CHAPTER 8

PHASE EQUILIBRIUM

In this chapter we shall consider applications of the result derived in the last chapter that (provided surface effects are negligible) two phases of the same substance can only coexist in equilibrium if they possess the same Gibbs function per unit mass. The examples we shall treat are the equilibrium of the solid, liquid and vapour phases of a substance at various pressures and temperatures, the phase diagrams of the two isotopes of helium, and the equilibrium between the normal and superconducting phases of a metal, for which we must introduce the magnetic field as an additional parameter. These examples should be sufficient to illustrate the methods involved in the treatment of phase equilibrium. No essentially new ideas are involved in the extension of these methods to more complex systems, such as solids which may exhibit many allotropic forms (ice, sulphur). Further, a full understanding of these examples should enable the reader, if he wishes, to grasp the thermodynamic theory of chemical reactions and of the phase diagrams of alloys with little difficulty, as the methods there employed are fundamentally of the same nature.

The phase diagram of a simple substance

We consider a simple substance which under suitable conditions exhibits three modifications, solid, liquid and vapour; by 'simple' we imply no more than that only these three modifications exist, at any rate under the conditions of temperature and pressure with which we are concerned. In order to determine the circumstances under which any of these phases can coexist it is convenient to study the variation with temperature and pressure of the Gibbs function $g$ (in what follows it will be taken for granted that we are considering unit mass of each phase). Since for any change

$$dg = -sdT + vdP,$$

therefore

$$\left( \frac{\partial g}{\partial T} \right)_P = -s, \quad \left( \frac{\partial g}{\partial P} \right)_T = v. \quad (8.1)$$

If then we exhibit $g$ as a function of $P$ and $T$, the surface representing $g$ ($g$-surface) will always slope upwards in the direction of increasing pressure, the gradient being small and nearly constant for a liquid or solid, and steep for a gas, decreasing as $P$ increases. The slope in the
direction of increasing temperature will depend on the choice of the arbitrary constant in \( s \), but if, as is usual, this is chosen so that \( s \) is positive at all temperatures the slope of the surface will always be negative, increasingly so as \( T \) increases since \( c_p \) and therefore \( (\partial s/\partial T)_P \) are always positive. Thus the surface has everywhere a negative curvature,† but the detailed shape may be expected to vary considerably for different phases of the same substance.

Let us suppose that we can construct one of these \( g \)-surfaces for each phase, irrespective of the question of whether the phase is observable at all pressures and temperatures. We then have three surfaces of which any two in general intersect along a line, the three lines so constructed meeting at the point at which all three surfaces intersect one another. The projection of these three lines onto the \( P-T \) plane will give a diagram of the type shown in fig. 25. Along these lines the two phases corresponding to the intersecting surfaces may coexist in equilibrium, since they have the same value of \( g \), and at \( p_c \) all three phases may coexist. The point \( p_t \) is thus the triple point of the substance, and our experimental knowledge of the behaviour of normal substances enables us to interpret \( O p_b \) as the sublimation curve, along which solid and vapour are in equilibrium, \( p_b p_c \) as the vapour pressure curve, along which liquid and vapour are in equilibrium, and \( p_t S \) as the melting curve, along which liquid and solid are in equilibrium. At points removed from these lines one of the \( g \)-surfaces lies lower than

† Strictly this statement is true only if the set of quadratic terms in the expansion of \( g \) as a power series in \( P \) and \( T \) is essentially negative. It may be left as an exercise for the reader to demonstrate that this is so if \( c_p > 0 \).
the others and this determines which phase is stable, since the equi-
librium state of the system at given $P$ and $T$ is that for which the Gibbs
function is minimized. It is clear that in the region below $O p_r p_e$ the
vapour phase is stable, for it possesses the largest volume and therefore
the Gibbs function falls most steeply as the pressure is reduced. It is
not so obvious that the region to the left of $O p_r S$ corresponds to the
stable existence of the solid and the remaining region to the stable
existence of the liquid, and here we must rely on experimental obser-
ation to ascribe the regions correctly. As the curves are drawn in the
figure it will be seen that in crossing the line $p_r S$ vertically upwards we
move from a region of liquid stability to one of solid stability; this
implies that $(\partial g_i / \partial P)_T > (\partial g_i / \partial P)_T$, i.e. that $v_i > v_r$, or that the substance
expands on melting. For substances such as water or bismuth which
contract on melting, $p_r S$ will have the opposite slope. If we move
across an equilibrium line horizontally ($P$ constant, $T$ increasing) it is
obvious that the phase which is stable on the high-temperature side
must have the greater negative slope $- (\partial g / \partial T)_P$, that is, by (8.1), the
higher entropy. Therefore in a reversible transition from the low-
temperature to the high-temperature phase heat must always be
absorbed, and the latent heat is in consequence always positive.

It might be argued that since only one phase is stable except along
the equilibrium lines it is not justifiable to imagine the $g$-surfaces to
extend over the whole plane for each phase, and indeed it is quite
unnecessary to make this supposition. We might equally well have
started constructing the surface from three points, one in the middle
of each region, making use of experimental information to decide
which phase to consider in each region; the intersections could then be
found without supposing the surfaces to be capable of crossing one
another. In fact, for many substances, particularly if they are highly
purified, it is possible to observe the metastable existence of a phase
in a region where it should have made a transition to another phase.
The most striking examples of this behaviour are the supercooling of
vapours, which may stay uncondensed at pressures four times or more
higher than the equilibrium vapour pressure (the Wilson cloud cham-
ber owes its operation to this fact), and the supercooling of liquids
without solidification. For instance, small drops of water in a cloud
may be cooled to $-40^\circ C.$ before they freeze. The converse effects may
also be demonstrated, as, for example, the superheating of liquids,
which is often manifested as 'bumping', and which is the basis of the
operation of the bubble chamber used to detect high energy particles.
There is therefore no real obstacle to imagining each surface to con-
tinue beyond its intersection with another, and the foregoing argu-
ment could be dismissed as trivial except for the fact that much
confusion has been generated in discussions of higher-order transitions
Phase equilibrium

(see Chapter 9) by a too-facile assumption that $g$-surfaces are always
continuable beyond an equilibrium line. Before leaving the question
of the metastable persistence of phases, it may be pointed out that the
equilibrium lines may be imagined prolonged through the triple point,
as $p_1A$, $p_1B$ and $p_1C$ in fig. 24. Along $p_1A$, for example, $g_i = g_v$, but both
are greater than $g_v$. There is no reason in principle why a superheated
liquid should not be made to solidify by crossing the curve $p_1A$, though
the author is not aware of any observation of this phenomenon. On the
other hand, the coexistence of a supercooled liquid with its vapour
along the line $p_1C$ is a commonplace of meteorology; the fact that the
vapour pressure of the supercooled liquid is higher than that of the
solid at the same temperature (as shown in fig. 25) means that any ice
crystal in a cloud containing supercooled water drops tends to grow
rapidly, since the latter maintain a high vapour pressure.

It is a result of general validity that the vapour pressure of a super-
cooled liquid is higher than that of the solid at the same temperature.
For if this were not so the line $p_1C$ would lie in the vapour region below
$Op_1p_c$; but in this region $g_v$ is lower than either $g_1$ or $g_s$, while at the
point $C$, $g_v = g_l$. It follows then that around a triple point there is only one
metastable line in each region, and that therefore the angles between
neighbouring equilibrium lines are never greater than $180^\circ$.

Clapeyron's equation

Along any equilibrium line separating two phases in the $P$-$T$
le diagram the Gibbs functions are equal, $g_1 = g_2$. The suffix 1 denotes
that phase which is stable on the low-temperature side of the equi-
librium line. For small variations of pressure and temperature, $\delta P$ and
$\delta T$, which alter the state of the system to a neighbouring state still on
the equilibrium line, the variation of $g_1$ and $g_2$ must therefore be equal, so that

$$
\left(\frac{\partial g_1}{\partial T}\right)_P \delta T + \left(\frac{\partial g_1}{\partial P}\right)_T \delta P = \left(\frac{\partial g_2}{\partial T}\right)_P \delta T + \left(\frac{\partial g_2}{\partial P}\right)_T \delta P,
$$

or

$$(s_2 - s_1) \delta T = (v_2 - v_1) \delta P \quad \text{from (8.1)}.
$$

Now the ratio $\delta P/\delta T$ tends, as $\delta T \to 0$, to the slope $dP/dT$ of the equi-
librium line, so that

$$
dP = \frac{s_2 - s_1}{v_2 - v_1} \frac{l}{T(v_2 - v_1)},
$$

(8.2)

where $l$ is the latent heat of the transition, $T(s_2 - s_1)$, per unit mass.
This is Clapeyron's equation which we derived (5.12) in Chapter 5
by a different argument. From this point of view it is clear that
Clapeyron’s equation is simply an expression of the fact that along a transition line the $g$-surface has a sharp crease. If one describes the slope of the $g$-surface by the two-dimensional vector $\text{grad } g$, at the transition line there is a discontinuity $\Delta(\text{grad } g)$ in the slope, and Clapeyron’s equation states that the vector $\Delta(\text{grad } g)$ is directed normal to the transition line.

Since $l$ cannot be negative it may be seen from equation (8.2), as we deduced by a geometrical argument in the last section, that a solid which expands on melting ($v_2 > v_1$) has a positive pressure coefficient of the melting temperature, and one which contracts has a negative coefficient. The comparison, by James and William Thomson in 1849–50, of the actual pressure variation of the melting-point of ice with that predicted by Clapeyron’s equation is of historical interest as being perhaps the first successful application of thermodynamics to a physical problem, and the success of this simple test undoubtedly contributed largely to the spirit of confidence which underlay and encouraged the rapid development of the subject.

