PHYSICAL REVIEW VOLUME 98, NUMBER 6 JUNE 15, 1955

Thermodynamic Properties of Liquid Helium Three. I. The Specific Heat and Entropy*

THOMAS R. ROBERTS AND STEPHEN G. SYDORIAK
University of California, Los Alamos Scientific Laboratory, Los Alamos, New Mexico

(Received March 7, 1955)

Specific heats of saturated liquid He^3 have been measured between 0.37° and 2.36°K. The data fit the empirical equation, $C=0.577+0.388T+0.0613T^3$ (cal/mole deg), to about ±1.0 percent between 0.5° and 1.7°K. The standard deviations of most of the individual points are between 1 and 2 percent.

Entropy differences are calculated from the above equation and combined with a value of entropy of 1.44 cal $mole^{-1}$ deg^{-1} at 0.5°K to give the total entropies.

The difference between the total entropy and the entropy of nuclear spin disorder is remarkably linear with and nearly proportional to T.

The present and earlier warmup experiments give no indication of existence of a specific heat anomaly in liquid He^3 between 3.21°K and 0.37°K. The present work also shows that a λ transition comparable to that occurring in liquid He^4 will not be found in liquid He^3 at any temperature below 0.37°K.

INTRODUCTION

THIS is the first of a series of papers whose ultimate objective is the establishment of a thermodynamically consistent vapor pressure equation for liquid He^3. Subsequent papers will describe vapor pressure and thermomolecular pressure ratio measurements and the combination of these results into a thermodynamic equation.

Measurements of specific heats and vapor pressures are of interest in themselves because of their usefulness in designing cryogenic apparatus and planning experiments. In the case of He^3 these measurements take on added interest because they provide answers to the questions: (a) Is there a specific heat anomaly corresponding to a lambda type transition in the readily accessible temperature range? and (b) Is there any reason to expect that such a transition will occur at temperatures below the range of the experiments? Because of recent interest and activity in measuring specific heats,[1,2] this first paper will describe and analyze the specific heat measurements reported briefly earlier.[3]

EARLY WARMUP EXPERIMENT

The earliest experimental evidence on the specific heat of liquid He^3 was of a qualitative nature intended only to answer question (a). In 1949, Hammel and one of us[4] showed that no λ-type transition exists for He^3 in the temperature range from 0.86° to 3.21°K by observing the warmup of 20 mm^3 of liquid He^3 in a miniature glass Dewar. Since the slides shown at the 1949 M.I.T. conference were not reproduced in the published proceedings, they are repeated here as Fig. 1. Figure 1(c) gives the results of a check run on liquid He^4 which clearly demonstrates the existence of its λ transition by a strong inflection at 37.6 mm Hg. Absence of any such inflection in the He^3 warmup experiments shows that He^3 does not undergo a second order transition of the same type as He^4 in the temperature range covered.

APPARATUS

The specific heat measurements which are described in this paper were performed in a Dewar also used for vapor pressure measurements and shown in Fig. 2. At the bottom of the all-metal Dewar, shown immersed in a bath of He^4, is a seamless 1-cm diameter sphere spun from a 10-mil copper sheet. The sphere usually is filled at 50 percent packing with paramagnetic salt particles of about 1-mm size. Twin coils wound directly on the He^3 vacuum jacket and immersed in the He^4 bath are used to measure the salt susceptibility temperature, T^*. Further details will be given in the vapor pressure paper.

The sphere is connected by 70 Cu 30 Ni tubing to a brass block, S, which thermally shorts the inner wall of the Dewar to the He^4 bath. An axial hole through this block connects the upper and lower vacuum spaces. Various inserts, shown in Fig. 2, can be screwed into the threads in this block.

Mercury and oil manometers are used to observe pressure warmups and to calibrate the alum. The liquid temperature is controlled by a sensitive needle valve and a mechanical fore pump of special design.[5]

A sensitive 0 to 250 mm Hg bellows-type gauge on the exhaust side of this pump is used to measure N, the total number of moles of He^3 in the Dewar and manometer. The gauge can be calibrated against the Hg and oil manometers mentioned above and is found

---

* Work performed under the auspices of the U. S. Atomic Energy Commission.

[1] G. de Vries and J. G. Daunt, Phys. Rev. **92**, 1572 (1953); Phys. Rev. **93**, 631 (1954).

[2] Osborne, Abraham, and Weinstock, Phys. Rev. **94**, 202 (1954).

[3] T. R. Roberts and S. G. Sydoriak, Phys. Rev. **93**, 1418 (1954).

[4] S. G. Sydoriak and E. F. Hammel, Proceedings of the International Conference on the Physics of Very Low Temperatures (Massachusetts Institute of Technology, Cambridge, 1949), p. 42.

