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Specific Heat, Entropy, and Expansion Coefficient of Liquid Helium-Three†

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The specific heat of liquid He³ has been measured over the temperature range 0.015 to 0.3°K at pressures of 0.12, 6.45, 14.6, 21.4, and 28.8 atm. The specific-heat curves have been fitted to polynomials suitable for the calculation of absolute entropies. The isobaric thermal expansion coefficient has been measured over the same temperature interval at pressures of 14.4, 21.1, and 28.5 atm and is found to be negative over the entire region investigated. The thermodynamic consistency of these two sets of measurements is discussed.

A NUMBER of investigations of the low-temperature specific heat of He³ have been carried out from saturated vapor pressure to the pressure of the minimum of the melting curve.[1-4] These investigations differed primarily in the extrapolation to the absolute zero of temperature, reasonable agreement existing between the higher temperature results of the various investigations. In the present work the measurements have been made over a sufficiently wide range of temperature (0.015–0.3°K) and pressure (0.12–28.8 atm) to allow, at least at the lower pressures, a reasonable extrapolation to the absolute zero and a reasonable overlap with earlier higher temperature work. The measurements at pressures just less than the minimum in the melting curve also serve as a reference for related work on the solid-liquid phase equilibrium and on the solid.

In contrast with the specific-heat data, no uniform agreement can be found concerning the value, or even the sign, of the isobaric thermal expansion coefficient. One method which has been used to measure the expansion coefficient is to determine the change of temperature accompanying an isentropic compression,[3-5] the expansion coefficient being given by

$$\alpha = (C_p/VT)(\Delta T/\Delta P)_S, \qquad (1)$$

where α is the isobaric thermal expansion coefficient, C_p is the molar specific heat at constant pressure, T is the absolute temperature, V is the molar volume, and ΔT is the change of temperature accompanying the change of pressure ΔP when isentropic conditions prevail. A second method has been to determine the temperature variation of the dielectric constant by measuring the capacity of a condenser filled with liquid He³ and to relate this to the change of density of He³ with temperature using the Clausius-Mossotti relation.[6,7]

The measurements of the dielectric constant have yielded values of the expansion coefficient which are algebraically larger than those determined by the thermodynamic method in the low temperature region. Below 0.1°K and above 20 atm, the dielectric constant measurements have yielded a positive sign for the expansion coefficient[7] while the thermodynamic measurements yield a negative sign.[4] One objection which might be raised regarding the previous thermodynamic measurement is that a rather large pressure change (several atmospheres) was used, so that it might be difficult to make this expansion adiabatically.

In the present work, we have measured the expansion coefficient using the thermodynamic method described by Eq. (1) where the pressure change was less than 1 atm. Our measurements, for which the adiabatic expansions and compressions were reversible within experimental error, yield a negative sign for the expansion

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[1] D. F. Brewer, J. G. Daunt, and A. K. Sreedhar, Phys. Rev. 115, 836 (1959).
[2] A. C. Anderson, G. L. Salinger, W. A. Steyert, and J. C. Wheatley, Phys. Rev. Letters 7, 295 (1961).
[3] M. Strongin, G. O. Zimmerman, and H. A. Fairbank, Phys. Rev. Letters 6, 404 (1961); in Proceedings of the Eighth International Congress on Low Temperature Physics (to be published).
[4] D. F. Brewer and J. R. G. Keyston, Nature 191, 1261 (1961).
[5] D. F. Brewer and J. G. Daunt, Phys. Rev. 115, 843 (1959).

[6] D. M. Lee, H. A. Fairbank, and E. J. Walker, Phys. Rev. 121, 1258 (1961).
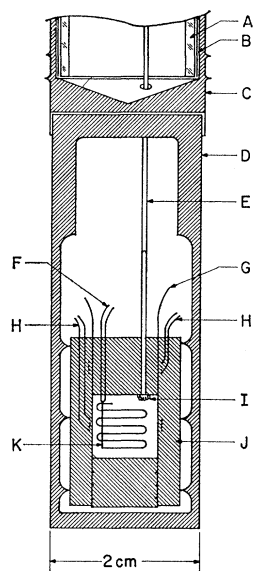[7] J. E. Rives and H. Meyer, Phys. Rev. Letters 7, 217 (1961).

