup>8</sup> ter Haar and Wergeland,<sup>3</sup> Wilson,<sup>19</sup> and Zemansky.<sup>4</sup>

liquid and gaseous states explains qualitatively the entropy changes which accompany the processes of melting, evaporation and sublimation. But the statistical approach can deal with phase changes to a very limited degree only, and we shall use the methods of thermodynamics.

We now have the possibility of the transfer of matter between different phases (e.g. in a mixture of ice and water, some or all of the ice may melt). For different phases to be in equilibrium certain conditions must hold so that no mass transfer occurs. These conditions are additional to those we had earlier for temperature and pressure equilibrium. These additional conditions will be derived in sections 8.1 and 8.2, and we shall discuss them in section 8.3. The Clausius–Clapeyron equation and its applications will occupy sections 8.4 and 8.5, while section 8.6 will deal with the critical point and related topics.

## 8.1 EQUILIBRIUM CONDITIONS

We consider a one-component system and shall derive the conditions for two phases to coexist in equilibrium. The two phases could be solid and liquid (e.g. ice and water), liquid and vapour, solid and vapour, and there are other possibilities, such as different crystalline forms of the same substance, e.g. grey and white tin.

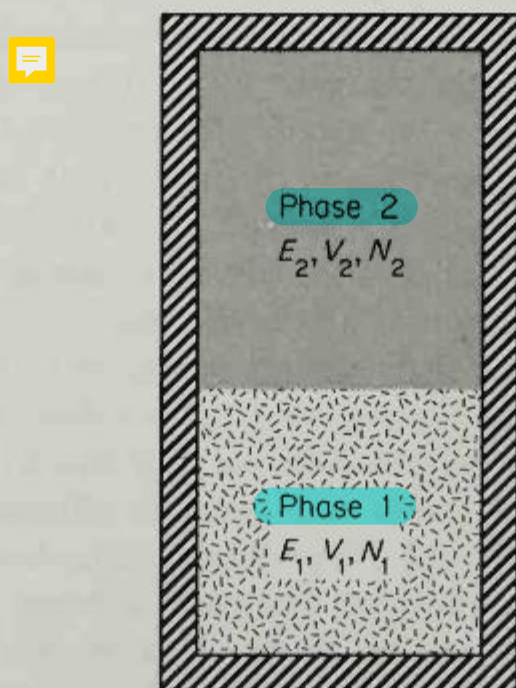


Fig. 8.1. Equilibrium of two phases of a one-component system in total isolation.



Our approach will be a direct generalization of that used in section 2.3, i.e. we shall assume the system totally isolated, as shown in Fig. 8.1, so that Eqs. (2.4a) to (2.4c) hold, namely

$$E_1 + E_2 = E \quad (8.1a)$$

$$V_1 + V_2 = V \quad (8.1b)$$

$$N_1 + N_2 = N \quad (8.1c)$$

which express the division of constant energy  $E$ , volume  $V$  and particle number  $N$  between the two phases. The entropy of the system is (cf. Eq. (2.6))

$$S(E, V, N, E_1, V_1, N_1) = S_1(E_1, V_1, N_1) + S_2(E_2, V_2, N_2) \quad (8.2)$$

where, as throughout this chapter, subscripts 1 and 2 label quantities in the two phases 1 and 2 respectively. For equilibrium of the system the entropy must be a maximum, i.e. from Eq. (8.2), treating  $E_1$ ,  $V_1$ , and  $N_1$  as the independent variables and eliminating  $E_2$ ,  $V_2$  and  $N_2$  by means of Eqs. (8.1),

$$\begin{aligned} dS = & \left[ \left( \frac{\partial S_1}{\partial E_1} \right)_{V_1, N_1} - \left( \frac{\partial S_2}{\partial E_2} \right)_{V_2, N_2} \right] dE_1 \\ & + \left[ \left( \frac{\partial S_1}{\partial V_1} \right)_{E_1, N_1} - \left( \frac{\partial S_2}{\partial V_2} \right)_{E_2, N_2} \right] dV_1 \\ & + \left[ \left( \frac{\partial S_1}{\partial N_1} \right)_{E_1, V_1} - \left( \frac{\partial S_2}{\partial N_2} \right)_{E_2, V_2} \right] dN_1 = 0 . \end{aligned} \quad (8.3)$$

Since  $E_1$ ,  $V_1$  and  $N_1$  are independently variable, each of the square parentheses in Eq. (8.3) must vanish for the system to be in equilibrium. The first two of these conditions (coefficients of  $dE_1$  and  $dV_1$  zero) are the conditions for equal temperatures (cf. Eq. (2.9)) and equal pressures (cf. Eq. (2.12)) for the two phases, as we discussed in section 2.3. The third condition

$$\left( \frac{\partial S_1}{\partial N_1} \right)_{E_1, V_1} = \left( \frac{\partial S_2}{\partial N_2} \right)_{E_2, V_2} , \quad (8.4)$$

mentioned in passing in Eq. (2.13), is the condition for particle equilibrium, i.e. no transfer of molecules between the two phases. We define the *chemical potential*  $\mu_i$  for each phase by

$$\mu_i = -T_i \left( \frac{\partial S_i}{\partial N_i} \right)_{E_i, V_i} , \quad i = 1, 2 . \quad (8.5)$$

Condition (8.4) then becomes

$$\mu_1 = \mu_2 \quad (8.6)$$

in equilibrium the chemical potentials of the two phases must be the same.

Before considering this condition further, we want to extend the thermodynamic relations which were derived in Chapters 2 and 4 to allow for the variable particle number. Considering only a single phase for the moment and so omitting the suffix  $i$ , we have for  $S = S(E, V, N)$ :

$$\begin{aligned} dS &= \left( \frac{\partial S}{\partial E} \right)_{V,N} dE + \left( \frac{\partial S}{\partial V} \right)_{E,N} dV + \left( \frac{\partial S}{\partial N} \right)_{E,V} dN \\ &= \frac{1}{T} dE + \frac{1}{T} P dV - \frac{1}{T} \mu dN, \end{aligned} \quad (8.7)$$

where we used Eqs. (2.9), (2.12) and (8.5), or on slight rearrangement

$$dE = T dS - P dV + \mu dN. \quad (8.8)$$

Eq. (8.8) is the generalization of the fundamental thermodynamic relation (4.12) for a one-component system whose size, i.e. particle number, is not kept fixed.

From Eq. (8.8) the chemical potential can be expressed in various ways depending on which of the variables  $E$ ,  $S$  and  $V$  are held constant. We can also introduce different independent variables and thermodynamic potentials, as in sections 4.4 and 4.5. It is left as an easy exercise for the reader (compare the derivations of Eqs. (4.43) and (4.49)) to show that, expressed in terms of the Helmholtz and Gibbs free energies, Eq. (8.8) becomes

$$dF = -S dT - P dV + \mu dN, \quad (8.9)$$

$$dG = -S dT + V dP + \mu dN, \quad (8.10)$$

whence

$$\mu = \left( \frac{\partial F}{\partial N} \right)_{T,V} = \left( \frac{\partial G}{\partial N} \right)_{T,P}. \quad (8.11)$$

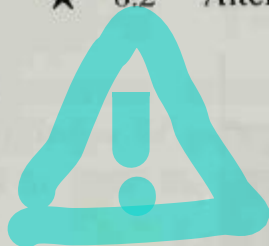
We see from Eqs. (8.8) to (8.10) that the chemical potential is always the derivative with respect to the particle number  $N$ .

