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The Vapor Pressure, Critical Point, Heat of Vaporization, and Entropy of Liquid He^3

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The vapor pressure of pure liquid He^3 was measured from 1.025° to 3.35°K, and the data are represented accurately by the equation $\log_{10}p_{\mathrm{mm}}=-0.97796/T+2.5\log_{10}T+0.000302T^3+1.91594$. The normal boiling point is 3.195±0.001°K. The critical temperature and pressure were determined to be 3.35±0.02°K and 890±20 mm Hg, respectively. The calculated heat of vaporization has a maximum value of 11.4±0.4 cal. mole^{-1} at 2.1°K, and the extrapolated value at 0°K is 4.47 cal. mole^{-1}. The calculated entropy of liquid He^3, excluding the nuclear spin entropy, is 0.75±0.1 cal. deg.$^{-1}$ mole^{-1} at 1°K, and the extrapolated value at 0°K is 0.42±0.1 cal. deg.$^{-1}$ mole^{-1}. This extrapolated value of the entropy suggests that below 1°K there is either a triple point or an anomaly in the heat capacity.

I. INTRODUCTION

THE vapor pressure and critical point of pure liquid He^3 were first measured by Sydoriak, Grilly, and Hammel.[1] Prior to their measurements certain theoretical considerations seemed to lead to the conclusion that He^3 could not condense to a liquid under its own vapor pressure.[2,3] De Boer and Lunbeck, however, by means of a quantum theory of corresponding states had made predictions of the approximate vapor pressure and critical temperature and pressure, which agreed with the subsequent measurements.[4]

Because of the theoretical importance of the properties of liquid He^3, particularly for an understanding of the behavior of liquid He^4, independent measurements seemed advisable. Furthermore, determinations of greater accuracy appeared necessary for the calculation of the heat of vaporization and the entropy of the liquid, as well as for the proper treatment of data on the vapor pressures of solutions of He^3 and He^4.

This paper presents comparative measurements of the vapor pressures of He^3 and He^4 from 1.025° to 3.35°K, measurements of the critical temperature and pressure, a vapor pressure equation which fits the He^3 data accurately, and calculations of the heat of vaporization and entropy of liquid He^3.

II. He^3 SAMPLE

The He^3 used in these experiments was obtained from the decay of tritium gas, which was prepared by neutron irradiation of lithium in a chain-reacting pile. The tritium was initially separated from He^4, also formed in the nuclear reaction, by diffusion of the tritium through a heated palladium thimble. Subsequently, the He^3 which had grown in was separated from the tritium by the same technique and was purified from traces of tritium by circulating the gas through a U-tube immersed in liquid helium. In this way 29.9 cc (NTP) of He^3 gas was obtained with a He^4 content, according to mass spectrometric analysis, of 0.03±0.03 percent.

III. APPARATUS

A schematic diagram of the cryostat is shown in Fig. 1. The nitrogen and helium dewars (*A* and *B*) had unsilvered viewing strips one cm wide. The helium dewar was held against a Neoprene gasket (*E*) in the cap (*D*) by means of three small stainless steel cables (*F*) and turnbuckles (*G*). The cap was bolted to an angle iron frame, which was in turn bolted to the floor. The vacuum space of the helium dewar was evacuated through tube (*C*), which was also used to admit dry nitrogen gas so that the apparatus could be precooled to liquid nitrogen temperatures. Ordinary helium was liquefied with a Collins liquefier and was transferred directly from the liquefier into the cryostat through the vacuum jacketed transfer tube[5] (*P*).

The pumping lead (*J*) was connected to a Kinney vacuum pump, with a displacement of 52 l/sec., through a 4-in. diameter iron pipe. A 4-in. diaphragm valve manufactured by the Hills-McCanna Company was used to regulate the pumping rate, so that the temperature could be held constant at any desired value between 1.025° and 4.2°K. An inclined differential manometer, filled with dibutyl phthalate, was connected to the cryostat pressure tube (*K*) and indicated the necessary adjustments of the valve. The reference volume was a 200-cc bulb immersed in an ice bath. Since this manometer had a 1:10 inclination, a one-mm change corresponded to a pressure difference of 0.008 mm of mercury. With this system the temperature could be held constant indefinitely to better than 0.001° for temperatures above about 1.4°K. Below this temperature the valve was set as closely as possible to maintain the desired pressure, and the pressure was then allowed to reach an equilibrium value.

