International Journal of Thermophysics, Vol. 6, No. 1, 1985

Equation of State for Liquid Helium from 1.4 to 4 K and Asymptotic Limits at the Lamda Line

V. Arp[1,2] **and K. Agatsuma**[1]

Received July 6, 1984

A liquid helium state equation has been constructed for the range 1.4 to 4 K for pressures up to 25×10^5 Pa consistent with the known asymptotic behavior of state properties at the lamda line. It utilizes a slightly different form of state equation than used in previous studies at the lamba line, resulting in simpler expressions for all thermodynamic variables while retaining good agreement with experimental data. The amplitude ratio, A/A', of the logarithmic term is found to be 1.14 ± 0.03, independent of pressure, in contrast to earlier work which indicated that this ratio was pressure dependent above 15×10^5 Pa. The state equation can also be used to show that the entropy variation along the lama line is independent of A or A' and to predict a finite value of C_V at the lamda line.

KEY WORDS: equation of state; helium; lamda line; logarithmic singularity; low temperature.

1. INTRODUCTION

Previous studies of asymptotic state functions at the λ line have generally focused on a narrow temperature range around that line. In this paper we construct a state equation which is valid over a wide temperature range including the λ line. This wide-range equation yields a more complete description of asymptotic behavior at the λ line and is used here to explore certain features which were not evident in previous work. Also included in the study is a slight variation on the thermodynamic formulation used in prior analyses, leading to a more succinct and easily integrated state equation.

---

[1] Electrotechnical Laboratory, 1-1-4 Umezono, Sakura-Mura, Niihari-Gun, Ibaraki 305, Japan.

[2] Permanent address: National Bureau of Standards, Boulder, Colorado 80303, U.S.A.

1.1. Previous Data Compilations

The primary reference for helium I, above 2.5 K, is the work of McCarty [1], in which diverse experimental data have been synthesized into a single state equation. A computer package originally developed by McCarty but now enhanced by iterative and approximate subroutines has been described by Hands [2] and is now maintained at Oxford by Hands and at NBS. More recently McCarty has incorporated his original computer package into a larger and more general one for the properties of several different fluids [3]. All input data for $T \geqslant 2.5$ K used in this study have been obtained from Ref. 1, and no attempt has been made to refit original experimental data.

Basic references for helium II data are Maynard [4], Brooks and Donnelly [5], and McCarty [6]. Maynard's data span the range from 1.2 to about 0.05 K below T_λ, derived primarily from precise sound velocity measurements. He gives both numerical equations and tabular data. The Brooks and Donnelly data span from 0.1 to about 0.05 K below T_λ, derived from the lattice vibrational spectrum. Only tabular data are presented. McCarty [6] synthesized these two data sets into a single computer package whose input and output formal is consistent with his for the helium I properties [3]. This means that the input variables are density and temperature and that iteration is required if other input variables, e.g., pressure and temperature, are used. His published report does not include thermal expansion data.

The primary reference for lamda line properties is the work of Ahlers [7]. His work includes experimental data and derived properties (specific heats, entropy, thermal expansion, and compressibility) in the range $10^{-5}\,\mathrm{K} \leqslant |T - T_\lambda| \leqslant 10^{-2}\,\mathrm{K}$ on either side of the lamda line. He also discusses the singularity at the lamda line in considerable detail. It is his work which we consider first, as it gives the major input to the form of the desired wide-range state equation.

1.2. Thermodynamic Variables

Two thermodynamic identities which form the basis of the equations developed here are

$$\frac{\partial^2 S}{\partial P\, \partial T} = \frac{1}{T}\left(\frac{\partial C_p}{\partial P}\right)_T = -\left(\frac{\partial^2 V}{\partial T^2}\right)_P \tag{1}$$

and

$$\frac{\partial^2 S}{\partial T\, \partial V} = \frac{1}{T}\left(\frac{\partial C_v}{\partial V}\right)_T = \left(\frac{\partial^2 P}{\partial T^2}\right)_V \tag{2}$$

A careful reading of references 4, 5, and 7 discloses that these second-order identities are not cited, and apparently are not used, in these respective studies. They are central to this work.

It will be seen that the Grüneisen parameter

$$\Phi = V\left(\frac{\partial P}{\partial U}\right)_V = \frac{V}{C_V}\left(\frac{\partial P}{\partial T}\right)_V \tag{3}$$

is very useful in analyzing internal consistency and asymptotic features of data as the lamda line is approached. It should be noted that this definition of Φ is consistent with that used for many years in studies of lattice properties of solids [8, 9]. More recently, the same name has occasionally been applied to the parameter

$$\Gamma = (\rho/c)(\partial c/\partial \rho)_S \tag{4}$$

in studies of many body problems and helium dynamics in the limit of zero temperature. These quantities are conceptually related, but the numerical values are different, though always of unity order of magnitude.

2. BASIC EQUATIONS

2.1. Logarithmic Singularity at the Lamda Line

Ahlers has shown that C_p near the lamda line is given by

$$C_p = A(P) \cdot \log|T - T_\lambda| + BDE \tag{5}$$

where A is a function of pressure, and BDE represents pressure- and temperature-dependent terms which remain finite at T_λ. The magnitudes of both A and BDE differ on either side of the lamda line. The empirical equations for A ($\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$) as a function of P (bar) are given by Ahlers as

$$A = 5.357 - 0.03465\,P + 8.447 \times 10^{-4}\,P^2, \qquad T > T_\lambda \tag{6a}$$

for helium I and

$$A' = 5.102 - 0.05652\,P + 9.643 \times 10^{-4}\,P^2, \qquad T < T_\lambda \tag{6b}$$

for helium II.

