Secondary Variables in Critical Phenomena

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Received February 16, 1971

1. Introduction

A wide variety of systems exhibit critical phenomena. In liquid-vapor systems the critical point is displayed in a pressure–density diagram as the point of vanishing slope and curvature of the isotherm for the critical temperature. In binary liquid systems, the chemical potential and the mole fraction of one of the components are the appropriate variables, instead of pressure and density.

The isotherms for a ferromagnetic material are exhibited schematically in Figure 1, in which it is seen that the magnetic field H and magnetization M take the place of pressure and density, respectively. It is assumed that the magnetic field is always in a fixed direction, but may be positive or negative. At high temperatures the magnetization decreases gradually as the field is decreased but at low temperatures a permanent magnetization remains at zero field, which changes sign as the sign of the field is reversed. The temperature dividing these two regions is known as the critical temperature, the λ temperature, or the Curie temperature.

In all these cases the variables mentioned may be regarded as those primarily associated with the order–disorder phenomena. In other cases, the order–disorder variables are more subtle, and cannot be experimentally manipulated. Such is the situation, for example, at the λ transition of liquid helium, or at the order–disorder transition of a binary alloy.

As further examples, we may consider certain theoretical models. In particular, we may make note of the Ising lattice.[1] At each point on the lattice there is supposed to be located an elementary spin, with a magnetic dipole which can be oriented in one of two directions (say, up or down) and which interacts with a nearest neighbor so that the mutual potential energy depends upon whether they are oriented in the same or opposite directions. Such a lattice is also mathematically equivalent[2] to a lattice gas (where some of the lattice positions are occupied by atoms and some are empty) or a mixture (in which some of the positions are occupied by atoms of one kind and the rest by atoms of another). The model is thus relevant not merely to

magnetic systems but also to liquid–vapor systems, to binary solutions, and to the order–disorder phenomena in binary alloys.

The critical point is a singular point or near singular point for the thermodynamic functions.[3] Holding the density constant for the liquid–vapor system (or the equivalent variable for other systems), the specific heat rises rapidly as the critical temperature, T_c, is approached from below (within the two-phase region in the liquid–vapor system), then falls even more rapidly as the critical temperature is exceeded, as in Figure 2. Indeed, it has been commonly supposed that the specific heat rises to a logarithmic infinity or that of a very small power, α, of $1/|T - T_c|$. Here α, which is called a critical exponent, is close to zero, but may be different for $T > T_c$ and $T < T_c$. It may be that the specific heat curve is in some or all cases actually rounded off at a fairly high value,[4] but we shall treat the approach to infinity as the normal situation. It is known to be logarithmically infinite in the two-dimensional rigid Ising lattice.[5] In the three-dimensional case an exact solution has not been possible, but the thermodynamic functions have been expressed in terms of series expansions[6] whose behavior indicates that the specific heat approaches infinity logarithmically or as a small power of $1/|T - T_c|$.

Other properties[3] also show singularities. For example, in the liquid–vapor system $|\rho - \rho_c|$ along the coexistence curve (where ρ is density and ρ_c critical density) depends on $|T - T_c|$ as $|T - T_c|^\beta$, where $1/\beta$ is close to 3, and hence is not a simple parabola as expected from the classical van der Waals theory. The slope of the isotherms, e.g., $(\partial P/\partial \rho)_T$, approaches zero as $(T - T_c)^\gamma$ above the critical point with $\gamma \approx 5/4$. The critical isotherm is always much flatter than would be predicted by the van der Waals theory. Similar results, in the appropriate variables, are obtained in other systems.

The variables listed in the introductory paragraph, those directly associated with the order–disorder phenomena, are the primary variables. There are other variables which affect the critical phenomena, to which we shall refer as secondary variables.

(1) E. Ising, *Z. Physik*, **31**, 253 (1925).
(2) G. S. Rushbrooke, in "Changements de Phases," Société de Chimie Physique, Paris, 1952, p 177.
(3) M. E. Fisher, *Rep. Progr. Phys.*, **30**, 615 (1967); P. Heller, *ibid.*, **30**, 731 (1967).
(4) M. E. Fisher, *Phys. Rev.*, **176**, 257 (1968); M. E. Fisher and P. E. Scesney, *ibid.*, **A2**, 825 (1970).
(5) L. Onsager, *Phys. Rev.*, **65**, 117 (1944); B. Kaufman and L. Onsager, *ibid.*, **76**, 1244 (1949); H. S. Green and C. A. Hurst, "Order–Disorder Phenomena," Interscience, New York, N. Y., 1964; T. Schultz, D. Matthis, and E. Lieb, *Rev. Mod. Phys.*, **36**, 856 (1964).
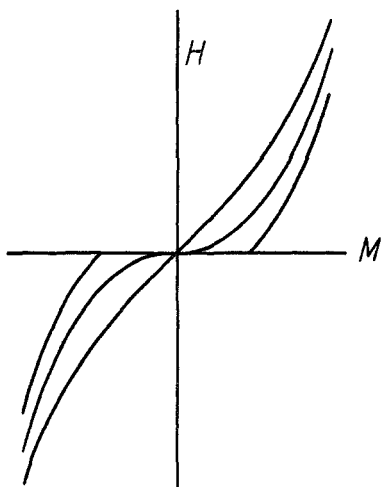(6) See C. Domb, *Advan. Phys.*, **19**, 339 (1970).

Figure 1. Isotherms for a ferromagnet. Middle curve for T_c; inner curve $T > T_c$; outer curve $T < T_c$, showing first-order transition.

Figure 2. Specific heat (cal mole^{-1} deg^{-1}) of liquid helium near its λ point.

For example, in the magnetic case the λ temperature will depend upon the pressure or the density. Thus, pressure and density are secondary variables in this case, though they are primary variables for a liquid–vapor system. If one constructs a diagram in the plane of a pair of secondary variables (e.g., pressure and density in the case of a magnet or liquid helium), then it is seen that a λ line in this plane (or, what is the same thing, a locus of critical points) is a line of singularities.

It is possible to apply thermodynamic reasoning to such a line provided one is careful in approaching the limits in which certain thermodynamic quantities become infinite.[7] One can also venture slightly beyond thermodynamics[8] by making the assumption that the partition function of the system can be factored into a lattice part, depending upon the properties of the system as it would be if no order–disorder phenomena occurred, and an order–disorder part, depending upon a dimensionless parameter J/kT, where J is an energy parameter describing the interaction between the entities responsible for the order–disorder effects. The characteristics of the partition function as a function of J/kT are responsible for the singularities at the critical point. J itself is supposed to depend only on the density or the pressure (or one of another pair of secondary variables). These assumptions lead to further relations which are almost thermodynamic in character and which are helpful for understanding the nature of the critical phenomena.

