

basis of the most highly corrected TFD-like equation, the general availability of TFD solutions favors their use. It is felt that at normal or above-normal crystal density, the best statistical-theory pressures will not differ greatly from the TFD values except in the cases of the aforementioned rare gases, alkalis, and alkaline earths.

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Statistical Thermodynamics of λ Transitions, Especially of Liquid Helium*

O. K. RICE

Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina

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The thermodynamic properties of systems in the immediate neighborhood of a locus of λ transitions have been investigated. It is assumed that the transitions arise from spin orientation (or some other order-disorder phenomenon), and that the partition function can be broken down into a product of a lattice part and a spin part, the latter dependent only on $I = J/kT$, where J is an energy parameter. If J depends only on the volume V , then the specific heat at constant volume C_v tends to become infinite along the λ line, but as is well known, an instability sets in before this point is reached. It is shown that this instability occurs only very close to the λ line, and C_v and $(\partial P/\partial T)_V$ may be expected to parallel each other much farther from the λ line. If an intrinsic volume change is associated with the ordering phenomenon, J is more appropriately taken as an enthalpy parameter, and may be supposed to depend on the pressure P rather than on V . Isothermal-isobaric partition functions are used. C_p tends to become infinite and to parallel $(\partial V/\partial T)_P$ a considerable distance from the λ line. Only very close to the λ line does $(\partial V/\partial P)_T$ become negatively infinite. The results are applied to liquid helium under pressure, and shown to accord with the data. The behavior of C_v is discussed. A possible generalization of the theory is suggested.

SOME years ago I examined some of the problems which arise when a λ transition occurs in a compressible substance.¹ It was shown that if the constant-volume specific heat C_v rises steeply enough as the λ line is approached, especially if it becomes infinite, there will be a van der Waals loop in the pressure-volume isotherm. Thus an instability will result, and the transition will become first-order. At that time I believed that the specific heat at constant pressure C_p would be unlikely to exhibit a locus of infinities, but the thermodynamics of such a situation was worked out. The relations were derived independently and cast in a different form by Pippard² and were somewhat extended and applied to liquid helium (which *does*, apparently, exhibit a locus of infinite C_p 's) by Buckingham and Fairbank.³

The theory was discussed from the point of view of statistical mechanics by Domb,⁴ and recently has been the subject of several papers by various authors.^{5,6}

Most recently a statistical formulation has been given by Garland and Renard,⁷ and applied to the transition in ammonium halides, where there is evidence of instability and hysteresis. It is the purpose of the present paper to give a brief review of the theory of Garland and Renard and to point out certain of its general consequences. A related theory for the case where C_p becomes infinite will then be given, and applied to the λ transition of liquid helium.

1. LOCUS OF INFINITE C_v

We shall discuss an Ising lattice, in which the spins are located on atoms in a compressible lattice. The formulation would apply equally well, however, to a case in which some other kind of order-disorder phenomenon were substituted for that associated with spin orientation. This particular case is used as a kind of semantic tool.

We follow the assumption of Garland and Renard that the partition function can be expressed as the product of a function depending only on the lattice vibrations and one depending on the spin system. Thus

* Work assisted by the Army Research Office.

¹ O. K. Rice, *J. Chem. Phys.* **22**, 1535 (1954).

² A. B. Pippard, *Phil. Mag.* **1**, 473 (1956); *Elements of Classical Thermodynamics* (Cambridge University Press, London, 1957), Chap. 9.

³ M. J. Buckingham and W. M. Fairbank, in *Progress in Low Temperature Physics*, edited by C. J. Gorter (North-Holland Publishing Company, Amsterdam, 1961), Vol. III, pp. 80ff.

⁴ C. Domb, *J. Chem. Phys.* **25**, 783 (1956).

⁵ C. P. Bean and R. S. Rodbell, *Phys. Rev.* **126**, 104 (1962).

⁶ D. C. Mattis and T. D. Schultz, *Phys. Rev.* **129**, 175 (1963).