The basic postulate of this work, suggested by the factor of T in Eq. (1), is that the logarithmic term in Eq. (5) should be multiplied by T, i.e., a more simple equation which fits the data quite well is

$$C_p = aT\log|T - T_\lambda| + T\Sigma \tag{7}$$

where Σ is a function which remains finite at the lamda line. Evaluating the parameter a in Eq. (7) from Eqs. (6a) and (6b) and tabulated values of $T_\lambda(P)$ from Ref. 4, one finds

$$a = -0.61(\pm 1\%)\,\mathrm{J \cdot g^{-1} \cdot K^{-2}}, \qquad T > T_\lambda \tag{8a}$$

for helium I and

$$a' = -0.57(\pm 2\%)\,\mathrm{J \cdot g^{-1} \cdot K^{-2}}, \qquad T < T_\lambda \tag{8b}$$

for helium II, independent of pressure within the error limits shown. The exception is that Eq. (8a) does become a function of pressure above 15×10^5 (Pa). The apparently anomalous behavior of helium I above this pressure is discussed in some detail by Ahlers. Aside from this high-pressure anomaly, it is reasonable that the 1 to 2% residual variation with pressure in Eqs. (8) could be eliminated by a small adjustment of the A and BDE terms.

The form of Eq. (7) leads to a state equation $V(P, T)$ which is quite simple compared to that which would be consistent with Eq. (5). Rewriting Eq. (7) to separate pressure-dependent and pressure-independent terms in Σ, we have

$$C_\mathrm{p} = aT \log|T - T_\lambda| + T\Sigma_\mathrm{b}(P, T) + T\Sigma_\mathrm{d}(T) \tag{9}$$

where the Σ terms are functions which remain finite at the lamda line, defined later. Then, from Eq. (1)

$$\frac{\partial^2 S}{\partial P\,\partial T} = \frac{a}{T - T_\lambda} \cdot \frac{\partial T_\lambda}{\partial P} + \frac{\partial}{\partial P}\Sigma_\mathrm{b} \tag{10}$$

$$\left(\frac{\partial V}{\partial T}\right)_P = a\frac{\partial T_\lambda}{\partial P} \cdot \log|T - T_\lambda| - \int dT \frac{\partial}{\partial P}\Sigma_\mathrm{b} + \Sigma_\mathrm{e}(P) \tag{11}$$

$$V = a\frac{\partial T_\lambda}{\partial P} \cdot \mathrm{ilog}(T - T_\lambda) - \int dT' \int dT \frac{\partial}{\partial P}\Sigma_\mathrm{b} + T\Sigma_\mathrm{e} + \Sigma_\mathrm{f}(P) \tag{12}$$

$$\left(\frac{\partial V}{\partial P}\right)_T = a\left[\frac{\partial^2 T_\lambda}{\partial P^2} \cdot \mathrm{ilog}(T - T_\lambda) - \left(\frac{\partial T_\lambda}{\partial P}\right)^2 \cdot \log|T - T_\lambda|\right]$$
$$- \int dT' \int dT \frac{\partial^2}{\partial P^2}\Sigma_\mathrm{b} + T\frac{\partial}{\partial P}\Sigma_\mathrm{e} + \frac{\partial}{\partial P}\Sigma_\mathrm{f} \tag{13}$$

The functions $\Sigma_\mathrm{d}(T)$, $\Sigma_\mathrm{e}(P)$, and $\Sigma_\mathrm{f}(P)$ are constants of integration, and

$$\mathrm{ilog}\, x = \int \log|x|\, dx = x(\log|x| - 1)$$

The equations as written here are correct for either sign of $T-T_\lambda$. An auxiliary equation for $T_\lambda(P)$ is required.

With simple polynomials for P and T in the Σ terms, this set of equations turns out to be quite successful in reproducing specific heats, thermal expansion, compressibility, (first) sound velocity, and density in the reference data and ranges cited above, in both helium I and helium II. Numerical details are discussed in a later paragraph. At this point it is appropriate to discuss certain features of Eqs. (9)–(13) at the lamda line, independent of any particular assignments for the Σ terms.

2.2. Entropy Gradient Along the Lamda Line

The entropy variation along the lamda line is

$$dS_\lambda=\left(\frac{\partial S}{\partial P}\right)_T dP+\left(\frac{\partial S}{\partial T}\right)_P dT=\left[-\left(\frac{\partial V}{\partial T}\right)_P+\frac{C_\mathrm{p}}{T}\cdot\frac{\partial T_\lambda}{\partial P}\right]dP$$

Substitution from Eqs. (8) and (10) shows that dS_λ is independent of the magnitude of the logarithmic term. More generally, $S_\lambda(P)$ is independent of any function in Eq. (9) whose entire dependence on P and T occurs through the arguement $[T-T_\lambda(P)]$.

There has been considerable discussion in the literature whether the coefficient A in Eq. (5) is the same on either side of the lamda line. Ahlers concludes that $A/A'=1.06$, while Elwell and Meyer [10] conclude that $A/A'=0.9$ (the unprimed coefficients refer to helium I and the primed coefficients refer to helium II). Whatever may be the true value of this ratio, it should not have any effect on the value of $S_\lambda(P)$. Conversely, if $S_\lambda(P)$ is known accurately, this independence of the logarithmic term can be useful in the numerical evaluation of the Σ terms.