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FIG. 1. Specific heat cell. A—Pyrex support tube, B—coil foil, C—nylon cylinder, D—nylon yoke of rectangular cross section (3 mm depth), E—$\frac{1}{64}$ in. 70–30 cupronickel filling tube, F—heater leads, G—pure copper cooling wires, H—leads to strain gauges, I—cotton filter plug, J—Epibond 100a, and K—cavity for powdered CMN and He^3.

coefficient. Our results for expansion coefficients are confined to the region of pressures above 14.0 atm.

APPARATUS AND TECHNIQUE

The demagnetization cryostat used for these measurements was similar to that described elsewhere[8] with the exception of the construction and mounting of the cell for the He^3 sample. A scale drawing of this cell and mount is shown in Fig. 1. The body of the cell was molded of Epibond 100a[9] using Teflon molds. The cavity was filled with 0.805 g of powdered cerium magnesium nitrate C(MN) and the lower plug then glued in place with Epibond 121. The packing was such that a volume of 0.218 cc was left for He^3. The He^3, which contained no more than 0.004% He^4 impurity, was admitted to this volume via the $\frac{1}{64}$-in. o.d.$\times$0.003-in. wall, 70–30 cupronickel tube. A strain gauge was also incorporated in the wall of the cell for use in measurements at pressures higher than the minimum of the melting curve. As it served no purpose in the measurements described in this paper, its description will be deferred to a later paper.[10]

The inner surface of the He^3 cell was lined with 300 insulated, 0.004-in. diam, 99.999% pure, copper cooling wires which extended through the top of the cell to two lead thermal switches. The thermal switches had an area to length ratio of 5×10^{-3} cm and were attached to the cooling wires by one of two alternative methods, each of which gave comparable results. The first method was that described by Reese and Steyert[11] and the other was to solder the cooling wires to a short length of 0.04-

in.-diam copper wire which in turn was soldered to the lead thermal switch. The upper ends of the thermal switches were similarly attached to cooling wires which extended down from the adiabatic demagnetization refrigerator of chromium potassium alum (CrK alum). The thermal switches were controlled by a small electromagnet which was external to the cryostat. This magnet was also used to provide a localized magnetic field for a second stage demagnetization of the CMN when desired. The design of the switches and the amount of CMN used in the cell determined the upper limit for this work of about 0.3°K; above this temperature the thermal coupling through the switches was so large and the sensitivity of the thermometer was so low as to make higher temperature work unprofitable.

The He^3 cell was rigidly mounted in a nylon yoke. The yoke was designed to provide a maximum thermal impedance between the CrK alum refrigerator and the He^3 cell, otherwise the lead thermal switches might be thermally bypassed. The upper end of the nylon yoke slid over the lower end of the rigid Pyrex central support for the demagnetization cryostat but was separated from the Pyrex by a layer of coil foil[12] to minimize the heat leak. This foil was cooled by the CrK alum refrigerator. The residual heat leak to the He^3 cell was about 3 ergs/min. About half of this heat leak was due to rf fields in the 100-Mc/sec range from FM and TV transmitters. This was detected by correlating a sudden decrease in the heat leak with the time at which these transmitters ceased to broadcast.

A different mounting arrangement was used for the He^3 cell at temperatures less than about 0.03°K. For these measurements the lead thermal switches were removed and the cell connected thermally to the CrK alum refrigerator as tightly as possible. The thermal boundary resistance between the He^3 and the cell walls provided the necessary thermal isolation for specific heat measurements. The nylon yoke was replaced with a nylon tube to which the cell was bound tightly in an attempt to reduce the likelihood of vibrational heating.

An electrical heater, consisting of a 30-cm length of 0.002-in.-diam manganin wire formed into a bifilar loop and bent into a spiral, was located within the cavity in the cell. Platinum leads, silver soldered to the heater, extended through the top of the cell. Potential and current measurements in the heater circuit were taken with a Leeds and Northrup type K-3 potentiometer. Power was usually applied for periods of 100 sec, the rate of heating being adjusted to provide a fractional temperature change ranging from 2% at low temperatures to 10% at the highest temperatures where the specific heat is a very slowly varying function of temperature. The procedure used to apply power was such that the heat input to the He^3 was known to better than 0.1%.