⁷ (a) C. W. Garland and R. Renard, *J. Chem. Phys.* **44**, 1120 (1966); (b) R. Renard and C. W. Garland, *ibid.* **44**, 1125 (1966); (c) C. W. Garland and R. Renard, *ibid.* **44**, 1130 (1966); (d) C. W. Garland and C. F. Yarnell, *ibid.* **44**, 1112 (1966). (e) R. Renard and C. W. Garland, *ibid.* **45**, 763 (1966).

we write

$$Q = Q_l Q_s, \quad (1)$$

where the subscript l refers to lattice and s to spin. We write $J = (\epsilon_a - \epsilon_p)/2$, where ϵ_a is the spin interaction energy of an adjacent pair of antiparallel spins, and ϵ_p that of a pair with parallel spins. More generally, J can be taken simply as some energy parameter. It is assumed that Q_s is a function only of $I = J/kT$, where k is the Boltzmann constant, T is the absolute temperature, and J is assumed to be a function only of the volume V . This, together with Eq. (1), is what Garland and Renard called the assumption of weak interaction. It should be noted that it includes the case of strong interactions as defined by Mattis and Schultz since the effect of the volume can be great, the only requirement being that J depend only on V . Direct interactions between the spin and the lattice vibrations may be of importance,⁸ and, indeed, Mattis and Schultz⁶ have shown that they are of importance in one dimension. These authors have, however, given reasons for supposing that such direct interactions are much less important in three dimensions, and experimental evidence for this conclusion has been discussed by Garland and Renard.^{7a} Indeed, it would be expected on purely physical grounds, for in one dimension there can be a very direct correlation between the spin orientations and the average distance between a pair of nearest neighbors, whereas in three dimensions such correlation would be hindered by the other near neighbors.

Accepting for the time being the assumption of weak interaction as formulated in the above paragraph, we note that the pressure P and the energy E of the system, by application of the standard statistical mechanical equations, will be given by logarithmic differentiations with respect to V and T , respectively. Thus

$$P = kT(\partial \ln Q_l / \partial V)_T + (Q_s' / Q_s) dJ/dV = P_l + P_s, \quad (2)$$

and

$$E = kT^2(\partial \ln Q_l / \partial T)_V - (Q_s' / Q_s) J = E_l + E_s, \quad (3)$$

where the prime indicates differentiation with respect to I . From Eq. (3) we obtain

$$C_v = C_{v,l} + C_{v,s} = C_{v,l} - (Q_s' / Q_s)^2 J^2 / kT^2 + (Q_s'' / Q_s) J^2 / kT^2, \quad (4)$$

and by appropriate use of Eqs. (2), (3), and (4)

$$\begin{aligned} \left(\frac{\partial P}{\partial V}\right)_T &= \left(\frac{\partial P}{\partial V}\right)_{T,l} - \frac{1}{kT} \left(\frac{Q_s'}{Q_s}\right)^2 \left(\frac{dJ}{dV}\right)^2 \\ &\quad + \frac{1}{kT} \frac{Q_s''}{Q_s} \left(\frac{dJ}{dV}\right)^2 + \frac{Q_s'}{Q_s} \frac{d^2 J}{dV^2} \\ &= \left(\frac{\partial P}{\partial V}\right)_{T,l} + \frac{T}{J^2} \left(\frac{dJ}{dV}\right)^2 C_{v,s} - \frac{E_s}{JkT} \frac{d^2 J}{dV^2}, \end{aligned} \quad (5)$$

⁸ M. E. Fisher (private communication).

and

$$\begin{aligned} \left(\frac{\partial P}{\partial T}\right)_V &= \left(\frac{\partial P}{\partial T}\right)_{V,l} + \left(\frac{Q_s'}{Q_s}\right)^2 \frac{J}{kT^2} \frac{dJ}{dV} - \frac{Q_s''}{Q_s} \frac{J}{kT^2} \frac{dJ}{dV} \\ &= \left(\frac{\partial P}{\partial T}\right)_{V,l} - \frac{C_{v,s}}{J} \frac{dJ}{dV}. \end{aligned} \quad (6)$$