2.3. Asymptotic Limits

If we assume that Eqs. (9)–(13) remain valid for arbitrarily small values of $\Delta T=|T-T_\lambda|$, one can then decrease ΔT to the point where the Σ terms are negligible in all equations. To explore the limiting values under this condition it is convenient to use a thermodynamic identity involving the Grüneisen parameter

$$\frac{c^2}{\Phi}=C_\mathrm{p}\Big/\left(\frac{1}{V}\cdot\frac{\partial V}{\partial T}\right)_P=\frac{C_\mathrm{p}}{\beta} \tag{14}$$

where the second equality is used to define β. In the above limit, substitution from Eqs. (9) and (11) yields

$$\Phi \approx \frac{c^2}{VT} \cdot \frac{\partial T_\lambda}{\partial P} \tag{15}$$

Figure 1 shows a comparison of this theoretical limit with values determined from Ahlers' data at respectively $\pm 10^{-5}$ K. Order-of-magnitude agreement is obtained, but the limit has not been obtained. Nevertheless, even this approximate agreement between this limit and Ahlers' data is probably significant considering that the theoretical limit is obtained from sound velocity measurements, while the experimental data are obtained from heat capacities.

An approximation of the same degree leads to

$$C_V = \frac{C_p}{1 + T\beta\Phi} \approx \frac{C_p}{T\beta\Phi} \approx \frac{c^2 T}{V^2} \left(\frac{\partial P}{\partial T_\lambda} \right)^2 \tag{16}$$

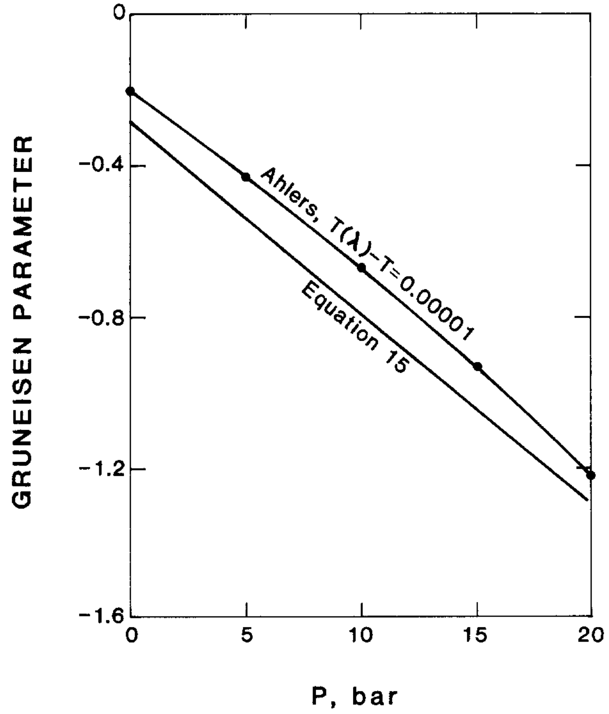

Fig. 1. The Grüneisen parameter ϕ as a function of pressure P. The data points are from Ahlers [7] at $T_\lambda - T = 10^{-5}$ K. The solid line is the asymtotic value given by Eq. (15).

for the asymptotic value at the lamda line. A finite value of C_V has been postulated in past work, e.g., in Ref. 7, but its values has not heretofore been calculated. From Eq. (16) the limiting value of C_V/R ranges from 128 at saturated vapor pressure to 13 at 25×10^5 Pa pressure. These are far greater than any measured value in this region. In order to estimate the extent to which ΔT must be reduced for this limiting value to be reached, one can equate C_V from Eq. (16) to C_p from Eq. (7) and solve for ΔT. Of course this calculation will overestimate ΔT because the specific heat ratio also becomes very large in this limit. The calculated ΔT varies from 10^{-100} K (!) at saturated vapor pressure to "only" 10^{-11} K at 25×10^5 Pa. If nothing else, statistical fluctuations from the finite number of atoms in a sample would belie these limits. More probably, higher-order divergences and/or corrections to the assumed logarithmic divergence must be considered.

It should be noted that none of these deductions concerning $S_\lambda(P)$ and asymptotic limits at the lamda line is obtained from an equation of state starting with Eq. (5).

2.4. Scaling Laws

The logarithmic term in Eqs. (5) and (7) is in fact inconsistent with accepted scaling laws at a critical point, as pointed out by Ahlers. An appropriate generalization of Eq. (7) is

$$C_\mathrm{p} = \frac{aT}{\alpha}(|T - T|^{-\alpha} - 1) + T\Sigma \tag{17}$$

Equation (7) is obtained from Eq. (17) in the limit that α goes to zero. Ahlers states that his data are better fitted by Eq. (5) than by Eq. (17) (without the factor of T, in his work) but that an acceptable fit might be obtained with $\alpha = -0.02$. This value of α would be in much better agreement with universal scaling laws. It should be noted here that none of the isentropic or limiting values at the lamda line as derived above is changed if one starts with Eq. (17) in place of Eq. (7), provided that $\alpha \geqslant 0$.

2.5. The Form of the Σ Terms

To this point the only restriction which has been placed on the Σ terms is that they remains finite at the lamda line. The constants of integration Σ_b, Σ_d, and Σ_f must each be functions of only one variable; it is reasonable to assume that they are analytic and can be represented, for example, by simple polynomials in P or T. The Σ_b term, however, can in principle be written

$$\Sigma_\mathrm{b} = \Sigma_\mathrm{b}'(P, T) + \Sigma_\mathrm{b}''[T - T_\lambda(P)] \tag{18}$$

The $\Sigma_{\rm b}'$ contribute to the observed $S_\lambda(P)$ and must be analytic in that limit. This means that they could be written

$$\Sigma_{\rm b}' = b_{ij} P^i T^j$$

though it is possible that other functional dependencies might be more effective. If the Σ'' terms were analytic, they could be represented to any desired degree of accuracy by the Σ' terms, and the separation into prime and double-prime contributions would become redundant. It is reasonable to assume that the Σ'' terms are nonanalytic at the lamda line.

Ahlers writes the BDE term of Eq. (5)

$$BDE = B \cdot (T - T_\lambda) \log |T - T_\lambda{}' + D \cdot (T - T_\lambda) + E \tag{19}$$

with B, D, and E as functions of pressure. Thus his B term, neglecting its pressure dependence, corresponds to Σ'', while the D and E terms correspond to Σ'.