**Liquid-vapour equilibrium and the critical point**

Along the curve $p_t p_c$ in fig. 25 the $g$-surfaces for the liquid and vapour intersect and the two phases are in equilibrium. This line does not, however, continue indefinitely, for at the critical point $p_c$ the liquid and vapour become indistinguishable. The critical phenomenon is clearly illustrated by the isotherms of a typical liquid-vapour system shown in fig. 26. If the system is in the vapour phase at a temperature below the critical temperature $T_c$, and is compressed isothermally, a stage is reached, as at $C$, when liquid begins to form and the system becomes inhomogeneous. Subsequent compression, at constant pressure, eventually leads to the state $C'$ where the vessel is wholly filled with liquid, which is far less compressible than the gas phase. In the inhomogeneous region $CC'$ the isothermal compressibility, defined as

$$-\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T,$$

is of course infinite. At the critical temperature the compressibility decreases at first as the volume is reduced, and then rises to infinity at the horizontal point of inflexion $p_c$, which corresponds to $p_c$ in fig. 25; further compression reduces the compressibility steadily. At no point is there a separation into two phases. At temperatures well above $T_c$ the compressibility decreases monotonically as the volume is reduced, so that although at large volumes the substance may be regarded as vapour-like, and at low volumes as liquid-like, there is no point at which any transition from one phase to another may be said to have occurred. It is therefore possible, by travelling around the point $p_c$ in fig. 25, to make a transition from
what is undoubtedly the vapour phase to the equally undoubted liquid phase, without any abrupt change in the properties of the system. This means that the $g$-surfaces for the liquid and the vapour must both be parts of the same surface, which, however, is not of a simple form, but intersects itself along the line $p_t, p_c$, though not beyond $p_c$. In order to obtain a picture of the form of this surface it is

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**Fig. 26.** Isotherms of xenon near the critical point (H. W. Habgood and W. G. Schneider, *Canad. J. Chem.* 32, 98, 1954). The broken line marks the region of coexistent phases, and the dotted line is the critical isotherm according to the van der Waals equation.

convenient to make use of the equation of state proposed by van der Waals (p. 75 footnote) to express the continuity of the liquid and vapour phases. The critical isotherm of a van der Waals gas and a typical isotherm for a temperature below $T_c$ are shown in fig. 27, together with the conjectured horizontal line $C'C'$ which corresponds to the mixture of phases. We shall for the moment ignore this line and suppose that the whole of the curve for a temperature less
than $T_c$ is experimentally realizable, in spite of the fact that in the central region the compressibility is negative and the hypothetical homogeneous phase is intrinsically unstable.

We now use this isotherm to calculate the variation of $g$ with pressure at constant temperature, since $(\partial g/\partial P)_T = v$, and therefore

$$g(P, T) = g(P_0, T) + \int_{P_0}^{P} v\,dP,$$

the integral being taken along the isotherm from $P_0$ to $P$. Let us take the point $D$ to correspond to the initial pressure $P_0$. The first stage of

![Diagram](image)

**Fig. 27.** Van der Waals isotherms: (a) $T = T_c$, (b) $T = 0.9T_c$.

the integration, from $D$ to $E$, is straightforward, and leads to the curve $DE$ in fig. 28. Between $E$ and $F$ the contribution of the integral is negative, and $g$ falls, but at the same time $P$ also falls, so that $(\partial g/\partial P)_T$ is still positive (as it must be, being equal to $v$). The curve for $g$ shows a cusp at $E$, the tangents to the two curves becoming coincident at $E$. Similarly, there is another cusp at $F$, and then the curve proceeds steadily upwards towards and beyond $G$. Clearly the portion $DE$ corresponds to the vapour phase and the portion $FG$ to the liquid phase, and equilibrium of the two phases is possible at the pressure $P_c$ where they intersect. The difference in gradient between
DE and FG at this point represents the volume difference between the two phases. Since \( g \) takes the same value at \( C \) and \( C' \), it is clear that the line \( CC' \) must be drawn at such a pressure \( P' \) that \( \int_{C}^{C'} v \, dP = 0 \), that is, the areas \( C'FC' \) and \( CEC' \) must be equal.† Now this argument, and that given in the footnote, both assume that the whole of the van der Waals isotherm is physically realizable as a succession of equilibrium states of the system. As this is not true it is very doubtful what validity the arguments possess. From a logical point of view they are worthless, but still it is probable that they lead to the correct conclusion. It would require a much more detailed investigation of the model to justify this result completely.

![Graph showing the Gibbs function obtained by integrating the van der Waals equation.](image)

Fig. 28. Gibbs function obtained by integrating the van der Waals equation.

Returning now to fig. 28 we can see that as the temperature is raised and \( v_v - v_i \) diminishes, the two branches \( DE \) and \( FG \) intersect more and more nearly tangentially, and the cusped region becomes steadily smaller, until at the critical temperature the curve degenerates into a single continuous curve. Just at the critical temperature the gradient of the curve, which is equal to \( v \), is everywhere continuous, but the curvature \( (\partial v/\partial P)_T \) becomes momentarily infinite at the critical pressure, since at this point the van der Waals gas is infinitely compressible. Above \( T_c \) the curves for \( g \) are everywhere continuous in all their

† An alternative argument leading to the same conclusion runs as follows: imagine the substance to be taken through the cycle \( CEC'FC'C'C \) reversibly. This cycle is completely isothermal, so that its efficiency must be zero, i.e. no work must be done in the cycle. Hence the area of the cycle must vanish, a condition satisfied by making the two areas \( C'FC' \) and \( CEC' \) equal.
derivatives. A sketch of the surface for $g$ is shown in fig. 29. The top portion, between the two lines of cusps, is the completely unrealizable region; a part of the regions between the line of intersection and the lines of cusps may be realized by superheating of the liquid or supercooling of the vapour.

![Gibbs surface for the van der Waals gas in vicinity of the critical point.](image)

Along with anomalous compressibility in the neighbourhood of the critical point the specific heat also shows certain anomalies, which we may exhibit qualitatively with the help of van der Waals's equation. It will be recalled (see p. 60) that according to this equation $(\partial c_p/\partial v)_T = 0$, so that if, as is a good approximation for many gases, $(\partial c_p/\partial T)_v$ is effectively zero, $c_p$ is the same for all states of the gas or liquid. This is certainly not true in practice, and illustrates one of the limitations of van der Waals's equation, but, nevertheless, it serves to show that we need not expect any markedly unusual behaviour in $c_p$ near the critical point. On the other hand, as the isothermal compressibility $k_T$ goes to infinity at the critical point, so does $c_p - c_v$, since, as follows easily from (6·9),

$$c_p - c_v = vT k_T \left( \frac{\partial P}{\partial T} \right)_v^2.$$  \hspace{1cm} (8·3)

A quantitative calculation from van der Waals's equation is straightforward. If we take the critical point as our origin of coordinates, and work in reduced coordinates, writing

$$x = \frac{v - v_c}{v_c}, \quad y = \frac{P - P_c}{P_c}, \quad z = \frac{T - T_c}{T_c},$$
the equation takes the form (when all powers of {$x$} above {$x^3$} are neglected),
\[
3x^3 + (2 + 3x)y - 8z = 0.
\]
(8.4)

Equation (6.9) may be rewritten in the form
\[
c_p - c_v = \frac{Pv_cT}{T_c^2} (\frac{\partial y}{\partial z})_v (\frac{\partial x}{\partial z})_v,
\]
and near the critical point, where $T$ may be put equal to $T_c$, and
\[
P_cv_c = \frac{3}{8} \pi T_c,
\]
\[
c_p - c_v = \frac{8\pi}{(2 + 3x)(y + 3x^2)}.
\]
(8.5)

From this result it will be seen that if the pressure is maintained at the critical value ($y = 0$) and the volume altered by changing the temperature, $c_p - c_v$, and hence $c_p$, approach infinity as const.$/x^2$. Since, from (8.4), $y \propto x^3$ when $y = 0$, we see that at the critical pressure $c_p$ approaches infinity as const.$/(T_c - T)^\frac{3}{4}$. If the volume is maintained at $v_c$ ($x = 0$), $c_p$ approaches infinity as const.$/(T_c - T)$.

We may further use this model to demonstrate that although $c_p$ and $k_T$ become infinite at the critical point, the adiabatic compressibility remains finite as asserted in Chapter 7. For, from (8.5), as the critical point is approached $\gamma (= c_p/c_v)$ tends to infinity,
\[
\gamma \rightarrow \frac{8\pi/c_v}{(2 + 3x)(y + 3x^2)},
\]
while the isothermal compressibility tends to the form
\[
\frac{1}{P_c3(y + 3x^2)}.
\]

Therefore
\[
k_s = k_T/\gamma \rightarrow \frac{c_v}{24\pi P_c} (2 + 3x)^2,
\]
which remains finite when $x = 0$.

It is important to remember, however, that although the van der Waals model illustrates qualitatively the thermodynamic behaviour near the critical point, it is very far from being quantitatively exact. The isotherms of a real substance in the vicinity of the critical point tend to be much flatter than those predicted by van der Waals's equation, as may be seen in fig. 26. It seems that not only $(\partial^2 P/\partial V^2)_T$, but $(\partial^3 P/\partial V^3)_T$ and $(\partial^4 P/\partial V^4)_T$ also vanish at the critical point, and it is likely that the behaviour cannot be adequately represented, as in van der Waals's and similar equations, by functions which are capable of expansion as a Taylor series involving values of the derivatives at the critical point itself. But this is too complex a problem to be entered into here.
Solid-liquid equilibrium

Let us now examine the question whether the transition line between the solid and liquid phases ($p_s S$ in fig. 25) continues indefinitely, or whether it also terminates abruptly in a critical point. It may be said at the outset that there are weighty theoretical arguments against the possibility of a critical point. For if such a point existed it would be possible, by going around it, to make a continuous transition from the liquid to the solid phase. Now the properties of normal liquids are strictly isotropic; they possess no crystalline structure which singles out any one direction as different from another, while true solids (excluding glasses and similar amorphous phases) possess non-spherical symmetries which are characteristic of the regular arrangement of their molecules in a crystalline lattice. In order to go from the liquid to the crystalline phase, therefore, it is necessary to make a change of the symmetry properties, and this is of necessity a discontinuous process. The symmetry properties of a lattice are describable in terms of certain geometrical operations, such as translation or reflexion, which displace every atom on to another identical atom and so leave the lattice unaltered. A given phase either possesses or does not possess any given symmetry property, and thus no continuous transition is possible and no critical point can exist.

This is the theoretical argument, which has appeared to some to be a little too straightforward to be absolutely convincing. There is little doubt, however, that the experimental evidence all points strongly to the truth of its conclusion. Of this evidence the most complete is that of Simon and his coworkers on solid and liquid helium. The choice of helium as a suitable substance for extensive investigation was governed by the following considerations. According to the law of corresponding states, the phase diagrams of most simple substances are very similar in form and scale if they are plotted in reduced coordinates, $P/P_c$, $V/V_c$ and $T/T_c$. There are, of course, differences in detail, but on the whole the law is well obeyed. It is therefore desirable to study a substance for which the highest values of $P/P_c$ and $T/T_c$ are attainable, and this is achieved by using helium, whose critical pressure and temperature are 2.26 atmospheres and 5.2° K. respectively. Since the melting curve of helium can be followed up to pressures of several thousand atmospheres, it follows that values of $P/P_c$ of more than one thousand may be attained, far more than is possible with any other substance.

Apart from the lowest temperature region, in which helium behaves unlike any other substance (this will be discussed more fully in the next section), the melting curve takes a form which closely resembles that of many other substances, in that the melting pressure varies with
temperature according to the law \( P/a = (T/T_0)^c - 1 \), in which \( a \) and \( T_0 \) are constants for a given substance and \( c \) is an exponent which varies somewhat from one substance to another, but usually lies between 1.5 and 2. The melting curve for helium is shown in fig. 30. There is thus no indication of a critical point for the liquid-solid transition even at temperatures eight times as high as that of the liquid-vapour critical point. It is interesting to note that if the same law for the melting pressure holds beyond the range of existing data, helium could be solidified at room temperature by application of a pressure of 110,000 atmospheres, not so much higher than the highest pressures produced by Bridgman. There are, however, technical reasons limiting the pressure which can be applied to helium at a much lower value.