[5] We are indebted to R. L. Mills for design of this pump. It is uniquely adapted for work with He^3 because of its low displacement (50 cc), its requirement of only 10 drops of oil, and its reversible operation.

to be reproducible to 0.2 mm Hg at full scale and 0.05 mm Hg at low pressures. The calibrated volume of gauge and pump exhaust (when running) ranges from 72.1 cc to 75.2 cc in the range 0–250 mm Hg. To facilitate the measurement of N, a fixed 542 cc volume can be added.

The He^3 used in these experiments contained 0.12 percent He^4.

METHODS OF MEASUREMENT

The measurements were made by three methods which differ in the temperature range covered and in the means used to evaluate the heat input, $\dot{Q}$. In Method I, best suited to measurements above 1°K, $\dot{Q}$ is primarily the measured power input to an electrical heater but includes also a small correction for normal heat leak to the liquid. In Method II, employed at selected temperatures between 0.5° and 1.25°K, the heater is dispensed with and $\dot{Q}$ derived from the carefully measured evaporation rate of the liquid and the calculated latent heat.

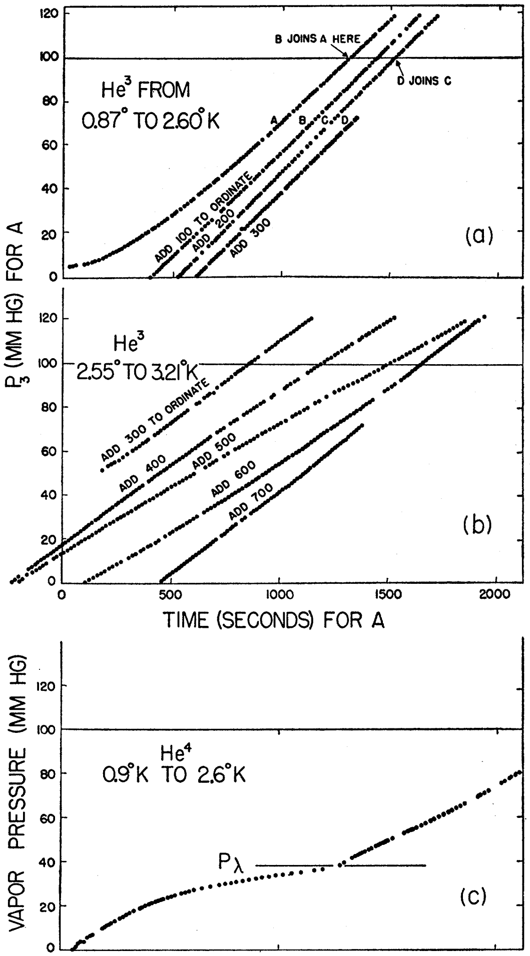

FIG. 1. Previously unpublished figures showing results of early liquid He warmup experiments of Hammel and Sydoriak performed in the Dewar in which He^3 was first liquefied. Figure 1(c) shows a He^4 warmup with a strong inflection at the lambda point. Note the absence of any such inflection in the He^3 warmups of Figs. 1(a) and 1(b).

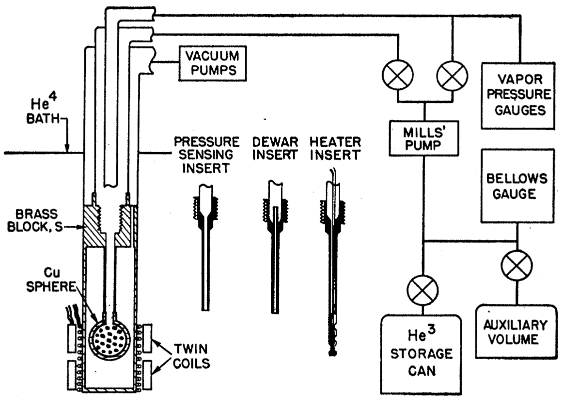

FIG. 2. He^3 Dewar and manifold.

Method III is used at temperatures below 0.5°K attainable to us only by adiabatic demagnetization, $\dot{Q}$ being inferred by fitting the warmup rate when above 0.5°K to the specific heat from Method II.

The liquid He^3 was contained in the copper sphere which served as the calorimeter. The noxious volume, i.e., the volume outside the calorimeter, was quite large in order to prevent excessive thermomolecular pressure ratios during vapor pressure measurements. Although this noxious volume was reduced considerably for the higher-pressure specific heat measurements, its effect was large on a single warmup. Therefore an experimental technique was used which canceled out the corrections for the noxious volume as well as for the calorimeter heat capacity. Warmup measurements were repeated with several different amounts of liquid. From the variation in warmup rate *versus* amount of liquid an apparent specific heat, C_a, is obtained. The calculated conversion to the actual specific heat, C, takes account of vapor warming and evaporation into that part of the dead space which changes with liquid level. To the extent that this region is isothermal, which is experimentally borne out, we show below that $C-C_a$ is dependent only on properties of He^3. The conversion factor $C-C_a$ can then be in error only to the extent that calculable quantities such as latent heat, vapor density, etc., are in error.