The volume of the cell was measured by measuring the amount of gas boiled off when the cell, initially full

[8] A. C. Anderson, W. Reese, and J. C. Wheatley, Phys. Rev. 127, 671 (1962).
[9] Furane Plastics Inc., 4516 Brazil Street, Los Angeles 39, California.
[10] A. C. Anderson, W. Reese, and J. C. Wheatley (to be published).
[11] W. Reese and W. A. Steyert, Rev. Sci. Instr. 33, 43 (1962).
[12] A. C. Anderson, G. L. Salinger, and J. C. Wheatley, Rev. Sci. Instr. 32, 1110 (1961).

of liquid, was very rapidly warmed to liquid nitrogen temperatures. Three such determinations were made. An additional determination was made by measuring the amount of gas required to fill the cell with liquid when it was initially full of gas. As the uncertainties involved in this determination were thought to be greater than in the other method, the volume so determined was given half-weight with respect to the volumes determined by the first method. The average of these four determinations led to a cell volume of (0.218±0.0045) cm³. This uncertainty in the volume will lead to an overall uncertainty of about 2% in the measurements made in this series of experiments. Some of the results of our measurements, namely, the values found for the entropy of the liquid at saturated vapor pressure, the value of the entropy at the minimum of the melting curve, and the agreement of our values of the specific heat at higher temperatures with other workers who used cells with volumes more amenable to accurate measurement, give us some confidence that our volume determination is really more accurate than the value assigned above.

Temperatures were determined by measuring the magnetic susceptibility of the CMN with an electronic bridge operated at 17 cps.[13] In a separate experiment, the magnetic susceptibility of CMN measured with the 17-cps bridge was compared with the susceptibility measured ballistically and found to agree within 0.5% down to 0.015°K. The sensitivity of the bridge was such that temperatures could be determined to a precision of $\Delta T/T = 10^{-4}$. Hence, the changes of temperature upon heating could be determined to better than 1%. The temperature calibration is believed to be accurate to about 1%; errors in the temperature calibration producing an over-all shift in all of the results of this investigation.

The calibration of the CMN required two steps. First, the He³ cell was maintained near 70°K and the magnetic susceptibility of the Pyrex vacuum case was measured as a function of temperature, the temperature being determined by the He⁴ vapor pressure. Then heat exchange gas was admitted and the susceptibility of the CMN plus Pyrex vacuum case was measured. The difference between the two measurements then gave the temperature dependence of the susceptibility of the CMN since the only other magnetic material present in sufficient quantity to produce a significant error in the calibration was that of the Pyrex vacuum case.[14] During an experimental run the vacuum case was held at a constant temperature near 1°K. In the mutual inductance circuit both the measuring coil and the bucking coil were maintained at He temperatures to circumvent possible errors due to changes of coil mutual inductance with temperature changes.

Pressure was applied to the He³ using a pressure system which has been described elsewhere.[8] Pressures

were measured using a Mansfield and Green dead weight tester which is accurate to 0.1%. In performing measurements of the expansion coefficient, a weight corresponding to the desired pressure change was removed from the dead weight tester and the accompanying temperature change was noted. An idea of the method employed in this measurement can be gained by reference to Fig. 2 which shows the result of one measurement made at an initial pressure of 423.4 psi (1 atm = 14.70 psi) and a temperature near 0.047°K. Mutual inductance bridge readings [changes proportional to $\Delta(1/T)$] were taken for a period long enough to establish an initial slope due to the residual heat-leak, then the pressure was reduced, in this case by 10 psi, and the temperature variation followed. As can be seen, the temperature very rapidly took a new value and then continued drifting in response to the residual heat leak. When the drift curve was again well established, the pressure was increased to the initial pressure, and, as can be seen, the temperature quickly returned to an extrapolation of the initial drift curve indicating that the process was very nearly reversible. The procedure was then repeated using a different pressure change, in this case 5 psi. Pressure changes varying from 2 to 20 psi were used, always using at least two different pressure changes for each determination. In all cases the temperature changes were proportional to the pressure changes to within 2%.