Interestingly, the character of the results depends greatly upon which one of the secondary variables J depends on. When the density ρ and the pressure P are the secondary variables, it is found that, if J depends only on P, so that it is the specific heat at constant pressure, C_p, which tends to become infinite, no difficulties arise. On the other hand, if J depends on
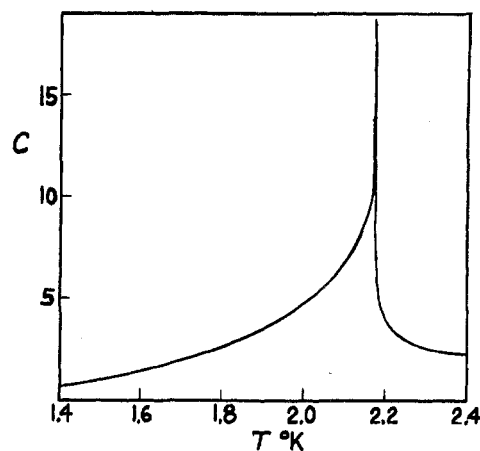
the density and C_v, the specific heat at constant volume, tends to become infinite, an instability results: either the transition turns into a first-order one, or the infinity in C_v is in some way avoided. Put in another way, the conditions of thermodynamic stability put an upper limit on C_v but none on C_p.

In order to gain a better insight into the physical significance of these results, let us fix our attention upon an Ising lattice. The theory of the magnetic behavior of the Ising lattice is based on the assumption that the lattice is rigid and that the distance between the magnetic spins is thus fixed. One would naturally suppose that the interaction between the magnets would depend upon the distance between them. Thus the critical point would depend on the density, but since, at constant pressure, the density depends upon the temperature, it is seen that there will be an interaction between the spins and the lattice forces. For example, it can be seen that if the distance between spins affects the orientation of the spins, the thus-induced spin forces, in turn, contribute to the forces between the atoms, and so affect such properties as the compressibility and coefficient of expansion. It is this interaction between the various forces involved that we wish to discuss.

According to this description the interaction energy J depends on the density. Then it is C_v which tries to become infinite; hence an instability sets in and the transition should change to first order. In real systems this has not been often observed, and, as we shall see, it may be that the infinity is avoided because of the fluctuations of individual atoms about their lattice points, or (what is not entirely unrelated) because of the presence of domains in magnetic materials, or because of a microcrystalline structure, even without the intervention of a first-order transition.

The foregoing involves the approximation that the interaction energy J depends upon one of the macroscopic variables, such as pressure or density. It was early recognized,[7a] however, that, on account of fluctuations, the interaction energy might have local variations, which in any more precise theory would need to be taken into account. It was suggested by Fisher[4]

(7) (a) O. K. Rice, J. Chem. Phys., 22, 1535 (1954); (b) R. B. Griffiths and J. C. Wheeler, Phys. Rev., A2, 1047 (1970).
(8) (a) C. Domb, J. Chem. Phys., 25, 783 (1956); (b) C. W. Garland and R. Renard, ibid., 44, 1120 (1966); (c) O. K. Rice, Phys. Rev., 153, 275 (1967).

that through such local variations the infinities in the specific heat might be avoided, and this appears to be the case for some models which have recently been proposed and worked out.[9] In perhaps the most realistic of these models,[9d] allowance was made for the possible variation of J with the distance between nearest neighbors, the normal lattice interactions were taken into account, and a shear-resisting force was introduced so that a simple cubic lattice could be used without excessive fluctuations along the lines of atoms. In this case a first-order transition did appear in the critical region, so that some of the properties of the simple thermodynamic model were retained.

In so-called mean-field theories, the behavior of any given spin in a magnetic lattice is assumed to depend only on the average value of the interaction (that is, the result of averaging J over all neighbors and then of further averaging over all sites in the lattice). This type of theory can explain the existence of critical points, but does not give the correct values of the critical exponents. The assumption that J, itself, depends only on a macroscopic variable, which we may call the mean-position theory, is a weaker assumption, but one that is somewhat related to (and, indeed, included in) the mean-field theory. The true situation, which involves local fluctuations, can be likened to a superposition of a range of cases of the mean-position theory, which results in a rounding off of infinities. The mean-position theory can thus explain, perhaps not completely, but in a simple and reasonably satisfactory fashion, many of the phenomena which occur, and this paper will be largely devoted to working out the thermodynamics and statistical thermodynamics of this model.

If rounding off lowers C_v sufficiently, then the instability does, indeed, disappear, but even a tendency for C_v to exceed a certain value will result in an instability. This, indeed, appears to occur in the ammonium halides, which we will discuss in Section 6. Ammonium chloride and bromide show λ transitions with marked anomalies in the specific heat. These appear to be connected with an order–disorder transition involving the orientation of the NH_4^+ ions. Above the λ point these crystals have the cesium chloride structure in which each NH_4^+ is surrounded by eight halide ions at the corners of a cube, and two orientations of the NH_4^+ tetrahedra are possible in which each hydrogen is pointed toward a halogen. The orientations of NH_4^+ ions are random at high temperatures but correlated at low; in NH_4Br the transition is accompanied by a change in crystal structure, but not in NH_4Cl.

An example in which C_p apparently tends to infinity is furnished by the λ transition of liquid helium, which is discussed in Section 5. At normal pressures helium remains liquid to $0°K$ because of its large zero-point motion. It has zero entropy under these conditions, and hence at $0°K$ it is a liquid in its ground state. The

(9) (a) H. Wagner, *Phys. Rev. Lett.*, **25**, 31 (1970); (b) H. Wagner and J. Swift, *Z. Physik*, **239**, 182 (1970); (c) G. A. Baker, Jr., and J. W. Essam, *Phys. Rev. Lett.*, **24**, 447 (1970); (d) G. A. Baker, Jr., and J. W. Essam, *J. Chem. Phys.*, **55**, 861 (1971).

excitations which occur at high temperatures are of two principal types, phonons and rotons (with some of intermediate character which because of the higher energy required are unimportant). The phonons are of the nature of sound waves, and are like the longitudinal waves in the Debye spectrum of a solid. They are excited at the lowest temperatures. The rotons are localized excitations, something like the vibration of a single atom in the field of its neighbors, and require about 16 cal/mole for their excitation. They become important above $1°K$. Because of the energy required, the specific heat rises since the rotons are excited more readily as the temperature increases. However, near the λ temperature the specific heat rises extraordinarily rapidly (see Figure 2) and appears to approach infinity logarithmically as this temperature is approached. (Incidentally a number of remarkable changes in the properties of the liquid occur at the λ point; for example, below the λ point it is a superfluid, which offers no viscous resistance to flow at small velocities, while above the λ point it is normal in this respect.) As will be noted in Section 5, the energy quantity primarily involved with the λ phenomenon seems to be the energy of interaction between the rotons, which we again call J, rather than the energy of excitation. This being the case, we can give a plausibility argument to explain the apparent dependence of J on pressure rather than density. The rotons, themselves, have a slightly different density than the rest of the fluid. Since the number of rotons increases rapidly with pressure, it may well be that the material between them would remain in a more uniform state at constant pressure than at constant density. Since the interaction between rotons is presumably transmitted through the intervening material, it should not be surprising if J depends primarily on P rather than on ρ. No instability, then, is to be expected.

