THE

PHYSICAL REVIEW

A journal of experimental and theoretical physics established by E. L. Nichols in 1893

SECOND SERIES, VOL. 106, NO. 2 APRIL 15, 1957

Thermodynamic Properties of Liquid Helium Three. Vapor Pressures below 1°K*

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

(Received January 14, 1957)

Vapor pressures of liquid He^3 have been measured between 0.45° and 1.0°K. Temperatures were measured by the paramagnetic susceptibility of either ferric ammonium or chrome methylamine alum. The salts were calibrated above 1°K against He^3 vapor pressures using the data of Abraham, Osborne, and Weinstock and the He^4 temperature scales of Clement (55*E*) and of van Dijk and Durieux (*L*55). The data obtained with the two salts were in good agreement with each other and indicate no preference between the two He^4 scales.

In order to fit the data by a simple equation over the entire temperature range, explicit account had to be taken of the effect on the vapor pressure of the variation of the spin entropy, S_σ. An equation valid between the critical point and 0°K is

$$\ln p_{\mathrm{mm}}=2.5\ln T_E+i_0-(1/RT)\int_0^T S_\sigma dT-2.53853/T_E-0.20644T_E+0.07728T_E^2-0.00919T_E^3,$$

where i_0 is the vapor pressure constant, 5.31733, and the subscript E designates use of the 55*E* scale throughout the calibration and subsequent equation fitting. By this equation the latent heat at absolute zero is 5.044 cal/mole. Between 0.25°K and the critical point, 3.327°K, the entropy integral is fitted by the empirical equation, $(1/RT)\int_0^T S_\sigma dT=0.5020+0.1786\ln T-0.00912T^2$.

1. INTRODUCTION

THIS paper describes measurements of the vapor pressure of liquid helium three below 1°K. These results are complementary to the specific heat measurements reported in an earlier paper,[1] hereafter referred to as I.

He^3 was first liquefied and its vapor pressures were measured as a function of He^4 bath pressure by Sydoriak, Grilly, and Hammel.[2] Abraham, Osborne, and Weinstock[3] made a more accurate series of measurements comparing He^3 and He^4 vapor pressures between 1.025° and 3.35°K. These measurements are hereafter referred to as the Argonne data.

This paper presents the results of He^3 vapor pressure measurements to 0.45°K. Temperatures were measured by means of paramagnetic salts and were obtained by extrapolation of their calibration equations, obtained in the temperature region above 1°K by using the Argonne vapor pressure data. Various vapor pressure equations are presented and discussed.

2. APPARATUS

The apparatus has already been described in some detail in I. Further details especially pertinent to the measurement of pressure and temperature are given below. With the description of each component of the apparatus we shall combine a discussion of techniques used with the component and the possible effect on the percentage accuracy of the measurements. The same percentage error in T and p are not equally significant. For example, at 0.5°K a 0.1% error in T is equivalent to 0.7% in p.

Figure 1 shows the all-metal helium-three Dewar and the susceptibility coils, both immersed in a bath of liquid He^4. He^3 is condensed in the half-inch diameter seamless copper sphere. The sphere also contains the paramagnetic salt crystals. The primary and secondary coils are wound directly on the brass vacuum jacket. This jacket extends upward to a brass block which thermally shorts the He^4 bath to the He^3 Dewar wall. The copper sphere is suspended from the brass block

---

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

[1] T. R. Roberts and S. G. Sydoriak, Phys. Rev. **98**, 1672 (1955).