DERIVATION OF WARMUP EQUATIONS

Since no expressions were found in the literature which applied to Methods I and II, the equations will be derived in some detail.

$\dot{Q}$, the heat flux reaching the calorimeter, is spent in warming (1) N_L moles of liquid, (2) the calorimeter of heat capacity C_{cal} and (3) n moles of vapor within the calorimeter, whose entire volume, v, is assumed to be at the liquid temperature, T. The heat flux is also spent in the evaporation of liquid which accompanies its rise in temperature. With L as the latent heat of vaporization, C and c as the specific heats of the saturated liquid and vapor, respectively, and $\dot{T}$ and $\dot{N}_L$ as the warmup and evaporation rates, the heat flux is equal to:

$$\dot{Q}=(CN_L+C_{\text{cal}}+cn)\dot{T}-L\dot{N}_L. \tag{1}$$

Let n' be the number of moles of vapor in the noxious volume. During a warmup no He^3 is removed from the system, so $\dot{N}_L+\dot{n}+\dot{n}'=0$ and

$$\dot{N}_L=-[(dn/dT)+(dn'/dT)]\dot{T}. \tag{2}$$

In this paper all total derivatives with respect to T are taken along the saturation curve.

With V_v and V_L as the molal volumes of the vapor and liquid and β defined as V_L/V_v, the calorimeter volume is equal to $N_LV_L+V_v$ and

$$n=(v/V_v)-\beta N_L. \tag{3}$$

By appropriate substituting in Eq. (1) and dividing by $\dot{T}$, we find that

$$\begin{aligned}\dot{Q}/\dot{T}=CN_L+C_{\text{cal}}+c[(v/V_v)-\beta N_L]\\ -L(1-\beta)^{-1}[(v/V_v^2)(dV_v/dT)\\ +N_L(d\beta/dT)-(dn'/dT)].\end{aligned} \tag{4}$$

Up to this point the derivation has been essentially the same as that given by Osborne and Van Dusen[6] with the addition of the term n' for the vapor in the external dead space. Direct application of their experimental technique would involve the determination of C from Eq. (4) by a single determination of the average value of $\dot{Q}/\dot{T}$ over a small temperature interval. The calculation would involve detailed corrections for C_{cal}, n', and (dn'/dT).

Instead, we have canceled out these latter corrections experimentally by measuring $\dot{Q}/\dot{T}$ for several different values of N_L. Since n', and hence (dn'/dT), may be assumed independent of N_L, at any given temperature $\dot{Q}/\dot{T}$ should be a linear function of N_L with slope

$$C_a=[\partial(\dot{Q}/\dot{T})/\partial N_L]_T=C-\beta c-L(1-\beta)^{-1}(d\beta/dT), \tag{5}$$

as the apparent specific heat.

Actually N_L is not measured directly in our experiment, but N, the total number of moles of He^3 in the system, is. Since

$$N=N_L+n+n'=N_L(1-\beta)+(v/V_v)+n', \tag{6}$$

and n' is independent of N_L, it follows that $C_a=(1-\beta)[\partial(\dot{Q}/\dot{T})/\partial N]_T$. Thus the resulting expression for the specific heat of the saturated liquid,

$$C=(1-\beta)[\partial(\dot{Q}/\dot{T})/\partial N]_T+\beta c+L(1-\beta)^{-1}(d\beta/dT), \tag{7}$$

does not require any knowledge of the geometry or mass of the calorimeter, of the amount of liquid, or of the noxious volume.

The second and third terms of Eq. (7) are referred to as the vapor warming and evaporative terms, respectively. Their net sum is shown in Fig. 4.

Latent heats have been derived from the thermodynamic vapor pressure equation by a method equivalent to the use of the Clausius-Clapeyron equation. These results will be discussed in a later paper.

β and $d\beta/dT$ have been calculated from the data of Kerr[7] and the second virial coefficients, B, calculated by Kilpatrick, Keller, Hammel, and Metropolis.[8] Kerr's experimental vapor volumes are fitted best below 2.6°K by the virial equation in the inverse volume expansion:

$$V_v=(RT/p)(1+B/V_v). \tag{8}$$

This equation has been used for all vapor volume calculations in this paper.