Equation (5) has been given by Domb⁹ and by Garland and Renard,^{7a} and Eq. (6) has been given by the latter authors.^{7c} At a locus of singularities with infinite C_v , it is of course $C_{v,s}$ which becomes infinite. The last term in the final expression of Eq. (5) is probably negligible, the first term is negative and the second term is positive. As has been pointed out,^{7,9} it is now easy to see how the infinity in $C_{v,s}$ produces the van der Waals loops and consequent instability by making the positive term larger in magnitude than the negative one. The larger $(dJ/dV)/J$ and the smaller $(\partial P/\partial V)_{T,l}$ (that is, the greater the intrinsic compressibility of the lattice), the sooner this effect will be noticed. The parallelism between $(\partial P/\partial T)_V$ and C_v , previously noted from the thermodynamic equations, is brought out and sharpened by Eq. (6).

Domb⁹ has used Eq. (5) as the basis for an explanation of the fact that it often appears that C_p becomes infinite rather than C_v . He has noted that in a magnetic system there are domains of finite and rather small size. One thus has actually to deal with an aggregate of small systems, and this results in the sharp peak of C_v being rounded off. Domb estimates that the maximum value might be around $8k$ per atom. Because of the slow logarithmic increase of C_v this still corresponds to a temperature difference from the λ point, $|T - T_\lambda|$, of the order¹⁰ of only 10^{-6} or 10^{-7} times T_λ . Under some circumstances, therefore, the second term on the right-hand side of Eq. (5) might not become greater than the first term in absolute value, and thus the instability would not occur.

If, as appears probable, the domain structure is an equilibrium phenomenon, and if there is a strict analogy between magnetic ordering and other types of ordering, one might expect the domain phenomenon to be general. However, there may be differences in this respect, and it may be significant that the cases in which Garland and co-workers found evidences of instability and hysteresis associated with going along the metastable portions of the van der Waals loop in the isotherm where ammonium halides, in which the order-disorder phenomena are not associated with magnetic ordering. Domb's mechanism would not be expected to apply to helium, but Goldstein¹¹ has brought up a somewhat similar point. He has called attention to the slow rise of the specific heat near the singularity and has pointed out that it is not possible to decide unequivocally by

⁹ C. Domb, Proc. Phys. Soc. (London) 88, 260 (1966).

¹⁰ C. Domb, Proc. Phys. Soc. (London) 86, 933 (1965).

¹¹ L. Goldstein, Phys. Rev. 135, A1471 (1964).

experiment whether the specific heat actually becomes infinite. The closer one comes to the singularity, the greater will be fluctuations in energy, and hence in temperature. Goldstein has noted that eventually the fluctuations in temperature will exceed $|T - T_\lambda|$, and then the temperature of the sample cannot actually be determined. Under such circumstances the specific heat (either C_v or C_p) will appear to be rounded off; but the fluctuations are smaller the larger the sample, and in the case of helium it seems possible, in principle at least, to take a very large sample, so that the rounding off will occur at a very low value of $|T - T_\lambda|$. So conceptually an infinite specific heat seems possible in this case.

One interesting conclusion can be drawn from a comparison of Eqs. (5) and (6), which I believe has not been previously pointed out. One may compare the ratio of the lattice terms to the ratio of the spin terms, and thus come to some conclusion as to the relative effect of the spin orientation on $(\partial P/\partial V)_T$ and $(\partial P/\partial T)_V$. The ratio of the lattice terms is

$$R_l = (\partial P/\partial V)_{T,l} / (\partial P/\partial T)_{V,l} = -(\partial T/\partial V)_{P,l}. \quad (7)$$