In the case of a single one-component phase, the Gibbs free energy  $G(T, P, N)$  is an extensive variable, i.e. it is proportional to the particle number  $N$ :

$$G(T, P, N) = NG(T, P, 1) \equiv Ng(T, P) \quad (8.12a)$$



where



$$g(T, P) = \frac{1}{N}G(T, P, N) \quad (8.12b)$$

is the corresponding *Gibbs free energy per particle*. It follows from Eqns. (8.11) and (8.12) that

$$\mu = g(T, P) : \quad (8.13)$$

the chemical potential  $\mu$  is simply the Gibbs free energy per particle. But this result (8.13), like Eq. (8.12), *is only true for a homogeneous one-component system. It is not valid generally.*

Reverting now to our system consisting of one component in two phases, each phase by itself is, of course, a homogeneous one-component system so that Eq. (8.13) applies to it. Hence we can write the equilibrium condition (8.6) in the form:

$$g_1(T, P) = g_2(T, P) : \quad (8.14)$$

the *Gibbs free energies per particle for the two phases must be the same.*

So far one of our equilibrium conditions has always been that the system be at a uniform pressure. This condition frequently applies, but it depends on the neglect of surface effects. If, for example, we consider drops of liquid suspended in their vapour then surface tension effects will be important if the drops are small, and the pressures within and outside them are no longer the same.\*

In the next section we shall give an alternative derivation of the equilibrium conditions between phases.

## ★ 8.2 ALTERNATIVE DERIVATION OF THE EQUILIBRIUM CONDITIONS

In the last section we considered a one-component system in two phases, which was completely isolated. The more usual experimental conditions are that the temperature and pressure of the system are held constant, for example the system is immersed in a heat bath and is subject to atmospheric pressure. An idealized arrangement of such a system existing in two phases is shown in Fig. 8.2. We shall obtain the equilibrium conditions for this system. We know from section 4.5 that for a system at fixed temperature  $T$  and pressure  $P$ , the Gibbs free energy  $G$  is a minimum in equilibrium. We can write the Gibbs free

\* This problem is treated, for example, by Pippard<sup>2</sup> and Wannier.<sup>18</sup>

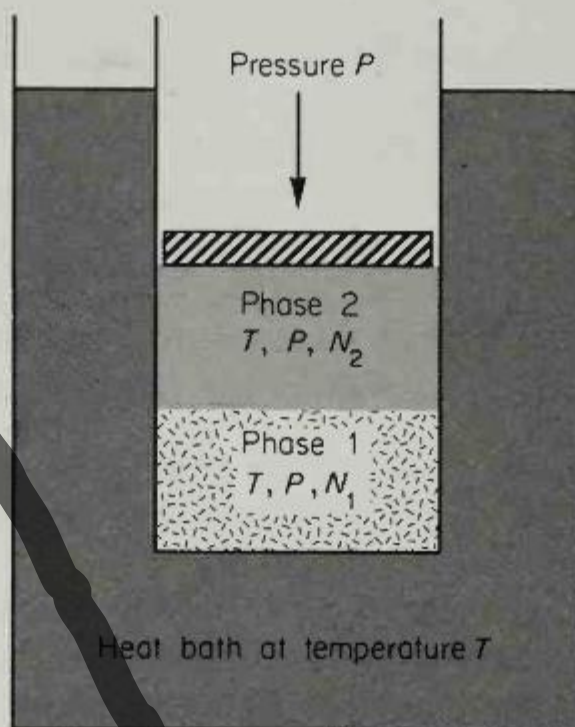


Fig. 8.2. Equilibrium of two phases of a one-component system in a heat bath and at constant pressure.

energy as

$$G \equiv G(T, P, N_1, N_2) = N_1 g_1(T, P) + N_2 g_2(T, P) \quad (8.15)$$

where we used the fact that each phase by itself is a homogeneous one-component system (cf. Eqs. (8.12));  $g_i$  and  $N_i$  are the Gibbs free energies per particle and the particle numbers of the two phases. From Eq. (8.15) we have

$$\begin{aligned} dG = & \left[ N_1 \frac{\partial g_1}{\partial T} + N_2 \frac{\partial g_2}{\partial T} \right] dT \\ & + \left[ N_1 \frac{\partial g_1}{\partial P} + N_2 \frac{\partial g_2}{\partial P} \right] dP \\ & + g_1(T, P) dN_1 + g_2(T, P) dN_2. \end{aligned} \quad (8.16)$$

For equilibrium we require  $G$  to be a minimum, i.e.

$$dG = 0 \quad (8.17)$$

subject to the constraints

$$dT = 0 \quad (8.18a)$$

$$dP = 0 \quad (8.18b)$$

$$N_1 + N_2 = N \quad (8.18c)$$



which express constant temperature, constant pressure and constant total number of particles for the system. From Eqs. (8.16) to (8.18) we obtain at once the equilibrium condition

$$dG = [g_1(T, P) - g_2(T, P)] dN_1 = 0, \quad (8.19)$$

whence the original equilibrium condition Eq. (8.14),  $g_1 = g_2$ , follows since  $N_1$  is freely variable. These equilibrium conditions for a system at constant pressure and temperature are the same as those for an isolated system. This is to be expected. For equilibrium between two phases they must be at the same pressure, temperature and chemical potential, irrespective of the applied constraints. Condition (8.14) ensures equilibrium with respect to particle transfer between the two phases.

### 8.3 DISCUSSION OF THE EQUILIBRIUM CONDITIONS

The condition (8.14),

$$g_1(T, P) = g_2(T, P), \quad (8.14)$$

defines a curve in the  $(T, P)$  plane, as shown in Fig. 8.3. At a point on the curve the chemical potentials of the two phases are the same; at a point off the curve they differ. Let us denote by 1 and 2 the regions in

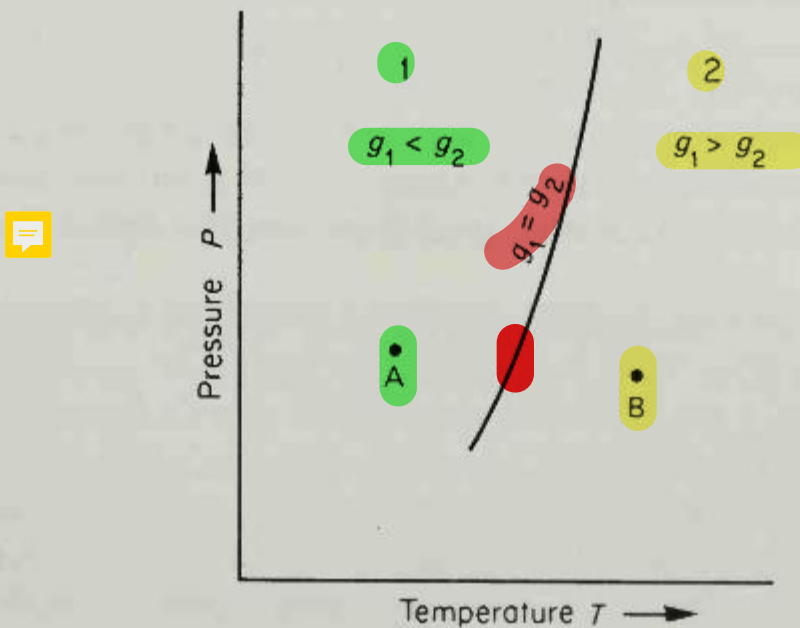


Fig. 8.3. The phase equilibrium curve ( $g_1 = g_2$ ) separating regions in which phases 1 and 2 respectively are the stable phases.

which we have  $g_1 < g_2$  and  $g_2 < g_1$  respectively. If  $N_1$  and  $N_2$  are the number of molecules in phases 1 and 2 respectively (with  $N_1 + N_2 = N = \text{constant}$ ) the Gibbs free energy of the system is

$$G = N_1 g_1(T, P) + N_2 g_2(T, P) . \quad (8.20)$$

For a system at a pressure and temperature given by the point A of Fig. 8.3, where  $g_1 < g_2$ , the Gibbs free energy (8.20) is a minimum if all the substance is in phase 1 (i.e.  $N_1 = N$ ,  $N_2 = 0$ ,  $G = N g_1(T, P)$ ). Similarly corresponding to point B,  $G$  is a minimum if all the substance is in phase 2. Thus the curve (8.14) divides the  $(P, T)$  plane into regions where the one or other phase represents the stable equilibrium state. It is only on the curve (where  $g_1 = g_2$  so that  $G = N g_1$  irrespective of the values of  $N_1$  and  $N_2 = N - N_1$ ) that the two phases can coexist in equilibrium. This curve is called a *phase equilibrium curve*. If the two phases are liquid and vapour it is called the vapour pressure curve, if solid and vapour the sublimation curve, and if solid and liquid the melting curve. For two coexisting phases of a one-component system we cannot choose the temperature *and* pressure arbitrarily. Given the temperature, the pressure is determined, and vice versa. For example, water vapour in contact with water at  $100^\circ\text{C}$  always has a pressure of one atmosphere.