The cryostat pressure tube (*K*) projected 43 cm below the top of dewar (*B*) into a region where the gas flow was laminar. A copper-constantan thermocouple was wound around the tube and soldered to the lower end, so that the temperature of that point could be measured for calculation of the thermomolecular pressure dif-

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[1] Sydoriak, Grilly, and Hammel, Phys. Rev. **75**, 303 (1949).

[2] F. London and O. K. Rice, Phys. Rev. **73**, 1188 (1948).

[3] L. Tisza, Phys. Tod. **1**, 4 (1948).

[4] J. de Boer and R. J. Lunbeck, Physica **14**, 510 (1948).

[5] Similar to one described by M. C. Desirant and W. J. Horvath, Rev. Sci. Inst. **19**, 718 (1948), with the exception that the liquid nitrogen shield was omitted.

ference. The tube was connected to a dibutyl phthalate manometer (1.2 cm i.d.) for measuring pressures below 20 mm of mercury and to a mercury manometer (1.85 cm i.d.) for higher pressures, as well as to the inclined differential oil manometer.

The U-tube (N) was used for purification of the He^3 from traces of tritium.

In the first set of vapor pressure measurements (Series I), duplicate bulbs (M) were used for He^3 and He^4. These were drilled into a single block of copper and were of 0.05-cc capacity. The bulbs were suspended from the top of the cap by monel tubes (L) (0.051 cm i.d.), which were in turn connected to the manometers and filling line by means of small copper tubing. A constant volume mercury manometer (1.8 cm i.d.) was used for measuring the He^3 pressures. A similar mercury manometer was used for measuring He^4 pressures above 20 mm of mercury, and a dibutyl phthalate manometer (1.2 cm i.d.) was used for He^4 pressures below 20 mm of mercury. The metal tubes were protected from mercury vapor by means of glass capillary U-tubes immersed in liquid nitrogen.

The apparatus was modified for the critical point measurements (Series II). The connecting tubes were replaced with 0.05 cm i.d. glass capillary, and the bulbs were replaced by 3.5-cm lengths of 0.15 cm i.d. glass capillary. In addition, a stirrer for the helium bath was added. This consisted simply of a copper cage which was alternately raised and lowered by a solenoid at the top of the cryostat.

A further modification of the apparatus was made for Series III. As in Series I, the vapor pressure bulbs were made of a single block of copper, but the He^4 bulb was increased in volume to 0.20 cc, and the monel connecting tubes were made larger. The connecting tubes for the He^4 were of 0.508 cm i.d. and 0.005-cm wall thickness, and those for the He^3 were of 0.097 cm i.d. and 0.013-cm wall thickness. A radiation baffle was soldered into the He^4 connecting tube 20 cm above the bulb. The reasons for making these changes will be discussed below.

IV. VAPOR PRESSURE MEASUREMENTS

The entire sample of 29.9 cc (NTP) of He^3 gas was used for the vapor pressure measurements from 3.35° to 2.8°K, but to avoid possible overfilling of the bulb a smaller quantity was used at lower temperatures. The presence of a condensed phase was assured at the highest temperature for each sample size by establishing that the pressures in the He^3 and He^4 systems were independent of changes in the volumes of the systems.