The specific heat of the saturated vapor is calculated from:

$$c=c_{\text{vol}}+T(\partial p/\partial T)_V(dV_v/dT), \tag{9}$$

where c_{vol}, the specific heat of the vapor at constant volume, is taken as $(3/2)R$, and the derivatives are expressed in terms of dp/dT and dB/dT by differentiating Eq. (8). The values of p and dp/dT are calculated from an equation which fits our vapor pressure data between 0.4 and 1.0°K and data up to 1.5°K given by Abraham, Osborne, and Weinstock.[9] The temperature scale advanced by these authors, based on the Kistemaker corrections to the "Agreed" scale, has been used throughout the present work. Discussion of the pressure equation and possible variations in the temperature scale will be deferred to future papers.

Method I: Heater Measurements

For a Method I specific heat measurement, the paramagnetic salt is dissolved and siphoned out to make room for more liquid. The heater, shown in Fig. 2 with current and potential leads, is inserted, and the attached needle valve is closed to reduce the dead space.

The specific heat measurement consists in following pressure *versus* time as the liquid warms up several tenths of a degree. The measurement is repeated for three or four different liquid levels, all at the same heater power and bath temperature, to measure the proportionality of $\dot{Q}/\dot{T}$ to N. Table I shows the results of three such runs. Run I-B results will be discussed in sufficient detail to show that $\dot{Q}/\dot{T}$ is a linear function of N. In this run the N's were respectively equal to 18.51, 12.92, 7.89, and 3.57 millimoles, a fivefold variation in N. The variation in N_L, the moles of

---

[6] N. S. Osborne and M. S. Van Dusen, Bull. Natl. Bur. Standards **14**, 397 (1917).

[7] E. C. Kerr, Phys. Rev. **96**, 551 (1954).

[8] Kilpatrick, Keller, Hammel, and Metropolis, Phys. Rev. **94**, 1103 (1954).

[9] Abraham, Osborne, and Weinstock, Phys. Rev. **80**, 366 (1950).

liquid, is even greater than this since N includes the He^3 vapor. Specific heats calculated from the two highest levels show no consistent difference from C's calculated from the two lowest levels. Thus for a more than fivefold variation in amount of liquid, $\dot{Q}/\dot{T}$ at a given temperature varies linearly with N as expected if Eq. (7) is valid.

$\dot{Q}$ includes a correction for conduction heat leaks and therefore gradually falls as T rises. Just prior to Run I-B, a measurement was made of normal heat leak at a low sphere temperature where high accuracy is possible. The result agreed to within 5 percent with a calculation based on the geometry of the Dewar and heater leads and on recently compiled thermal conductivity data for copper and Cu Ni.[10] Since the observed heat leak in Run I-B amounts at most to only 4.6 percent of the heater power input, it was felt that calculation of this small correction would be preferable to more extensive measurements at each value of T. In Run I-A the heater power was three times as great, so the calculated correction ranges only between 1.5 percent and 0.8 percent of the total $\dot{Q}$. The fact that there are no consistent differences in the results of these two runs is further evidence that the conduction calculations are not a serious source of error.

The values from Run I-C are based on only two warmups and hence have been weighted $\frac{1}{3}$ in calculating a specific heat equation. The relative weights are shown in the table.

Errors in Method I

All errors given in the tables or in the text are the calculated standard deviations or their estimated equivalent. Where data were not available for calculation of a standard deviation, the deviation was taken as one-half the estimated limit of error.

The errors in Table I are the total standard deviations for each value of C and include estimated deviations of ±0.2 percent in both $\dot{Q}$ and N and ±1 percent in the evaporative and vapor warming terms. The average total deviation for all the values below 2°K is about ±2.0 percent with no systematic increase with pressure. This number represents mainly statistical errors calculated from the spread in observed C_a values due to dead space variations and timing errors. No estimate has been made of absolute errors in the temperature differences taken from the He^3 scale.

TABLE I. Specific heats from Method I in cal/mole deg.

	Run I-A		Run I-B			Run I-C			Relative
T°K	C_{ab}	C_{bc}	C_{ab}	C_{bc}	C_{cd}	C_{ab}	C	Std dev	weight
1.070	1.039	1.095	1.066	1.026	1.086		1.062	±0.017	1
1.157	1.069	1.132	1.144	1.135	1.190		1.114	0.019	1
1.256	1.170	1.161	1.181	1.190			1.176	0.012	1
1.364	1.198	1.259	1.255	1.273			1.246	0.022	1
1.452	1.403	1.283	1.273	1.356			1.329	0.032	1
1.527	1.404	1.349	1.371	1.405			1.382	0.020	1
1.608	1.470	1.369	1.485	1.422			1.436	0.030	1
1.695			1.553	1.526			1.540	0.028	$\frac{1}{2}$
2.231						2.047	2.047	0.047	$\frac{1}{3}$
2.358						2.391	2.391	0.049	$\frac{1}{3}$