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

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

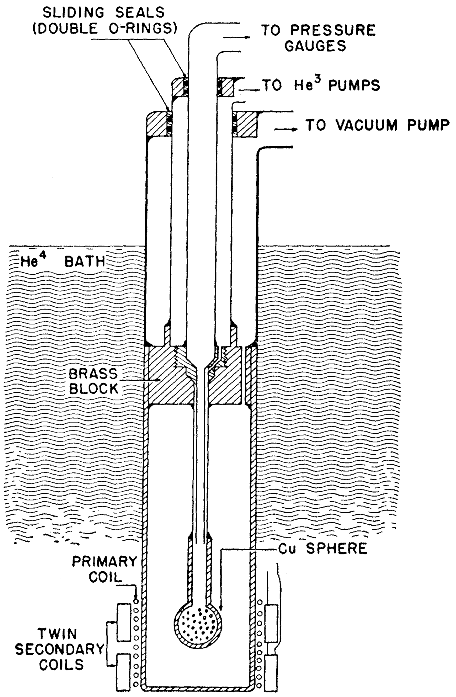

FIG. 1. Schematic diagram of helium 3 Dewar.

by an 8-inch length of 70 Cu 30 Ni tubing of $\frac{1}{8}$-inch o.d. and 0.010-inch wall thickness. Various inserts could be screwed into the brass block for specific heat or vapor pressure measurements, as described in I. Only the pressure-sensing insert is shown in the figure. The He^3 is cooled below the bath temperature by pumping via the annular space surrounding the pressure-sensing tube. The sliding double O-ring seals at the top allow for differential contraction of the concentric Inconel or stainless steel tubes extending from the room-temperature end to the brass block.

a. Pressure Measurement

Vapor pressures were measured by means of mercury and oil manometers in the salt calibration region (above 1°K) and by the oil manometer and a special McLeod gauge below 1°K. A Consolidated Electrodynamics Corporation capacitative micromanometer, sensitive to a fraction of a micron at all pressures, was used to ascertain that Taconis oscillations were not present and to indicate the maintenance of steady pressures during equilibration of the McLeod gauge.

The manometer scales were mirrored Pyrex calibrated to an accuracy of ±0.01 mm and mounted in a frame which guided a slide rule indicator. Pressures read from the manometers are believed correct to ±0.2 mm Hg and ±0.3-mm oil. The Hg manometer, made of 1-cm i.d. Truebore tubing, was used to calibrate the butyl phthalate oil manometer, which was made of 2-cm i.d. Truebore tubing. The oil was boiled under vacuum to remove absorbed gases. Since the oil manometer was not thermostatted, it was calibrated at about 90-mm Hg during each run. Data collected over a period of a year at various ambient temperatures in the range 23°C to 33°C are consistent with the density ratio equation,

$$\rho_{\mathrm{oil}}/\rho_{\mathrm{Hg}}=0.07818-0.000046t,$$

where t is the temperature in degrees Celsius. At 20°C this equation is fitted to give 0.07726, the 1955–56 Chemical Rubber Publishing Company handbook value. Pressures are all expressed in mm Hg at 0°C and standard gravity ($g=980.655$ cm/sec^2) using $g=979.135$ cm/sec^2 at Los Alamos and $(\rho/\rho_0)_{\mathrm{Hg}}=1-0.0001812t$.

The McLeod gauge was the same one described in an earlier paper on thermomolecular pressure ratios.[4] The gauge was calibrated and used as a $p=h^2K(h)$ instrument, where h is both the height of the compressed gas column and the mercury pressure head on it as measured by a cathetometer. By this method a given p corresponds to a single gauge reading so the calibration is unique. Variations in $K(h)$ due to irregularities in capillary bore were determined by a mass balance method in which He^3 was expanded from a small fixed volume and measured pressure into the McLeod system. The linear relation between amount of gas in the system and pressure was established at a high value of h by a direct comparison of h and the pressure indicated by the oil manometer, about 40 mm oil. This was read with a cathetometer to ±0.01 mm during the calibration measurement. By the above method K was measured at a score of points to an estimated accuracy ranging from 1% at 80 μ to 0.5% at 3000 μ. All pressure measurements were made with a Truebore tubing McLeod capillary about 500 mm long×0.5 mm bore for which $K(h)$ was found to vary smoothly by about 1%.