From the point of view of determining whether a liquid-solid critical point exists, an even more instructive set of measurements is that of the entropies of the liquid and solid phases, which have been computed from specific heat measurements at high pressures. It is found
that the entropy difference between liquid and solid helium increases slightly as the melting pressure is increased. Since at a critical point the two phases, being identical, must have the same entropy, the experiments make it highly probable that no critical point will be found.†

The phase diagram of helium

Naturally occurring helium consists almost entirely of $^2\text{He}^4$, the isotope of mass 4 (two protons and two neutrons comprising the nucleus), with an admixture of one part in $10^5$–$10^6$ of $^2\text{He}^3$, the light isotope of mass 3 (two protons and one neutron). Until recently little was known of the properties of the latter, but with the development of methods of separating the two isotopes and, still more, with the production on a comparatively large scale of $^2\text{He}^3$ in nuclear reactors,‡ it has become possible to carry out experiments on the thermodynamic and other properties of this very interesting substance, and even to use it as a liquid bath in cryostats. Since it behaves in a rather more simple manner than $^4\text{He}$ we shall discuss it first.

Both isotopes have the property, unlike any other substance, that they may remain liquid down to the lowest temperatures. The reason for this, which is essentially quantum-mechanical, need not concern us here,§ since we shall limit our discussion to thermodynamical aspects of the phase diagram. The diagram for $^2\text{He}^3$ is shown in fig. 31, from which it will be seen that there is no triple point.

The form of the melting curve is unique among liquid-solid transitions. At all temperatures the solid is the denser phase, but whereas above 0-32° K. the entropy of the liquid exceeds that of the solid, as is usual, below 0-32° K. the reverse is true. There is a range of temperatures and pressures within which the liquid is the low temperature phase and the solid the high temperature phase. If a vessel containing $^2\text{He}^3$ is maintained at a pressure of 30 atmospheres and warmed up from a very low temperature, it starts as a liquid, freezes at 0-18° K., and melts once more at 0-49° K. It is worth noting in passing that solid iron behaves somewhat analogously, as may be seen in fig. 41; on heating it makes a transition from the $\alpha$-modification to the $\gamma$-modification, and at a higher temperature reverts to the $\alpha$-modification.

The melting curve of $^2\text{He}^3$ has been studied down to 0-06° K.,|| and is

‡ The reaction $^6\text{Li}^+ + n \rightarrow ^2\text{He}^4 + ^1\text{H}^3$, creates tritium $^1\text{H}^3$, which decays by $\beta$-emission with a half-life of twelve years to $^2\text{He}^3$.
still rising steadily. Ultimately it must become level, since according to the third law $S_s - S_i$ must vanish at the absolute zero, but the temperature at which this occurs may prove to be very low indeed.

The melting curve of $\text{He}_4$ is more normal, though again there is no triple point, and a pressure of at least 25 atmospheres is needed to produce the solid. Of particular interest in the phase diagram (fig. 32) is the line separating two different forms of the liquid phase.

![Phase diagram for $\text{He}_3$.](image)

Fig. 31. Phase diagram for $\text{He}_3$.

The higher-temperature form, $\text{He}_1$, shows no markedly unusual properties; but as the temperature is lowered a sharp transition to a new form, $\text{He}_2$, occurs, which possesses such remarkable and unique properties of high heat conductivity and low viscosity as have earned it the title ‘superfluid’. Undoubtedly, the great fascination of helium is due to its transport properties and hydrodynamic peculiarities, but its thermodynamic behaviour is not devoid of interest, since it is typical of a large class of transitions which hitherto we have not considered.
The specific heat of liquid $^4$He in contact with its vapour, that is, very nearly at constant pressure, varies with temperature in the manner shown in fig. 33. The sharp rise at 2·172° K. corresponds to the transition from He II to He I, and is called, on account of its shape, the $\lambda$-point. The most careful measurements have been unable to determine with certainty how high the peak really is, and it is quite probable that an ideal experiment would reveal that it is virtually unbounded. If $C_P$ does in fact tend to infinity at the $\lambda$-point it must do so more slowly than as $(T_\lambda - T)^{-1}$, since the energy change associated with the transition, $\int C_P \, dT$, must remain finite. In fact the rise is much slower than this, being represented rather closely by a function of the form $A + B \ln |T_\lambda - T|$ on both sides of the transition, with $A$ taking different values on the two sides;† the specific heat has been determined within a few microdegrees of $T_\lambda$. There is no latent heat associated with this transition; if an isolated vessel of He II is supplied with heat at a constant rate, the rate of temperature rise steadily decreases as $T_\lambda$ is approached, and appears to become momentarily zero at $T_\lambda$ before increasing suddenly once more, but there is no

halting of the temperature for a measurable time at $T_\lambda$ as would occur if there were a latent heat. The entropy is thus a continuous function of temperature, though there may be a discontinuity in $(\partial S/\partial T)_P$. It is easy to see that the volume is also continuous by applying M.3 to the liquid. In crossing the $\lambda$-line (AB in fig. 32) at constant tempera-

![Graph](image1)

Fig. 33. Specific heat of liquid $^4$He in contact with its vapour.

![Graph](image2)

Fig. 34. Variation of volume of liquid $^4$He near the $\lambda$-point. Note the vertical tangent at $T_\lambda$.

ture the entropy is a continuous function of pressure, although $(\partial S/\partial P)_T$ may become infinite on the line; correspondingly the volume is a continuous function of temperature, although $(\partial V/\partial T)_P$ may become infinite on the line, with the opposite sign to that of $(\partial S/\partial P)_T$. This is illustrated in fig. 34. We have then to deal with a new type of transition which in some respects resembles a smeared-out phase
transition—the latent heat is, as it were, absorbed over an interval of temperature instead of at one fixed temperature. It also resembles, and perhaps more closely, the specific heat behaviour at the critical point. Here, however, instead of a single point on the phase diagram at which $C_p$ becomes infinite, we have a line of such points. Clapeyron's equation cannot be applied as it stands to relate the slope of this line to discontinuities of entropy and volume at the transition, since there is no discontinuity of either. We shall consider in the next chapter how to derive thermodynamic relationships analogous to Clapeyron's equation for this type of transition and others.

The Gibbs function for the liquid phase exhibits singular behaviour along the $\lambda$-line, but of course in a less striking fashion than the specific heat or entropy. If $C_p$ rises to infinity, the corresponding curve for $s$ shows momentarily a vertical tangent, and the curve for $g$ at a point at which the curvature becomes momentarily infinite. The surface $g(P, T)$ is therefore not folded along the $\lambda$-line, as it would be if there were a latent heat at the transition, but shows, as it were, an 'incipient fold', the gradient changing rapidly but continuously. The intersection of the $g$-surface for the liquid with that for the solid, which is quite regular and free from kinks, should in principle reflect the singularity of the liquid in the shape of the liquid-solid equilibrium line. Just as at a triple point, where a regular surface meets a folded surface, there is a sharp change in the gradient of the equilibrium line, so here, where a regular surface meets an almost-folded surface, the equilibrium line exhibits a region of rapidly changing gradient, with one point at which the curvature becomes infinite. The same behaviour should occur at the liquid-vapour equilibrium line. Unfortunately, neither for the liquid-solid nor for the liquid-vapour transition are the experimental data sufficient to show this clearly. Certainly as far as the former is concerned the region of rapidly changing gradient on the melting-curve ought to be readily apparent,† but it would be very hard to recognize on the vapour-pressure curve. The reason for this is easily understood. The volume of unit mass of vapour is a rapidly varying function of temperature, so that the curvature of the vapour-pressure curve is high, as follows from Clapeyron's equation, and the change in entropy of the liquid resulting from the specific heat maximum is small compared with the difference in entropy between the liquid and vapour phases. In consequence, the anomalous variations in curvature resulting from the existence of a $\lambda$-transition are comparable with the curvature already present only within a few thousandths of a degree of the $\lambda$-point, and give rise to no perceptible deviation in the general trend of the vapour-pressure curve.

† See C. A. Swenson, Phys. Rev. 79, 626 (1950), where the available data are clearly displayed.
In concluding this section the properties of mixtures of the two helium isotopes deserve mention, since they illustrate the third law most strikingly. We have not entered into the subject of chemical thermodynamics, and have thus neglected to introduce the concept of 'entropy of mixing'. We shall therefore not go into details but merely remark that the entropy of a mixture of isotopes is greater than that of the separated isotopes, unless the isotopes can achieve an ordered arrangement, analogous to the ordered state of an alloy shown in fig. 49. The third law demands that the isotopes either order themselves as zero temperature is approached, something that is hard to conceive in a liquid, or else that the two liquids become mutually insoluble. For all that they are so similar it is in fact the latter that occurs. For instance, if a solution containing $3 \text{He}^3$ atoms to $2 \text{He}^4$ atoms is cooled, phase separation begins just below $0.9^\circ K$. At first a solution richer in $\text{He}^3$ floats on a solution richer in $\text{He}^4$, but with further cooling each phase expels its minority constituent so that as zero temperature is approached the system tends towards the ideal state of zero entropy, pure $\text{He}^3$ floating on pure $\text{He}^4$.