Let us next consider the *equilibrium of three different phases* of a one-component system, solid, liquid and vapour, say, and let us label these *1, 2 and 3 respectively*. If we repeated the derivations of sections 8.1 or 8.2 we would obtain the equilibrium conditions

$$g_1(T, P) = g_2(T, P) = g_3(T, P) . \quad (8.21)$$

But we can also see this directly, since equilibrium between all three phases demands equilibrium between any pair of them. So we obtain a condition like Eq. (8.14) for each pair of phases, and hence Eqs. (8.21) follow.

We have seen that an equation such as Eq. (8.14) defines a phase equilibrium curve (Fig. 8.3). For points on this curve the two phases are in equilibrium. Eqs. (8.21) represent the intersection of the two curves  $g_1 = g_2$  and  $g_2 = g_3$  in the  $(T, P)$  diagram. This intersection defines a point in the  $(T, P)$  diagram: the *triple point*. This is shown in Fig. 8.4 which is known as the *phase diagram* of the system. (In general, the phase diagram even of a one-component system will be more complex. See, for example, Fig. 8.5 below.) Of course, at the triple point we also have  $g_1 = g_3$ . The triple point is the intersection of three phase equilibrium curves: the vapour pressure curve, the sublimation curve and the melting curve. At the triple point all three phases are in



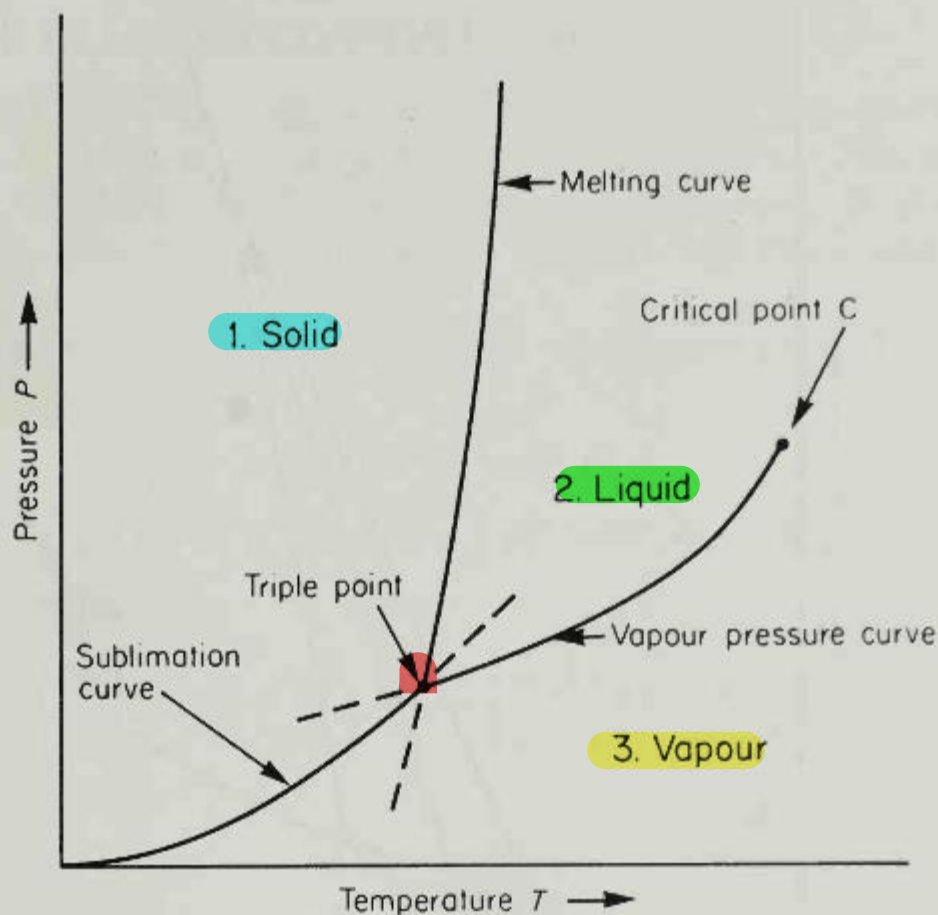


Fig. 8.4. Phase diagram of a one-component system possessing one triple point only.

equilibrium with each other. The triple point of water, for example, occurs at  $P = 4.58 \text{ mmHg}$  and  $T = 0.01^\circ\text{C}$ . Because ice, water and water vapour coexist at a unique temperature, the triple point of water is used as the fixed point of the absolute temperature scale (see section 1.2). It follows from Eqs. (8.21) (two equations in two unknowns) that the maximum number of coexisting phases of a one-component system is three.

On the other hand a pure substance may be capable of existing in more than one allotropic form and it will then have several triple points. Fig. 8.4 is a particularly simple phase diagram. Fig. 8.5 shows schematically the phase diagram for sulphur which can exist in two different crystalline forms, rhombic and monoclinic. It has three triple points which occur at: (A)  $10^{-6}$  atmospheres,  $95.5^\circ\text{C}$ ; (B)  $4 \times 10^{-6}$  atmospheres,  $119^\circ\text{C}$ ; (C) 1,400 atmospheres,  $153.7^\circ\text{C}$ .

Reverting to Fig. 8.4, the three phase equilibrium curves divide the  $(T, P)$  plane into three regions in which the solid, liquid and gaseous phases respectively are the stable state (i.e. have the lowest chemical potential). Although not true equilibrium states (i.e.  $G$  is not a minimum)

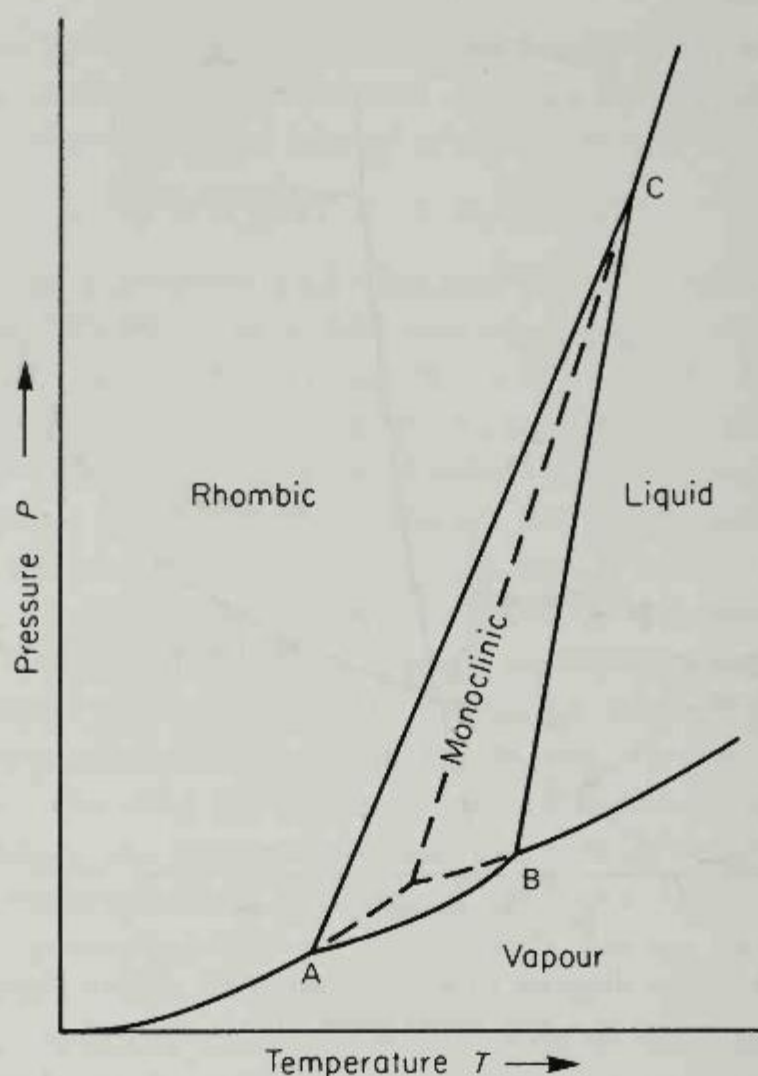


Fig. 8.5. Schematic phase diagram for sulphur.

metastable states can exist for quite long times under suitable conditions. For example, it is possible for a supersaturated vapour to exist in region 2 (of Fig. 8.4), well above the saturation vapour pressure. Similarly one can have supercooled liquids in region 1, or superheated liquids in region 3. In each case the persistence of the metastable state depends on the absence of nuclei which can start condensation, etc.