The correction for the thermomolecular pressure ratio, p_c/p_w, in the pressure-sensing tube is the subject of a separate paper.[4] The subscripts c and w indicate the pressures at the cold and warm ends of the pressure-sensing tube of radius R. The Weber-Schmidt[5] equation for He^4 can be used for He^3 with no change in coefficients or exponents for pressures such that Rp_c is no less than 1 cm μ.

The pressure-sensing tube consisted of two sections of different radii. The upper section of radius 0.211 cm extended from the McLeod gauge down to the thermal short (the brass block in Fig. 1) at the He^4 bath temperature, usually maintained at 2.8°K. From this point to a level 2 to 3 cm above the liquid He^3, the tubing radius of the pressure-sensing insert was 0.10 cm. The correction is negligible in the lower section for pressures greater than 30 microns as shown by Table VII of reference 4. In the larger tube the calculated p_c/p_w is 0.766 at the lowest measured pressure. The upper tube had the same radius as the tubing used for the direct measurements of He^3 thermomolecular pressure ratios.

---

[4] T. R. Roberts and S. G. Sydoriak, Phys. Rev. **102**, 304 (1956).
[5] S. Weber and G. Schmidt, Leiden Comm. No. 246C (1936).

The direct measurements covered the same temperature interval and were extended to even lower pressures than the present work. The error in p_c/p_w calculated from the Weber-Schmidt equation is therefore believed to be no greater than the mean deviation of the data of Table IV of reference 4, or about 0.5%.

The amount of He^4 present in the liquid was small and somewhat uncertain. At the start of each run about 0.12% He^4 was condensed corresponding to the storage can concentration. The percentage of He^4 in the liquid rose during pump-down because the He^3 was preferentially evaporated due to its higher vapor pressure. To get an upper limit to the error we can assume that all the He^4 remained in the capsule. In a typical run about half the liquid evaporates so the He^4 concentration would be doubled. A detailed analysis was made for run 1. From the known amount of liquid in the capsule during each measurement and the assumption that Raoult's law is valid, a corrected salt calibration equation was derived and applied to the subsequent vapor pressure measurements. The net correction to p_c due to increasing He^4 content was estimated to range from −0.06% at 0.86°K to −0.18% at 0.46°K. This calculation should represent an upper limit to the error involved. Hence, the correction for He^4 impurity is seen to be negligible and has been ignored.

A calculation of error due to the greater hydrostatic head of vapor in the cold Dewar than in the warm manometers or gauges showed this, too, to be negligible, the error ranging from 0.030% of p_c at 2.8°K to 0.054% at 0.45°K.

b. Temperature Measurement

The temperature of the liquid below 1°K was determined from the magnetic susceptibility of a paramagnetic salt by use of the ballistic measurement technique described by Hull.[6] The primary coil is wound directly on the brass vacuum jacket surrounding the capsule and hence is immersed in the bath liquid He^4 as shown in Fig. 1. The twin secondary coils are wound directly on top of the primary and are connected in opposition. A variable mutual inductometer is used to adjust the circuit to a suitable range of galvanometer deflections.

The primary current is approximately constant during calibration and measurements below 1°K and is measured to 0.01% with a potentiometer circuit. As described in I, the current is reversed automatically every 30 seconds by a rapid-action solenoid. Thus the two current pulses passing through the galvanometer are completed in a time interval (the "off" time) which is reproducible and very short compared to the period of the galvanometer.

The galvanometer has a 16-sec period, a 200-ohm critical damping resistance, and a sensitivity of 0.0054 μcoul/mm at one meter. The scale used was about 4.2 meters from the galvanometer mirror. The usual tangent correction, amounting to 0.44% at full-scale deflection, was applied to the observed deflection. All galvanometer deflections are expressed as θ, the ratio of angular deflection to primary current.

During the course of a run, the primary of the immersed coils was replaced periodically with an equal fixed resistance and the galvanometer deflection was observed due to reversal of the current in the primary of the balancing inductometer. Thus a measurement was obtained of the over-all effect on the galvanometer sensitivity of room temperature variations and of variations in R_g, the resistance of the secondary circuit. As the bath level falls, the resistance of the leads from the galvanometer to the immersed secondary coils increases. In the vicinity of critical damping, a 0.3% fall in sensitivity is observed for a 1% increase in R_g. Deflections were corrected in accordance with the observed drift in sensitivity, usually ranging over several tenths of a percent during a day's running time.