Based on the accuracy with which the heat input and the temperature changes could be measured, one would expect the scatter in our specific-heat measurements to be about 1% and the absolute accuracy to be about 4% based on a possible 2% volume error and 1% temperature calibration error. Actually, this ignores two effects which were occasionally present. The first effect was one of occasional large stray heat bursts which were well correlated with the operation of a local FM communications transmitter. By monitoring these transmissions it was usually possible to eliminate data which were affected by this cause. The second was systematic errors
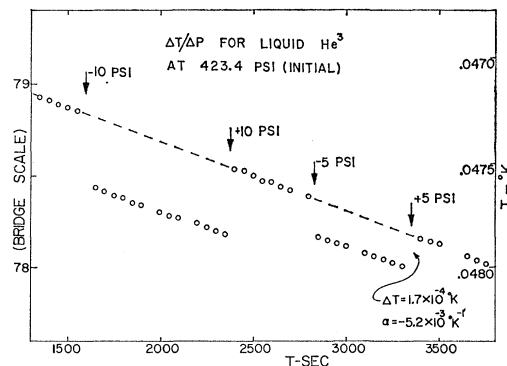

FIG. 2. Typical measurement of the expansion coefficient of liquid He³. The absolute temperature corresponding to the arbitrary bridge scale on the left side is given on the right side. Note that decreasing temperatures are upwards. Every second reading is plotted.

[13] Cryotronics Inc., Clinton, New Jersey.
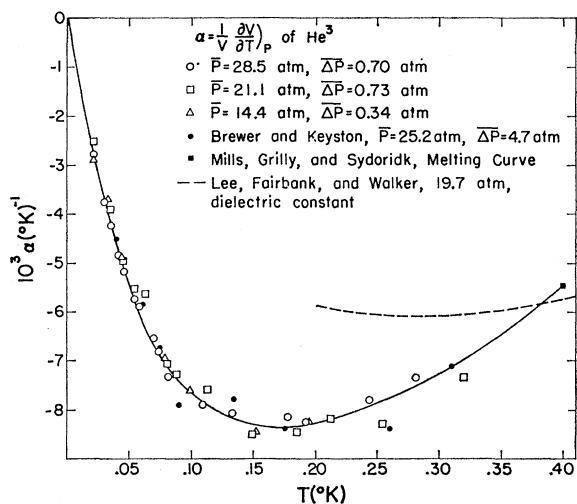[14] G. L. Salinger and J. C. Wheatley, Rev. Sci. Instr. 32, 872 (1961).

FIG. 3. The expansion coefficient of liquid He³ at various temperatures as a function of pressure. The measurements of Brewer and Keyston are those of reference 4, those of Mills, Grilly, and Sydoriak are those of reference 14, and those of Lee, Fairbank and Walker are those of reference 6.

throughout the data taken on a particular run due to a shifting of the zero in the relation between bridge reading and magnetic susceptibility which occurred despite the precaution of keeping all coils at He temperatures. The cause of this effect, which appeared to happen infrequently, if at all, is unknown and was uncorrelated with such possible factors as the helium level in the experimental cryostat. Of the data reported in this paper, it is our opinion that the data taken in one run at a pressure of 14.6 atm between the temperatures of 0.06 and 0.3°K represent the only data which could possibly have been so affected. The reasons for this belief will be discussed subsequently.

In the measurement of the expansion coefficient the temperature changes were smaller than those involved in the specific heat measurement, so a precision of 2% is assigned in the measurement of ΔT; the pressure changes were known to 1%. As smoothed values of the heat capacity were used, these should lead to a negligible random error in the evaluation of the expansion coefficient. However, one might expect a shift of up to 3% in the expansion coefficient due to systematic errors in the specific heat resulting from uncertainties in the value of the cell volume and the temperature scale. Errors in the calibration constant do not enter in the quantity $\Delta T/T$ which enters into Eq. (1).