We may also imagine the phase equilibrium curves continued beyond the triple point as shown by the dashed curves in Fig. 8.4. For example, along the dashed continuation of the vapour pressure curve supercooled liquid and vapour may coexist in a metastable state (along this curve  $g_2 = g_3 > g_1$ ). For sulphur, Fig. 8.5, the existence of metastable phase equilibrium curves leads to a metastable triple point at which rhombic sulphur coexists with the liquid and vapour.

In Fig. 8.4 the vapour pressure curve comes to an abrupt end at the critical point, the significance of which will be discussed in section 8.6.



## 8.4 THE CLAUSIUS–CLAPEYRON EQUATION

The Clausius–Clapeyron equation which we shall now derive is the differential equation for a phase equilibrium curve. The equation specifies the slope  $dP/dT$  at each point of the curve. It thus gives information about the dependence on pressure and temperature of the phase equilibrium.

For two points A and B on a phase equilibrium curve, Fig. 8.6, we have

$$g_1(T, P) = g_2(T, P) \quad (8.22a)$$

$$\text{[icon]} \quad g_1(T + dT, P + dP) = g_2(T + dT, P + dP) , \quad (8.22b)$$

whence by subtraction

$$\left(\frac{\partial g_1}{\partial T}\right)_P dT + \left(\frac{\partial g_1}{\partial P}\right)_T dP = \left(\frac{\partial g_2}{\partial T}\right)_P dT + \left(\frac{\partial g_2}{\partial P}\right)_T dP \quad (8.23)$$

so that

$$\frac{dP}{dT} = - \frac{\Delta \left(\frac{\partial g}{\partial T}\right)_P}{\Delta \left(\frac{\partial g}{\partial P}\right)_T} . \quad (8.24)$$

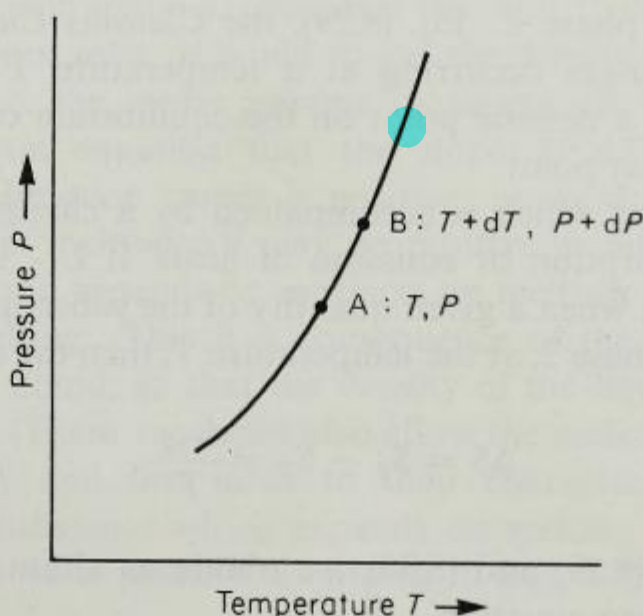


Fig. 8.6. The phase equilibrium curve  
 $g_1(T, P) = g_2(T, P)$ .

Here we introduced the notation

$$\Delta f \equiv f_2 - f_1 \quad (8.25)$$

for the difference of the quantity  $f$  in the two phases.

We can write Eq. (8.10) for each phase separately as

$$dG_i = -S_i dT + V_i dP + \mu_i dN_i. \quad (8.26)$$

For a one-component phase, we have from Eqs. (8.12) and (8.13) that  $\mu_i = g_i$  and  $G_i = N_i g_i$ . Hence Eq. (8.26) becomes

$$N_i dg_i = -S_i dT + V_i dP, \quad (8.27)$$

so that

$$\left(\frac{\partial g_i}{\partial T}\right)_P = -\frac{S_i}{N_i}, \quad \left(\frac{\partial g_i}{\partial P}\right)_T = \frac{V_i}{N_i}. \quad (8.28)$$

Substituting expressions (8.28) into Eq. (8.24) gives

$$\frac{dP}{dT} = \frac{\Delta\left(\frac{S}{N}\right)}{\Delta\left(\frac{V}{N}\right)} = \frac{\Delta S}{\Delta V}, \quad (8.29)$$

where in the last expression on the right-hand side  $\Delta S$  and  $\Delta V$  must refer to the *same* quantity of substance: it could be one molecule or one mole.  $\Delta S$  is the change in entropy,  $\Delta V$  the change in volume of this same quantity of substance as it undergoes a phase transformation from phase 1 to phase 2. Eq. (8.29), the *Clausius-Clapeyron equation*, relates these changes occurring at a temperature  $T$  and pressure  $P$  corresponding to a definite point on the equilibrium curve to the slope of the curve at that point.

A phase change, which is accompanied by a change in entropy  $\Delta S$ , involves the absorption or emission of heat. If  $L_{12}$  is the latent heat of transformation when a given quantity of the substance is transformed from phase 1 to phase 2, at the temperature  $T$ , then the entropy change is

$$\Delta S = S_2 - S_1 = \frac{L_{12}}{T}. \quad (8.30)$$

Combining Eqs. (8.29) and (8.30), we obtain as alternative form of the *Clausius-Clapeyron equation*

$$\frac{dP}{dT} = \frac{L_{12}}{T\Delta V}. \quad (8.31)$$



Again, the extensive quantities  $L_{12}$  and  $\Delta V$  must refer to the same amount of substance.

The phase change we have considered is characterized by the discontinuities (as one goes from one phase to the other) of the numerator and denominator of Eq. (8.24). These discontinuities imply differences in entropy and molar volume (i.e. density) between the phases. The entropy difference implies that the phase change involves a latent heat. This type of phase change is called a *first-order transition*. Solid-liquid-vapour phase changes and many allotropic transitions, e.g. grey to white tin, are of this kind. There are phase changes in which the numerator and denominator of Eq. (8.24) are continuous, i.e. entropy and density are continuous (so that no latent heat is involved) but some higher-order derivatives of  $g_i$  and other thermodynamic quantities, such as the specific heat, are discontinuous or may become infinite. We shall not consider these kinds of phase changes.