The investigation of liquefied helium isotopes, both pure and mixed, has revealed many new phenomena and contributed notably towards the understanding of the quantum physics of condensed systems, but these are matters beyond our scope and the reader is referred to specialized texts for further study.†

The superconducting phase transition

Certain metals, for example, lead, mercury, tin, aluminium, niobium and tantalum, have the remarkable property of losing all trace of electrical resistance when cooled sufficiently. The disappearance of resistance may take place gradually, over a temperature interval of \(\frac{1}{10}\) to \(1^\circ\), but it is found that if sufficient care is taken to ensure chemical and physical purity, by using single crystals of highly refined metal, the transition usually becomes very sudden. With a good sample of tin, between the point at which the resistance is first observed to diminish and that at which it has entirely vanished, there may lie a temperature interval of only one or two thousandths of a degree. For tin the transition occurs at \(3.73^\circ K\); for other elementary metals it varies between \(9^\circ K\) for niobium and \(0.14^\circ K\) for iridium. Metal-like compounds have been found which have transition temperatures as high as \(18^\circ K\), but there seems little doubt that the phenomenon is one which only occurs at temperatures very far below room temperature. As with liquid helium, the chief fascination of the study of superconductors lies in properties which are not strictly

thermodynamic, and which it is beyond our scope to discuss here. We shall only use superconductivity as an example of a phase transition which involves three independent variables, in this case \( P, T \) and \( \mathcal{H} \), and because it exhibits under certain circumstances a type of phase transition which is different from any we have encountered hitherto.†

The most important single property of superconductors is not their absence of resistance but their perfect diamagnetism. A magnetic field is unable to enter a superconducting sample, being restrained from entry by shielding currents which flow in a very thin surface layer. The property of perfect diamagnetism implies that the magnetic field at the surface of a superconductor is everywhere parallel to the surface (a normal magnetic field cannot be prevented from entering and is therefore prohibited by the property of perfect diamagnetism), and if the strength of the field is \( \mathcal{H} \) outside and zero inside there must be a surface current density of \( \mathcal{H}/4\pi \) (since \( \text{curl} \mathcal{H} = 4\pi \mathbf{J} \), \( \mathbf{J} \) being the volume density of current). A typical example of the magnetic field distribution around a superconductor is shown in fig. 35, where the sample is a sphere. If the mean direction of the field is regarded as defining an axis of the sphere (vertical in fig. 35), the surface currents flow along lines of latitude. Since a magnetic field may be maintained indefinitely by means of a permanent magnet, without any external source of power, it follows that the screening currents are

† For a detailed account of superconductivity see D. Shoenberg, *Superconductivity* (Cambridge University Press, 1952).
entirely non-dissipative, and in this case the property of perfect conductivity is an immediate corollary of the perfect diamagnetism. This is not so obviously true for multiply-connected superconductors, or superconducting wires fed by an external circuit, but it is rather probable that, although no rigorous deduction of perfect conductivity from perfect diamagnetism has been given, it is nevertheless not far from physical reality to regard the latter as the primary property to which the former owes its existence. The present discussion will be confined to simply-connected bodies where this element of doubt is absent. We shall also consider only massive superconductors for which the thickness of the surface layer carrying the screening currents is negligibly small, so that the description of the body as perfectly diamagnetic ($B = 0$) is entirely adequate.

If a long cylindrical superconductor is placed in a magnetic field parallel to its length, the field does not enter until a certain critical field, $H_c$, is reached. When the critical field is exceeded the metal reverts to its normal, resistive state and the external field penetrates, so that within the metal $B = H$. In reality the susceptibility of the normal metal is not exactly zero, but it is so small that the error involved in putting $B$ and $H$ equal is negligible in practice. There is no difficulty in modifying the following arguments to include the normal susceptibility. If the field is slowly reduced from its value greater than $H_c$ the metal reverts to its perfectly diamagnetic state at the field strength $H_c$, with expulsion of all the magnetic flux from its interior, a striking phenomenon known, after its discoverers, as the Meissner-Ochsenfeld effect.† Thus the magnetic transition between the superconducting and the normal states is reversible in the thermodynamic sense, and the curve (fig. 36) showing how $H_c$ depends on temperature

† Or often, with inequitable brevity, simply the Meissner effect. It should be pointed out that this description of the effect is an idealization on two counts. First, it is very commonly observed, particularly with pure metals, that the field must be reduced below $H_c$ before the superconducting state is re-established. This behaviour is analogous to the supercooling of vapours, and does not occur if a nucleus of superconducting material is formed either in regions of impurity or physical strain, or by artificial means. The phenomenon of supercooling is attributed, as in the vapour-liquid system, to the influence of a high interphase surface energy inhibiting the formation of small nuclei from which the transition may proceed. A second idealization is that the magnetic flux is entirely expelled at the transition. In fact a little is always trapped within the specimen, but in a well-prepared specimen it need not be more than $\frac{1}{10} \%$ of the flux present before the transition started. This trapped flux is not uniformly distributed over the specimen, but is confined to small channels which do not become superconducting. In the superconducting regions $B = 0$. Neither of these effects invalidates our assumption in what follows that the magnetic behaviour may be idealized as in the text without essentially falsifying the physical picture.
is a transition curve between two phases in the same sense as the term
was used in discussing the phase diagram of simple substances.

An extra degree of freedom enters the discussion when it is realized
that the transition temperature and the value of \( H_c \) at a given tem-
perature are affected, if only to a small extent, by pressure. If we
include the influence of pressure we must regard the state of the metal
as determined by three parameters of state, for which \( T, H \) and \( P \)
are the most convenient choice, and the transition line now becomes
extended into a transition surface in \((T, H, P)\) space. Since the effect
of pressure is small (the transition temperature of tin is changed from

3.73 to 3.63° K. by a pressure of about 1700 atmospheres), sections of
the transition surface at different attainable pressures do not differ
greatly from the form of fig. 36.

Let us now consider the analogues of Clapeyron’s equation for this
three-parameter system. We shall confine our attention to a specimen
of unit mass in the form of a long cylinder, for which the demagnetizing
factor is zero.† It may easily be seen, by extension of the arguments
developed in the last section, that the two phases are in equilibrium at
such points that their ‘magnetic Gibbs functions’, \( g' \), are equal, \( g' \)
being defined by the equation (see (3.13) for the significance of the
primes),

\[
g' = u' - Ts + P v - H m, \tag{8.6}\]

where \( m \) is the magnetic moment per unit mass. For the supercon-
ducting phase \( m_s = -v_s H / 4\pi \), since the volume susceptibility of

† See Shoenberg, loc. cit., for a full discussion of shape effects, and a more
complete account of the thermodynamic properties of superconductors.
a perfect diamagnetic is \(-1/4\pi\), while for the normal phase \(m_n=0\) and \(g'_n=g''_n\). From (8·6), since \(du'=T\,ds-P\,dv+\mathcal{K}\,dm\),
\[
dq' = -s\,dT + v\,dP - m\,d\mathcal{K},
\]
so that
\[
\left(\frac{\partial g'}{\partial T}\right)_{P,\mathcal{K}} = -s, \quad \left(\frac{\partial g'}{\partial P}\right)_{T,\mathcal{K}} = v \quad \text{and} \quad \left(\frac{\partial g'}{\partial \mathcal{K}}\right)_{T, P} = -m. \quad (8·8)
\]
The analogues of Clapeyron's equation now follow immediately by the same argument as before. By considering a section of the transition surface at a constant pressure we have
\[
\left(\frac{\partial \mathcal{H}_c}{\partial T}\right)_P = -\left(\frac{\partial g'_n}{\partial T}\right)_{P, \mathcal{K}} - \left(\frac{\partial g'_s}{\partial T}\right)_{P, \mathcal{K}} = -\frac{s_n-s_s}{m_n-m_s} = -\frac{4\pi}{v_s\mathcal{H}_c}(s_n-s_s). \quad (8·9)
\]
Similarly
\[
\left(\frac{\partial \mathcal{H}_c}{\partial P}\right)_T = \frac{4\pi}{v_s\mathcal{H}_c}(v_n-v_s) \quad (8·10)
\]
and
\[
\left(\frac{\partial P}{\partial T}\right)_{\mathcal{H}_c} = \frac{s_n-s_s}{v_n-v_s}, \quad (8·11)
\]
the last equation being identical with Clapeyron's. The values of \(s_n, s_s, v_n\) and \(v_s\) to be used in these equations are of course the values taken on the transition surface, although in fact their variation with magnetic field is extremely small. Since, by the magnetic analogue of M.3, \((\partial s/\partial \mathcal{K})_{T,P} = (\partial m/\partial T)_{\mathcal{K}, P}\), we see that neither \(s_n\) nor \(s_s\) are sensibly field-dependent, the former because \(m_n=0\) and the latter because \(m_s = -v_s\mathcal{H}/4\pi\), independent of temperature, except for a minute effect caused by thermal expansion. And from (8·7) it follows that \((\partial v/\partial \mathcal{K})_{P, T} = -(\partial m/\partial P)_{\mathcal{K}, T}\), so that \(v_n\) is field-independent and \(v_s\) also, apart from an equally minute effect which results from the finite bulk modulus of the superconductor. Thus, except perhaps for the term \((v_n-v_s)\) which is a small difference of large quantities, it is precise enough in practice to use in (8·9), (8·10) and (8·11) the values of \(s_s\) and \(v_s\) in zero magnetic field, and to regard \(s_n\) and \(v_n\) as the values which the normal state would possess if it could exist in zero field.

From (8·9) it is seen that the change of entropy at the transition is given by the equation
\[
s_n-s_s = -\frac{v_s\mathcal{H}_c}{4\pi} \left(\frac{\partial \mathcal{H}_c}{\partial T}\right)_P. \quad (8·12)
\]
Fig. 36 shows that \(s_n-s_s\) vanishes at 0°K. in accordance with the third law and also at the critical temperature where \(\mathcal{H}_c=0\) and
(\partial \mathcal{H}_c/\partial T)_P \) is finite. The transition in zero field at \( T_c \) is therefore accomplished without any latent heat. This introduces us to a type of transition different from either the simple phase transition or the \( \lambda \)-transition, for here there is a finite discontinuity in specific heat, not infinite as in the \( \lambda \)-transition. This may be seen from (8.12), since

\[
c_{P_n} - c_{P_s} = -\frac{v_s T}{\pi} \left( \frac{\partial^2}{\partial T^2} (\mathcal{H}_c^2) \right)_P.
\]

Near \( T_c \) the critical field is approximately proportional to \( T_c - T \), so that the second derivative of \( \mathcal{H}_c^2 \) is a well-defined finite quantity; since

\[
\begin{align*}
\text{Fig. 37. Specific heat of normal and superconducting tin (W. H. Keesom} \\
\text{and P. H. van Laer, } \textit{Physica, 5, 193, 1938).}
\end{align*}
\]

it is positive, \( c_{P_s} > c_{P_n} \) at the transition temperature. The specific heat of tin is shown in fig. 37 for both the normal and superconducting phases. From this experimental curve and (8.13) the variation of \( \mathcal{H}_c \) with temperature may be calculated, and is found to agree well with what is measured directly.