RESULTS AND DISCUSSION

The results of the measurements of the expansion coefficient are shown in Fig. 3. For comparison we have included the results of Brewer and Keyston,[4] with which we are in substantial agreement, and the results of Lee, Fairbank, and Walker,[6] with which we disagree. We found that there was substantially no change in the expansion coefficient as a function of pressure between the

lowest pressure at which we made measurements, 14.4 atm, and the highest pressures at which we made measurements, 28.5 atm. The points shown in Fig. 3 are all averages obtained by performing at least one expansion and one compression for two different pressure changes. The pressure changes ranged from 2 to 20 psi, the average values of the pressure change used at a given pressure as well as the average pressure of the measurement are used to label the points.

The point at 0.4°K is taken from the work of Mills, Grilly, and Sydoriak[15] who directly measured the molar volume of the liquid along the melting curve. They extrapolated the expansion coefficient to zero at the temperature of the minimum of the melting curve (about 0.32°K), basing their extrapolation on the apparent observation that the change of molar volume with pressure along the melting curve was nearly constant as the minimum in the melting curve was approached. As can be seen, our results, and those of Brewer and Keyston, while consistent with the lowest temperature expansion coefficient given in reference 15, are definitely not in agreement with the extrapolation made there, and hence are in disagreement with any observations which led to this conclusion.

In the present measurements one finds that the expansion coefficient is negative down to the lowest temperatures and highest pressures investigated in contrast to the results of dielectric constant measurements.[7] In fact, the dielectric constant results would predict that the measurement shown in Fig. 2 should display cooling on expansion and warming on compression while the opposite is the case. Additionally, at lower pressures (about 21 atm) the results of the present measurements, while agreeing with measurements of Brewer and Daunt[5] who used the thermodynamic method using expansions only, are about a factor of 2 more negative than values deduced from the dielectric constant measurements of Lee, Fairbank, and Walker.[6] The reason for these deviations between the values of the expansion coefficient derived from the dielectric constant measurements and those employing the thermodynamic method are unknown to us, although the results reported here are thermodynamically consistent with the heat capacity measurements, while the dielectric constant results are not.

Specific-heat measurements were made at pressures of 0.12, 6.45, 14.6, 21.4, and 28.8 atm over a temperature range from about 0.015 to 0.30°K. The molar volumes used to reduce the heat capacity data to molar specific heats were the molar volumes given by Sherman and Edeskuty[16] for He³ at 1°K. Such a procedure will introduce an error of less than 1% into the resulting specific heats and is consistent with the treatment of previous work in this field.[1] Our results are given in Figs. 4(a)–(e).