2. Thermodynamics

Consider first the situation in which J depends on P and C_p tends to become infinite. We shall wish to follow C_p as the temperature changes along an isobar. We may write[7a]

$$(\partial C_p/\partial T)_P = -(\partial C_p/\partial P)_T(\partial P/\partial T)_{C_p} \quad (2.1)$$

Since $C_p = T(\partial S/\partial T)_P$, we have

$$(\partial C_p/\partial P)_T = T(\partial^2 S/\partial T \partial P)_V = -T(\partial^2 V/\partial T^2)_P \quad (2.2)$$

from the Maxwell relation $(\partial S/\partial P)_T = -(\partial V/\partial T)_P$. Substituted into eq 2.1 this gives

$$(\partial C_p/\partial T)_P = T(\partial^2 V/dT^2)_P(\partial P/\partial T)_{C_p} \quad (2.3)$$

Along the λ line C_p is infinite, so we write

$$\lim_{C_p \to \infty} (\partial P/\partial T)_{C_p} = dP_\lambda/dT \quad (2.4)$$

and substituting into eq 2.3 we find that, in the immediate neighborhood of the λ line

$$(\partial C_p/\partial T)_P = T(\partial^2 V/\partial T^2)_P dP_\lambda/dT \quad (2.5)$$

which may be integrated approximately to give[10]

$$C_p = T(\partial V/\partial T)_P dP_\lambda/dT + \kappa_p(P) \qquad (2.6)$$

where κ_p is a constant of integration which is negligible close to the λ line where C_p is very large. If κ_p is truly constant at constant P, then, since $C_p = T(\partial S/\partial T)_P$ and $(\partial V/\partial T)_P = -(\partial S/dP)_V$, we see that $\kappa_p = T_\lambda dS_\lambda/dT$.

Equation 2.5 is analogous to the Clapeyron and the Ehrenfest equations. Since the ratio of C_p to $(\partial V/\partial T)_P$ and the ratio of $(\partial C_p/\partial T)_P$ to $(\partial^2 V/\partial T^2)_P$ are virtually constant very close to the λ line, we may integrate between two temperatures T' and T'' very close to the λ line such that $T'' > T_\lambda > T'$. We find

$$T \frac{dP_\lambda}{dT} = \frac{\int_{T'}^{T''} C_p dT}{\int_{T'}^{T''} (\partial V/\partial T)_P dT} = \frac{\Delta H}{\Delta V} \qquad (2.7)$$

where ΔH is the "heat of transition" and ΔV is the "volume change of transition" between the temperatures T' and T''. The analogy to the Clapeyron equation is now clear. The analogy to the Ehrenfest equation is seen by writing

$$T \frac{dP_\lambda}{dT} = \frac{\int_{T'}^{T''} (\partial C_p/\partial T)_P dT}{\int_{T'}^{T''} (\partial^2 V/\partial T^2)_P dT} = \frac{\Delta C_p}{V \Delta \alpha} \qquad (2.8)$$

where $\alpha = V^{-1}(\partial V/\partial T)_P$ is the coefficient of expansion.

The behavior of the other differential coefficients can be determined from the equation

$$(\partial V/\partial T)_{C_p} = (\partial V/\partial T)_P + (\partial V/\partial P)_T(\partial P/\partial T)_{C_p} \qquad (2.9)$$

Since we see that

$$\lim_{C_p \to \infty} (\partial V/\partial T)_{C_p} = dV_\lambda/dT \qquad (2.10)$$

which is in general finite, and since $(\partial V/\partial T)_P$ becomes infinite, we see that $(\partial V/\partial P)_T$ must become infinite. Furthermore, since $(\partial V/\partial T)_P dP_\lambda/dT$ must have the same sign as C_p, which is always positive, it is seen from eq 2.9 and 2.4 that $(\partial V/\partial P)_T$ must remain negative. The isotherms in this case appear as in Figure 3.

We may derive one further relation from eq 2.11,

$$(\partial P/\partial T)_{C_p} = (\partial P/\partial T)_V + (\partial P/\partial V)_T(\partial V/\partial T)_{C_p} \qquad (2.11)$$

Inasmuch as $(\partial P/\partial V)_T = (\partial V/\partial P)_T^{-1}$ approaches zero as the λ line is approached it is seen that

$$dP_\lambda/dT = (\partial P/\partial T)_V \qquad (2.12)$$

Very similar equations can be derived for the case in which C_v tends to become infinite. All that is necessary is to interchange P and V in the equations. But it must be noted that, because the relevant Maxwell equation, $(\partial S/\partial V)_T = (\partial P/\partial T)_V$, has no minus sign, we derive, instead of eq 2.5

$$(\partial C_v/\partial T)_V = -T(\partial^2 P/\partial T^2)_V dV_\lambda/dT \qquad (2.13)$$

with a minus sign. Integrating

$$C_v = -T(\partial P/\partial T)_V dV_\lambda/dT + \kappa_v(V) \qquad (2.14)$$

(10) A. B. Pippard, *Phil. Mag.*, 1, 473 (1956); "Elements of Classical Thermodynamics," Cambridge University Press, Cambridge 1957, Chapter 9.
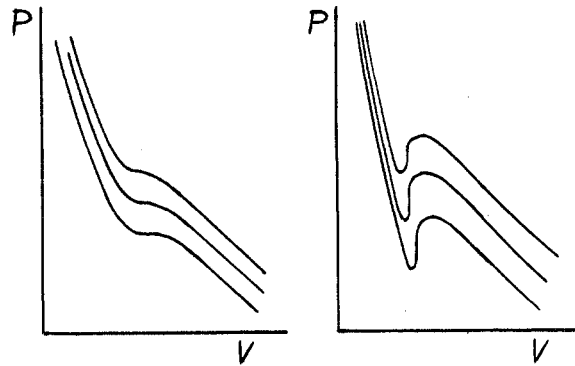

Figure 3 (left). *P–V* isotherms when C_p becomes infinite.
Figure 4 (right). *P–V* isotherms when C_v becomes infinite.

In this case $(\partial P/\partial T)_V$ becomes infinite, but since $(\partial P/\partial T)_V dV_\lambda/dT$ must have the opposite sign to C_v and hence be negative, it is seen from eq 2.10 and 2.11, which are of general validity, that $(\partial P/\partial V)_T$ must become positively infinite if $(\partial P/\partial T)_{C_p}$ is to remain finite. This gives isotherms such as shown in Figure 4, with a van der Waals loop, leading to an instability, so an infinite C_v can never actually be attained. This can be resolved by a first-order transition occurring at a pressure determined by the Maxwell equal-area construction.

In this case we may also derive

$$dV_\lambda/dT = (\partial V/\partial T)_P \qquad (2.15)$$

where V and V_λ refer to the volume in the unstable region where C_v would be infinite. It is also clear from these results that, quite aside from the instability, infinite C_p's and infinite C_v's would be mutually incompatible along the same λ line.