In this work we have tried

$$\Sigma'' = b_{n1} \cdot \mathrm{ilog}(T - T_\lambda) + b_{n2} \cdot \mathrm{i2log}(T - T_\lambda)$$

$\mathrm{ilog}(x)$ was defined earlier. $\mathrm{i2log}(x)$ is defined

$$\mathrm{i2log}(x) = (x^2/2)(\log |x| - 3/2) = \int \mathrm{ilog}(x)\, dx$$

Different coefficients b_N may be assumed on either side of the lamda line without affecting the fit to $S_\lambda(P)$ in accordance with the analysis above.

3. NUMERICAL EVALUATION

3.1. An Equation for $T_\lambda(P)$

Equations (9)–(13) all involve $T_\lambda(P)$ and its derivatives. To obtain this equation, Kierstead's [11] equation for $P_\lambda(T)$ has been used to generate data for a curve-fitting routine. His equation consists of a four-term polynomial plus an exponential term which is necessary to represent the marked change in $\partial P/\partial T$ which occurs near and below atmospheric pressure. The equation

$$T_\lambda = K_0 + K_1 \pi + K_2 \pi^2 + K_3 \pi^3 + K_4 (1 - e^{-2\pi}) \tag{20}$$

where $\pi = 10^{-6} P$ (Pa) reproduces his values of T_λ within 0.1 millidegree and his derivative $\partial T_\lambda / \partial P$ with a maximum error of 0.2%. The constants K_i are given in Table I.

Table I. The Constants K_i [Eq. (20)], s_i [Eq. (21)], and h_i [Eq. (22)][a]

$K_0 = 2.17247$
$K_1 = -0.117615$
$K_2 = -0.0038655$
$K_3 = -0.00147339$
$K_4 = 0.0138789$

$s_1 = -0.210359$
$s_2 = 0.111850$
$s_3 = -0.117229$
$s_4 = 0.054780$
$s_5 = -0.0088230$

$h_1 = 6.385471$
$h_2 = -0.234656$
$h_3 = -0.0982606$
$h_4 = 0.0755214$
$h_5 = -0.0137764$

[a] The units for S and H are, respectively, $\mathrm{J \cdot g^{1} \cdot K^{-1}}$ and $\mathrm{J \cdot g^{-1}}$.

3.2. Least-Squares Procedures

Two different state equations have been developed for this work, one for helium I and one for helium II. For each equation, the adjustable parameters were determined by a linear least-squares fitting to five different physical parameters: C_p, thermal expansion, density, isothermal compressibility, and entropy at the lamda line. The first four parameters were evaluated at each of approximately 100 data points within the pressure and temperature range of interest. $S_\lambda(P)$ was evaluated at increments of 10^5 Pa over the pressure range. Thus a total of about 500 data points are supplied to the least-squares fitting routine, which determines optimum values for 28 adjustable coefficients. The overall accuracy of the fit can be varied by giving different weights to these separate thermodynamic components. In general we have given a little lower weight to the thermal expansion than to other components, espcially where it is small and difficult to determine from the original experimental data. In general terms, the accuracy of the helium II fit was 2% or better, while with the same number of adjustable parameters the helium I fit was only about 5%. It is appropriate to discuss these two equations separately.

3.3. The Helium II Equation

There is no indication in Refs. 4 and 5 that Eq. (1) was used in any way, e.g., for constructing, testing, or smoothing of their compiled results. For this work spot checks were made by simple linear differencing of

$$\Delta C_p/\Delta P$$

and

$$\Delta(\partial V/\partial T)/\Delta T$$

in their tabulated values at several points. Maynard's data passed this test very well, exhibiting equality of these factors within about 2%. The Brooks and Donnelly data, on the other hand, were thermodynamically inconsistent by up to 17%, essentially because of erratic behavior of their thermal expansion data (they noted trouble with this parameter in their paper). Thermal expansion data are not given in Ref. 6, and it is not apparent whether they were used in determining the state equation. On the other hand, McCarty presents some evidence for systematic error in Maynard's density data.

For numerical curve fits in this work, only Maynard's data were used. The data at 131 different (P, T) points were selected from the tables of reference 4, along with all 26 data points in Table VII of Ref. 6. [An apparent misprint in the latter data has been corrected: it appears from cross-plots that K_T for helium I at $P = 20$ bars and $(T - T_\lambda) = 10^{-3}$ K should be 0.0670 rather than 0.0700 bar^{-1}.]

3.3.1. Entropy at the Lamda Line

One of the first questions to be considered was the accuracy of Ahlers' data for the entropy along the lamda line. Since his evaluation of this quantity utilized specific heat data within 10^{-2} K of T_λ, where the logarithmic term dominates, a priori suspicion of the result is reasonable because $S_\lambda(P)$ is independent of the logarithmic term. In effect, the Σ' term must be separated from the logarithmic and Σ'' terms.

A least-squares fit to C_p, thermal expansion, compressibility, and density was obtained. S_λ from this fit agreed with that of Ref. 7 to within about ± 0.006 J $\cdot$ g^{-1} $\cdot$ K^{-1}, after an arbitrary zero shift. In subsequent curve fitting, Ahlers' S_λ data were included and given reasonable weight. The fitting of the helium II data was essentially unaffected, but the helium I was aided considerably. One cannot help but admire the precision of Ahlers' work in this very narrow temperature range.