Analogous results to (8.13) may be obtained by differentiating (8.10) with respect to pressure and temperature. In this operation only a negligible error will result from taking \( v_s \) in the denominator as a constant and equal to \( v \); the results of interest arise from the
variations of the small difference \((v_n - v_s)\) caused by changes of pressure and temperature. Thus

\[
\frac{1}{8\pi} \left( \frac{\partial^2}{\partial P^2} (\mathcal{H}_c) \right)_T^2 = \frac{1}{v} \left\{ \left( \frac{\partial v_n}{\partial P} \right)_T - \left( \frac{\partial v_s}{\partial P} \right)_T \right\} = -(k_n - k_s)
\]

(8.14)

and

\[
\frac{1}{8\pi} \left( \frac{\partial^2}{\partial P \partial T} (\mathcal{H}_c) \right)^2 = \frac{1}{v} \left\{ \left( \frac{\partial v_n}{\partial T} \right)_P - \left( \frac{\partial v_s}{\partial T} \right)_P \right\} = \beta_n - \beta_s,
\]

(8.15)

where \(k\) is written for the isothermal compressibility, and \(\beta\) for the volume expansion coefficient. The results (8.13)–(8.15) hold at all points on the transition surface. When \(\mathcal{H}_c = 0\), i.e., along the transition line in zero field, they can be cast into simpler forms:

\[
c_{p_n} - c_{p_s} = -\frac{vT}{4\pi} \left( \frac{\partial \mathcal{H}_c}{\partial T} \right)_P^2,
\]

(8.16)

\[
k_n - k_s = -\frac{1}{4\pi} \left( \frac{\partial \mathcal{H}_c}{\partial P} \right)_T^2,
\]

(8.17)

\[
\beta_n - \beta_s = \frac{1}{4\pi} \left( \frac{\partial \mathcal{H}_c}{\partial P} \right)_T \left( \frac{\partial \mathcal{H}_c}{\partial T} \right)_P,
\]

(8.18)

from which it follows, by combining these equations in pairs, that

\[
\left( \frac{\partial T_c}{\partial P} \right)_{\mathcal{H}_c = 0} = vT_c \frac{\beta_n - \beta_s}{c_{p_n} - c_{p_s}} = \frac{k_n - k_s}{\beta_n - \beta_s},
\]

(8.19)

since

\[
\left( \frac{\partial \mathcal{H}_c}{\partial P} \right)_T \left( \frac{\partial \mathcal{H}_c}{\partial T} \right)_P = -\left( \frac{\partial T_c}{\partial P} \right)_{\mathcal{H}_c}.
\]

The experimental verification of these results is not easy, for although the change in specific heat is measurable with considerable accuracy, the expansion coefficients in both states are very small indeed, while on account of the small value of \(\partial T_c/\partial P\) (itself not easily measured) the compressibility changes by only a few parts in a million. Such data as have been obtained, however, agree satisfactorily with (8.19). These equations, which we have derived by considering the special case of a superconductor, are in fact the analogues to Clapeyron's equation applicable, as we shall see in the next chapter, to any transition in which there is no latent heat and a finite discontinuity in \(C_p\).
CHAPTER 9

HIGHER-ORDER TRANSITIONS

Classification of transitions

In the last chapter we noted three distinct types of thermal behaviour occurring along lines separating different phases or modifications of a substance, the normal transition with latent heat, the \( \lambda \)-transition without latent heat but a very high (perhaps infinite) peak of specific heat, and the so-called second-order transition in which there is no latent heat and a finite discontinuity in specific heat. The first and last are members of a classification introduced by Ehrenfest, in which the ‘order’ of a transition is determined by the lowest order of differential coefficient of the Gibbs function which shows a discontinuity on the transition line. Thus in a phase transition which involves latent heat, \( g \) is continuous across the line, but its derivatives \( (\partial g/\partial T)_P \) and \( (\partial g/\partial P)_T \) — \( s \) and \( v \) respectively, are discontinuous; such a transition is said to be of the first order. In the transition of a superconductor in zero magnetic field there is no latent heat and no volume change, so that the first derivatives of \( g \) are continuous, but the second derivatives, representing specific heat, expansion coefficient and compressibility are discontinuous, so that this is a transition of the second order. The classification may be extended indefinitely, though as the order of the transition increases it becomes less and less clear that it is appropriate to think of the process as a change from one phase to another since the discontinuity in properties becomes progressively less significant. For instance, in a third-order transition the specific heat is a continuous function of temperature, only its gradient showing a sharp break, while in a fourth-order transition the \( C_T-T \) curve is distinguished merely by possessing a discontinuity of curvature. Thus in practice it is only the first- and second-order transitions which usually arouse interest, and we shall mainly confine our discussion to these.

Now this classification of Ehrenfest’s, while having served a valuable purpose in pointing to a distinction between different types of transition, is of only limited application, since true second-order transitions are exceedingly unusual. It is probably true to say that of physically interesting systems (that is, excluding ad hoc models, of which we shall discuss one in detail) there is only one class, the superconducting transition, which bears any resemblance to an ideal second-order transition. On the other hand, there are many transitions known to
occur in widely different varieties of substance which do not comfortably conform to Ehrenfest's scheme. The transition in liquid helium is an example, and others will be mentioned later. A few conceivable specific heat curves are drawn diagrammatically in fig. 38,

\[ C_p \]
\[ T \]

\[ C_p \]
\[ 2 \]
\[ 2a \]
\[ 2b \]
\[ 2c \]
\[ T \]

\[ C_p \]
\[ 3 \]
\[ 3a \]
\[ 3b \]
\[ 3c \]
\[ T \]

Fig. 38. Classification of transitions.

and arranged so as to present the variants of Ehrenfest's classification. Type 1 is the simple first-order transition, with latent heat. Types 2, 2a, b and c show no latent heat but a discontinuity in \( C_p \); in 2a \( \partial C_p / \partial T \) tends to infinity as the transition is approached from one side, in 2b it tends to infinity from both sides; in 2c the discontinuity in \( C_p \) is infinite. The third-order transitions are analogous variants of the standard Ehrenfest third-order transition (type 3).
Not all these types have been observed in practice, but there appears to be no thermodynamical reason why they should not occur. A few examples of those which have been observed are given below,† together with some idealized theoretical models which have been calculated exactly and found to exhibit interesting transitions. The latter are placed in square brackets.

(1) First-order transitions: Solid-liquid-vapour transitions. Many allotropic transitions in solids, e.g. grey to white tin.

(2) Second-order transitions: Superconducting transition in zero field (fig. 37). [Weiss model of ferromagnetism, † Bragg-Williams model of the order-disorder transformation in β-brass.§]

(2c) λ-transitions: Order-disorder transformation in β-brass∥ (fig. 39), ammonium salts,¶ crystalline quartz∥ (fig. 40), solid hydrogen† † (fig. 41) and many other solids.


$C_p$ (cal. g$^{-1}$ deg.$^{-1}$) vs $T$ (°C.)

Fig. 40. Specific heat of crystalline quartz.

$C_p$ (cal. mole$^{-1}$ deg.$^{-1}$) vs $T$ (°K.)

Fig. 41. Specific heat of solid hydrogen containing 74% orthohydrogen, 26% parahydrogen.
(3) Third-order transitions: The Curie points of many ferromagnetics† (fig. 42).

(3c) Symmetrical λ-transitions: The antiferromagnetic transition in MnBr₂‡ (fig. 43). Liquid ⁴He (fig. 33). [Two-dimensional Ising model of the order-disorder transformation.§]

One might also include in category (3c) the critical point of liquid-vapour systems, as discussed in the last chapter. This is rather different from the rest, however, as the infinity in $C_p$ occurs only at one point, and not along a transition line.

It is well to remember that the distinctions made between different types of transition in this catalogue may prove to have been too nice. It is very easy for the character of a transition to be falsified through imperfections in the samples or experimental inaccuracy, and it is not unlikely that almost every transition which is not of first order would be found to be of type 3c under ideal conditions. The only exception to this statement is the superconducting transition, which obstinately persists in exhibiting a finite discontinuity in $C_p$ in the most refined experiments.

**Analogues of Clapeyron’s equation**

For all transitions except those of the first order, not only the Gibbs function but the entropy is continuous across the transition line, since there is no latent heat. It follows at once from Clapeyron’s equation, since in general the slope of the transition line, $dP/dT$, is finite and non-zero, that the volume also is continuous, and Clapeyron’s equation degenerates to the form $dP/dT = 0/0$. But now the continuity of $s$ and $v$ enables arguments similar to those applied to $g$ in deriving Clapeyron’s equation to be applied to $s$ and $v$. We shall first consider a second-order transition of type 2 (Ehrenfest’s second-order transition). For this $s$ and $v$ are continuous, but $(\partial s/\partial T)_P$ is not on account of the jump in $C_p$. We therefore write immediately,

$$\frac{dP}{dT} = \frac{\left(\frac{\partial s_2}{\partial T}\right)_P - \left(\frac{\partial s_1}{\partial T}\right)_P}{\left(\frac{\partial s_2}{\partial P}\right)_T - \left(\frac{\partial s_1}{\partial P}\right)_T} = \frac{\left(\frac{\partial v_2}{\partial T}\right)_P - \left(\frac{\partial v_1}{\partial T}\right)_P}{\left(\frac{\partial v_2}{\partial P}\right)_T - \left(\frac{\partial v_1}{\partial P}\right)_T},$$

or, from M. 3,

$$\frac{dP}{dT} = \frac{1}{\nu T} \frac{c_{P_2} - c_{P_1}}{\beta_2 - \beta_1} = \frac{\beta_2 - \beta_1}{k_2 - k_1}, \tag{9.1}$$

in which, as usual, $\beta$ is the volume expansion coefficient and $k$ the isothermal compressibility. Equations (9.1), which are of course identical with (8.19), are Ehrenfest’s equations for a second-order

transition. We discussed in the last chapter the degree of success with which they have been verified for the superconducting transition, the only type of transition to which they may strictly be applied.

Fig. 42. Specific heat of iron.

Fig. 43. Specific heat of anhydrous MnBr₂.
For Ehrenfest's third-order transition (type 3), not only $g$, $s$ and $v$ are continuous, but also $c_p$, $\beta$ and $k$, while the derivatives of the latter are discontinuous. There are in consequence three analogues of Clapeyron's equation for a third-order transition, which the reader will easily verify to have the form

$$\frac{dP}{dT} = \frac{1}{\nu T} \left( \frac{\partial c_p}{\partial T} \right)_P - \left( \frac{\partial c_p}{\partial T} \right)_P = \frac{\partial \beta_2}{\partial T} \left( \frac{\partial \beta_1}{\partial T} \right)_P - \left( \frac{\partial \beta_1}{\partial T} \right)_P = \frac{\partial k_2}{\partial T} \left( \frac{\partial k_1}{\partial T} \right)_P - \left( \frac{\partial k_1}{\partial T} \right)_P.$$

(9.2)

Relations between higher derivatives similarly exist for transitions of higher order. No experimental verification has been attempted for any transitions of higher than second order.

![Diagram showing variation of entropy with temperature at a $\lambda$-point.](image)

Fig. 44. Variation of entropy with temperature at a $\lambda$-point.