3. Generalized Thermodynamics

These results can be generalized. There is an infinite category of variables, Y, which we shall call volume-like, the condition being that $(\partial Y/\partial V)_T$ and $(\partial Y/\partial T)_V$ are finite and $(\partial Y/\partial V)_T$ is nonvanishing. We can also define a variable complementary to Y by the equation $[(Y)$ signifies path of constant $Y]$

$$Z = \int_{T'}^{T} (\partial S/\partial Y)_T dT_{(Y)} \qquad (3.1)$$

where T' is an arbitrary constant. Differentiating, we obtain a generalized Maxwell equation

$$(\partial Z/\partial T)_Y = (\partial S/\partial Y)_T \qquad (3.2)$$

Dividing both sides of eq 3.2 by $(\partial Z/\partial Y)_T$ gives the complementary Maxwell relation

$$(\partial Y/\partial T)_Z = -(\partial S/\partial Z)_T \qquad (3.3)$$

and by integrating

$$Y = -\int_{T'}^{T} (\partial S/\partial Z)_T dT_{(Z)} \qquad (3.4)$$

We shall see that Z is a pressure-like variable in the sense that $(\partial Z/\partial P)_T$ is everywhere finite and nonvanishing and $(\partial Z/\partial T)_P$ is everywhere finite, if Y is volume-like. In the meantime, the relations between Y and Z

being just like those between V and P, we may generalize the equations of Section 2.

If C_y tends to approach infinity along a λ line

$$dY_\lambda/dT = (\partial Y/\partial T)_Z \tag{3.5}$$

$$C_y = -T(\partial Z/\partial T)_Y dY_\lambda/dT + \kappa_y(Y) \tag{3.6}$$

and

$$(\partial Z/\partial Y)_T \longrightarrow \infty \tag{3.7}$$

with the same sign as C_y.

If C_z approaches infinity along a λ line

$$dZ_\lambda/dT = (\partial Z/\partial T)_Y \tag{3.8}$$

$$C_z = T(\partial Y/\partial T)_Z dZ_\lambda/dT + \kappa_z(Z) \tag{3.9}$$

and

$$(\partial Y/\partial Z)_T \longrightarrow \infty \tag{3.10}$$

with the opposite sign to C_z. Similarly to C_p and C_v, C_y and C_z could not both be infinite along the same line.

It is also possible to relate C_y to C_v and C_z to C_p. Thus,

$$C_y = T(\partial S/\partial T)_Y = T(\partial S/\partial T)_V +$$
$$T(\partial S/\partial V)_T(\partial V/\partial T)_Y$$
$$= C_v + T(\partial P/\partial T)_V(\partial V/\partial T)_Y$$
$$= C_v + T(\partial S/\partial Y)_T(\partial Y/\partial V)_T(\partial V/\partial T)_Y$$
$$= C_v - T(\partial Z/\partial T)_Y(\partial Y/\partial T)_V \tag{3.11}$$

and, similarly

$$C_z = C_p - T(\partial V/\partial T)_P(\partial P/\partial T)_Z$$
$$= C_p + T(\partial Y/\partial T)_Z(\partial Z/\partial T)_P \tag{3.12}$$

Also

$$C_z = T(\partial S/\partial T)_Z = T(\partial S/\partial T)_Y +$$
$$T(\partial S/\partial Y)_T(\partial Y/\partial T)_Z$$
$$= C_y + T(\partial Z/\partial T)_Y(\partial Y/\partial T)_Z \tag{3.13}$$

which, like the relation between C_v and C_p, can be transformed in various ways.

Since $(\partial Y/\partial T)_Z$ will not in general be equal to $(\partial Y/\partial T)_V$, comparison of eq 3.6 and the last line of eq 3.11 shows that C_v and C_y would become infinite together if the stability criterion did not need to be considered.

Similarly, the infinities of C_z and C_p are bound together. Thus, it is seen that there is a category of specific heats, C_y, where Y is volume-like, which have a common line of singularities, and another category, C_z, where (as we shall show) Z is pressure-like, which have a common line of singularities, and these lines cannot coincide or cross.

We shall now show that, if Y is volume-like, Z is pressure-like. In general, no problem arises, except at λ lines. First consider one where C_y becomes infinite. Along such a line C_z and C_p are finite (again, of course, this is a mathematical conclusion, obtained by ignoring

the instability); therefore, by eq 3.12 and since $(\partial Y/\partial T)_Z$ is, by eq 3.5, not zero, $(\partial Z/\partial T)_P$ is finite. To investigate $(\partial Z/\partial P)_T$ divide the Maxwell relation $(\partial V/\partial T)_P = -(\partial S/\partial P)_T$ by eq 3.3. This yields

$$(\partial Z/\partial P)_T = (\partial V/\partial T)_P/(\partial Y/\partial T)_Z \tag{3.14}$$

and shows at once that $(\partial Z/\partial P)_T$ is finite and nonzero if the λ line has a finite nonzero slope in the V–T and Y–T planes.

On the other hand, if C_z and C_p become infinite along the λ line, we note that $(\partial Z/\partial T)_Y$ is finite and nonzero, and, since $(\partial P/\partial V)_T$ is zero and $(\partial V/\partial T)_Y$ is finite, $(\partial P/\partial T)_Y = (\partial P/\partial T)_V$. Thus

$$(\partial Z/\partial T)_Y = (\partial Z/\partial T)_P + (\partial Z/\partial P)_T(\partial P/\partial T)_V \tag{3.15}$$

Similarly, since P and Z, and V and Y, are simultaneously interchangeable

$$(\partial P/\partial T)_V = (\partial P/\partial T)_Z + (\partial P/\partial Z)_T(\partial Z/\partial T)_Y \tag{3.16}$$

Now $(\partial Z/\partial T)_Y$ and, by eq 2.12, $(\partial P/\partial T)_V$ are finite and nonzero. If C_p and C_z become infinite in the same way we see from eq 3.12 that $(\partial Z/\partial T)_P$ and $(\partial P/\partial T)_Z$ are finite, so, by eq 3.15–3.16, $(\partial Z/\partial P)_T$ and $(\partial P/\partial Z)_T$ are both finite, and hence nonzero, and we see that Z fulfills the condition for being pressure-like. If we do not wish to assume that C_p and C_z necessarily become infinite in the same way, we can, by an argument similar to that of the preceding paragraph, show at least that if Z is pressure-like then Y must be volume-like; so in any case we must have a large class of pairs of complementary variables, one of the pair being volume-like, the other pressure-like.

The relations of this section can be used to derive some useful results. For example, an equation found by Buckingham and Fairbank[11] for C_v along a λ line where C_p becomes infinite can be found from the second line of eq 3.11 if we set $Y = C_p$. Of course C_p is not a volume-like variable, but eq 3.11 does not depend on this. So we find

$$C_v = C_{C_p} - T(\partial P/\partial T)_V(\partial V/\partial T)_{C_p}$$

or, letting $C_p \longrightarrow \infty$ and noting eq 2.10 and 2.12

$$C_{v,\lambda} = T_\lambda dS_\lambda/dT - T_\lambda(dP_\lambda/dT)dV_\lambda/dT \tag{3.17}$$

so that $C_{v,\lambda}$ can be determined from the properties of the λ curve alone.

It is interesting that eq 3.17 gives the largest value that C_v may have if the system is to remain thermodynamically stable.[12] Indeed, this is general for any line of constant Y. Write

$$(\partial P/\partial T)_V = (\partial P/\partial T)_Y + (\partial P/\partial Y)_T(\partial Y/\partial T)_V$$
$$= (\partial P/\partial T)_Y + (\partial P/\partial V)_T(\partial V/\partial Y)_T(\partial Y/\partial T)_V$$
$$= (\partial P/\partial T)_Y - (\partial P/\partial V)_T(\partial V/\partial T)_Y \tag{3.18}$$

Substituting into eq 3.11

(11) M. J. Buckingham and W. M. Fairbank, *Progr. Low Temp. Phys.*, **3**, 80 (1961).