From the Clausius–Clapeyron equation several interesting deductions are possible. For the processes of melting, evaporation and sublimation, the entropy changes  $\Delta S$  (and hence the corresponding latent heats) are positive.\* That  $\Delta S$  is positive for these phase changes is a consequence of the fact that these are changes from more to less ordered states of the system. The atoms in a crystal are arranged regularly at the lattice sites so that one here has long-range order over the whole size of the crystal. Except near the boiling point, liquids show a considerable degree of short-range order, i.e. liquids possess localized structure, as in a crystal except that there are many vacant sites; about one in ten. In a gas there is almost no structure left. These different degrees of order show up in x-ray diffraction experiments (see Hill,<sup>23</sup> section 6.3). For a transformation from solid or liquid to gas the density decreases so that  $\Delta V$  is positive (i.e. the molar volume increases). It follows from the Clausius–Clapeyron equation that the slope  $dP/dT$  of the vapour-pressure and sublimation curves is positive; as we drew it in Fig. 8.4. For the process of melting  $\Delta V$  may be positive or negative depending on whether the solid expands or contracts on melting. Most substances expand upon melting. This is a consequence of the large number of vacant sites in a liquid, so that the density of the liquid is lower than that of the solid. (These vacancies also allow the molecules in the liquid to migrate easily and this leads to their characteristic property of fluidity.) For a substance which expands on melting the slope  $dP/dT$  of the melting curve is positive, as drawn in Fig. 8.7(a). But there are

\* The behaviour of the isotope helium 3 ( $^3\text{He}$ ) at temperatures below 1 °K and at pressures in the range of about 29 to 38 atm is an exception. If we heat liquid  $^3\text{He}$  at a constant pressure in this range, starting at a sufficiently low temperature, the liquid will first solidify and then melt again. See, for example, Adkins<sup>1</sup> or Zemansky.<sup>4</sup>



exceptional substances such as water (ice floats on water!) which contract on melting and for which the melting curve has a negative slope as shown in Fig. 8.7(b).<sup>\*</sup> This behaviour in ice is due to its very open tetrahedral crystal structure. On melting, both the nearest-neighbour distance and the number of nearest neighbours increases, and the latter effect outweighs the former.

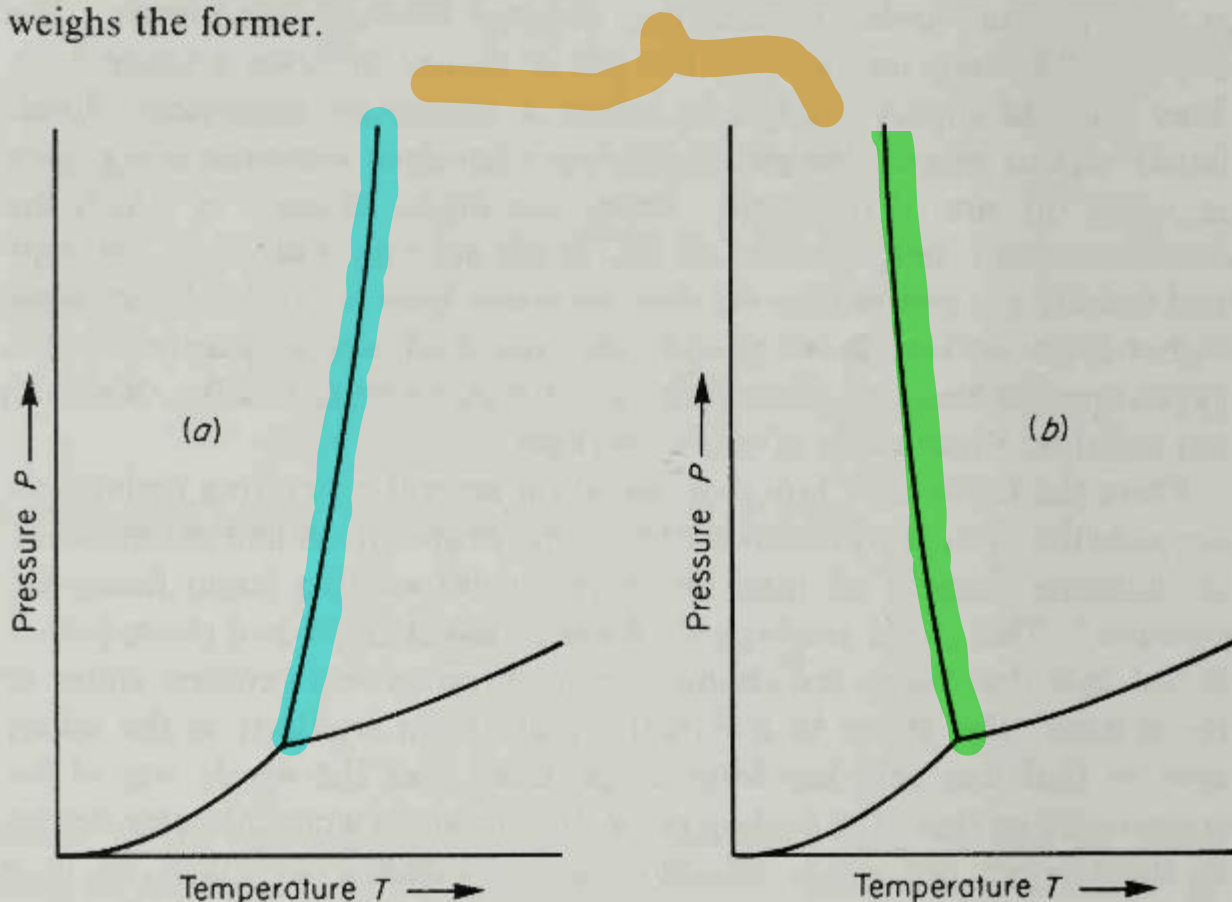


Fig. 8.7. Phase diagram for a substance which possesses only one triple point, and which: (a) expands on melting, (b) contracts on melting.

## 8.5 APPLICATIONS OF THE CLAUSIUS-CLAPEYRON EQUATION

We give some simple illustrative applications of the Clausius-Clapeyron equation in this section.

### 8.5.1 Pressure dependence of the melting point

We consider the equilibrium between ice and water as an example of the pressure dependence of the melting point. To calculate this effect from the Clausius-Clapeyron equation (8.31) we require: (i) the latent heat of fusion  $L_{12}$  of water: at  $0^\circ\text{C}$

$$L_{12} = 335 \times 10^7 \text{ erg/g} ;$$

<sup>\*</sup> Actually water has a much more complicated phase diagram since ice can exist in several modifications.



(ii) the volumes per gram in the solid and liquid phase are, respectively,

$$V_1 = 1.09070 \text{ cm}^3/\text{g}, \quad V_2 = 1.00013 \text{ cm}^3/\text{g},$$

so that  $\Delta V = V_2 - V_1 = -0.0906 \text{ cm}^3/\text{g}$ . Hence from Eq. (8.31)

$$\begin{aligned} \frac{dP}{dT} &= -\frac{335 \times 10^7}{273.2 \times 0.0906} = -1.35 \times 10^8 \text{ dyn cm}^{-2} (\text{°C})^{-1} \\ &= -134 \text{ atm/°C}. \end{aligned}$$

Thus an increase in pressure of 134 atmospheres lowers the melting point by 1 °C. An increase in pressure of 1,000 atmospheres lowers the melting point by 7.5 °C, in excellent agreement with the observed value of 7.4 °C. Similarly good agreement is obtained for other substances. The lowering of the melting point of ice under pressure is responsible for the motion of glaciers. The deeper parts of a glacier melt under the weight of ice on top of them allowing them to flow. They freeze again when the pressure decreases. In this way ice against a rock on the bed of the glacier can flow round the obstructing rock. Ice skaters similarly depend for lubrication on the melting of the ice in contact with the skate.

### 8.5.2 Pressure dependence of the boiling point

Since  $\Delta V$  is always positive for the transformation of liquid to vapour, increasing the pressure on a liquid always increases the boiling point. We again take water at the normal boiling point as an example. In this case we have: (i) the latent heat of vaporization

$$L_{12} = 2,257 \times 10^7 \text{ erg/g};$$

(ii) the volume per gram in the liquid and vapour phase at  $T = 373.15 \text{ °K}$  and  $P = 1 \text{ atm}$  are, respectively,

$$V_1 = 1.043 \text{ cm}^3/\text{g}, \quad V_2 = 1,673 \text{ cm}^3/\text{g}. \quad (8.32)$$

Hence Eq. (8.31) gives

$$\begin{aligned} \frac{dP}{dT} &= \frac{2,257 \times 10^7}{373.15 \times 1,672} = 3.62 \times 10^4 \text{ dyn cm}^{-2} (\text{°C})^{-1} \\ &= 27 \text{ mmHg/°C}. \end{aligned} \quad (8.33)$$

A pressure of 1 atmosphere is  $1.0132 \times 10^6 \text{ dyn/cm}^2$ . Thus at a pressure of  $3.6 \times 10^5 \text{ dyn/cm}^2$  (approximately atmospheric pressure at an altitude of 8 km, the height of Mount Everest)

$$\Delta P = -6.5 \times 10^5 \text{ dyn/cm}^2,$$

whence

$$\Delta T \approx -\frac{65}{3.6} = -18^\circ\text{C}$$

i.e. water boils at about  $80^\circ\text{C}$  at this height.