Since in transitions of the types (2a) and (2b) the discontinuities in $c_p$ are finite, even though $\partial c_p/\partial T$ may become infinite at the transition, Ehrenfest's equations for the second-order transition are applicable to them. On the other hand, the discontinuities in $c_p$ for types (2c) and (3c) and the discontinuities in $\partial c_p/\partial T$ for types (3a) and (3b) convert equations like (9.1) and (9.2) into indeterminacies of the form $\infty/\infty$. Although this circumstance rules out Ehrenfest's method of approach, it enables an alternative approach to be made, which may be illustrated by consideration of types (2c) and (3c). Here the specific heat rises to infinity, so that as the transition is approached from below $(\partial s/\partial T)_P$ and $(\partial^2 s/\partial T^2)_P$ tend to infinity, and the variation of entropy with temperature, at constant pressure, takes the form shown diagrammatically in fig. 44. At the transition temperature $T_\lambda$, the curve reaches a point of
inflexion, $\Lambda$, with vertical tangent, and either continues without discontinuity of gradient, for a transition of type (3c), or breaks sharply at the inflexion, for a transition of type 2c. The value, $s_\Lambda$, of the entropy at $T_\Lambda$ will normally be a smoothly varying function of pressure, so that the surface $s(T, P)$ will have a regular fold along the transition line, and at any point near this fold (on either side for (3c), but only on the left-hand side for (2c)) there will be a very great second derivative in a plane normal to the transition line, and only a much smaller one in a plane tangential to the transition line. We may therefore hope to approximate to the shape of the entropy surface by treating it, over a short range of pressure, and in the vicinity of $T_\Lambda$, as a cylindrical surface:

$$s = s_\Lambda(P) + f(P - \alpha T).$$

In this approximation it is taken to be adequate to treat the line of inflexion points $\Lambda$ as straight; this is equivalent to the assumption that the second derivative of this line is negligible in comparison with the second derivative of the function $f$ which describes the shape of the curve in fig. 44. Clearly $\alpha$ is equal to $(dP/dT)_\Lambda$, the slope of the transition line. Then, since $\alpha$ is taken as constant and $s_\Lambda(P)$ to contain no quadratic or higher terms, (9.3) yields the results

$$\left(\frac{\partial^2 s}{\partial T^2}\right)_P = \alpha^2 f^\prime\prime, \quad \left(\frac{\partial^2 s}{\partial T \partial P}\right) = -\alpha f^\prime\prime \quad \text{and} \quad \left(\frac{\partial^2 s}{\partial P^2}\right)_T = f^\prime\prime,$$

in which $f^\prime\prime$ is the second derivative of $f$ with respect to its argument. Hence

$$\left(\frac{dP}{dT}\right)_\Lambda = \alpha = -\left(\frac{\partial^2 s}{\partial T^2}\right)_P \bigg/ \left(\frac{\partial^2 s}{\partial T \partial P}\right) = -\left(\frac{\partial^2 s}{\partial T \partial P}\right) \bigg/ \left(\frac{\partial^2 s}{\partial P^2}\right)_T,$$

or, by use of M.3,

$$\frac{\partial}{\partial T} \left(\frac{\partial s}{\partial T}\right)_P = \alpha \frac{\partial}{\partial T} \left(\frac{\partial v}{\partial T}\right)_P \quad \text{and} \quad \frac{\partial}{\partial P} \left(\frac{\partial s}{\partial T}\right)_P = \alpha \frac{\partial}{\partial P} \left(\frac{\partial v}{\partial T}\right)_P.$$ 

The results (9.5) imply that in the vicinity of the transition line, $(\partial s/\partial T)_P$ is a linear function of $(\partial v/\partial T)_P$, or that

$$c_p = \alpha v T_\Lambda^\beta + \text{const.}$$

It follows from (9.6) that as $c_p$ tends to infinity, so does $\beta$, and therefore that the surface representing $v(T, P)$ also has a fold like that for $s(T, P)$. The same argument may then be applied to $v(T, P)$, to yield the equation

$$\beta = \alpha k + \text{const.}$$

Equations (9.6) and (9.7) are based upon a cylindrical approximation to the form of the entropy and volume surfaces, and may not apply at
any great distance from $T_\lambda$; they should, however, become increasingly more exact as the $\lambda$-point is approached.

It will be noted that there is a marked similarity between these equations and Ehrenfest's equations (9·1), and indeed Ehrenfest's equations are readily derived from (9·6) and (9·7). At a transition of type 2 the entropy surface has a sharp fold where the gradient changes abruptly. If this fold is smoothed out into a cylinder of high curvature,

\[ C_P \text{ v. } \beta \text{ for NH}_4\text{Cl in vicinity of } \lambda\text{-point. The temperatures involved are shown along the line.} \]

(9·6) holds on this cylinder, so that between one side of the cylinder and the other $\Delta C_P = \alpha \nu T_\lambda \Delta \beta$; when the radius of curvature of the cylinder is allowed to tend to zero, this result becomes identical with one of Ehrenfest's equations. The other is similarly derived from (9·7).

There is very little experimental material available to provide a test of these equations, but the $\lambda$-transition in ammonium chloride has been sufficiently studied to enable (9·6) to be applied to it. In fig. 45 values of $C_P$ and $\beta$ measured at the same temperature are plotted against one another, and it is clear that the linear relation predicted from (9·6) holds over an interval of several degrees below $T_\lambda$ (the data
Higher-order transitions

above $T_\lambda$ are insufficiently reliable to be useful). From the slope of the line $\alpha$ may be found, and it is predicted that the $\lambda$-temperature should be raised by 1° by applying a pressure of 113 atmospheres. Fig. 46 shows the only measurements of $T_\lambda$ as a function of pressure. In view of the scanty data the agreement of predicted and measured slopes is satisfactory. Much more information is available concerning the $\lambda$-transition in liquid helium, but it turns out that the slope deduced for $\alpha$ when $C_p$ is plotted against $\beta$, or $\beta$ against $k$, may be incorrect to the extent of a factor of nearly two if the temperature scales used in

![Graph](image)

Fig. 46. Variation of $\lambda$-point of NH$_4$Cl with pressure. The line is calculated from (9·6).

the determination of these quantities (by different groups of workers) differ from one another by as little as 0·001° K. As an error of this magnitude is too likely in practice, we cannot regard liquid helium as providing a satisfactory test. However, the validity of (9·6) and (9·7) is not open to serious doubt in the vicinity of a $\lambda$-point, and it is possible that their chief application lies in testing critically the experimental data for a transition such as that of helium, and in eliminating relative errors in the temperature scales of different workers.†

We have seen earlier that, although $c_p$ may become infinite, $c_T$ must

† For further discussion, see the article by Buckingham and Fairbank referred to on p. 126 (footnote). For the application of (9·6) and (9·7) to the $\alpha$-\$\beta$ transition in quartz, see A. J. Hughes and A. W. Lawson, J. Chem. Phys. 36, 2098 (1962).
Classical thermodynamics

remain finite (except under the most unusual circumstances), and this analysis of the \( \lambda \)-transition provides a convenient illustration. Writing (9.6) and (9.7) in the form

\[
c_P - c_0 = \alpha v T_\lambda \beta, \\
\beta - \beta_0 = \alpha k,
\]

and making use of (6.10), we find that near the \( \lambda \)-point

\[
c_P - c_v = (c_P - c_0) \left( 1 - \frac{\beta_0}{\beta} \right)^{-1} \\
= (c_P - c_0) \left( 1 + \frac{\beta_0}{\beta} + \frac{\beta_0^2}{\beta^2} + \ldots \right),
\]

or

\[c_v = (c_0 - \alpha v T_\lambda \beta_0) - \alpha v T_\lambda \beta_0 \left( \frac{\beta_0}{\beta} + \ldots \right).\] (9.8)

Now since the area under the curve of \( c_P \) must be finite, \( c_P \), and hence \( \beta \), must go to infinity less rapidly than \( (T_\lambda - T)^{-1} \), so that \( 1/\beta \) must go to zero with a vertical tangent at \( T_\lambda \). This means that as the \( \lambda \)-point is approached \( c_v \) rises (if \( \alpha \) is positive) with a vertical tangent to the finite value given by the first bracket in (9.8). The contrast between \( c_P \) and \( c_v \) is thus very marked, and indeed in ammonium chloride an analysis of the data leads to no evidence of any significant change in \( c_v \) as \( T_\lambda \) is approached. This result has importance in connexion with attempts to analyse in detail the mechanisms responsible for \( \lambda \)-points. In most calculations by statistical methods it is much easier to handle a system maintained at constant volume than one at constant pressure. But it must always be remembered that in the former the symptoms of a \( \lambda \)-transition may be much less pronounced than in the latter, and it may even be possible to lose the transition altogether by employing approximate means of calculation on a constant-volume system.

Critique of the theory of higher-order transitions

After Ehrenfest's thermodynamical treatment of second-order transitions was published it became a target for several critical attacks which, taken at face value, appeared to be not without substance. Following these attacks the literature on the subject has become rather unnecessarily confused, and we shall attempt by the following discussion to remove some of the resulting obscurity. A complete discussion can be made more easily with the aid of statistical mechanics, but we shall avoid this elaboration by analysing artificial models which may be regarded as analogues of the real physical systems of interest.
Higher-order transitions

First let us look at the criticisms of the theory, of which the two of importance are essentially concerned with pointing out a contrast between transitions of the first and second orders. Fig. 47 shows how the Gibbs function varies with temperature for the two types of transition. For the first-order transition the curves for \( g \) in the two phases (at a given pressure) cut each other at the equilibrium temperature, so that phase 1 is stable below and phase 2 above the equilibrium temperature. In the second-order transition, since there is no entropy difference between the two phases at the equilibrium temperature, but a difference in specific heat, the two curves osculate, and the difference in curvature at the point of contact ensures that there is no cross-over (in a third-order transition there would be a three-point contact at the equilibrium temperature and the curves would cross). It may now be pointed out in criticism of the conception of a second-order transition that

1) whereas two lines in general cross each other at some point, the chance of their meeting so as to osculate exactly is so small as never to be observed in the world of physical phenomena;

2) if the two lines osculate without crossing, the line corresponding to phase 1 remains below that for phase 2 both above and below the equilibrium temperature, and phase 1 is therefore stable at all temperatures.

On both these counts the critics of Ehrenfest’s theory have claimed that the second-order transitions cannot occur in nature, in spite of the fact that the superconducting transition appears to provide convincing refutation of their view.

It is now convenient to analyse in some detail a simple physical system which simulates a second-order transition, in order to see how
the criticisms can be explained away. This model of a second-order transition was suggested by Gorter, who did not give a detailed analysis, no doubt regarding its behaviour as obvious to the instructed imagination. As however even this model has been denounced as imperfect it will be as well, and in addition it will provide an instructive example of thermodynamical reasoning, to show how it leads to Ehrenfest’s equations. Gorter’s model is depicted in fig. 48. A vessel contains a small amount of liquid, the remaining space being filled with its vapour; the walls of the vessel have negligible thermal capacity and are not quite inextensible, so that the volume of the vessel is altered by a variation of the difference, $\Pi$, between the external pressure $P$ and internal pressure $P_i$. The vapour is assumed to behave as a perfect gas, having $C_p$ and $C_V$ independent of pressure and temperature. As the vessel is warmed, $P$ being constant, liquid evaporates into the vapour phase so as to keep $P_i$ equal to the vapour pressure, and the effective thermal capacity of the vessel includes not only the thermal capacities of liquid and vapour but also the latent heat of evaporation. At a certain temperature, $T_0$, the last drop of liquid evaporates (the amount of liquid is adjusted so that this occurs below the critical point), and thereafter there is no latent heat contribution to the effective thermal capacity, which thus shows a sharp drop, as in a second-order transition. At the same time the internal pressure $P_i$ which up to $T_0$ had been the vapour pressure, now begins to increase in proportion to $T$, following the perfect gas law. There is thus a discontinuity in $(\partial \Pi/\partial T)_P$, and hence in $(\partial V/\partial T)_P$, just as in a second-order transition. It will also be seen that the compressibility shows a discontinuity at $T_0$.