(12) J. C. Wheeler and R. B. Griffiths, *Phys. Rev.*, **170**, 249 (1968).

$$C_v = C_y - T(\partial P/\partial T)_r(\partial V/\partial T)_r +$$
$$T(\partial P/\partial V)_T(\partial V/\partial T)_r{}^2$$
$$\le C_y - T(\partial P/\partial T)_r(\partial V/\partial T)_r \quad (3.19)$$

since, for stability, $(\partial P/\partial V)_T \le 0$.

If along a line C_v tends to become larger than this, a first-order transition will occur, as described earlier, even if C_v does not tend to infinity, because of the implied positive (though now finite) value of $(\partial P/\partial V)_T$.

4. Statistical Thermodynamics

We shall now examine the consequences of the assumption,[8b] discussed in the Introduction, that the canonical partition function Q may be factored into a lattice part Q_1 and a "spin" (order–disorder) part Q_s,

$$Q = Q_1 Q_s \quad (4.1)$$

Q_s being a function of $I = J/kT$ where J, in turn, depends only on the density, ρ, or the volume, V, of a fixed amount of material. We shall write $dQ_s/dI = Q_s'$ and $d^2Q_s/dI^2 = Q_s''$.

The thermodynamic functions can be calculated from Q by logarithmic differentiation using the standard formulas, and they may be divided into lattice and "spin" parts. Thus, for the pressure and energy of the system we write

$$P = kT\partial \ln Q_1/\partial V + (Q_s'/Q_s)dJ/dV = P_1 + P_s \quad (4.2)$$

$$E = kT^2\partial \ln Q_1/\partial T - (Q_s'/Q_s)J = E_1 + E_s \quad (4.3)$$

By further differentiation of eq 4.3 we obtain

$$C_v = C_{v,1} + C_{v,s}$$
$$= C_{v,1} - (Q_s'/Q_s)^2 J^2/kT^2 + (Q_s''/Q_s)J^2/kT^2$$
$$= C_{v,1} - E_s{}^2/kT^2 + (Q_s''/Q_s)J^2/kT^2 \quad (4.4)$$

and by appropriate use of eq 4.2, 4.3, and 4.4

$$\left(\frac{\partial P}{\partial V}\right)_T = \left(\frac{\partial P}{\partial V}\right)_{T,1} + \frac{T}{J^2}\left(\frac{dJ}{dV}\right)^2 C_{v,s} - \frac{E_s}{J}\frac{d^2J}{dV^2} \quad (4.5)$$

and

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial P}{\partial T}\right)_{V,1} - \frac{C_{v,s}}{J}\frac{dJ}{dV} \quad (4.6)$$

The relations between $C_{v,s}$, $(\partial P/\partial V)_T$, and $(\partial P/\partial T)_V$ in the limit $C_{v,s} \to \infty$ are graphically brought out by eq 4.5 and 4.6, and eq 4.5 also illustrates the appearance of the instability when $C_{v,s}$ increases without limit, for it is seen that this will eventually cause $(\partial P/\partial V)_T$ to become positive.

Comparison of eq 4.6 with eq 2.14, allowing C_v and $C_{v,s}$ to become infinite, or division of eq 4.5 by eq 4.6 under the same conditions with subsequent use of eq 2.15, shows that

$$T_\lambda{}^{-1}dT_\lambda/dV = J^{-1}dJ/dV \quad (4.7)$$

where, of course, $dT_\lambda/dV = (dV_\lambda/dT)^{-1}$. Equation 4.7 is to be expected, since Q_s is assumed to depend only on J/kT. Thus any specially characterized temperature, such as T_λ, should be proportional to J. Equation 4.7

holds, of course, only for the hypothetical λ line, which lies in the unstable region which is never reached, but it and the subsequent equations, which have the same limitation, can have some practical value because the region of instability is usually very narrow.

Substituting eq 4.5 and 4.6 into eq 2.11 (with constant C_v in the latter substituted for constant C_p), using eq 4.7 and taking $T = T_\lambda$, we obtain

$$\left(\frac{\partial P}{\partial T}\right)_{C_v} = \left(\frac{\partial P}{\partial T}\right)_{V,1} + \left(\frac{\partial P}{\partial V}\right)_{T,0}\left(\frac{\partial V}{\partial T}\right)_{C_v} - \frac{C_{v,s}}{T_\lambda}\frac{dT_\lambda}{dV} \times$$
$$\left[1 - \frac{dT_\lambda}{dV}\left(\frac{\partial V}{\partial T}\right)_{C_v}\right] \quad (4.8)$$

where

$$(\partial P/\partial V)_{T,0} = (\partial P/\partial V)_{T,1} - (E_s/J)d^2J/dV^2$$
$$= (\partial P/\partial V)_{T,1} - (E_s/T_\lambda)d^2T_\lambda/dV^2 \quad (4.9)$$

If we let $C_v \to \infty$, then, since dP_λ/dT, $(\partial P/\partial T)_{V,1}$ and $(\partial P/\partial V)_{T,0}$ are finite, the final term in eq 4.8 must remain finite, and, indeed, it is seen that the term in brackets vanishes since $dT_\lambda/dV = (dV_\lambda/dT)^{-1}$. Further, if $C_{v,s}$ becomes infinite as $\ln |T - T_\lambda|$, or as a small power of $|T - T_\lambda|^{-1}$, it may be shown by application of l'Hospital's rule that the complete last term in eq 4.8 vanishes, so that (4.8) becomes

$$dP_\lambda/dT = (\partial P/\partial T)_{V,1,\lambda} + (\partial P/\partial V)_{T,0,\lambda}dV_\lambda/dT \quad (4.10)$$

This means that were it not for the last term in eq 4.9, which may generally be expected to be a relatively small correction, the change of pressure along the λ line would be the same as if the λ transition did not exist at all. Since $(\partial P/\partial T)_{V,1} = -(\partial P/\partial V)_{T,1}(\partial V/\partial T)_{P,1}$, and the change of volume with temperature along the λ line (since it is accompanied by a change in pressure) may be expected to be considerably larger than the rate of expansion at constant P_1, we see that the first term in eq 4.10 is less important than the second. Thus roughly speaking the compressibility along the λ line is not far different from that at constant temperature. The differences, however, are, as we shall see, of considerable interest.

If we set $Y = C_v$ in eq 3.11, we have

$$T(\partial S/\partial T)_{C_v} = C_v + T(\partial P/\partial T)_V(\partial V/\partial T)_{C_v}$$

Equations 4.6 and 4.7 then give

$$T(\partial S/\partial T)_{C_v} \approx C_{v,1} + T(\partial P/\partial T)_{V,1}(\partial V/\partial T)_{C_v} + C_{v,s}[1 - (\partial V/\partial T)_{C_v}(\partial T_\lambda/dV)] \quad (4.11)$$

Again the last term will vanish in the limit, leaving

$$dS_\lambda/dT = (\partial S/\partial T)_{V,1,\lambda} + (\partial P/\partial T)_{V,1,\lambda}dV_\lambda/dT \quad (4.12)$$

This shows, since $(\partial P/\partial T)_{V,1} = (\partial S/\partial T)_{V,1}$, that the order–disorder entropy does not change along the λ line, which, of course, could be anticipated, since the λ point occurs at a fixed value of J/kT.