Before each pressure measurement the temperature was held constant for at least 10 minutes. The stopcocks to the manometers were then closed simultaneously, and the manometer levels were read with cathetometers. Two cathetometers were used, one a Gaertner cathetometer which could be read to 0.03 mm, and the other a Henry Wild cathetometer which could be read to 0.01 mm. Both instruments were checked against a standard meter bar. The observed pressure readings were corrected to mm of mercury at 0°C and to the standard acceleration of gravity of 980.665 cm/sec.² (i.e., to international mm of mercury). The local acceleration of gravity[6] was taken to be 980.278 cm/sec.² Corrections were also applied for the temperature of the cathetometer scale, for the pressure exerted by the gas column in the tubes leading from the vapor bulbs to the manometer, and for the thermomolecular pressure difference.[7] The differences in meniscus heights were always small enough to make the meniscus corrections negligible. A factor to convert the readings of the

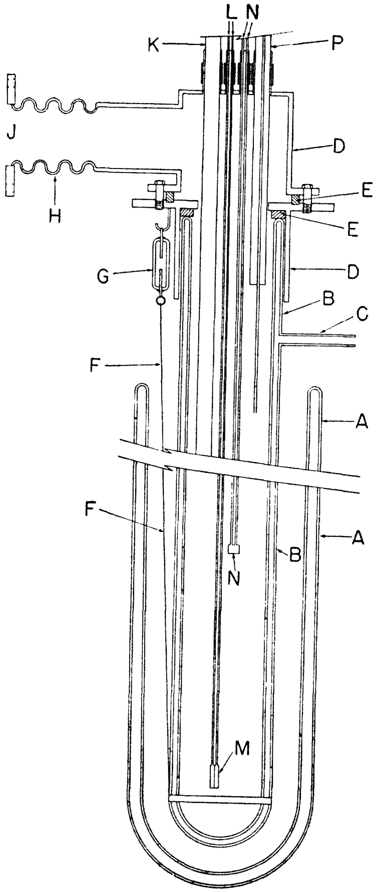

FIG. 1. Cryostat. A: liquid nitrogen dewar (Pyrex, 11.7 cm i.d., 90 cm inside length); B: liquid helium dewar (Pyrex, 5.9 cm i.d., 105 cm inside length); C: pumping lead for vacuum space of helium dewar; D: stainless steel cap; E: Neoprene gaskets; F: stainless steel cable; G: turnbuckle; H: brass bellows; J: pumping lead; K: cryostat pressure tube (monel, 0.823 cm i.d., 0.013 cm wall thickness); L: connecting tubes to vapor pressure bulbs (monel below cap, 0.051 cm i.d., 0.025-cm wall thickness; copper above cap); M: copper vapor pressure bulbs (0.05-cc capacity); N: monel U-tube for purification of He^3; P: vacuum-jacketed transfer tube from Collins helium liquefier.

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[6] *International Critical Tables* (McGraw-Hill Book Company, New York, 1926), Vol. I, p. 396.

[7] Weber, Keesom, and Schmidt, Communs. Kamerlingh Onnes Lab. Univ. Leiden No. 246a (1936); S. Weber and G. Schmidt, Communs. Kamerlingh Onnes Lab. Univ. Leiden No. 246c (1936).

dibutyl phthalate manometers at room temperature to international mm of mercury was determined in each series of measurements by comparing the readings of the oil and mercury manometers at a pressure of approximately 20 mm of mercury.

Above the lambda-point the pressure in the He^4 vapor pressure bulb rather than that in the cryostat was always used to indicate the temperature of the He^3. This was done in order to eliminate any uncertainty regarding the temperature of the He^3 arising from heat leak down the connecting tubes, temperature gradients in the bath, and possible cold spots on the connecting tubes.

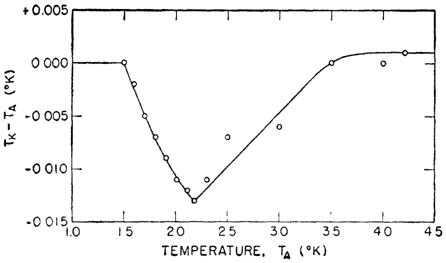

FIG. 2. Deviations of the temperature, T_K, according to Kistemaker (reference 11) from the "agreed" scale, T_A (reference 8).

TABLE I. Observed vapor pressure of liquid He^3.