We now analyse the model in detail (we shall leave the reader to verify some of the intermediate steps of the calculation). When $P = 0$, let $T_0$ be the ‘transition’ temperature at which the last drop of liquid disappears, and correspondingly let the internal pressure be $P_0$ and the volume of the vessel $V_0$. Let the elasticity of the vessel be such that $(dV/d\Pi) = -a$. First we calculate how the transition temperature depends on $P$. When $P$ is increased from zero to $\delta P$, let the transition temperature change from $T_0$ to $T_0 + \delta T$, and the internal pressure at the transition temperature from $P_0$ to $P_0 + \delta P_i$. Then at the transition temperature $P_i$ is equal to the vapour pressure, and from Clapeyron’s equation,

$$\delta P_i = A \delta T,$$
where
\[ A = \frac{l}{T_0(v_v - v_l)}. \]

Corresponding to the changes \( \delta P \) and \( \delta P_i \), \( V \) changes by \( \delta V \), where
\[ \delta V = a(\delta P_i - \delta P) = a(A\delta T - \delta P). \]

Now at the transition all the material is in the vapour phase, to which the perfect gas law applies, so that
\[ P_0 \delta V + V_0 \delta P_i = R \delta T, \]

or
\[ \delta T = \frac{aP_0}{A(V_0 + aP_0) - R} \delta P. \]

Thus the slope \( dP/dT \) of the transition line is given by the expression
\[ \alpha = \frac{dP}{dT} = \frac{A(V_0 + aP_0) - R}{aP_0}. \quad (9.9) \]

To find the expansion coefficient \( \beta \), we note that expansion is caused (\( P \) being constant) by the increase of \( P_i \) with temperature. Below \( T_0 \), by Clapeyron’s equation \( dP_i/dT \) is simply \( A \); above \( T_0 \), by the gas law, \( dP_i/dT \) is \( R/(V_0 + aP_0) \). Hence the discontinuity in \( \beta \) is given by the expression
\[ \Delta \beta = \frac{A R - A(V_0 + aP_0)}{V_0} \frac{1}{V_0 + aP_0}. \quad (9.10) \]

A similar analysis of the variation of \( V \) caused by changing \( P \) leads to the discontinuity in isothermal compressibility,
\[ \Delta k = -\frac{a^2 P_0}{V_0(V_0 + aP_0)}. \quad (9.11) \]

From (9.9), (9.10) and (9.11) it will be seen that one of Ehrenfest’s equations is satisfied, \( \Delta \beta/\Delta k = \alpha \).

To verify the other of Ehrenfest’s equations we must calculate the discontinuity in specific heat, \( \Delta C_p \), and for this purpose it is convenient to write down expressions for the entropy of the material in the vessel. Let there be unit mass of material altogether, and let \( s_l \) and \( s_v \) be the entropy if all the material were in the liquid and vapour phase respectively at temperature \( T_0 \) and pressure \( P_0 \). Then \( T_0(s_v - s_l) = l \). At a temperature \( T_0 - \delta T \) the entropy of the liquid at its saturation vapour pressure would be \( s_l - c_{p_l} \delta T/T_0 \), while that of the vapour would be
s_v - (c_{P_v} - AV_0) \delta T/T_0. \quad \text{If then at } T_0 - \delta T \text{ an amount } \delta q \text{ of liquid is present, the entropy of the system takes the form}

\[ S = s_v - \frac{l}{T_0} \delta q - \frac{c_{P_v} - AV_0}{T_0} \delta T. \]

Since it follows from the gas law and Clapeyron's equation that

\[ \delta q = AV_0 \frac{A(aP_0 + V_0) - R}{Rl} \delta T, \]

therefore

\[ S = s_v - \left( \frac{A^2V_0}{R} (aP_0 + V_0) - 2AV_0 + c_{P_v} \right) \frac{\delta T}{T_0}, \]

and the effective thermal capacity just below \( T_0 \),

\[ C_{P1} = \frac{A^2V_0}{R} (aP_0 + V_0) - 2AV_0 + c_{P_v}. \]

The thermal capacity just above \( T_0 \) is easily seen to take the form

\[ C_{P2} = c_{P_v} - \frac{RV_0}{aP_0 + V_0}. \]

Hence

\[ \Delta C_P \equiv C_{P1} - C_{P2} = \frac{T_0}{P_0} \left( \frac{A(aP_0 + V_0) - R}{aP_0 + V_0} \right)^2. \quad \text{(9.12)} \]

From (9.9), (9.10) and (9.12) it follows that \( \Delta C_P/\Delta \beta = V_0 T_0 \alpha \), in agreement with Ehrenfest's equation.

This model serves to show that there is no intrinsic violation of thermodynamic principles involved in the existence of a second-order transition, and we may now examine the criticisms mentioned above in the light of the model. It is immediately clear that they are based on an erroneous analogy with first-order transitions. To take the second criticism first, at temperatures below that at which the lines 1 and 2 (fig. 47b) meet, the stable phase 1 in Gorter's model is that in which the vessel contains both liquid and vapour, while phase 2 corresponds to supercooled vapour only. As the transition temperature is approached, the amount of liquid steadily diminishes until at the point of contact of the lines it finally vanishes. The continuation of line 1 above this
temperature is physically absurd—it could only mean a state in which the vessel contains a negative amount of liquid. Thus the true diagram should rather consist of a single line at temperatures above the transition, which breaks into two branches below the transition temperature. By the same token the first criticism is also disposed of. The two lines do not correspond to totally different phases, such as liquid and vapour, which can be considered independently of one another so that the phase transition results from an almost fortuitous meeting of the lines; rather, the two phases become more and more similar in constitution as the transition temperature is approached, and at that temperature they are actually identical.

We may see from this analysis what is the characteristic difference between first-order transitions and transitions of the second and higher orders. The two phases which are in equilibrium at a first-order transition are different in their physical constitution, greatly different when they are solid and vapour, not so greatly when they are solid and liquid, but always sufficiently different that they possess different energies, entropies and volumes. In a second-order transition, on the other hand, the two phases (and at this stage we may begin to doubt the wisdom of using this terminology to describe the two states on either side of the transition line) are identical in constitution, energy, entropy and volume. Where they differ is in the rates of variation with respect to temperature, pressure, etc., of these primary thermodynamical parameters. In fact whereas a first-order transition marks the point at which a major change in properties occurs, a second-order transition only marks the point at which a change begins to occur. Thus in Gorter’s model the jump in specific heat (as the temperature is decreased) occurs when the liquid phase begins to condense. Similarly the transition in β-brass, according to the simplified description of Bragg and Williams, marks the onset of an ordering process, not the establishment of an ordered state. Above the transition temperature copper and zinc atoms, present in equal numbers, are arranged at random on a body-centred cubic lattice; at very low temperatures the two types of atom take up a completely ordered arrangement on alternate lattice sites, as shown in fig. 49. At the transition temperature itself the arrangement is still quite random, in the sense that if we count the number of copper and zinc atoms on one set of sites (those denoted by open circles for example) we shall find them to be equal. But as the temperature is lowered the tendency begins to show for the copper atoms to favour one set of sites and the zinc atoms the other, and this tendency becomes more pronounced as the temperature falls until at 0°K. there is complete order. It should be emphasized that this is a simplified theoretical model which leads, when worked out in detail, to a second-order transition of the Ehrenfest type, while the
realism conforms more nearly to a transition of type 2c. This does not, however, detract from its value as an illustration of the way in which a second-order transition marks the beginning, not the achievement, of a change in character of a physical system.

We have seen how the critics of higher-order transitions were misled by a false analogy with first-order transitions, so that they implicitly assumed the existence of two g-surfaces, one for each 'phase' and each capable, as it were, of existing independently of the other. The justification for this assumption in the theory of first-order transitions, as was discussed in Chapter 8, essentially lies in the possibility of establishing superheated and supercooled states, and thus of demonstrating

![Ordered structure of β-brass.](image)

Fig. 49. Ordered structure of β-brass.

the actual intersection of the surfaces. Let us conclude our examination of higher-order transitions by inquiring into the extent to which any analogues of superheating and supercooling can be expected in the vicinity of the transition line. We may deduce immediately from Gorter's model and the ensuing discussion that superheating is inconceivable, since there is no continuation above the transition line of the surface corresponding to that phase which is stable at lower temperatures. We might also conclude that supercooling is a theoretical possibility, since the vapour in the vessel may remain in a supercooled, uncondensed state below $T_b$, but this conclusion will turn out to be misleading, since it is in this one, almost trivial, respect that Gorter's system is an unsound model of a real second-order transition.

The possibility of superheating and supercooling at a first-order transition is due to the essential difference in the constitution of the two phases concerned. Just as the volume contributions to their
energies and entropies are different, so in general we must expect the surface contributions to differ also, so that there will be a surface tension at a boundary between the phases. This surface tension imposes what may be thought of, in mechanical terms, as a potential barrier between the two phases. If we imagine the condensation of a slightly supercooled vapour to proceed by the formation and subsequent growth of a drop of liquid, we may represent the availability of the whole system as a function of the radius of the drop, making the crude approximation that the contribution of the drop is simply its mass times the availability per unit mass of liquid, plus the surface tension times the area of the drop. If the vapour is supercooled, \( g_v > g_l \), and the dependence of the availability on the radius of the drop is expressed by the equation

\[
A(r) - A(0) = 4\pi r^2 \sigma - \frac{4}{3} \pi r^3 \rho_l (g_v - g_l),
\]

in which \( A(r) \) is the availability of the system containing a drop of radius \( r \), \( A(0) \) is the availability of the system before the drop is formed, \( \sigma \) is the surface tension and \( \rho_l \) the density of the liquid. As on p. 110, \( g_v \) and \( g_l \) must both be calculated at the pressure and temperature of the vapour. This expression is shown in fig. 50, from which it will be seen that although the availability is lowered by the production of a large drop, the early stages of formation of a drop involve a raising of \( A \), which is precluded by the arguments of Chapter 7. This is in essence the reason why supercooling is possible, although the argument given
here is too superficial to be entirely correct; taken at its face value it would imply that however great the supercooling there could never be any condensation to the liquid phase, except by the introduction of an extraneous impurity on which condensation could readily occur. A more sophisticated approach to the problem, by fluctuation theory or by treating the early stages of formation of the drop as a quasi-chemical reaction between gas molecules,† shows that there will always be present a very small number of droplets, and that condensation may in principle always occur when the vapour is supercooled, by the growth of these droplets. The supercooled vapour is thus not metastable in the strict mechanical sense that it corresponds to a local, rather than an absolute, minimum of $A$; it is rather to be regarded as slowly transforming itself into the liquid phase, but at so slow a rate as to be inappreciable. The rate may be calculated, and it is found that water vapour at room temperature and at a pressure which is twice the equilibrium vapour pressure should condense, without external aid, in about $10^{40}$ years. As the pressure is increased the time for condensation diminishes, until at six times the vapour pressure the time is calculated to be only a few seconds, and this accords fairly well with careful observations on pure water vapour. It is clear that to the purist the supercooled state is not acceptable as an equilibrium state. Nevertheless if the supersaturation is not too great, the contribution to the Gibbs function of the system by the small number of droplets present after a reasonable time is quite immeasurably small, so that the $g$-surface apparently runs smoothly across the equilibrium line. Under these circumstances, as discussed in Chapter 2, we can afford for thermodynamical purposes to treat the supercooled system as if it were genuinely metastable.