The agreement between the fitted Eqs. (9) to (13) and the input data is summarized for each thermodynamic component in Table II. Complete

Table II. The rms Deviation of the Input Data from the Values Predicted by the Equation of State, for Five Different Thermodynamic Parameters and Four Different Equations[a]

	Helium II	Helium I		
		$P < 17$	Full range	$P > 12$
Percentage error in				
C_p	1.52	3.35	4.49	3.00
β	4.58	7.43	9.03	1.59
ρ	0.12	0.14	0.22	0.17
K_T	1.69	4.92	7.96	1.11
rms absolute error in				
$S_\lambda (\mathrm{J \cdot g^{-1} \cdot K^{-1}})$	0.0056	0.0057	0.0090	0.0032
Coefficient of logarithmic term $a (\mathrm{J \cdot g^{-1} \cdot K^{-2}})$	-0.5497 ± 0.0023	-0.6200 ± 0.0102	-0.6286 ± 0.0112	-0.6267 ± 0.0038

[a] Also shown is the value of the coefficient a of the logarithmic term, for each equation.

numerical results in the form of a computer equation can be obtained from the author. The largest source of error was associated with the highest temperature datum along each isobar in Ref. 4. These high-temperature points were often more than 3 SD from the computed curve.

The entropy and enthalpy gradients along the λ line, from this result, are given approximately by

$$S_\lambda(\pi) - S_\lambda(0) = \sum_{i=1}^{5} s_i \pi^i \tag{21}$$

$$H_\lambda(\pi) - H_\lambda(0) = \sum_{i=1}^{5} h_i \pi^i \tag{22}$$

where the coefficients s_i and h_i are given in Table I and, as before, $\pi = 10^{-6} P$ (Pa). The equations are not applicable below the saturation vapor pressure.

3.3.2. The Logarithmic Term

Returning now to the complete set of equations, (9)–(13), we find that the coefficient of the logarithmic term, determined from the least-squares fit, is

$$a = -0.5497 \pm 0.0023 \ \mathrm{J \cdot g^{-1} \cdot K^{-2}}$$

in reasonable agreement with Eq. (8b). It is important to note that neither this result for the coefficient a nor the predicted $S_\lambda(P)$ is a simple repeat of Ahlers calculations in Ref. 7. Using only Maynard's data, i.e., given zero weight to Ahler's data, a least-squares fit gave $a = -0.59\ \mathrm{J \cdot g^{-1} \cdot K^{-2}}$. A higher correlation between the two data sets is indicated.

The existing data for the thermal expansion coefficient are approximately linear with pressure above about 3×10^5 Pa but exhibit a noticeable decrease from the linear curve below this pressure. This can be seen, for example, in Fig. 2 of Ref. 4. In the present work, this qualitative effect is consistent with the decrease in dT_λ/dP in this same region, plus the fact that the logarithmic term is the dominant contribution in Eq. (11). However, the decrease in β at zero pressure predicted by the correlation of Ref. 4 is somewhat greater than that predicted here.

McCarty's suspicion of Maynard's density data was tested by giving zero weight to all densities except at $P = 1 \times 10^5$ and 2×10^5 Pa (necessary to determine integration constants). The resulting fit to the other four thermodynamic components yielded densities in agreement with Maynard's to within ±0.5%. Thus we see no strong evidence of systemic error in this component alone. However, further comparisons on this point should be made.

3.4. Helium I Equation

Fitting of the helium I data is complicated by two factors, (1) the temperature gap between Ahlers' data at the lamda line and McCarty's data above 2.5 K and (2) strong property variations as the liquid–vapor equilibrium line is approached, especially at near-critical pressures. Both of these constrain the data-fitting procedures.

Between T_λ and 2.5 K there occurs a minimum in C_p, seen in Fig. 2, and a change in the sign of the thermal expansion coefficient, seen in Fig. 3. This region corresponds approximately to the transition from dominance of the logarithmic term, near T_λ, to major contributions from the Σ terms, above 2.5 K. The fitting of $S_\lambda(P)$ using only the Σ' terms is of great help in constraining their behavior below 2.5 K. Nevertheless, it would be a serious mistake to use a large number of terms in Σ' just so as to obtain a fine fit at the liquid–vapor equilibrium line, especially as the critical pressure is approached. The lack of constraint in the T_λ to 2.5 K region could lead to unrealistic behavior in this transition region.

After some experimentation, it was decided that the upper limit of the fitted temperatures should be 4 K. Temperature up to 4.5 K were included in the fitted data but at reduced weight above 4.0 K. Thus, the resulting equations are not valid at the liquid–vapor equilibrium line except at subat-

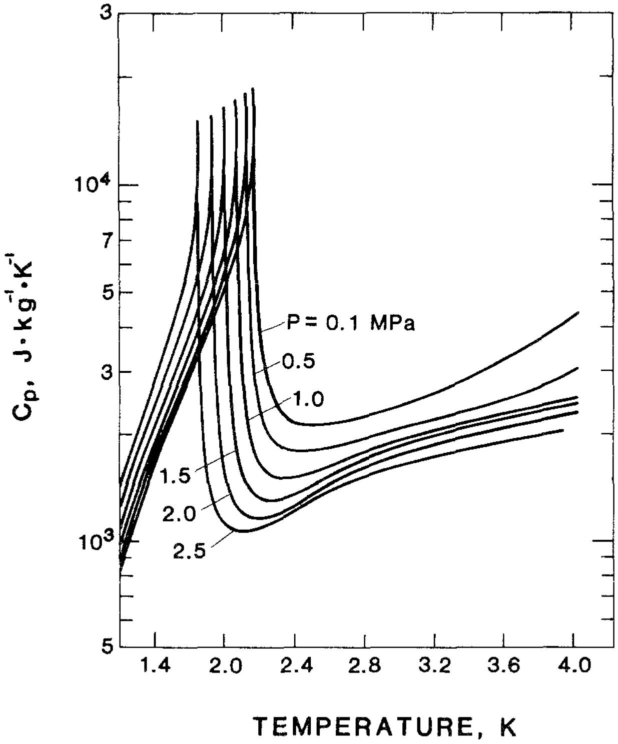

Fig. 2. The specific hear C_p as a function of temperature along selected isobar from 1.4 to 4.0 K. The maxima in the plotted curves correspond to $|T - T_\lambda| = 10^{-5}$ K.

mospheric pressure. Even in the latter case the accuracy is somewhat worse than the rms deviations listed in Table I.