The ratio of the spin terms is

$$R_s = -(T/J)dJ/dV. \quad (8)$$

We can just as well compare the dimensionless forms

$$|R_l V/T| = |(V/T)(\partial T/\partial V)_{P,l}|, \quad (9)$$

and

$$|R_s V/T| = |(V/J)dJ/dV|. \quad (10)$$

It is seen that Eq. (9) is the relative change of temperature with volume at constant P (related to the reciprocal of the coefficient of expansion of the lattice without spin), which is generally large for solids. On the other hand Eq. (10) is the relative change of J with V , which is expected to be relatively small. Even if J varies as a fairly large power of the interatomic distance, V itself varies as the third power, so Eq. (10) would not be expected usually to be greater than 3 or 4. Therefore the spin will have much less effect on $(\partial P/\partial V)_T$ than on $(\partial P/\partial T)_V$, and the latter can parallel the specific heat over a range of temperatures in which the compressibility is scarcely affected, and in which no signs of instability have appeared.

2. LOCUS OF INFINITE C_p

In the case of liquid helium it seems likely, as already remarked, that there is a locus of infinite C_p and not of infinite C_v . One feels that this must be associated with the fact that the excitations in liquid helium, which, by a cooperative phenomenon, are responsible for the λ transition, are associated with a change in volume, which is one of their intrinsic properties. If the system volume were held constant, changes in volume due to new excitations would be compensated by changes in density of the rest of the system. The energy of excita-

tion under constant volume would be equal to the enthalpy of excitation at constant pressure. The energy (or enthalpy at constant pressure) of excitation, and the energy (or enthalpy) of interaction between excitations (which is also an essential feature in any cooperative phenomenon) tend to remain nearly constant when the pressure, rather than the volume, remains constant. This is so because the surrounding medium, in which the excitation is formed, remains more nearly in the same state under constant pressure. It is thus at constant pressure rather than at constant volume, that any analogy to the theory of the Ising lattice would have to be applied. At the λ point there is an infinite rate of change of the number of excitations with temperature. This means, of course, not only an infinite value of C_p , but also an infinite value of $(\partial V/\partial T)_P$ (where V , T , and P are molal volume, absolute temperature, and pressure, respectively). It has been indicated several times that C_p and $(\partial V/\partial T)_P$ parallel each other near a λ line.¹⁻³

Some further insight into the behavior of a system which exhibits an infinite C_p can be obtained from a consideration of an Ising-type lattice in which an attempt is made to express the thermodynamic functions in terms of what has been called the isothermal-isobaric partition function.¹² This is essentially a canonical partition function based on enthalpy rather than energy, which we define as

$$Z = \sum_L e^{-H_L/kT}, \quad (11)$$

where H_L is the enthalpy of the L th state of the assembly. In this case the Gibbs free energy is given by

$$G = -kT \ln Z, \quad (12)$$

and we have

$$H = kT^2(\partial \ln Z/\partial T)_P \quad (13)$$

and

$$V = -kT(\partial \ln Z/\partial P)_T. \quad (14)$$

We now introduce the equivalent of the weak-interaction assumption

$$Z = Z_l Z_s, \quad (15)$$

where again Z_s is a function only of $I = J/kT$. But now J is assumed to be the difference in *enthalpy* of the antiparallel and parallel neighbors and is assumed to depend only on P . The latter assumption seems reasonable in the light of the foregoing discussion if the change in volume on going from the parallel to the antiparallel is an intrinsic property of the excitation and if the change on volume with temperature is chiefly that associated with the change in the density of excitations.

Then, in place of Eqs. (2) and (3) we will have

$$\begin{aligned} V &= -kT(\partial \ln Z_l/\partial P)_T - (Z_s'/Z_s)dJ/dP \\ &= V_l + V_s, \end{aligned} \quad (16)$$

¹² T. L. Hill, *Statistical Mechanics* (McGraw-Hill Book Company, Inc., New York, 1956).

and

$$H = kT^2(\partial \ln Z_l / \partial T)_P - (Z'_s / Z_s)J \\ = H_l + H_s. \quad (17)$$