If J depends on P rather than V, it becomes conveni-

ent to deal with the enthalpy $H = E + PV$ and to use the isothermal–isobaric partition function[8c]

$$Z = Z_1 Z_s = \Sigma_L e^{-H_L/kT} \qquad (4.13)$$

Here H_L is the enthalpy of the entire assembly of molecules when held in the Lth quantum state at constant pressure. We have, in this case, for the Gibbs free energy

$$G = -kT \ln Z \qquad (4.14)$$

and the various thermodynamic functions are found by differentiation

$$V = -kT(\partial \ln Z_1/\partial P)_T - (Z_s'/Z_s)\mathrm{d}J/\mathrm{d}P = V_1 + V_s \qquad (4.15)$$

$$H = kT^2(\partial \ln Z_1/\partial T)_P - (Z_s'/Z_s)J = H_1 + H_s \qquad (4.16)$$

$$C_\mathrm{p} = C_{\mathrm{p},1} - H_s^2/kT^2 + (Z_s''/Z_s)J^2/kT^2 \qquad (4.17)$$

$$\left(\frac{\partial V}{\partial P}\right)_T = \left(\frac{\partial V}{\partial P}\right)_{T,0} - \frac{T}{J^2}\left(\frac{\mathrm{d}J}{\mathrm{d}P}\right)^2 C_{\mathrm{p},s} \qquad (4.18)$$

$$\left(\frac{\partial V}{\partial T}\right)_P = \left(\frac{\partial V}{\partial T}\right)_{P,1} + \frac{C_{\mathrm{p},s}}{J}\frac{\mathrm{d}J}{\mathrm{d}P} \qquad (4.19)$$

In analogy to eq 4.10 and 4.12 we obtain

$$\mathrm{d}V_\lambda/\mathrm{d}T = (\partial V/\partial T)_{P,1,\lambda} + (\partial V/\partial P)_{T,0,\lambda}\mathrm{d}P_\lambda/\mathrm{d}T \qquad (4.20)$$

$$\mathrm{d}S_\lambda/\mathrm{d}T = (\partial S/\partial T)_{P,1,\lambda} - (\partial V/\partial T)_{P,1,\lambda}\mathrm{d}P_\lambda/\mathrm{d}T \qquad (4.21)$$

In eq 4.18 and 4.20

$$(\partial V/\partial P)_{T,0} = (\partial V/\partial P)_{T,1} + (H_s/T_\lambda)\mathrm{d}^2 T_\lambda/\mathrm{d}P^2 \qquad (4.22)$$

which is not the reciprocal of $(\partial P/\partial V)_{T,0}$. In eq 4.22 we have used the relation, analogous to eq 4.7

$$J^{-1}\mathrm{d}J/\mathrm{d}P = T_\lambda^{-1}\mathrm{d}T_\lambda/\mathrm{d}P \qquad (4.23)$$

from which $J^{-1}\mathrm{d}^2 J/\mathrm{d}P^2 = T_\lambda^{-1}\mathrm{d}^2 T_\lambda/\mathrm{d}P^2$.

Should J depend on some variable Y, or Z, other than V or P, we could derive similar equations, provided we could set up the corresponding partition function. However, if we continue to use one of the usual partition functions, say the isothermal–isobaric partition function, and assume that it can be factored as in eq 4.13, this will mean that J is a function of T as well as P. The larger terms in eq 4.17–4.19 will remain almost as before, but there will be extra small terms in these equations. In eq 4.18 they can be incorporated in $(\partial V/\partial P)_{T,0}$ and in eq 4.19 we can define a $(\partial V/\partial T)_{P,0}$. If we do this, we will obtain eq 4.20 with $(\partial V/\partial T)_{P,0}$ substituted for $(\partial V/\partial T)_{P,1}$. A similar situation holds with eq 4.21. As implied, the large terms in eq 4.17–4.19 will be slightly altered: J, where it occurs as a factor, will be replaced by $J - T\partial J/\partial T$. A similar change will occur in eq 4.23.

If $(\partial V/\partial P)_{T,0}$ were equal to $(\partial V/\partial P)_{T,1}$ and if $(\partial P/\partial V)_{T,0}$ were equal to $(\partial P/\partial V)_{T,1}$, then eq 4.10 and 4.20 would clearly be equivalent. This is approximately true if the second terms on the right-hand sides of eq 4.9 and 4.22 are relatively small, which is

true at least in the case of liquid helium. If, as we may generally expect, $\mathrm{d}^2 T_\lambda/\mathrm{d}V^2$ has the same sign as $\mathrm{d}T_\lambda^2/\mathrm{d}P^2$, the agreement will be improved.

If, as in the case of the λ transition of liquid helium, C_p appears to become infinite logarithmically, it is of interest to know how C_v behaves in the neighborhood of the λ line. In order to study this we may use the thermodynamic equation

$$C_\mathrm{v} = C_\mathrm{p} + T(\partial V/\partial T)_P^2(\partial P/\partial V)_T \qquad (4.24)$$

and substitute from eq 4.18 and 4.19, obtaining

$$C_\mathrm{v} = C_{\mathrm{p},1} - \frac{a + (T_\lambda/T)b + a^2/4C_{\mathrm{p},s}}{1 - (T_\lambda/T)b/C_{\mathrm{p},s}} \qquad (4.25)$$

where $a = 2T_\lambda(\partial V/\partial T)_{P,1}\mathrm{d}P_\lambda/\mathrm{d}T$ and $b = T_\lambda(\partial V/\partial P)_{T,0}(\mathrm{d}P_\lambda/\mathrm{d}T)^2$. Here we have set $T = T_\lambda$, since we are interested in the behavior of C_v close to the transition.

It is noted that a and b depend only on the slope of the λ line and the lattice quantities. They may, therefore, be taken as constants near the λ line. It is found, at least for the λ transition in liquid helium, that b is much greater than a and the behavior of C_v depends very largely on b. It may be seen that C_v is indistinguishable from C_p until $C_{\mathrm{p},s}$ becomes of the order of b. Then C_v will gradually fall away from C_p, finally reaching the finite limit

$$C_{\mathrm{v},\lambda} = C_{\mathrm{p},1,\lambda} - a_\lambda - b_\lambda \qquad (4.26)$$

which may be shown to be equivalent to eq 3.17 if we solve for $(\partial V/\partial P)_{T,0,\lambda}$ and $(\partial V/\partial T)_{P,1,\lambda}$ from eq 4.20 and 4.21. It may be shown by differentiation of eq 4.25 with respect to T (P constant), and passing to the limit $C_{\mathrm{p},s} \to \infty$, that C_v approaches its limiting value with a cusp.