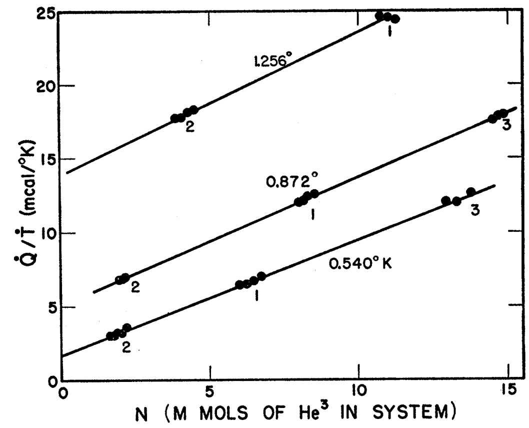

FIG. 3. The ratio of heat leak to warm-up rate plotted as a function of the total millimoles of He^3 in the Dewar and manometer. The least squares fitted slope of the straight line through the points at a given temperature is the apparent specific heat, C_a. The data shown are from Method II.

Method II: C/L Measurements

For Method II measurements iron alum is used to measure $\dot{T}$, and the Dewar tube insert replaces the heater. To measure $\dot{Q}$ it is necessary to remove vapor without significantly altering the conduction heat leak to the liquid. By removing vapor only via the capillary which forms the inner wall of this Dewar tube insert, we eliminate heat exchange between the effluent vapor and the Cu Ni tube which joins the copper sphere to the brass block, S. We estimate that even if the bottom of this insert made perfect thermal contact to the liquid, which is certainly does not do, the effect on the $\dot{Q}$ measurement would be only about 0.7 percent in the worst case.

In Method II measurements the warmup interval is much smaller, usually about 0.04°K, which requires up to 30 minutes for a full capsule. It is not practical to tabulate the data in detail, since ten to twenty warmups were observed in each temperature region. Figure 3 shows some typical $\dot{Q}/\dot{T}$-*vs*-N data. Each plotted point corresponds to one warmup, the sequence of warmups within a cluster being in the order of decreasing N. As a means of detecting any possible monotonic variation in dead space the data were usually taken in the order half-full, nearly empty, and full. No persistent variation is dead space is evident. However it was found necessary to allow about half an hour for equilibration of the dead space after having condensed or removed a large fraction of the liquid.

In measuring the heat flux to the refrigerant in a Dewar by means of its evaporation rate one can either (a) attempt to hold the temperature constant while

---

[10] R. L. Powell and W. A. Blanpied, National Bureau of Standards Circular 556, 1954 (unpublished).

TABLE II. Specific heats from Method II.

T°K	0.540	0.566	0.598	0.629	0.748	0.804	0.872	1.256
C cal/mole deg	0.811	0.790	0.815	0.854	0.895	0.930	0.956	1.223
Std dev	±0.013	0.012	0.010	0.011	0.013	0.014	0.017	0.035
L cal/mole	7.36	7.47	7.60	7.72	8.19	8.41	8.66	9.90

measuring $\dot{N}$ or (b) allow repeated warmup and cooldown over a narrow temperature interval, recording N for each warmup and time, t, at the moments the mean temperature is crossed during successive warmups. The latter technique was much better for our purposes. The amounts of gas withdrawn between successive warmups when divided by the time interval between arrivals at the average temperature, $\bar{T}$, and multiplied by the apparent latent heat[11] provided data for a continuous record of average heat leak including that during warmup. In fact, once a series of warmups was begun, very little time was spent in cooldowns, since these could be done quite rapidly. Thus the $\dot{Q}$ and $\dot{T}$ measurements were essentially concurrent.

This technique has several advantages besides a saving in time. Since the apparent latent heat is equal to $L/(1-\beta)$, the factor $(1-\beta)$ is canceled in Eq. (7), and no error is introduced due to errors in vapor density calculations except in the relatively small vapor warming and evaporative terms. The small changes in N between successive warmups used to calculate $\dot{Q}$ and the relatively large changes in N between series of measurements at the different liquid levels are both measured by the same metering system. Thus absolute errors in pressure calibration and volume measurements tend to be canceled.

Table II shows the results of Method II measurements. Latent heats have been calculated to an estimated accuracy of about ±0.5 percent. The latent heats used are shown in the table.

The standard error of temperature differences measured by the susceptibilities was ±0.2 percent. The error analysis shows that the net standard deviation for Method II measurements below 1°K is 1.5 percent of C.