In place of Eqs. (4), (5), and (6) we have¹³

$$C_p = C_{p,l} + C_{p,s} \\ = C_{p,l} - (Z'_s / Z_s)^2 J^2 / kT^2 + (Z''_s / Z_s) J^2 / kT^2 \quad (18)$$

$$\left(\frac{\partial V}{\partial P}\right)_T = \left(\frac{\partial V}{\partial P}\right)_{T,l} + \frac{1}{kT} \left(\frac{Z'_s}{Z_s}\right)^2 \left(\frac{dJ}{dP}\right)^2 \\ - \frac{1}{kT} \frac{Z''_s}{Z_s} \left(\frac{dJ}{dP}\right)^2 - \frac{Z'_s}{Z_s} \frac{d^2 J}{dP^2} \\ = \left(\frac{\partial V}{\partial P}\right)_{T,l} - \frac{T}{J^2} \left(\frac{dJ}{dP}\right)^2 C_{p,s} + \frac{H_s}{J} \frac{d^2 J}{dP^2}, \quad (19)$$

$$\left(\frac{\partial V}{\partial T}\right)_P = \left(\frac{\partial V}{\partial T}\right)_{P,l} - \left(\frac{Z'_s}{Z_s}\right)^2 \frac{J}{kT^2} \frac{dJ}{dP} + \frac{Z''_s}{Z_s} \frac{J}{kT^2} \frac{dJ}{dP} \\ = \left(\frac{\partial V}{\partial T}\right)_{P,l} + \frac{C_{p,s}}{J} \frac{dJ}{dP}. \quad (20)$$

The first thing to remark about Eq. (19) is that the second term on the right-hand side is now negative. Thus no matter how large $C_{p,s}$ becomes, no instability will result; although $(\partial V / \partial P)_T$ can become very large, it remains negative.

From Eq. (20) we see that $(\partial V / \partial T)_P$ will parallel $C_{p,s}$ near the singularity. It is again of interest to compare the relative sizes of the terms in Eqs. (19) and (20), as we previously compared the terms in Eqs. (5) and (6). We wish to compare

$$R_l / T = T^{-1} (\partial V / \partial P)_{T,l} / (\partial V / \partial T)_{P,l} = \kappa_l / T \alpha_l \quad (21)$$

(where κ_l is the lattice isothermal compressibility and α_l is the lattice coefficient of expansion) with

$$R_s / T = J^{-1} dJ / dP \quad (22)$$

(where R_s is actually the negative of the ratio).

We will attempt to evaluate these quantities near the λ point at 13 atm and 2.02°K, a point which has been investigated experimentally by Lounasmaa.¹⁴ If helium behaved like a simple Ising lattice we could assume that J was proportional to T_λ and write

$$J^{-1} dJ / dP = T_\lambda^{-1} (dT / dP)_\lambda. \quad (23)$$

Equation (23) would, indeed, follow, in the limit near the λ line, simply by dividing Eq. (19) by Eq. (20),

¹³ C. E. Chase [Physica 27, 1129 (1961)] has presented a theory in which the infinity in C_p is associated with an infinity in the second derivative of the excitation energy for rotons. This may not be as far removed from the present theory as it seems. Such an infinity in the second derivative may be associated with the interaction between rotons in a region in which the second derivative of their number is infinite, this in turn being associated with the infinity in Z''_s .

¹⁴ O. V. Lounasmaa, Phys. Rev. 130, 847 (1963).

remembering that $(dP/dT)_\lambda$ is equal to $(\partial P / \partial T)_V$ along the λ line.¹ Substitution of Eq. (23) in Eq. (20) gives the correct limiting thermodynamic expression very close to the λ line,^{1,3} which is verified experimentally.³