5. Application to Liquid Helium

To apply the equations of Section 4 to liquid helium we need to evaluate the "lattice" quantities. There is, of course, no rigid lattice in this case, so these are simply what the thermodynamic quantities (including V) would be as functions of T and P (since J is assumed to depend on P) if there were no order–disorder phenomenon. At first[13] it was assumed the lattice quantities could be identified with the contributions attributed to the phonons; this gives[14a]

$$C_{\mathrm{p},1} = 16\pi^5 k^4 T^3/15h^3 c^3 \rho \qquad (5.1)$$

where c is the velocity of sound, and[14b]

$$V^{-1}(\partial V/\partial T)_{P,1} = (16\pi^5 k^4 T^3/15h^3 c^3)\left(\frac{1}{c}\frac{\mathrm{d}c}{\mathrm{d}P} + \frac{1}{3}\kappa_T\right) \qquad (5.2)$$

where κ_T is the compressibility, this being evaluated at $0°K$. Since it varies slowly with temperature the compressibility at $0°K$ was also used directly to evaluate $(\partial V/\partial P)_{T,1,\lambda}$. Then $C_{\mathrm{v},\lambda}$ from eq 4.26 agreed fairly

(13) O. K. Rice, *J. Amer. Chem. Soc.*, **91**, 7682 (1969).
(14) K. R. Atkins, "Liquid Helium," Cambridge University Press, Cambridge, 1959: (a) p 63; (b) p 65; (c) p 128 ff.

well but not quite satisfactorily[15] with eq 3.17, using data of Lounasmaa and Kojo[16] and Kierstead[17] in the latter; dV_λ/dT, from the experimental data[18] involved on the right-hand side of eq 4.20, agreed similarly with direct experimental values.[17] But calculation of dS_λ/dT from eq 4.21, assuming $(\partial S/\partial T)_{P,1}$ to be negligible, as indicated by integrating eq 5.1, gave very poor results. Both[14c] c and[19] κ_T have singularities at the λ line, and eq 5.2 might break down for this or other reasons. Therefore, we tried, in unpublished work, simply using eq 4.21 to evaluate $(\partial V/\partial T)_{P,1,\lambda}$, but this effected no improvement in $C_{v,\lambda}$ or dV_λ/dT.

The difficulty could, of course, lie in the fundamental assumption, eq 4.13, of the factorizability of the partition function; however, it was felt that it might indicate that the rotons, as well as the phonons, contribute to the lattice properties, and that only the *interaction* between rotons has to do with the order–disorder phenomenon associated with the λ transition. Thus it might be more reasonable to find the appropriate value of $C_{p,1}$ and other quantities by interpolating the parts outside the region of the λ transition into that region.[20] If J depends only on P, the $C_{p,s}$ curves should have the same shape at different pressures. Modifying and generalizing an empirical equation of Buckingham and Fairbank,[11] $C_{p,s}$ (in joules g^{-1} deg^{-1}) was represented by the following equations (in which $x = T/T_\lambda$)

$$C_{p,s} = [61.8 - 90.9 \log (1 - x)]e^{-3.4/x}, \text{ for } T < T_\lambda$$

$$C_{p,s} = [-17.30 - 16.42 \log (x - 1)]e^{-1.7/x}, \text{ for } T > T_\lambda$$

$C_{p,1}$ was assumed to be proportional to $T^{5.27}$, the constant of proportionality being adjusted to fit the data, and with these values of $C_{p,s}$ and $C_{p,1}$ the specific heat data were very well represented.

With $(\partial V/\partial T)_P$ the situation is complicated because of the peculiar behavior of the coefficient of expansion in liquid helium. $(\partial V/\partial T)_P$ is positive at low T, becomes negative at $x \approx 1/2$, and again positive slightly above T_λ. So $(\partial V/\partial T)_{P,1}$ was evaluated at the points[14,18,21] on the saturated vapor curve where $(\partial V/\partial T)_P = 0$ by using eq 4.19, since the last term in this equation could be evaluated from eq 4.23. It was found that the empirical form $AT^{5.27}$ fits these two points around zero pressure and with adjustment of the constant A could be used at higher pressures. The calculated values fit the experimental values of $(\partial V/\partial T)_P$ closer than $\pm 0.1°$ from the λ point. If the rotons contribute to the lattice properties, then far from the λ

point, where the interaction between rotons is negligible but the negative coefficient of expansion (which is presumably attributable to them) is already evident, this feature should be reflected in $(\partial V/\partial T)_{P,1}$. The form $AT^{5.27}$ obviously cannot reproduce these intricacies, but it seems to be a sufficiently good representation near the λ point to make it possible to separate lattice and order–disorder contributions. Since $(\partial V/\partial T)_{P,1}$ is positive near the λ line it cannot be directly connected with the negative contribution of the rotons, but, rather, the effect of the rotons must be an indirect one, possibly connected with the apparent divergence of terms in eq 5.2.

Having $(\partial V/\partial T)_{P,1}$, we may find $(\partial V/\partial P)_{T,0,\lambda}$ from eq 4.20, and $(\partial V/\partial P)_{T,1,\lambda}$ may then be found by estimating $H_{s,\lambda}$ from $C_{p,s}$. It is then possible to calculate $(\partial V/\partial P)_T$ from eq 4.18 and C_v from eq 4.25. (C_v is needed for comparison with specific heat data at higher pressures.) Equation 4.20 is valid, of course, only in the immediate neighborhood of the λ line, where the lines of constant C_p parallel the λ line, and its use outside this region serves to give only a rough idea of the magnitude of $(\partial V/\partial P)_{T,0}$. This is satisfactory for C_v, because where the procedure breaks down the terms in b predominate in eq 4.25 and the error cancels. The values of $(\partial V/\partial P)_T$ and $(\partial P/\partial T)_V$ can be properly compared with experiment only close to the λ point. On the whole, the agreement in this region was good, so that the separation into lattice and order–disorder parts seemed successful.

Having found the values of the lattice quantities, it is now possible to check eq 4.21 for dS_λ/dT. The results are shown in Table I, which gives the lattice quantities as found by the procedures outlined in the preceding paragraphs. For comparison, the values obtained from eq 5.1 and 5.2, together with the assumption that the lattice compressibility is the same as that observed at 0°K, are shown in parentheses.

Table I bears out the general idea that the roton excitations contribute to the lattice quantities. The values of $C_{P,1,\lambda}$ are considerably larger than these calculated from eq 5.2 (shown in parentheses). The values of $(\partial V/\partial T)_{P,1,\lambda}$ are also greater than those inferred from eq 5.1 neglecting possible effects of divergence of terms in this equation.

Of interest is the fact that at the higher pressures $-(\partial V/\partial P)_{T,1,\lambda}$ is smaller than $-(\partial V/\partial P)_{T,1,\lambda} \equiv -(\partial V/\partial P)_T$ at 0°K. One would not expect the lattice compressibility to decrease with increasing temperature, but this appears to be a secondary effect, which occurs because of the negative coefficient of expansion. At the saturated vapor pressure the contraction between 0°K and the λ point is about 0.7%, but at 25 atm it is 2.0%, which would seem to be sufficient to have an appreciable effect on the lattice compressibility, affecting it similarly to compression by an external force.

6. Transitions in the Ammonium Halides

As noted in section 1, NH$_4$Cl and NH$_4$Br show λ

(15) H. C. Kramers, J. D. Wasscher, and C. J. Gorter, *Physica*, **18**, 329 (1952) (used to calculate H_s).