Method III: Demagnetizations

For a Method III measurement, the Dewar tube insert is removed and replaced by a radiation shield, since one is interested only in obtaining the highest possible pumping speed, and therefore the lowest temperature, prior to a demagnetization. As noted above, $\dot{Q}$ was inferred from the slope of the warmup curve in the Method II region (above 0.5°K).

The results of runs III-A and III-B, with N's of 10.54 and 3.90 millimoles, respectively, are shown in Table III. The results were calculated for each warmup according to Eq. (1). The evaporative term varied from 6 percent to 19 percent of the C value while the paramagnetic salt heat capacity term varied between 4 percent and 10 percent. The vapor warming term was negligible. The standard deviations and relative weightings are shown in the table.

INCIDENTAL TECHNICAL REMARKS

(a) Hand operation of the current reversing switch in the susceptibility apparatus primary circuit was not satisfactory. At each current reversal there is an interval when the magnetic field, due to the primary current, is low, the salt therefore is cooled, and some condensation takes place, resulting in a momentary surge of warm gas into the capsule. With manual operation the "off" interval and hence the magnitude of the surge are not reproducible, resulting in an erratic contribution to the average heat leak. The difficulty was solved by employing an electrical relay switch having a rapid and reproducible action, actuated every 30 seconds even during cooldown. With this arrangement the added heat leak came to several percent of the total at the highest primary current used but did not vary during a series of measurements and was therefore not a source of error.

(b) Use of exchange gas in the vacuum space was found to be highly undesirable. For an hour or so after beginning re-evacuation, temperature spurts of ~0.002° occurred on occasional warmups. The solution was to avoid breaking vacuum altogether.

(c) Removal of a large fraction of the liquid in the absence of heat exchange to the bath was accomplished by cycling a 10 kilogauss field several dozen times. The net irreversible heating was due to the effect noted in (a) above but on a grand scale. It reduced the removal time from several hours to several minutes.

(d) To protect the salt from dehydration the Dewar was kept cold for months at a time. A gradual rise in $\dot{Q}$ then occurred, amounting eventually to several times the calculated conduction heat leak. A small portion of the capsule was visible to room temperature radiation by way of the pumping port in block S. The rise in $\dot{Q}$ might have been due to an increase in emissivity of the capsule caused by gradual formation of ice on it. This explanation is consistent with the observation that the excess in $\dot{Q}$ was independent of bath or capsule temperature. For our purposes the added heat leak was actually an advantage since it helped mask out any remaining variation in conduction heat leak not taken care of by the Dewar tube insert. In the Method I measurements (without salt), this added heat leak was not present since the Dewar was allowed to warm up

TABLE III. Specific heats from Method III.

T(°K)	Run III-A	Run III-B	C	Std dev	Relative weight
0.369		0.742	0.742	±0.030	$\frac{1}{4}$
0.417	0.740	0.733	0.737	0.020	$\frac{1}{2}$
0.463	0.749	0.744	0.747	0.021	$\frac{1}{2}$

---

[11] See, for example, R. Berman and J. Poulter, Phil. Mag. 43, 1047 (1952).

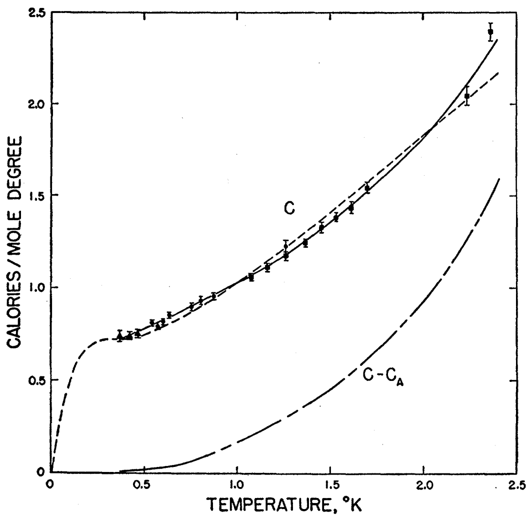

FIG. 4. The specific heat of saturated liquid He^3. The points plotted are the experimental results of all three methods with the vertical bars indicating the standard deviations. The solid curve is the fitted empirical relation, Eq. (10). The dashed curve is calculated from $C=C_{\text{spin}}+0.88T$ and shows qualitatively how C can be extrapolated to 0°K without postulating a phase change. The lowest curve shows the calculated difference between true and apparent specific heat.

between runs and the vacuum pump trap then removed any water vapor which had leaked in.

DISCUSSION OF RESULTS

The specific heat data are plotted in Fig. 4. Methods I and II seem to join smoothly at 1°K. The data between 0.5° and 1.7°K fit the empirical equation

$$C=0.577+0.388T+0.0613T^3 \text{ (cal/mole deg)}, \qquad (10)$$

with a mean deviation of 1.0 percent. The discussion of total errors in the various methods has shown that these errors are probably not much greater in magnitude than the scatter in the data and vary from 1.5 percent at 0.5°K to 2.0 percent at 1.7°K.