If J were strictly proportional to T_λ the "spin" part of the entropy would be the same all along the λ line. Actually the entropy increases somewhat along the λ line (and the lattice contribution must decrease), so it is clearly an oversimplification to assume that helium can be described with the aid of an order-disorder partition function which is a function of the single variable $I = J/kT$ with J a function of P alone. Still Eq. (23) may give a reasonable estimate of orders of magnitude. At $T_\lambda = 2.02^\circ\text{K}$, then^{3,14}

$$R_s / T = J^{-1} dJ / dP \approx -0.0065 \text{ atm}^{-1}. \quad (24)$$

The evaluation of Eq. (21) offers some difficulties: κ_l and α_l cannot be directly measured. We shall assume that κ_l is equal to the value of the compressibility at some temperature well below the λ point, where it seems to become fairly constant. At 1.25°K, and 13 atm, κ is approximately¹⁵ 0.0065 atm⁻¹. Although the rotons and photons in liquid helium are actually parts of the same excitation spectrum, it seems reasonable to assume that the rotons (which are associated with the volume changes mentioned at the beginning of this section), are principally concerned with the λ transition, whereas the phonons are identified with lattice vibrations. It thus seems reasonable to get α_l by extrapolating the coefficient of expansion from the phonon region to the temperature of interest. According to Atkins and Edwards¹⁶ the phonon part of the coefficient of expansion is given by $0.00108T^3$, so at $T = 2.02^\circ\text{K}$ we estimate $\alpha_l = 0.0089$. This is for essentially zero pressure; assuming it to be the same at 13 atm we estimate

$$R_l / T = \kappa_l / T \alpha_l \approx 0.36 \text{ atm}^{-1}.$$

This is about 50 times as large as R_s / T , so we expect $(\partial V / \partial T)_P$ to show the effects of the large $C_{p,s}$ much farther from the λ line than $(\partial V / \partial P)_T$.

Now Lounasmaa¹⁴ has found that at 13 atm $(\partial V / \partial P)_T$ changes only moderately with pressure to within about 10^{-3} atm of the λ line. Since the slope of the λ line is 76 atm/deg, 10^{-3} atm corresponds to about 10^{-5} deg. The increase in the magnitude of $(\partial V / \partial P)_T$ can only occur closer to the λ line than that. Lounasmaa did not measure $(\partial V / \partial T)_P$ directly but he did measure $(\partial P / \partial T)_V = -(\partial V / \partial T)_P (\partial P / \partial V)_T$. This coefficient reflects the behavior of $(\partial V / \partial T)_P$, showing a logarithmic change with $|T - T_\lambda|$ at constant pressure. However, the slopes are different above and below the λ point. This may be because of a difference in the behavior of $(\partial V / \partial P)_T$. It is known from thermodynamics that $(\partial P / \partial T)_V$ will not become infinite, but will eventually reach $(dP/dT)_\lambda$, the slope of the λ line.

¹⁵ W. H. Keesom, Helium (Elsevier Publishing Company, Inc., Amsterdam, 1942).

¹⁶ K. R. Atkins and M. H. Edwards, Phys. Rev. 97, 1429 (1955).

The logarithmic increase of $(\partial P/\partial T)_V$ starts some tenths of a degree from the λ point. If $(\partial V/\partial P)_T$ is 50 times too small at this point to show any anomaly, then, because of the slow logarithmic change of C_p with temperature, its anomaly will not be observed until one is many orders of magnitude closer to the λ point. The behavior of the thermodynamic coefficients is, therefore, that expected from the theory.¹⁷

Equations (19) and (20) can be used to give a very instructive insight into the behavior of C_v as the λ line is approached. From thermodynamics

$$C_v = C_p + T(\partial V/\partial T)_P^2(\partial P/\partial V)_T.$$

Then from Eq. (20), if one is *fairly* close to the λ line,

$$C_v \approx C_p + T(C_{p,s}/J)^2(dJ/dP)^2(\partial P/\partial V)_T. \quad (25)$$

However, if one is so close to the λ line that $(\partial V/\partial P)_T$ has become very large, Eq. (19) gives, with Eq. (25),

$$C_v \approx C_p - C_{p,s} \quad (26)$$

which simply means that, when $C_{p,s}$ becomes infinite, C_v remains finite and approaches a constant value as the λ line is approached, since the singularity in C_p arises wholly from that in $C_{p,s}$. Its actual value along the λ line is given by a formula derived by Buckingham and Fairbank.³