Although eddy currents in the copper sphere would result in a loss of sensitivity in measuring salt susceptibility, this loss was not found to be appreciable. A bare single crystal of salt placed at various positions in the secondary coil gave a maximum deflection which was about 10% greater than that given by the same mass of salt in the form of small particles within the copper sphere. A systematic error would be introduced only if the eddy currents varied with capsule temperature. Over the temperature range used, 0.5° to 2.5°K, the resistivity of copper changes less than 0.7%.[7] Hence, the variation in magnetic shielding, which would be expected to be roughly proportional to the variation in resistivity, can cause only a negligible error.

A 1-inch long copper cylinder is hard-soldered between the copper sphere and the Cu-Ni tubing. The purpose of this cylinder is to remove the Cu-Ni from the immediate vicinity of the measuring coils, because the tubing was found to have a slight magnetic effect when inside the coils. This effect could impair the accuracy of temperature measurements only to the extent of its temperature dependence. Care was also taken in assembly of the Dewar to eliminate soft solder or other superconducting metals from the vicinity of the susceptibility coils and hence to avoid the possibility of superconductors affecting the susceptibility measurements.

Two paramagnetic salts were used, ferric ammonium alum and chromium methylamine alum. The sphere was filled with salt particles of from 1 to 2 mm in size. A low filling factor, about 55%, was found to be necessary. When 77% filling was obtained by tamping, erratic vapor pressure measurements resulted and there was some indication that the interstices were not full of liquid.

---

[6] R. A. Hull, *Proceedings of the International Conference on Fundamental Particles and Low Temperatures, Cavendish Laboratory, Cambridge, 1946* (The Physical Society, London, 1947), Vol. II, p. 72.

[7] E. Mendoza and J. G. Thomas, Phil. Mag. **42**, 291 (1951).

During each run the salt was calibrated at several temperatures between 2.5° and 1.1°K. The susceptibility temperature for a spherical sample, T^*, was obtained from (a) the measured pressure, (b) a He^3 vapor pressure equation based on the Argonne data and (c) a table of T^* *vs* T. The salt calibration equation, $\theta=\theta_0+(K/T^*)$, was fitted by the method of least squares.

At each calibration point the pressure was observed several times and the galvanometer deflection either 10 or 20 times. Temperature gradients in the liquid were minimized by adjustment of the pumping speed to give a very slow decrease in pressure with time. For each vapor pressure measurement involving use of the McLeod gauge, 2 to 4 pressure readings and 4 to 8 deflections were recorded. To allow time for pressure equilibration McLeod gauge readings were spaced at least four minutes apart.

The least squares fitting of the calibration equation minimizes $(\bar{\theta}-\theta_{\text{eq}})^2$, where $\bar{\theta}$ is the mean of the 10 to 20 observations taken at each of the several calibration temperatures. For the iron alum runs, the root-mean-square-deviation of $\bar{\theta}$ from θ_{eq} varied from 0.17 to 0.46 mm/amp. The corresponding deviation of $\bar{T}$ from T_{eq} ranged from 0.6 to 1.2 millidegrees. At 0.5°K, the precision of temperature measurement using observed galvanometer deflections and the calibration equations is about 0.1%.

The conversion between T^* and T is calculated using the partition functions given by Hebb and Purcell[8] and the theoretical formulas of Van Vleck.[9] The Curie constant and crystalline splitting factor given by Cooke[10] have been used for iron ammonium alum. For $T\geqslant 0.2°\text{K}$,

$$T^*-T=0.00548/T \quad \text{(iron ammonium alum)} \quad (1)$$

to within 0.1 millidegree. For chrome methylamine alum the splitting factor of 0.275°K given by deKlerk and Hudson[11] and a calculated Curie constant of 0.00632°K yield

$$T^*-T=0.00315/T \quad \text{(chrome methylamine alum)}. \quad (2)$$

The results obtained with the two salts are in good agreement, as will be shown later.