$P(He^4)$ (int. mm Hg)	T_A (°K)	T_K (°K)	$P(He^3)$ (int. mm Hg)
Series I			
0.152	1.025	1.025	9.71
0.346	1.121	1.121	14.74
0.551	1.183	1.183	18.68
1.746	1.363	1.363	34.16
3.811	1.513	1.513	52.59
6.853	1.647	1.644	72.78
11.94	1.792	1.785	99.65
19.82	1.945	1.935	135.0
27.40	2.057	2.046	165.1
37.17	2.175	2.162	201.1
46.60	2.269	2.257	234.2
61.44	2.393	2.382	282.7
80.78	2.527	2.517	342.4
96.89	2.623	2.614	389.8
117.1	2.729	2.722	446.6
132.7	2.802	2.796	489.0
157.7	2.911	2.906	555.3
181.5	3.004	2.999	616.9
213.5	3.115	3.112	697.4
241.4	3.206	3.203	765.6
278.8	3.314	3.312	856.0
Series II			
0.154	1.026	1.026	9.81
0.179	1.042	1.042	10.46
0.205	1.058	1.058	11.29
267.2	3.282	3.280	827.7
276.3	3.307	3.305	849.9
278.9	3.314	3.313	856.5
280.3	3.318	3.316	859.5
292.4	3.351	3.350	888.7
Series III			
0.172	1.038	1.038	10.41
0.549	1.182	1.182	18.79
1.192	1.298	1.298	28.00

Below the lambda-temperature there were neither temperature gradients in the bath nor cold spots on the connecting tubes. The effect of heat leak was overcome by having the bulbs immersed in the bath to a depth of at least 2.5 cm. Under these conditions, the pressures in the cryostat and He^4 vapor pressure bulb were expected to agree in the range where the thermomolecular pressure corrections could be neglected, since the impact pressure and pressure drop due to gas flow in the cryostat were negligible. Experimentally, they were found to agree within a pressure difference corresponding to 0.001°K from the lambda-temperature down to 1.7°K.

Below 1.7°K the cryostat pressure in Series I and II did not agree with that of the He^4 vapor pressure bulb, even after correction for thermomolecular pressure differences. This was due chiefly to the impracticably long time required for pressure equilibrium in the He^4 vapor pressure bulb system. The cryostat pressure was therefore used to determine the temperature of the He^3. This choice was further desirable because the thermomolecular pressure corrections which had to be applied to the He^4 vapor pressure bulb were too large to be made with sufficient accuracy and because there was an uncertain (although probably negligible) correction due to film flow.

In Series III the diameter of the connecting tube for the He^4 vapor pressure bulb was large enough for the pressure equilibrium time to be short and for the thermolecular pressure corrections to be small even at the lowest temperature. In this series the cryostat and He^4 vapor pressure bulb agreed within 0.001°K.

For the He^3, the pressure equilibrium time was short and the thermomolecular pressure correction was negligible in all three series.

The experimental results are given in Table I. Columns 1 and 4 are the observed He^4 and He^3 vapor pressures, respectively, each entry being the average of two or more independent measurements. Column 2 is the "agreed" temperature, T_A, calculated from the He^4 pressure and the table given by van Dijk and Shoenberg,[8] which is essentially the Leiden 1937 scale[9] down to 1.6°K and the Bleaney and Simon scale[10] below 1.6°K. Column 3 is the temperature, T_K, calculated by applying to column 2 the corrections of Kistemaker,[11] smoothed as shown in Fig. 2. T_K rather than T_A was used in the derivation of the He^3 vapor pressure equation and in the thermodynamic calculations. This choice appears to be desirable because the heat of vaporization of He^4 at 0°K, calculated from Kistemaker's data, is much more nearly constant than that calculated from the 1937 scale. Also, van Dijk has recently obtained

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[8] H. van Dijk and D. Shoenberg, Nature **164**, 151 (1949).

[9] G. Schmidt and W. H. Keesom, Physica **4**, 963 (1937); **4**, 971 (1937).

[10] B. Bleaney and F. Simon, Trans. Faraday Soc. **35**, 1205 (1939).