(16) O. V. Lounasmaa and E. Kojo, *Ann. Acad. Sci. Fenn.*, Ser. A, **6**, No. 36 (1959); O. V. Lounasmaa, *Cryogenics*, **1**, 212 (1961).

(17) H. A. Kierstead, *Phys. Rev.*, **162**, 153 (1967).

(18) (a) C. Boghosian and H. Meyer, *Phys. Rev.*, **152**, 200 (1966); **163**, 206 (1967); (b) D. L. Elwell and H. Meyer, *ibid.*, **164**, 245 (1967).

(19) H. A. Kierstead, *Phys. Rev.*, **153**, 258 (1967).

(20) O. K. Rice and Do-Ren Chang in "Critical Phenomena in Alloys, Magnets, and Superconductors," R. E. Mills, E. Ascher, and R. I. Jaffee, Ed., McGraw-Hill, New York, N. Y., 1971, p 105.

(21) R. L. Mills and S. G. Sydoriak, *Ann. Phys.* (*New York*), **34**, 276 (1965).

Table I
Values of Thermodynamic Quantities for Liquid Helium

P_λ, atm	$C_{p,l,\lambda}$, cal mole^{-1} deg^{-1}	$(\partial V/\partial T)_{P,l,\lambda}$, cm^3 mole^{-1} deg^{-1}	$H_{s,\lambda}$, cal mole^{-1}	$-(\partial V/\partial P)_{T,l,\lambda}$, cal atm^{-1} mole^{-1}	$T_\lambda dS_\lambda/dT_\lambda$, cal mole^{-1} deg^{-1} Calcd	Exptl
0.050	1.43 (0.2)	0.70 (0.304)	2.16 (2.68)	0.00877 (0.00782)	5.5 (2.0)	5.6
14.69	0.333 (0.06)	0.44 (0.035)	1.98 (2.10)	0.00326 (0.00348)	1.88 (0.18)	1.74
29.81	0.256 (0.02)	0.49 (0.008)	1.75 (1.58)	0.00162 (0.00228)	1.41 (0.04)	1.40

phenomena associated with the orientation of NH_4^+ ions. A number of properties of these crystals (e.g., lattice distance, ultrasonic attenuation, elastic constants, and heat effects) have been investigated[22] in the neighborhood of the λ point, and hysteresis effects were observed of the type to be expected if an instability of the kind discussed in sections 2 and 4 occurs. These phenomena were treated by Garland and Renard[8b] using the separation of the partition function shown in eq 4.1, assuming that J depends upon V.

Renard and Garland[23] made a detailed investigation of the thermodymamics of ammonium chloride. Despite the fact that this seems to be a case where V is the proper independent variable, they plotted C_p/T against $(\partial V/\partial T)_P$ at 1 atm over a small range of T just below T_λ, and similarly they plotted $(\partial V/\partial T)_P$ against $(\partial V/\partial P)_T$. Finding nearly linear curves, they used the equivalent of eq 2.6 and 2.9 (with eq 2.10 and 2.12) to find dP_λ/dT (equal to 116.9 and 110 bar deg^{-1}, from eq 2.6 and 2.9, respectively), $dS_\lambda/dT = 2.73 \times 10^6$ erg deg^{-2} mole^{-1}, and $V_\lambda^{-1}dV_\lambda/dT = -3.60 \times 10^{-4}$ deg^{-1}. The actual determination of the curve was slightly ambiguous on account of the hysteresis, and the transition was measured best when approached *from above*. This gave $V_\lambda^{-1}dV_\lambda/dT = -3.85 \times 10^{-4}$ deg^{-1}, in good agreement.

Renard and Garland also tested eq 4.10. In calculating dP_λ/dT they assumed that $(\partial P/\partial V)_{T,0,\lambda}$ could be obtained by extrapolating $(\partial P/\partial V)_T$ from above the λ point, i.e., they neglected any changes in E_s above the λ point (actually they set $E_s = 0$, which is equivalent). The values obtained agreed reasonably well with experimental values obtained directly from the λ curve.

The results of Renard and Garland may be inserted into (3.17). This will give, at least approximately, the value C_v could attain if no instability occurred near the λ line. Equation 3.17 gives $C_{v,\lambda} \approx 25$ cal mole^{-1} deg^{-1}. Using measurements of the compressibility and the coefficient of expansion Lawson[24] calculated C_v from C_p and found that C_v was almost constant, increasing from around 19 to between 21 and 22 cal mole^{-1} deg^{-1} a few tenths of a degree below the λ temperature. At first sight this seems very strange, but the values of C_v are already so close to 25 cal

Figure 5. Isotherm for ammonium chloride, showing first-order transition. ΔL is the decrease in length of a specimen from its length at 600 bars, in microns; P is the pressure in bars.

mole^{-1} deg^{-1} as to be not far outside the limits of error. C_v may tend toward a high value, but it cannot get very high before the instability sets in. Probably this is why the instability is so easily observed in this case.

Of particular interest from our present point of view are recent experiments of Garland and Weiner,[25] in which they have measured the change in length of a single ammonium chloride crystal as a function of temperature and pressure. Isotherms at 250.04°K ($P_\lambda \approx 830$ bar) and 255.75°K ($P_\lambda \approx 1490$ bar) showed discontinuities, signaling a first-order transition, while no discontinuities were observed at 256.94 and 266.37°K. The curve for the lowest temperature is reproduced in Figure 5. From this figure it seems clear that even where the first-order transition is most pronounced the isotherms become very flat before the transition is reached, and there is no indication that the transition occurs to avoid a region where $(\partial P/\partial V)_T$ is infinite. It may, however, be avoiding a region where $(\partial P/\partial V)_T$ would tend to become barely positive. It must be, therefore, that C_v, though it increases markedly in the region of the transition, is not tending toward infinity, but on the other hand, at the lower temperatures it presumably is tending toward a value greater than that given by eq 3.17. If $(\partial P/\partial V)_T$ is given by eq 4.5, there is presumably near-cancelation between the negative $(\partial P/\partial V)_{T,0}$ and the positive $(T/J^2)(dJ/dV)^2C_{v,s} = (T/T_\lambda^2)(dT_\lambda/dV)^2C_{v,s}$. According to the data of Renard and Garland,[8] $|dT_\lambda/dV|$ decreases slightly with increasing temperature and pressure, whereas $-(\partial P/\partial V)_{T,0}$ is expected to increase with increasing pressure. Thus it is not surprising that the negative term predominates at high temperatures.

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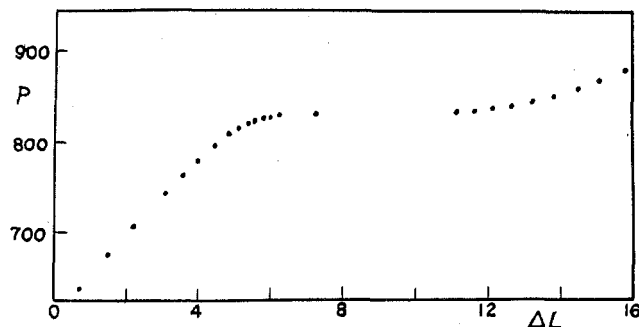(24) A. W. Lawson, *Phys. Rev.*, 57, 417 (1940).

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