### 8.5.3 The vapour pressure curve

The Clausius–Clapeyron equation for the vapour pressure curve admits the following approximate treatments.

Firstly, we may neglect the volume of the liquid compared with that of the gas:  $V_1 \ll V_2$  so that

$$\Delta V = V_2 - V_1 \approx V_2. \quad (8.34)$$

For water at its normal boiling point, for example, we see from Eq. (8.32) that this introduces an error of less than 0.1 per cent. Secondly, we shall assume that the vapour behaves like a perfect gas. For one gram of vapour we then have

$$PV_2 = RT/M, \quad (8.35)$$

where  $M$  is the gram-molecular weight. Substitution of Eqs. (8.34) and (8.35) in Eq. (8.31) leads to

$$\frac{d}{dT} \ln P = \frac{1}{P} \frac{dP}{dT} = \frac{ML_{12}}{RT^2}. \quad (8.36)$$

For water at its normal boiling point, the data in section 8.5.2 give  $dP/dT = 3.56 \times 10^4 \text{ dyn cm}^{-2} \text{ K}^{-1}$ , in very good agreement with the value  $3.62 \times 10^4$ , Eq. (8.33), obtained in the exact calculation.

If we treat the latent heat of vaporization  $L_{12}$  as a constant, Eq. (8.36) can be integrated analytically to give

$$P = \text{const.} \exp \left[ -\frac{ML_{12}}{RT} \right]. \quad (8.37)$$

Eq. (8.37) will always hold for small temperature changes. For larger variations of  $T$ , Eq. (8.37) gives only a very rough value for the vapour pressure, as the latent heat varies appreciably for large temperature changes. Fig. 8.8 illustrates this for water.

Eq. (8.37) should be compared with the Sackur–Tetrode vapour pressure formula (7.54). The latter, derived from statistical mechanics, contains *no* undetermined constant. Furthermore in deriving Eq. (7.54) the latent heat was *not* assumed independent of temperature (the most objectionable feature in the derivation of Eq. (8.37)). The only approxi-



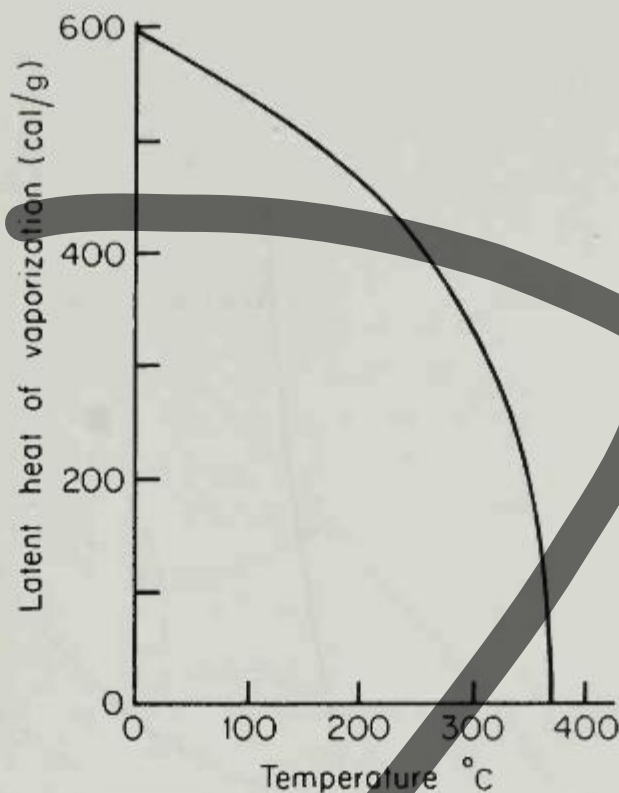


Fig. 8.8. The temperature dependence of the latent heat of vaporization of water.

mation made in obtaining the Sackur–Tetrode equation was to treat the vapour as a perfect gas, and this is generally a good approximation.

## ★ 8.6 THE CRITICAL POINT

At the end of section 8.3 we mentioned that the vapour pressure curve which separates the liquid and gaseous phases in the phase diagram comes to an abrupt end at the critical point, labelled C in Fig. 8.9. We now want to discuss the significance of the critical point.

As one follows the vapour pressure curve towards the critical point (see Fig. 8.9) the latent heat and the volume change  $\Delta V$  associated with the phase transformation decrease until they become zero at the critical point. Fig. 8.8 showed the temperature dependence of the latent heat of vaporization of water. The latent heat vanishes at 374.15°C, the critical temperature of water. In Fig. 8.10 the temperature dependence of the specific volumes of liquid water and water vapour in equilibrium are shown. At 374.15°C, the specific volumes of the liquid and vapour become equal; their difference  $\Delta V$  vanishes. The phase diagram 8.10 is typical. At temperatures below the critical temperature  $T_c$  the fluid can co-exist in two states with different specific volumes; the liquid phase with specific volume  $V_1 < V_c$ , and the vapour phase with specific

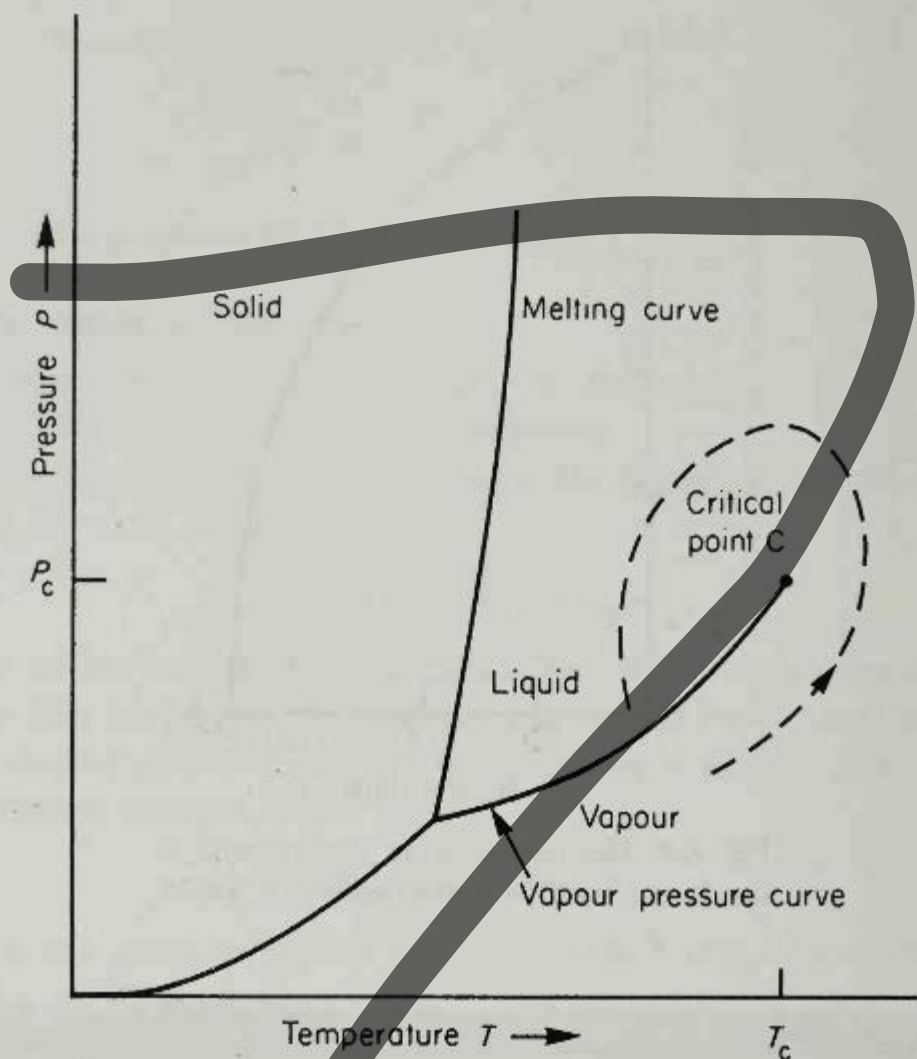


Fig. 8.9. The vapour pressure curve and critical point C. The dashed path represents a change from vapour to liquid without abrupt phase transition.

volume  $V_2 > V_c$ . At the critical temperature  $T_c$  both specific volumes become equal to  $V_c$ . Above the critical temperature the substance exists in one fluid phase only.