The two points above 2°K are less consistent with the equation. These points, as well as the data from Method III were only weighted between $\frac{1}{4}$ and $\frac{1}{2}$ as much as the other points in fitting the equation because they were obtained from fewer warmups. The weightings are shown in Tables I–III.

Our data are quite consistent with the equation published by Osborne, Abraham, and Weinstock[2] over the range of their measurements. The data of de Vries and Daunt[1] were obtained with much less liquid and show considerable scatter. Within their stated limits of accuracy of ±10 percent, their results are in agreement with the present work up to about 1.5°K but are 30 percent higher at 2.2°K.

Equation (10) is obviously unsatisfactory for extrapolation to zero degrees, since integration of C/T would yield a negatively infinite entropy at absolute zero. The terms of the equation have no theoretical significance. The equation may be integrated, however, to give entropy differences over the range of specific heat measurements. The resulting differences are combined with a value of the entropy at 0.5°K of 1.44 cal mole^{-1} deg^{-1} obtained from the thermodynamic vapor pressure equation and yield the entropies of the saturated liquid tabulated in Table IV and plotted in Fig. 5. A discussion of the derivation of the entropy at 0.5°K and comparisons with entropies derived solely from the vapor pressures will be deferred to a later paper. Entropy values reported by Weinstock, Abraham, and Osborne[2,12] are also plotted and are in good agreement.

NONSPIN ENTROPY AND SPECIFIC HEAT

The contribution to the entropy due to the disordering of the spins of the He^3 nuclei has a limiting value of $R\ln 2$ or 1.377 cal/mole degree. As T approaches 0°K the nuclear spins become more and more ordered in anti-parallel pairs, and this entropy of spin disorder, S_{spin}, also decreases to zero. Pomeranchuk[13] has predicted that the spin ordering will begin to occur appreciably at temperatures of the order of 1°K due to the exchange effects in the liquid. The detailed variation of S_{spin} with T has been considered by Goldstein,[14] who establishes the relation

$$S_{\text{spin}}=[\chi(T)/\chi_0(T)]R\ln 2, \qquad (11)$$

where $\chi(T)$ is the actual nuclear magnetic susceptibility and $\chi_0(T)$ is given by the limiting Curie-Langevin susceptibility law. Thus the measurements of χ by Fairbank, Ard, and Walters[15] can be used to calculate the spin entropy. Their Fig. 1 can be read as a plot of $S_{\text{spin}}/R\ln 2$. These spin entropies are given in Table IV and have been subtracted from calculated total entropy values to give the nonspin entropy, S_n.

TABLE IV. Total entropy, spin entropy, and nonspin entropy of saturated liquid He^3 in cal/mole deg.

T(°K)	S	S_{spin}[a]	S_n
0.4	1.27	1.04	0.23
0.5	1.44	1.14	0.30
0.6	1.58	1.20	0.38
0.8	1.83	1.28	0.55
1.0	2.04	1.29	0.75
1.2	2.24	1.31	0.93
1.4	2.43	1.32	1.11
1.5	2.52	1.33	1.19
1.6	2.61	1.33	1.28
1.8	2.79	1.33	1.46
2.0	2.97	1.34	1.63
2.2	3.16	1.34	1.82
2.4	3.35	1.35	2.00
2.5	3.45		

[a] Spin entropies read from an enlarged copy of the figure of Fairbank, Ard, and Walters (see reference 15).

---

[12] Weinstock, Abraham, and Osborne, Phys. Rev. **89**, 787 (1953).

[13] I. Pomeranchuk, J. Exptl. Theoret. Phys. (U.S.S.R.) **20**, 919 (1950).

[14] L. Goldstein, Phys. Rev. **96**, 1455 (1954).

[15] Fairbank, Ard, and Walters, Phys. Rev. **95**, 566 (1954).