[11] J. Kistemaker, Physica **12**, 272, 281 (1946).

TABLE II. Vapor pressure of liquid He^3 at even temperature intervals, from Eq. (4).

T_K (°K)	T_A (°K)	P (int. mm Hg)	dP/dT (mm/°)
1.0	1.000	8.68	41.3
1.1	1.100	13.51	55.9
1.2	1.200	19.93	72.7
1.3	1.300	28.13	91.7
1.4	1.400	38.33	112.6
1.5	1.500	50.72	135.5
1.6	1.603	65.50	160.3
1.7	1.705	82.85	186.9
1.8	1.807	102.94	215.2
1.9	1.909	125.94	245.2
2.0	2.011	152.04	276.9
2.1	2.112	181.38	310.2
2.2	2.213	214.13	345.1
2.3	2.312	250.46	381.6
2.4	2.411	290.50	419.6
2.5	2.510	334.44	459.3
2.6	2.609	382.41	500.5
2.7	2.708	434.59	543.2
2.8	2.807	491.13	587.6
2.9	2.906	552.18	633.6
3.0	3.005	617.89	681.1
3.1	3.104	688.45	730.3
3.2	3.203	764.02	781.2
3.3	3.302	844.74	833.8
3.195	3.198	760	

preliminary confirmation of Kistemaker's scale by magnetic measurements.[12]

It can be shown by equating the expressions for the Gibbs free energies of the liquid and of the saturated vapor, and neglecting the effects of nuclear spin, that the vapor pressure equation must be

$$\ln p = -\frac{\Delta H_0^0}{RT} + 2.5\ln T + \ln(2\pi m)^{3/2}k^{5/2}h^{-3} - \frac{1}{RT}\int_0^T S_{\text{liq}}dT + \frac{1}{RT}\int_0^T V_{\text{liq}}\left(\frac{dp}{dT}\right)_{\text{sat}}dT - \frac{Bp}{RT} + \frac{1}{2}\left(\frac{Bp}{RT}\right)^2, \quad (1)$$

provided the liquid exists in equilibrium with the vapor at 0°K and the equation of state of the vapor can be expressed by

$$pV = RT[1 + B(T)/V]. \quad (2)$$

ΔH_0^0 is the heat of vaporization at 0°K, R is the gas constant, m is the mass of a He^3 atom, k is Boltzmann's constant, h is Planck's constant, S_{liq} is the molal entropy of the liquid, V_{liq} is the molal volume of the liquid, and $(dp/dT)_{\text{sat}}$ is the slope of the vapor pressure curve. Equation (1) can be written in the form

$$\log_{10}p_{\text{mm}} = -A/T + 2.5\log_{10}T + C + f(T), \quad (3)$$

where A and C are constants and $f(0) = 0$.

Since $f(T)$ is only a correction term, it seemed reasonable to try $f(T) = DT^n$, and this function with $n = 3$ was found to be satisfactory. The constants A, C, and D were evaluated from the vapor pressure data in columns 3 and 4 of Table I by a least squares procedure in which the sum of the squares of the temperature deviations was minimized. The resulting vapor pressure equation is

$$\log_{10}p_{\text{mm}} = -0.97796/T_K + 2.5\log_{10}T_K + 0.000302T_K^3 + 1.91594. \quad (4)$$

Values of the pressure and of dp/dT calculated from Eq. (4) at 0.1° intervals from 1° to 3.3°K are given in Table II. The normal boiling point calculated from this equation is 3.195±0.001°K, in agreement with the previously reported value[1] of 3.20°K.

The deviations of the experimental data from Eq. (4) are plotted in Fig. 3 as temperature differences, $\Delta T = (p_{\text{calc}} - p_{\text{obs}})(dp/dT)^{-1}$, where p_{calc} and dp/dT are the pressure and slope calculated from the vapor pressure equation, and p_{obs} is the observed pressure. The deviations are within 0.001° except at the temperature extremes. In the neighborhood of the critical temperature there is a maximum deviation of 0.003°, and at the lowest temperature the deviations are within

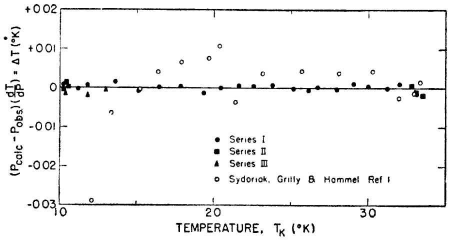

FIG. 3. Deviations from vapor pressure Eq. (4).