In Gorter's model the possibility of supercooling at the second-order transition arises from the possibility of supercooling of a vapour which, we have seen, is the consequence of a non-zero surface tension. But if we take account of surface tension in the model the transition ceases to be strictly of the second order. We may imagine the vessel just below the transition temperature to contain one droplet suspended in the vapour. On account of surface tension the equilibrium pressure in the vessel will be modified in accordance with Kelvin's vapour-pressure relation, (7.16), and will be higher than the vapour pressure over a plane surface. Now although (see p. 111) a drop surrounded by vapour maintained at constant pressure is at best in unstable equilibrium, if the vapour is confined to a fixed volume the equilibrium is stable for drops greater than a certain critical size; this is because the act of evaporating a little liquid from the drop increases the pressure of the vapour at a greater rate than is required by (7.16). But below

this critical size the drop is unstable and collapses suddenly. Thus in Gorter’s model the introduction of surface tension implies that the amount of liquid does not fall smoothly to zero, and in fact the transition becomes one of the first order, albeit with a very minute latent heat. If we wish to simulate precisely a second-order transition we must put the surface tension equal to zero, and then we automatically eliminate the prime cause of supercooling in the vapour.

By this analysis we have removed any justification for taking the Gorter model as favouring the possibility of supercooling in a second-order transition, and indeed there is no reason to expect supercooling to occur. For, in contrast to a first-order transition, no meaning is attachable to the idea of a phase-boundary at a second-order transition, since the two ‘phases’ are identical along the transition line.† No discontinuity of properties occurs in crossing the transition line, and there is therefore nothing to inhibit the transition. In fact no supercooling has even been observed at any transition of higher than first order.‡ The behaviour of some superconductors exemplifies clearly the contrast between first- and second-order transitions. In a magnetic field the transition is of the first order and one may expect superheating and supercooling to be observed. Both phenomena have in fact been observed, and the latter is particularly striking in aluminium, which may when very pure be maintained in the normal (non-superconducting) state in a magnetic field whose strength is only one-twentieth of the critical field, $H_c$. It has never, however, been found possible to reduce the field to zero at any temperature below $T_c$ without the superconducting state being established. Diagrammatically the behaviour may be represented as in fig. 51; the central curve shows $H_c$, the field at which $g_n = g_p$, while the upper and lower curves represent the limits of superheating and supercooling respectively. At any non-zero value of $H$ both supercooling and, to a lesser extent, superheating are possible, but when $H = 0$ the transition proceeds without hysteresis at the transition temperature $T_c$. At temperatures below $T_c$, with $H = 0$, the normal state cannot exist in any sort of equilibrium, stable or metastable.

We must therefore conclude that from a thermodynamical point of

† This is true only for a homogeneous sample. In an inhomogeneous sample, as for instance a very tall cylinder in which, on account of gravity, the pressure varies with height, it is in principle possible to establish a phase boundary in equilibrium, and the stable position of the phase boundary will alter as the temperature is changed.

‡ It is often observed with alloys such as β-brass, which exhibit the order-disorder phenomenon, that the disordered state may be maintained at temperatures well below the transition temperature by sufficiently rapid cooling. The reason why this should not be regarded as analogous to supercooling will be explained on pp. 157–8.
view (and this conclusion is strengthened by a detailed analysis of real physical systems by statistical means) we are not justified in drawing a diagram like fig. 47b to represent a second-order transition. No physical meaning can in general be attached either to the line representing phase 1 above $T_c$ or to the line representing phase 2 below $T_c$. It is far better to regard the $g$-surface as a single-valued function of $P$ and $T$, which shows a discontinuity in its second derivatives along a certain line, the transition line. This provides the simplest, and physically most exact, picture of a second-order transition, and leads

\[ \mathcal{H} \]
\[ T \]

Fig. 51. Superheating and supercooling of a superconductor.

immediately to Ehrenfest's equations without admitting any validity to the criticisms which were based on analogy with a first-order transition. In no useful sense can the second-order transition be regarded as the limiting form of a first-order transition in which the latent heat has been allowed to tend to zero.

This conclusion is just as valid for other higher-order transitions, as may be illustrated by two simple examples. The perfect Bose-Einstein gas shows a third-order transition at its point of condensation (fig. 42). The theory of this phenomenon allows one and only one state of the gas for any given values of pressure and temperature, and reveals how the $g$-surface possesses a line of discontinuities in the third differential coefficients. There is no question here of any conceivable continuation of either branch of the surface across the transition line. As a second example let us consider a $\lambda$-transition such as that of $\beta$-brass. The theory of Bragg and Williams, mentioned above, led to a second-order transition at the point where the ordering process began as the temperature was lowered, but this is not true to the facts (fig. 41). In particular the rounded portion of the curve for $C_P$ just above $T_\lambda$ is evidence, as more refined theories show, that order is not completely destroyed
at $T_\lambda$, but that there is a persistence of 'local order' to higher temperatures, in the sense that there remain in the equilibrium state small groups of atoms in which there is a marked tendency for alternation of copper and zinc atoms. If we choose any copper atom at random we shall find on the average that its nearest neighbours are rather more likely to be zinc that copper atoms, and the next nearest neighbours rather more likely to be copper than zinc. As we move away from the chosen atom, however, we shall find that this discrimination between lattice sites becomes less and less marked. It is possible to define the range of local order along the following lines. Starting from a given copper atom we may label alternate sites as $C$ (copper) or $Z$ (zinc) sites according to their occupants in a perfectly ordered arrangement. Then, selecting those sites which lie at a distance $R$ from the chosen central copper atom we may count the number, $r$, of copper atoms on $C$-sites and zinc atoms on $Z$-sites, and the number, $w$, of copper atoms on $Z$-sites and zinc atoms on $C$-sites, and define the degree of order $\omega(R)$ by the equation

$$\omega(R) \equiv \frac{r-w}{r+w}.$$

In a completely ordered lattice $\omega = 1$, since $w = 0$; in a completely disordered lattice $\omega = 0$, since there is random occupation of the sites, and $r = w$. Let us now plot $\omega$ as a function of $R$; we may expect to find, after repeating this procedure many times for different central atoms, an average diagram such as fig. 52 and $R_0$, the width of the plot (to a value of $R$ at which $\omega(R_0) = \frac{1}{2}\omega(0)$, say) is a measure of the range of local order. As the temperature is lowered towards $T_\lambda$, both $\omega(0)$ and $R_0$ increase until at $T_\lambda$ the range of order becomes infinite; $\omega(R)$ does not tend to zero as $R$ tends to infinity. Further lowering increases both $\omega(0)$ and the value to which $\omega(R)$ tends as $R$ tends to infinity, which is a measure of the degree of long-range order. This picture of the transition fixes the transition point as the temperature at which long-range order first appears on cooling. But it will be seen that now there is no sharp distinction between disordered and partially ordered states; there is no definable state at temperatures above $T_\lambda$ which can be extrapolated into metastable existence below $T_\lambda$ without being in itself a state of long-range order.

In the preceding description of the ordering process it has been assumed that at every temperature there is an equilibrium state of order (either of short or long range), and that any experiment is performed sufficiently slowly that at each temperature the equilibrium state is established. It may now be argued that of necessity this precludes the occurrence of supercooling, just as a sufficiently slow cooling of a vapour through its condensation temperature would avoid the establishment of the supersaturated vapour phase. If the alloy is cooled
rapidly from a temperature well above $T_\lambda$ to one well below $T_\lambda$ it may retain its disordered state virtually indefinitely on account of the very slow rate of migration of the atoms at low temperatures. There is, however, an important distinction to be made between these two cases. On the one hand a vapour just above its condensation temperature reaches equilibrium in a very short time, and on cooling to the supersaturated state just below the condensation temperature still retains this property of reaching what is apparently equilibrium extremely rapidly. As we have said before, the state is not strictly one of equilibrium since over a very long period condensation will occur. Still there is a sufficiently large margin between the short time for apparent equilibrium of the vapour ($10^{-8}$ sec., say) and the long time of condensation (perhaps $> 10^{100}$ years for small supercooling of a pure vapour) that a meaning may be attached to the concept of a supercooled vapour in equilibrium. On the other hand the time taken for an alloy just above $T_\lambda$ to reach its equilibrium state of partial short-range order is not significantly different from the time taken to establish long-range order just below $T_\lambda$, since the same migration mechanism is involved in both cases. When a disordered alloy is quenched by rapid cooling to a temperature well below $T_\lambda$, it is frozen into a particular configuration which is not analogous to the state of a supercooled vapour. For the state of the vapour is thermodynamically well defined, in that it does not depend on how fast the vapour was cooled or from what temperature, whereas the state of the quenched alloy shows more or less order according to the rate of cooling and the initial temperature. The only way in which the state of the whole alloy below $T_\lambda$ may be made independent of the manner in which it was achieved is by allowing sufficient time for migration to occur, and this necessarily involves, as pointed out above, the production of the long-range ordered state, as
being the only well-defined state at temperatures below $T_{\lambda}$. The existence of the quenching phenomenon does not therefore invalidate the view that true supercooling is never observed, and is indeed unobservable, in any but first-order transitions.

This last example has taken our reasoning well beyond the confines of classical thermodynamics, but the conclusion we arrive at is not dependent on the illustrations given of its application. The relations which may be derived for the thermodynamic behaviour in the vicinity of a transition line, of first or higher orders, in no case depend on the assumption that such a line marks the intersection or meeting of different surfaces; only for first-order transitions can such an assumption lead to a clarification rather than an actual misinterpretation of the physical situation.