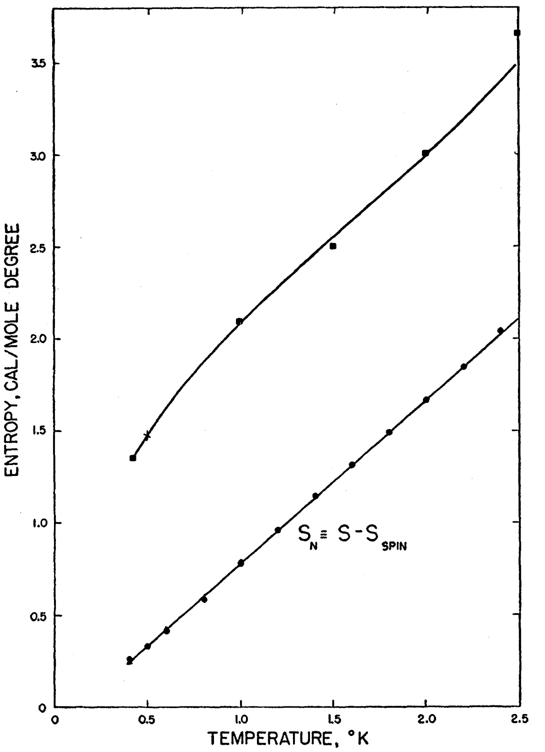

FIG. 5. Total entropy, S, and nonspin entropy, S_n, of saturated liquid He^3. Entropies given by Weinstock, Abraham, and Osborne are plotted as squares and are in reasonable agreement. The nonspin entropy is seen to be remarkably linear over its entire range and at 0.4°K is only 0.23 cal/mole deg. This value is an approximate upper limit to an entropy change which could be associated with a phase change in the liquid below 0.4°K.

The nonspin entropy points are plotted in Fig. 5. They are very nearly a straight line and fit the equation,

$$S_n = -0.12 + 0.88T \text{ (cal/mole deg)}, \qquad (12)$$

within ±0.01 entropy unit. The negative constant either indicates the order of magnitude of error in the calculated absolute value of the entropy at 0.5°K or the deviation of S_n from a straight line below 0.4°. An error in the entropy scale may be introduced in any of several ways: by errors in the Kistemaker temperature scale or in the virial coefficients used, as well as by errors in the specific heat and vapor pressure measurements. These factors will be discussed in detail with respect to the thermodynamic vapor pressure relation. For example, recent measurements by Keller[16] indicate that the second virial coefficient is calculated[17] more closely by use of the Exp-6 potential instead of the Lennard-Jones potential. Use of these Exp-6 potential virial coefficients changes all the entropy values by about +0.07 unit, thus reducing the constant in Eq. (12) from −0.12 to −0.05. This value is just within the limits of error of the absolute entropy determination. Therefore there is no valid reason at the present time to assume that the nonspin entropy is not well represented by a straight line passing through the origin.

The nonspin entropy is only about 0.23 cal mole^{-1} deg^{-1} at 0.4°K. Even if all this entropy were attributed to a phase change below 0.4°K, the transition would involve only 11 percent of the entropy change which Burton, Grayson Smith, and Wilhelm[18] associated with the He^4 λ transition by integrating over the specific heat anomaly.

Since the present work plus the early warmup experiments show that no second order phase occurs in liquid He^3 down to 0.4°K, we conclude that no transition comparable to the He^4 λ transition occurs in He^3 at any temperature. In fact, the analysis of the data indicates no reason whatsoever to postulate the existence of any phase change or specific heat anomaly below 0.4°K because all the entropy at this temperature is accounted for by S_{spin} and the simple linear S_n expression given above.

A reasonable extrapolation of the specific heat to temperatures below 0.4°K can be made by assuming that the proportionality of S_n to T persists in this range. The total specific heat is calculated as the sum of the specific heat of spin disorder, C_{spin}, and the nonspin specific heat, C_n. The latter, obtained by differentiating Eq. (12), is $C_n = 0.88T$. C_{spin} could be obtained by differentiating the experimental curve of χ/χ_0. Such differentiation is not warranted until the susceptibility data are better fitted by an empirical curve. Therefore we have used the values for C_{spin} calculated by Goldstein by differentiating the expression for χ/χ_0 for an ideal Fermi-Dirac gas of degeneracy temperature 0.45°K, which Fairbank has selected as the best fit to his data. The total specific heat, calculated according to the relation

$$C = C_{\text{spin}} + 0.88T, \qquad (13)$$

is shown as a dashed curve in Fig. 4. The extrapolation should be qualitatively correct, depending in detail on the analytical expressions for χ/χ_0 and C_n.

The remarkably high and apparently linear nonspin specific heat remains to be explained.

The authors gratefully acknowledge helpful discussions during the course of the present work with Dr. Louis Goldstein, Dr. J. E. Kilpatrick, and the entire staff of the Cryogenics Group, especially Dr. E. F. Hammel, Dr. W. E. Keller, Dr. E. C. Kerr, and Dr. H. S. Sommers.

---

[16] W. E. Keller (private communication).

[17] Kilpatrick, Keller, and Hammel, Phys. Rev. **97**, 9 (1955).

[18] Burton, Grayson Smith, and Wilhelm, *Phenomena at the Temperature of Liquid Helium* (Reinhold Publishing Corporation New York, 1940), p. 330.