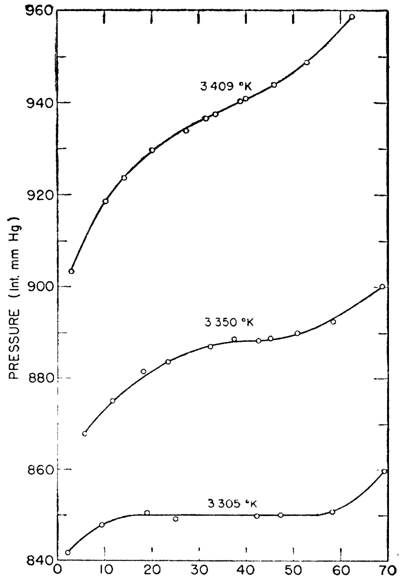

FIG. 4. Critical point determination.

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[12] H. van Dijk, Proceedings of the International Conference on the Physics of Very Low Temperatures, Massachusetts Institute of Technology (1949), p. 117.

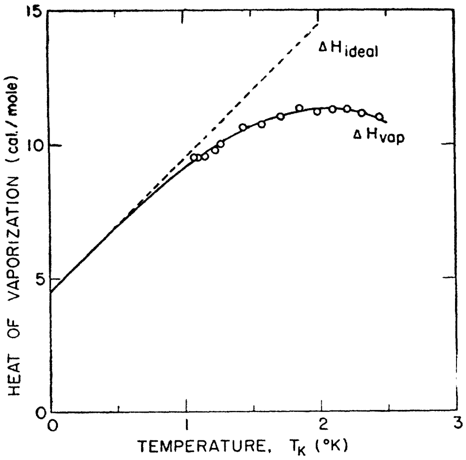

FIG. 5. Heat of vaporization of liquid He^3.

0.002°. It can also be seen from this figure that the three series of measurements are in excellent agreement with one another.

The deviations of the data of Sydoriak, Grilly, and Hammel[1] (corrected to the Kistemaker temperature scale) from Eq. (4) are also given in Fig. 3. Their deviations are considerably larger than those in the present work but appear to be within the experimental uncertainty of their measurements.

V. CRITICAL POINT

An attempt was made to locate the critical point of liquid He^3 by the classical visual method. Within experimental error the temperatures of appearance and disappearance of the meniscus were the same, namely, 3.317±0.001°K, and the corresponding measured pressure was 860±1 mm of mercury.

Since the visual method gives only a lower limit to the critical point,[13] further experiments were made by studying the dependence of the pressure on the volume of gas in the manometer at various temperatures. The observed pressures have been plotted in Fig. 4 against the height of the lower mercury level in the manometer, at temperatures of 3.305°, 3.350°, and 3.409°K. Although these curves are not $p-V$ isotherms, they can be used to locate the critical point. Below the critical temperature, as the manometer level is raised, there is an initial rise in pressure due to compression of the gas; next, there is a flat portion due to condensation to the liquid; and finally, there is a rise in pressure as the liquid in the capillary rises above the bath level. At the critical temperature the flat portion becomes an inflection with a horizontal tangent, since the densities of the liquid and vapor become equal. These measurements indicate a critical temperature of 3.35±0.02°K and a critical pressure of 890±20 mm of mercury, in agreement with the previously reported values of 3.34°K and 875 mm of mercury obtained by the same method.[1]

VI. HEAT OF VAPORIZATION

The heat of vaporization of He^3 was calculated from the thermodynamic relation,

$$\Delta H_{\text{vap}} = T(V_{\text{gas}} - V_{\text{liq}})dp/dT. \tag{5}$$

The molal volume of the gas, V_{gas}, was obtained from the equation of state (2), where the second virial coefficient, B, was taken from the computations of van Kranendonk, Compaan, and de Boer.[14] The molal volume of the liquid, V_{liq}, was taken from the experimental results of Grilly, Hammel, and Sydoriak,[15] and values of p and dp/dT were computed from Eq. (4).