Exactly the same form of equations, and the same number of fitted constants, was used for the helium I data as had been used for the helium II data. The resulting fit for helium I was generally less accurate than for helium II, as can be seen in the standard deviations listed in Table II. The largest source of error seemingly was associated with the compressibility and/or thermal expansion in the approximate range from 5 to 15 times atmospheric pressure. It is possible that McCarty's compilation [1] deviates systematically from Ahlers' data [7] in this region.

Ahlers discusses an apparent anomaly in the magnitude of the logarithmic term in Eq. (5) above 15×10^5 Pa. In the context of this work, his observations are equivalent to a pressure-dependent increase in the magnitude of the parameter α, Eq. (8a), from -0.61 at $P \leqslant 15 \times 10^5$ Pa to approximately -0.69 at $P = 25 \times 10^5$ Pa. For this reason, our initial fitting

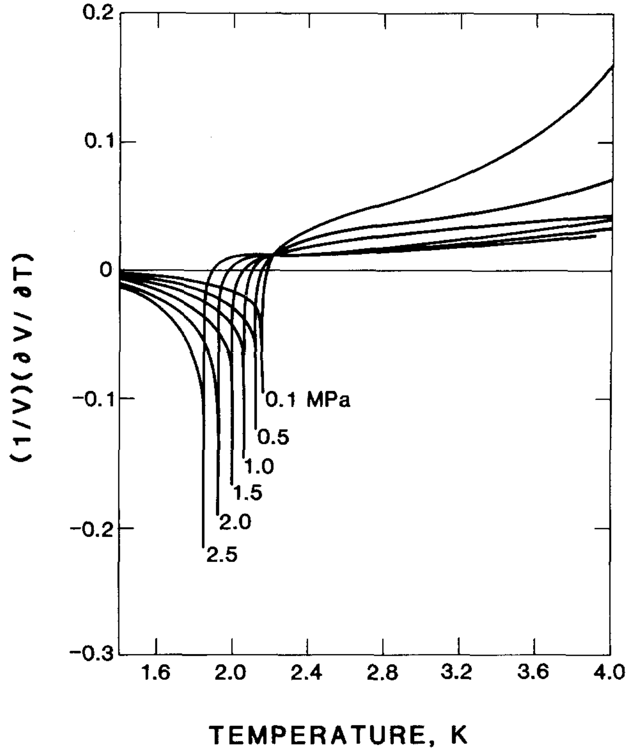

Fig. 3. The dimensionless thermal expansivity $(T/V)(\partial V/\partial T)_p$ as a function of T from 1.4 to 4.0 K, along selected isobars. The minima in the plotted values correspond to $|T - T_\lambda| = 10^{-5}$ K.

was limited to pressures of 16×10^5 Pa. This fitting yielded $a = -0.6200 \pm 0.0102$ $\text{J} \cdot \text{g}^{-1} \cdot \text{K}^{-2}$, in good agreement with Eq. (8a). Subsequently the data base was enlarged to include pressures up to 25×10^5 Pa. The corresponding value of a increased by a statistically insignificant amount, to -0.6286 ± 0.0112 $\text{J} \cdot \text{g}^{-1} \cdot \text{K}^{-2}$, but there was no serious degradation of the fit, as might have been expected. Subsequently, a separate fit was made for data from 12 to 25×10^5 Pa. This fit was somewhat more accurate than either of the two earlier fits at lower pressures, as can be seen in Table II. The important result, however, is that the coefficient a [Eq. (8a)] did not increase as would be expected from Ref. [7] but remained essentially unchanged at $a = -0.6267 \pm 0.0038$ $\text{J} \cdot \text{g}^{-1} \cdot \text{K}^{-2}$.

For pressures up to 15 bars the entropy gradient along the λ line from the wide-range fit is slightly smaller than given by Eq. (21), accumulating to an entropy difference of -0.033 $\text{J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$ at that pressure. For pressures from 15 to 25 bars, $S_\lambda(P) - S_\lambda(15)$ agrees with Eq. (21) to within ± 0.001

$\mathrm{J \cdot g^{-1} \cdot K^{-1}}$. Similarly, for pressures up to 15 bars the enthalpy gradient along the λ line is slightly smaller than given by Eq. (22), accumulating to an enthalpy difference of –0.067 $\mathrm{J \cdot g^{-1}}$ at that pressure. From 15 to 25 bars, $H_\lambda(P) - H_\lambda(15)$ agrees with Eq. (22) to within ±0.002 $\mathrm{J \cdot g^{-1}}$. This good agreement between the helium I equation and the helium II equation at pressures above 15 bars gives some confidence to our assumption that no substantial errors exist in this high pressure range.

4. SCALING LAWS AND ASYMPTOTIC VALUES

The important conclusion at this point is that the ratio of the logarithmic amplitudes

$$\frac{\alpha(\text{helium I})}{\alpha'(\text{helium II})} = \frac{0.6286 \pm 0.0112}{0.5497 \pm 0.0023} = 1.140 \pm 0.032$$

is independent of pressure within the above analysis. This pressure independence is expected by scaling laws, at least in their simplest form, but was not found by Ahlers from analyses of his narrow-range data. It is appropriate to discuss the approach to asymptotic values at the λ line and the difficulties of separating the logarithmetic, Σ', and Σ'' terms from narrow-range data.

Figure 4 shows the Grüneisen parameter as a function of $|T - T_\lambda|$ along several isobars in both helium I and helium II. Important observations from Fig. 4 are as follows.