[15] R. L. Mills, E. R. Grilly, and S. G. Sydoriak, Ann. Phys. (N. Y.) 12, 41 (1961).
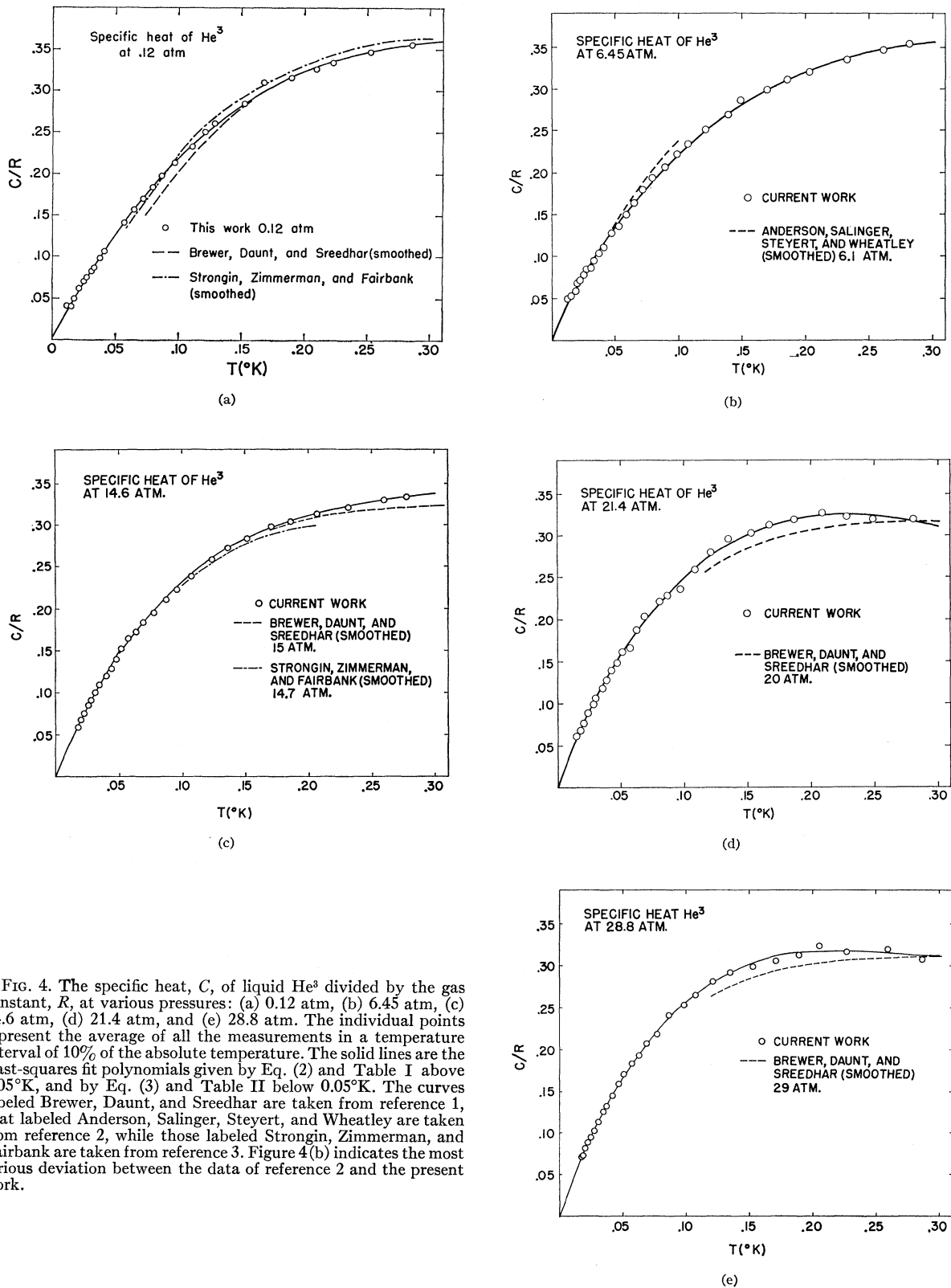[16] R. H. Sherman and F. J. Edeskuty, Ann. Phys. (N. Y.) 9, 522 (1960).

FIG. 4. The specific heat, C, of liquid He³ divided by the gas constant, R, at various pressures: (a) 0.12 atm, (b) 6.45 atm, (c) 14.6 atm, (d) 21.4 atm, and (e) 28.8 atm. The individual points represent the average of all the measurements in a temperature interval of 10% of the absolute temperature. The solid lines are the least-squares fit polynomials given by Eq. (2) and Table I above 0.05°K, and by Eq. (3) and Table II below 0.05°K. The curves labeled Brewer, Daunt, and Sreedhar are taken from reference 1, that labeled Anderson, Salinger, Steyert, and Wheatley are taken from reference 2, while those labeled Strongin, Zimmerman, and Fairbank are taken from reference 3. Figure 4(b) indicates the most serious deviation between the data of reference 2 and the present work.

TABLE I. The coefficients in the fit of polynomial 2 to the specific-heat data and the rms deviation of the polynomial from the data.

Pressure (atm)	a	b ($°K^{-1}$)	c ($°K^{-2}$)	d ($°K^{-3}$)	Δ_{rms}	No. of points
0.12	0.000	2.89	-7.80	7.09	0.0026	60
6.45	0.012	2.82	-8.04	8.14	0.0027	54
14.6	0.011	3.25	-12.0	16.1	0.0028	49
21.4	0.024	3.24	-10.9	11.0	0.0052	59
28.8	0.010	3.84	-15.8	21.1	0.0030	103

The smooth curves are least square fits to the data. The other curves are the smoothed results of Brewer, Daunt, and Sreedhar,[1] Anderson, Salinger, Steyert, and Wheatley,[2] and Strongin, Zimmerman, and Fairbank.[3] The points plotted in Fig. 4 are the unweighted average of all the points taken in each interval of 10% of the center temperature of that interval. The agreement between our present results and specific-heat measurements which were obtained in a previous, completely independent experiment[2] performed in this laboratory under much less favorable conditions is, in all cases, less than the 10% accuracy claimed for the previous experiment, and in most cases the agreement is closer to 2–3%.