The results are given in column 2 of Table III and by the solid curve in Fig. 5. The dashed curve in this figure shows the ideal heat of vaporization,

$$\Delta H_{\text{ideal}} = RT^2(d\ln p/dT). \tag{6}$$

The circles in Fig. 5 were obtained by using in Eq. (5) $\Delta p/\Delta T$ calculated from the successive experimental points of Series I and III (Table I) instead of dp/dT from Eq. (4). No calculations were made above 2.5°K because Eq. (2) is inadequate for the saturated vapor above this temperature.

The uncertainty in the heat of vaporization shown in Table III was estimated in the following way. Since the calculated values[14] of B for He^4 agree with the experimental ones[16] within about 10 percent, the uncertainty in the values of B calculated[14] for He^3 was taken to be 10 percent. An error in B of this magnitude causes an error in the heat of vaporization of 0.5 cal./mole at 2.5°K, 0.03 cal./mole at 1.0°K, and less at lower temperatures. The estimated error in the experimental values of the molal volume of the liquid is two to three percent,[15] and this results in an error in the heat of vaporization of 0.05 cal./mole at 2.5°K and less than 0.01 cal./mole at 1.0°K. Uncertainties in the slope of the temperature scale and in the measurements of the pressures together cause a one percent uncertainty in the heat of vaporization.

TABLE III. Heat of vaporization and entropy of liquid He^3.

T_K (°K)	ΔH_{vap} (cal. mole^{-1})	$\Delta H_{\text{vap}}/T$ (e.u.)[a]	$S_{\text{ideal gas}}$ (e.u.)	$S_{\text{real}}-S_{\text{ideal}}$ (e.u.)	S_{liq} (e.u.)
0	(4.47)	∞	∞	0.00	(0.42±0.11)
0.5	(6.95)	(13.89)	(14.34)	0.00	(0.45±0.12)
1.0	9.12±0.12	9.12	9.87	0.00	0.75±0.14
1.5	10.65±0.24	7.10	8.37	−0.02	1.25±0.17
2.0	11.34±0.41	5.67	7.62	−0.06	1.89±0.22
2.5	10.81±0.69	4.32	7.16	−0.11	2.73±0.29

[a] e.u. =cal. deg.$^{-1}$ mole^{-1}.

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[13] Mason, Naldrett, and Maass, Can. J. Research **18B**, 103 (1940); S. N. Naldrett and O. Maass, Can. J. Research **18B**, 118 (1940).

[14] van Kranendonk, Compaan, and de Boer, Phys. Rev. **76**, 1728 (1949).

[15] Grilly, Hammel, and Sydoriak, Phys. Rev. **75**, 1103 (1949).

[16] J. Kistemaker and W. H. Keesom, Physica **12**, 227 (1946).

The values of the heat of vaporization previously reported by others[15] are in poor agreement with those presented here, chiefly because they were calculated from less accurate vapor pressure data.

VII. ENTROPY OF He^3

The entropy of liquid He^3 was calculated from the difference between the entropy of the saturated vapor and the entropy of vaporization. The entropy of the vapor was obtained from the Sackur-Tetrode equation,

$$S=2.5R\ln T-R\ln p_{\text{atmos}}+1.5R\ln M-2.314, \quad (7)$$

to which was added a small correction for non-ideality, calculated from Eq. (2). The effect of the Fermi-Dirac statistics is included in this correction. In accordance with the usual convention, the contribution of nuclear spin, $R\ln 2=1.377$ cal. deg.$^{-1}$ mole^{-1} for He^3, was not included. The entropy of vaporization was calculated from the heat of vaporization. The values of the fundamental constants used were those adopted in tabulations at the National Bureau of Standards.[17] The atomic weight, M was taken as 3.0162 on the chemical scale.[18]

The results are given in Table III. The indicated uncertainty in the entropy of the liquid from 1.0° to 2.5°K was calculated from the uncertainty in the heat of vaporization and an uncertainty of 0.002 to 0.004° in the temperature.