(1) In helium II, Φ is a very weak function of temperature, for all pressures. The small slope of the curves is consistent with our earlier estimate that $|T - T_\lambda|$ would have to be reduced to less than 10^{-11} K to reach the asymptotic limit [Eq. (15)] for Φ.

(2) In helium I, Φ is a strong function of temperature, changing sign a few millidegrees above T_λ. This change in sign is coincident with a change in sign of the thermal expansion coefficient as that point, as required by Eq. (14). The rapid temperature variation is a reflection of the rapidly changing balance between the logarithmic and the Σ terms in the state functions.

(3) For pressures below about 15×10^5 Pa, $\Phi(\text{helium I}) \simeq \Phi(\text{helium II})$ for $|T - T_\lambda{}' \leqslant 10^{-5}$ K, and it appears from the slopes that this equality will be maintained as the abscissa is further reduced.

(4) For pressures above about 15×10^5 Pa, $\Phi(\text{helium I})$ exhibits a variable slope even down to $|T - T_\lambda| = 10^{-5}$, and it appears that the abscissa would have to be reduced to 10^{-6} or 10^{-7} K in order to achieve equality in magnitude and slope with $\Phi(\text{helium II})$.

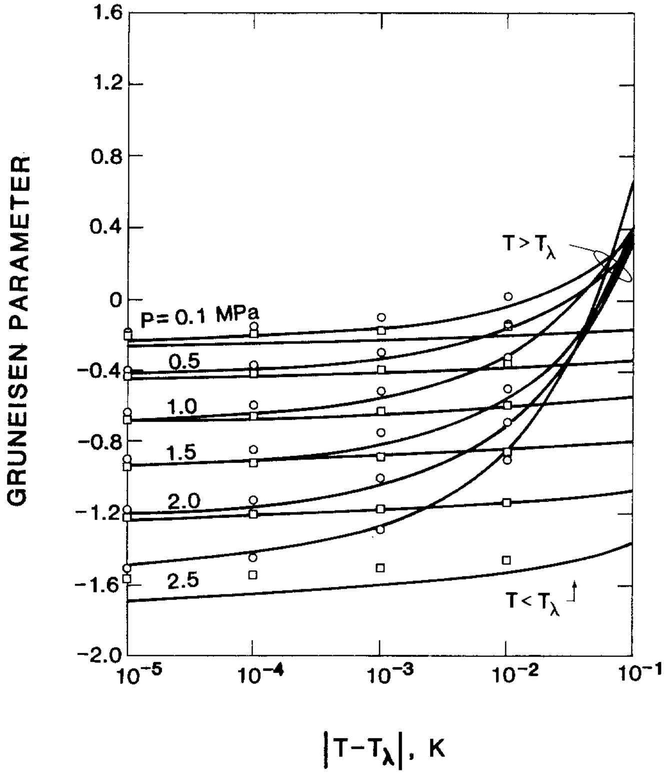

Fig. 4. The Grüneisen parameter ϕ as a function of $|T - T_\lambda(p)|$ along selected isobars. The data points are from Ahlers [7].

The conclusion from the curves is that strong and opposite temperature dependences of, respectively, the logarithmic and Σ terms are found in helium I as the λ line is approached, especially at higher pressures. As a consequence, more than just the D and E terms of Eq. (19) may be required to secure an accurate asymptotic representations of the analytic terms for helium I out to 10^{-2} K, especially for pressures about 15 bars. It might be a very difficult problem to separate higher-order analytic terms from the nonanalytic B term when data are available only out to $T = 10^{-2}$ K.

On the other hand, the accuracy of Ahlers' data-fitting was generally superior to that obtained in this work, especially for helium I. Thus, the discrepancy between his results and ours remains unresolved at this time.

5. A SINGLE EQUATION FOR 1.4 K < T < 4 K

It has been shown that $S_\lambda(P)$ depends only on analytic terms Σ which contain no explicit reference to the λ line. Thus, nothing in the analyses to this point requires that Σ' be any different in helium I than in helium II. Further, a hint of continuity in Σ' across the λ line is seen in Fig. 5, where the velocity of sound is plotted on isobars from 1 to 4 K. From this figure one could easily accept a model in which c is the sum of a dominant, continuous function minus a small λ-like perturbation of peak magnitude $\approx 13\ \mathrm{m \cdot s^{-1}}$, centered at the λ line. On the other hand, an awkward offset in the "continuous" function does become noticable at higher pressures. Perhaps this offset is related to the difficulties in fitting the compressibility of helium I, as mentioned above.

From these considerations an attempt was made to fit the complete range of data from 1.4 to 4.0 K using a single set of terms for Σ'. This

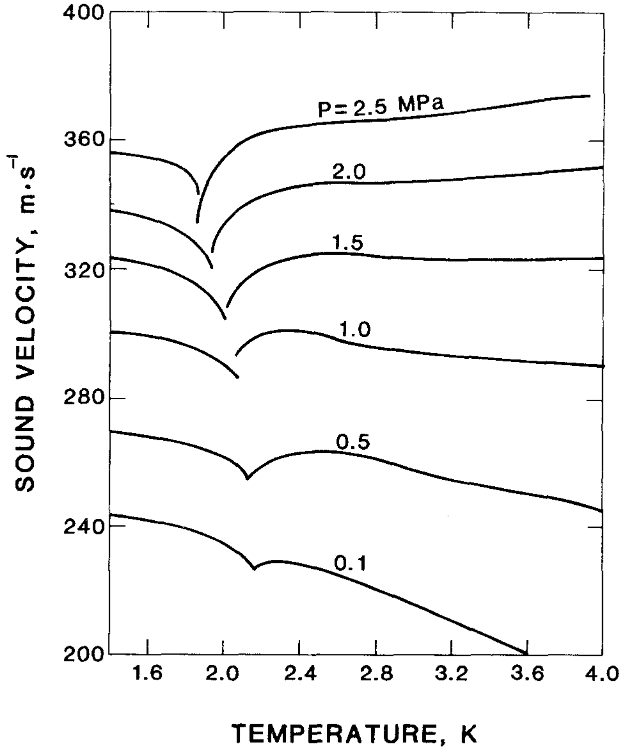

Fig. 5. The velocity of sound as a function of temperature from 1.4 to 4.0 K, along selected isobars. The discontinuities at the λ line are most probably due to unnaccuracies in the helium I state equation.