To understand this behaviour better, let us consider the isotherms of one gram of fluid in a ( $P, V$ ) diagram, shown schematically in Fig. 8.11. Consider one gram of fluid enclosed in a cylinder with a piston at one end, and immersed in a heat bath, as shown in Fig. 8.2. Suppose initially the cylinder is filled with vapour at a temperature  $T_1$ , corresponding to the point A in Fig. 8.11. If the system is compressed isothermally, the vapour pressure and density of the vapour increase as its volume decreases. At a certain point ( $A_2$  on the diagram) the vapour has just reached saturation at the given temperature. As the volume is reduced further, condensation occurs at constant pressure. We now have two phases present, liquid and vapour, and the system is at the



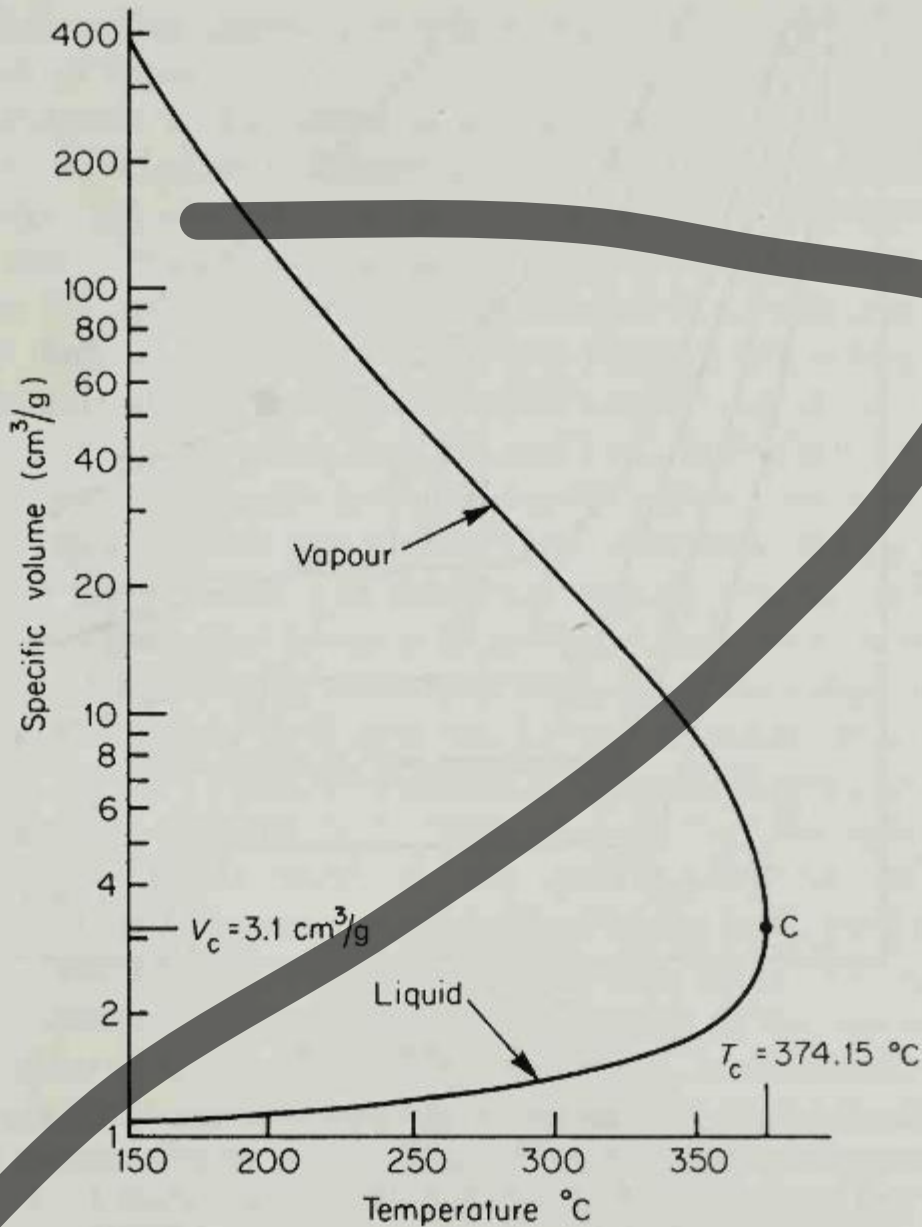


Fig. 8.10. The temperature dependence of the specific volume (in  $\text{cm}^3/\text{g}$ ) of liquid water and water vapour in equilibrium. C is the critical point.

saturation vapour pressure  $P_1$  corresponding to the temperature  $T_1$ . Eventually (point  $A_1$  on the figure) all the vapour is condensed; the cylinder is filled with liquid. Further reduction of the volume now requires very large pressures, due to the comparatively low compressibility of liquids, and results in a steeply rising isotherm (the portion  $A_1A'$  of it). During condensation (i.e., the portion  $A_2A_1$  of the isotherm) the fraction  $\alpha$  of fluid in the liquid phase and the volume  $V$  of the system are related by