TABLE II. The coefficients in the fit of polynomial 3 to the specific-heat data taken below 0.05°K and the rms deviation of the polynomial from the data.

Pressure (atm)	α ($°K^{-1}$)	β ($°K^{-2}$)	Δ_{rms}	No. of points
6.45	3.74	-23.7	0.070	26
14.6	3.84	-18.6	0.074	21
21.4	4.25	-23.6	0.072	16
28.8	4.44	-22.2	0.039	38

Our specific-heat data were fitted by least squares to the polynomial

$$C/R = a + bT + cT^2 + dT^3, \tag{2}$$

where C is the specific heat, R is the gas constant, and a, b, c, and d are functions of pressure given in Table I. In such a fit the higher temperature results, being larger, carry relatively more weight than the lower temperature results so that it is not surprising that the

curves, with the exception of 0.12 atm, do not pass through zero at $T=0$. Because of this feature, these polynomials are not suitable for the calculation of absolute entropies. To obtain curves suitable for such purposes the low temperature data (T less than 0.05°K) were treated separately and fitted to the polynomial

$$C/RT = \alpha + \beta T. \tag{3}$$

The results of this fit are given in Table II. It should be noted that the polynomial expression above gives a better fit to the data than did the expression $C/RT = \alpha' + \beta' T^2$ which would be most appropriate for a Fermi gas.[17] Except for the possibility of systematic errors in part of the 14.6 atm data, evidence for which will be discussed subsequently, these curves should represent the heat capacity of liquid He[3] with the exception of possible adjustments due to a 2% uncertainty of the volume of the cell and a 1% uncertainty in the temperature scale. It should be noted that the limiting value of C/RT obtained in this experiment at 0.12 atm, $(2.89 \pm 0.12)°K^{-1}$, is in satisfactory agreement with the previously reported value[2] of $(2.78 \pm 0.28)°K^{-1}$.

Entropy tables were constructed using Eq. (3) to 0.05°K, then Eq. (2) to 0.3°K. The resulting entropy table at 0.12 atm gave an entropy which was higher by an amount $\Delta S/R = 0.055$ than that tabulated by Brewer and Daunt in reference 5 at temperatures above 0.15°K. This difference stemmed primarily from the different specific-heat curve used below 0.10°K. Adding such a term to the saturated vapor pressure entropies given in reference 5 would bring them into agreement with the entropy determinations of Abraham, Osborne, and Weinstock,[18] who determined the entropy at 1.5°K by measurements of the heat of vaporization, but would cause them to disagree with the determination of Roberts and Sydoriak[19] who determined the entropy via the vapor pressure. Adding $\Delta S/R = 0.055$ to the entropy table of Brewer and Daunt would bring the higher pressure entries into substantial agreement with the values obtained in our work with the exception of the 14.6-atm case. These results are shown in Table III. Thus, the present work confirms, at least qualitatively, that the expansion coefficient data of Brewer and Daunt are thermodynamically consistent. We obtain that the entropy of the liquid along the melting line is equal to

TABLE III. A comparison of the entropy of liquid He[3] divided by the gas constant, as determined both in the present work and by Brewer and Daunt (reference 5). The results of Brewer and Daunt are in the columns labeled B. D.

T ($°K$)	0.12 atm	B. D.	6.4 atm	B. D.	14.6 atm	B. D.	21.4 atm	B. D.
0.15	0.354	0.299	0.382	0.329	0.403	0.360	0.435	0.381
0.20	0.442	0.386	0.468	0.414	0.489	0.445	0.525	0.466
0.25	0.516	0.461	0.543	0.488	0.560	0.514	0.598	0.534
0.30	0.581	0.524	0.606	0.547	0.621	0.575	0.655	0.592

[17] E. C. Stoner, Phil. Mag. **21**, 145 (1936).
[18] B. M. Abraham, D. W. Osborne, and B. Weinstock, Suppl. Physica 24, 132 (1958).
[19] T. R. Roberts and S. G. Sydoriak, Phys. Rev. **93**, 1418 (1954).