attempt was totally unsuccessful, using just the logarithmic and Σ'' terms as outlined here. Perhaps it could be made to work if a larger set of Σ'' terms were included in the fitting. On the other hand, the magnitudes of the Σ' terms are much different on either side of the λ line when the individual helium I and helium II fits are compared. This work was not pursued further.

6. INFLUENCE OF THE LOG TERM ON PROPERTIES FAR FROM T_λ

One of the interesting questions which we can now answer is the extent to which the logarithmic terms, required at the lamda line, contribute to the observed properties far from that line. In helium II, over the range of Maynard's data, the logarithmic term contributes 75 tp 90% of the specific heat and about 90% of the thermal expansion but less than about 5% of the compressibility. This result suggests that the logarithmic term should be included in any wide-range equation of state for helium II. Further, the known change in sign of $\partial V/\partial T$ at about 1 K would correlate approximately with the change in sign of the logarithm term above and below $T_\lambda - T = 1$. Small differences would be accomodated by the Σ terms. However, in this work the equations have not been extended below 1.4 K.

In helium I the logarithmic term contributes essentially the total specific heat up to 2.3 K and then drops rapidly to a small fraction. The thermal expansion changes sign a few millidegrees above T_λ where the logarithmic and Σ terms are equal and opposite, and order-of-magnitude equality of these terms persists to the upper temperature bound. Thus, the presence of the logarithmic term seriously perturbs the state functions above 3 K. The situation is comparable to the problem of creating a nonanalytic state equation valid at the critical point. In both cases the terms required for accurate description at the nonanalytic point (λ line or critical point) cause problems far from that point. Attempts have been made to introduce empirical terms to cut off the nonanalytic terms far from the critical point but without notable success. No such attempts have been made in this work.

7. DENSITY–TEMPERATURE COORDINATES

All of the work reported here is based upon integration of Eq. (1) with P and T as independent coordinates. An alternative approach would be to integrate Eq. (2) with V and T as independent coodinates. Ahlers has shown that his specific heat data may be expressed as

$$C_v = A(V) \log |T - T_\lambda(V)| + BDE \tag{23}$$

where, as before, A is a function of P and BDE represents terms which remain finite at T_λ. The fitting of his data to Eq. (23) shows residual deviations of 1 to 2% which are absent from his fitting to Eq. (5). Nevertheless, his observation offers the hope that an equation of the form

$$C_v = AT \log |T - T_\lambda(V)| + T\Sigma \tag{24}$$

might be reasonably successful in correlating wide-range data. The subsequent equations would be formally identical with Eqs. (9)–(13), but with P and V interchanged along with certain minus signs. The set of state equations would then be consistent with the usual state equations based upon density and temperature as independent coordinates. We have not performed this analysis.

8. CONCLUSIONS

The equation of state $V(P, T)$ given by Eq. (12), with simple polynomials for Σ' and Σ'', has been shown to represent helium properties from 1.4 to 4.0 K, up to 25×10^5 Pa, with an accuracy of 5% or better. The form of the equation allows simple evaluation of asymptotic fluid properties at the λ line, along with the observation that $S_\lambda(P)$ is independent of the logarithmic term. The calculated amplitude amplitude ratio $A/A' = 1.14$ is independent of pressure as required by the simplest form of universal scaling laws. A computer equation giving full numerical results is available from the author.

This work can be enlarged in several ways: (1) The helium II data base should be expanded to include Ref. 5, with temperatures down to 0.1 K. (2) It would be technologically useful to extend the helium I range to include the saturated liquid and, if possible, the near-critical fluid. (3) Second-sound velocities and two-fluid-model densities should be included in the helium II equation. (4) An equation of the form $P(V, T)$, based upon Eqs. (24) and (2), should be constructed and tested for numerical accuracy.

ACKNOWLEDGMENTS

This work was completed while V. Arp was a guest worker at the Electrotechnical Laboratory, sponsored by the Science and Technology Agency of Japan. The opportunity to work in a stimulating environment undisturbed by the normal miscellany of administrative procedures is gratefully acknowledged. The unstinting support of Drs. I. Todoriki, H. Koyama, H. Kaiho, and many others at ETL has been freely given. The patient assistance of T. Ohara in many aspects of computer work, often at the expense of his own work, has been invaluable.

REFERENCES

1. R. D. McCarty, NBS Technical Note 631 (1972).
2. B. A. Hands, *Cryogenics* **13**:423 (1973).
3. R. D. McCarty, NBS Technical Note 1025 (1980).
4. J. Maynard, *Phys. Rev.* **B**14:3868 (1976).
5. J. S. Brooks and R. J. Donnelly, *J. Phys. Chem. Ref. Data* **6**:51 (1977).
6. R. D. McCarty, NBS Technical Note 1029 (1982).
7. G. Ahlers, *Phys. Rev.* **A8**:530 (1973).
8. V. Arp, *Cryogenics* **15**:285 (1975).
9. V. Arp, *ASME J. Fluids* **106**:193 (1984).
10. D. L. Elwell and H. Meyer, *Phys. Rev.* **164**:245 (1967).
11. H. A. Kierstead, *Phys. Rev.* **126**:153 (1967).