$$V = \alpha V_1 + (1 - \alpha)V_2 \quad (8.38)$$

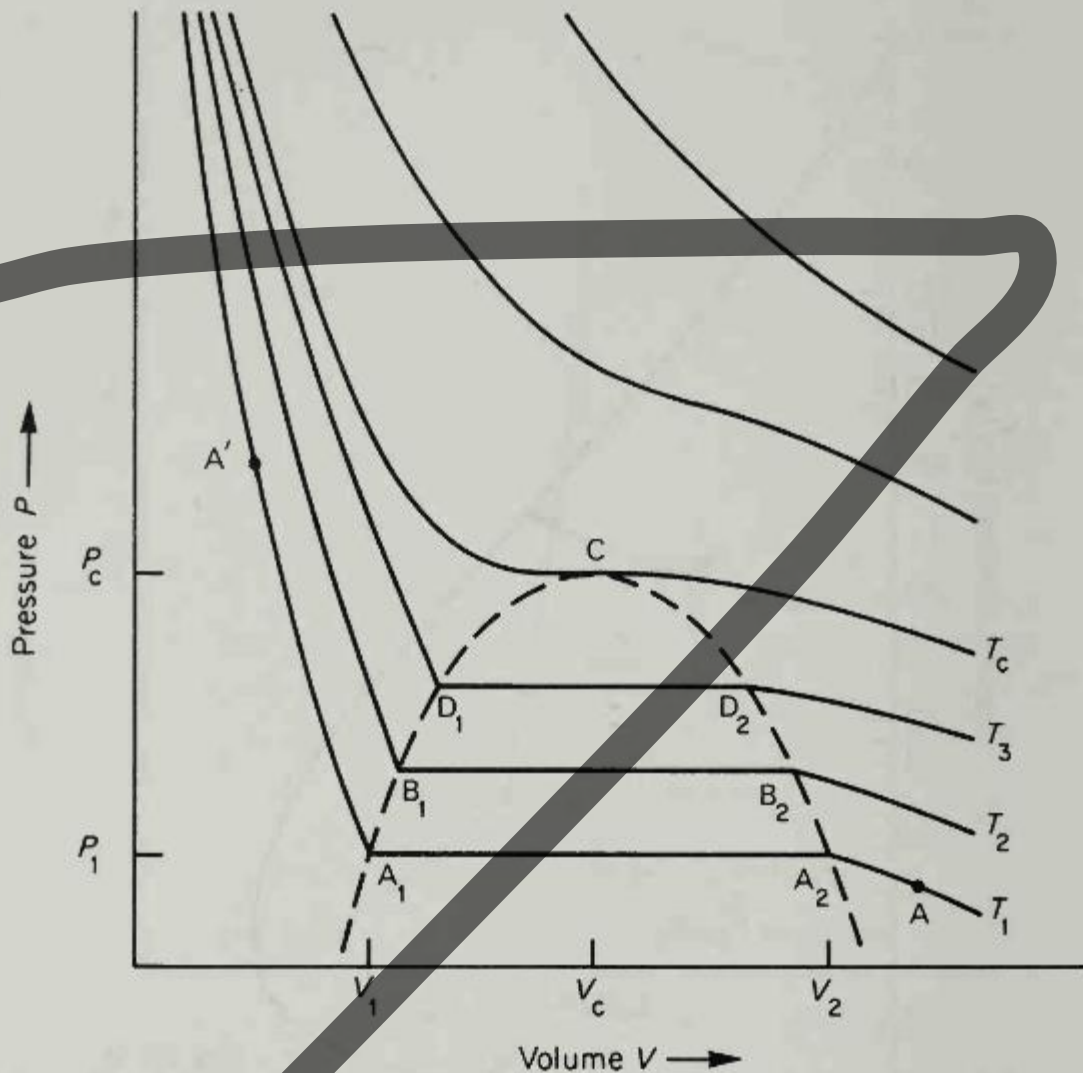


Fig. 8.11. Schematic diagram of the isotherms of a fluid,  $V$  is the specific volume (i.e., volume per gram),  $V_1$  and  $V_2$  are the specific volumes of the liquid and vapour coexisting in equilibrium at temperature  $T_1$ .  $C$  is the critical point, and  $T_c$ ,  $P_c$  and  $V_c$  are the critical constants.

where  $V_1$  and  $V_2$  are the specific volumes, at temperature  $T_1$ , of liquid and vapour respectively.

Fig. 8.11 shows two isotherms similar to that at temperature  $T_1$ . They correspond to temperatures  $T_3 > T_2 > T_1$ . We see that as the temperature increases, the horizontal portions of the isotherms ( $A_1A_2$ ,  $B_1B_2$ ,  $D_1D_2$ ), along which liquid and vapour are in equilibrium, become shorter. For the isotherm at the *critical temperature*  $T_c$ , this horizontal portion has shrunk to a horizontal point of inflection at the *critical point*  $C$ . The mathematical definition of the critical point is

$$\left(\frac{\partial P}{\partial V}\right)_{T=T_c} = \left(\frac{\partial^2 P}{\partial V^2}\right)_{T=T_c} = 0. \quad (8.39)$$



The corresponding critical pressure  $P_c$  and critical specific volume  $V_c$  are shown on Fig. 8.11.

The isotherms at temperatures above  $T_c$  are monotonic decreasing continuous curves, that is, following one of these curves in an isothermal compression the properties of the system change continuously; at no point is there a discontinuous change like a phase transition. Starting from very low density, where the fluid behaves like a gas, one can compress the fluid to high densities where it behaves like a liquid. These sort of considerations can also be carried out for one of the alternative forms of the phase diagram, Figs. 8.9 and 8.10. In Fig. 8.9, for example, the dashed curve represents a continuous transition from a gas-like to a liquid-like state without any abrupt phase transition having occurred. The dashed curve in Fig. 8.11 shows the specific volumes of the liquid and vapour phases as a function of pressure. It is very similar to Fig. 8.10 showing these specific volumes as functions of the temperature.

Experimentally one finds that the critical isotherm of a substance possesses a *very flat* point of inflection at the critical point, as indicated in the schematic diagram 8.11. This suggests that not only the first two derivatives (8.39) vanish at the critical point but also higher derivatives. This is in contrast to the predictions from van der Waals' equation:\* the critical isotherm which results from van der Waals' equation possesses a very sharp point of inflection. Thus van der Waals' equation gives at best a qualitative description. In particular, it always leads to a uniform density, whereas we know that under suitable conditions (underneath the dashed curve  $A_1CA_2$  in Fig. 8.11) two separate phases of different densities coexist. It seems that no simple equation of state, like van der Waals', which allows a power series expansion near the critical point can provide a correct description near the critical point. As mentioned previously (section 2.5, see also Flowers and Mendoza,<sup>21</sup> section 7.7, and Present,<sup>11</sup> section 9.2), a substance displays very peculiar properties near the critical point which result from large fluctuations in density, and an adequate description of these properties is very difficult.

The question naturally arises whether there also exists a critical point on the melting curve, Fig. 8.9. Experimental evidence strongly suggests that no such critical point exists (see Pippard,<sup>2</sup> pp. 122–24). This conclusion is supported by the following theoretical argument (which is not accepted by everyone). Liquids and crystalline solids are *in principle* very different. A crystalline solid has a geometrical structure which gives it preferred directions (lines of atoms, etc.). A liquid has no such

\* For a derivation and discussion of van der Waals' equation see the end of section 7.8.



preferred directions; its properties are isotropic. Now a system either possesses certain geometrical symmetries or it does not. No *continuous* transition from the one to the other state of affairs is possible. On the other hand we have seen that the existence of a critical point implies the occurrence of such continuous transitions. As one approaches the critical point along the phase equilibrium curve the properties of the two phases gradually become more and more similar until at the critical point they are identical. Since no such continuous transition seems possible for the symmetries of a system, a solid-liquid critical point cannot exist.

## PROBLEMS 8

- 8.1 Derive Eqs. (8.9) and (8.10) from Eq. (8.8).
- 8.2 The transition temperature of grey and white tin at a pressure of one atmosphere is 291 °K, grey tin being the stable modification below this temperature. The change in enthalpy for this transition is 535 cal/mol. The densities of grey and white tin are 5.75 and 7.30 g/cm<sup>3</sup> respectively, and the atomic weight of tin is 118.7. What is the change in the transition temperature if the system is at a pressure of 100 atm?
- 8.3 In the temperature range 700 to 730 °K, the vapour pressure of magnesium can be approximately represented by

$$\log_{10} P = -\frac{7,500}{T} + 8.6$$

( $P$  in mmHg,  $T$  in °K). What is the molar latent heat of sublimation of magnesium in this temperature range?

- 8.4 The latent heat of fusion and the latent heat of vaporization of neon at the triple point have the values 80 cal/mol and 431 cal/mol respectively. The temperature of the triple point is 24.57 °K. What is the latent heat of sublimation of neon at the triple point? What is the change in entropy when one mole of liquid neon at the triple point is vaporized?
- 8.5 The vapour pressure of water at 298.15 °K is 23.75 mmHg. What is the vapour pressure of water at 273.16 °K, given that the latent heat of evaporation of water at 298.15 and 273.16 °K is 10,514 and 10,767 cal/mol respectively?
- 8.6 The liquid and solid phases of helium 4 may coexist in equilibrium at 0 °K, the density of the solid being greater than that of the liquid. What is the slope  $dP/dT$  of the phase equilibrium curve at the absolute zero of temperature?
- 8.7 Derive an expression for the vapour pressure of a solid monatomic substance given that the vapour may be treated as a perfect monatomic gas and that the solid can be described by the Einstein model, the temperature of the system being large compared with the Einstein temperature  $\Theta_E$  of the solid.

(Hint: Look at the 'hints' to problem 6.2.)

- 8.8 Obtain the critical constants for Dieterici's equation of state

$$P(V - b) = RT \exp \left( -\frac{a}{RTV} \right).$$