The second term on the right-hand side of Eq. (25) is, of course, negative, since $(\partial P/\partial V)_T$ is negative. It is seen that as one approaches the λ line this negative term builds up relatively faster than C_p itself. Eventually a maximum in C_v is reached, unless the region in which $(\partial P/\partial V)_T$ suddenly drops off toward zero, is reached first. We can estimate where this maximum would occur, if we assume that the only quantity in the right-hand side of Eq. (25) which changes with appreciable rapidity is $C_{p,s}$. Then the maximum will occur when

$$0 = (\partial C_{p,s}/\partial T)_P + 2C_{p,s}(\partial C_{p,s}/\partial T)_P(T/J^2) \times (dJ/dP)^2(\partial P/\partial V)_T, \quad (27)$$

or

$$C_{p,s} = -(J^2/2T)(dJ/dP)^{-2}(\partial V/\partial P)_T. \quad (28)$$

Using our estimate of $(dJ/dP)/J$, and Lounasmaa's values of $V^{-1}(\partial V/\partial P)_T$ and V at 13 atm and 2.02°K, we find that this maximum would occur at $C_{p,s} \approx 27$ cal mole⁻¹ deg.⁻¹ Such a value of $C_{p,s}$ would be reached only extremely close to the λ , line but it is undoubtedly

¹⁷ These phenomena have been discussed from a different point of view by E. G. Batyev, A. Z. Patashinskii, and V. L. Pokrovskii, Zh. Eksperim. i Teor. Fiz. 47, 598 (1964) [English transl.: Soviet Phys.—JETP 20, 398 (1965)].

an underestimate (though of the right order of magnitude), since Buckingham and Fairbank's estimate for $C_{v,\lambda}$ at this pressure was 40 cal mole⁻¹ deg.⁻¹.

3. A POSSIBLE GENERALIZATION

It has been pointed out¹ that there is a whole category of specific heats which become infinite if C_v becomes infinite. If Y is some function of V and T such that $(\partial Y/\partial V)_T$ and $(\partial Y/\partial T)_V$ are everywhere finite and $(\partial Y/\partial V)_T$ is nonvanishing, then Y may be called a volume-like variable, and C_y is one of the category of specific heats mentioned. The following general formula (not dependent on the properties of Y) was derived for C_y :

$$C_y = C_v + T(\partial P/\partial T)_V(\partial V/\partial T)_Y. \quad (29)$$

If this is applied to the case where C_v and C_y are not finite but C_p is—in which case $(dP/dT)_\lambda = (\partial P/\partial T)_V$ at the λ line—and if Y is so defined that it is constant along the λ line, then this equation yields Buckingham and Fairbank's expression for the value of C_v along the λ line.

If, on the other hand, Y (considered as a function of P and T rather than a function of V and T) bears a relation to the pressure such that $(\partial Y/\partial P)_T$ and $(\partial Y/\partial T)_P$ are everywhere finite and $(\partial Y/\partial P)_T$ is nonvanishing, then Y is a pressure-like variable, and C_y belongs to one of a category of specific heats which become infinite along with C_p . We can write

$$(\partial S/\partial T)_Y = (\partial S/\partial T)_P + (\partial S/\partial P)_T(\partial P/\partial T)_Y, \quad (30)$$

whence

$$C_y = C_p - T(\partial V/\partial T)_P(\partial P/\partial T)_Y. \quad (31)$$

Since $(\partial P/\partial T)_Y = -(\partial P/\partial Y)_T(\partial Y/\partial T)_P$ cannot be infinite, it is seen that if C_y is infinite either $(\partial V/\partial T)_P$ or C_p is infinite. But these tend to become infinite together, unless $(dP/dT)_\lambda$ is zero, which would of course give rise to an impossible situation. Now J may not be a function solely of P but, if it is a function of any pressure-like variable, it should be possible, though this has not been carried out, to use Y as a variable and to find another variable X to use in place of V , such that XY has the dimensions of energy. Thus one could get a simple formulation for the derivatives involving the new variables. These could then be related to the more usual thermodynamic coefficients, but we would already know that the λ line would be one with infinite C_p , with all the thermodynamic consequences arising therefrom.