It is interesting to note that the entropy of the liquid at 0°K calculated by extrapolating the vapor pressure Eq. (4) is 0.42 ± 0.11 cal. deg.$^{-1}$ mole^{-1}. Since one would expect a value of zero from the third law of thermodynamics, it seems advisable to discuss the way in which the uncertainty in this value was obtained. The method was to estimate the limits of error in C, the constant term in the vapor pressure equation (3) or (4), since

$$S_{\text{liq, }0^\circ\text{K}}=(2.0085-C)R\ln 10. \quad (8)$$

For this purpose, a vapor pressure equation was fitted to the data from 1.0° to 1.5°K. The data at higher temperatures were not used because it was desired to reduce the effect on C of the correction terms, which are more important above 1.5°K. The equation

$$\log_{10}p_{\text{mm}}=-(0.9807/T)+2.5\log_{10}T+1.9198 \quad (9)$$

was found to fit the experimental data with the same precision as Eq. (4) from 1.0° to 1.5°K, and the corresponding value of the entropy of the liquid at 0°K is 0.41 cal. deg.$^{-1}$ mole^{-1}, which is in agreement with the previous value.

Further, the effect of uncertainties in the temperature scale and in our experimental measurements were considered. Kistemaker[11] has estimated that the uncertainty in his measurement of the vapor pressure of He^4 against a gas thermometer is 0.003° at 1.5°K. The vapor pressure-temperature relation for He^4 below 1.5°K is a calculated one,[10, 11] which joins Kistemaker's experimental results at 1.5°K. It can be shown that an error of 0.003° at 1.5°K will cause an error at 1.0°K of 0.0022° in the same direction. This error at 1.0°K could be changed by ±0.0016° if the error in the virial coefficient of gaseous He^4 at 1.5° is 10 percent, and by an additional ±0.0002° from the estimated one percent error[11] in the terms arising from the molal heat capacity and volume of liquid He^4 at lower temperatures. Our experimental error is 0.002° at 1.0°K and less than 0.001° at 1.5°K. The most unfavorable combination of these errors will change the temperature interval from 1.0° to 1.5°K by ±0.006°. This will result in a change in C of ±0.025, and hence a change in the entropy of the liquid at 0°K of ±0.11 cal. deg.$^{-1}$ mole^{-1}.

Another effect which must be considered is the possible alignment of the nuclear spins in the liquid at low temperatures, with a consequent loss of amount $R\ln 2$ in the entropy. Since this alignment cannot occur in the gas in the absence of a magnetic field, the entropy of the liquid at 0°K as calculated here would be smaller or negative, if there were any alignment in the liquid at 1°K. Hence, this effect cannot be used to explain the residual entropy of 0.4 cal. deg.$^{-1}$ mole^{-1}.

These considerations suggest that the extrapolation of the vapor pressure equation is not valid because there is a transition in liquid He^3 below 1°K. This transition may be to a solid in equilibrium with the vapor, with an entropy of fusion of 0.4 cal. deg.$^{-1}$ mole^{-1}, or there may be a hump in the heat capacity which will account for the remaining 0.4 cal. deg.$^{-1}$ mole^{-1}. The existence and nature of this transition, which is obviously of fundamental importance to the theory of liquid He^3 and He^4, will need to be investigated experimentally.

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[17] Rossini, Pitzer, Taylor, Ebert, Kilpatrick, Beckett, Williams, and Werner, *Selected Values of Properties of Hydrocarbons*, National Bureau of Standards Circular C461 (U. S. Government Printing Office, Washington, D. C., 1947), p. 8.

[18] J. Mattauch and A. Flammersfeld, "Isotopic report," Zeits. f. Naturforsch. (1949).