TABLE IV. A comparison of the specific-heat measurements with the expansion coefficient results. The comparison is made by subtracting the lower pressure quantity from the higher pressure quantity for the pairs of pressures indicated. The entropy change on expansion, $\Delta S/R$, and the change of specific heat on expansion $\Delta C_p/R$, are derived from measurements of the specific heat. The same quantities are calculated from the expansion coefficient results using Eqs. (4) and (5) and are labeled $\Delta S_\alpha/R$ and $\Delta C_{p\alpha}/R$.

| | 28.8–21.4 atm | | | | 21.4–14.6 atm | | | |
T (°K)	$\Delta S/R$	$\Delta S_\alpha/R$	$\Delta C_p/R$	$\Delta C_{p\alpha}/R$	$\Delta S/R$	$\Delta S_\alpha/R$	$\Delta C_p/R$	$\Delta C_{p\alpha}/R$
0.04	0.0087	0.0112	0.0098	0.0098	0.0125	0.0108	0.0085	0.0092
0.08	0.0150	0.0172	0.0078	0.0093	0.0213	0.0166	0.0166	0.0087
0.12	0.0191	0.0193	0.0049	0.0048	0.0277	0.0186	0.0187	0.0044
0.16	0.0204	0.0201	−0.0020	0.0000	0.0326	0.0193	0.0187	0.0000
0.20	0.0196	0.0200	−0.0092	−0.0019	0.0362	0.0192	0.0142	−0.0018
0.30	0.0170	0.0176	−0.0023	−0.0085	0.0347	0.0169	−0.0287	−0.0079

$R \ln 2$ at 0.321°K, in good agreement with the expected result if the solid entropy at the minimum in the melting curve is also $R \ln 2$. A similar result was obtained with an entropy table constructed by Strongin, Zimmerman, and Fairbank[3] from a compilation of all the previously available specific-heat data. The comparisons with the above higher temperature results can, of course, be reversed to indicate confidence in our determination of the cell volume and temperature scale.

A check on the consistency of our results which is independent of possible uncertainties in the cell volume and temperature scale is provided by the relation

$$(\partial S/\partial P)_T = - V\alpha. \qquad (4)$$

The results of such a calculation are shown in Table IV. One finds reasonably good agreement for the entropy differences between 28.8 and 21.4 atm calculated using the specific-heat values given by Eqs. (2) and (3) and those calculated from the expansion coefficient. However, the agreement between the two ways of calculating the entropy difference between the 21.4 and 14.6 atm curves is not at all satisfactory. However, if one were to adjust the entropies at 14.6 atm slightly upward so as to agree with those obtained if the entropy table of reference 5 is corrected as discussed above, one could obtain satisfactory agreement. Apparent discrepancies in the 14.6-atm data also manifest themselves in Table I where the coefficients needed to fit the data do not fall in regular sequence with the others.

The cause of the unsatisfactory nature of the 14.6-atm data is apparent if one employs the relation

$$(1/VT)(\partial C_P/\partial P)_T = - (\partial\alpha/\partial T)_P - \alpha^2. \qquad (5)$$

When this equation is used to examine the raw specific-heat data, the raw data obtained in one run extending from 0.06 to 0.30°K at 14.6 atm fail to be consistent with the specific heat curves at higher pressures over the temperature interval from 0.05 to about 0.17°K in a manner highly suggestive of a zero shift in the temperature measuring apparatus—a shift which gradually disappeared with time. Unfortunately, this run was not repeated except over the interval 0.06 to 0.07°K where the data also support the hypothesis advanced. However, the possible occurrence of such a systematic error in this one run is sufficient to make questionable the entropy values calculated at 14.6 atm for temperatures higher than 0.05°K.

One further test can be applied to our results to test the validity of the extensions to absolute zero resulting from using Eq. (3). This is to apply Eq. (5) in the limit of $T \rightarrow 0$. Since there is considerable difficulty in evaluating the derivatives accurately from the data at hand, this cannot be considered a precise tool. The two sides of Eq. (5) agree to better than 20% when evaluated over the pressure range from 14 to 29 atm. We consider this agreement to be satisfactory.