We have already shown that hydrostatic head corrections in the vapor are a negligible source of error in the pressure measurements. The potential seriousness of a hydrostatic head in the liquid is vastly greater, especially for liquid He^3. Let z be the hydrostatic head of liquid above the center of the salt. Let $T(\theta)$ be the average temperature of the salt and $T(p)$, the temperature of the surface of the liquid as determined by the vapor pressure. A theoretical upper limit to the correction for hydrostatic head assumes that the liquid is at saturation at all levels and hence that the temperature at any level corresponds to the measured pressure plus the hydrostatic pressure of the liquid at that level. This condition can be maintained in He^4 above the lambda temperature[12] and could conceivably occur in He^3 at all temperatures, especially below 1°K where a strong density-temperature dependence such as stimulates convection in He I does not exist.

The effect of liquid level was measured during run 1 at a low temperature, at which an increase of 1 cm in liquid depth would correspond to 40 millidegrees rise in temperature under saturation conditions. No liquid level dependence was evident as is seen in Table I, where $T_E(p)$ is calculated from Eq. (8) and $T(\theta)$ from the calibration constants of Table II. The variation in $T(\theta)-T_E(p)$ is random and is well within the expected uncertainty due to reading errors in p and θ. Use of the copper capsule evidently has achieved a sufficient degree of temperature equilibration.

3. RESULTS

The existing He^3 temperature scale of Abraham, Osborne, and Weinstock is based on the Kistemaker corrections to the 1948 "Agreed" scale. This $48K$ scale has not been used except in He^3 work and has been superseded by the two 1955 He^4 temperature scales, T_{55E} [13] and T_{L55}.[14]

TABLE I. Vapor pressure *vs* liquid level.

Liquid volume (mm^3)	320	184	111	70	42
Liquid head above center of salt (cm)	0.40	0.06	−0.11	−0.21	−0.29
p (microns)	90.0	89.6	90.8	90.5	90.5
Salt temperature minus vapor pressure temperature: $[T(\theta)-T_E(p)]$(mdeg)	−0.6	−0.2	−0.7	−0.7	−0.2

In order that our salt calibrations be based on the new He^4 scales we have calculated provisional equations from the Argonne table of p_3 *vs* p_4, reference 3. Small thermomolecular pressure corrections to p_3 have been made. The equations have the same form as the original Argonne equation and are obtained from a least-squares fit of the functional form

$$T\ln(p/T^{5/2})=a+bT+eT^4. \quad (3)$$

Since e is a small coefficient, this equation minimizes the sum of the squares of $(T_{\text{obs}}-T_{\text{calc}})$. On the $55E$ scale the coefficients are $a=-2.24008$, $b=4.39251$, and $e=0.001354$. On the $L55$ scale the coefficients are $a=-2.22359$, $b=4.39030$, and $e=0.001230$. On either

---

[8] M. H. Hebb and E. M. Purcell, J. Chem. Phys. **5**, 338 (1937).

[9] J. H. Van Vleck, J. Chem. Phys. **5**, 320 (1937).

[10] A. H. Cooke, Proc. Phys. Soc. (London) **A62**, 269 (1949).

[11] D. deKlerk and R. P. Hudson, Phys. Rev. **91**, 278 (1953).

[12] Corak, Garfunkel, Satterthwaite, and Wexler, Phys. Rev. **98**, 1699 (1955).

[13] J. R. Clement (private communication); W. E. Keller, Nature **178**, 883 (1956).

[14] H. van Dijk and M. Durieux, *Conference on Physics of Low Temperatures* (Centre National de la Recherche Scientifique and UNESCO, Paris, 1956), p. 599; Physica **22**, 760 (1956).

scale, the rms deviation of the Argonne data is about 1.5 millidegrees; hence no choice between the two scales is indicated.

Table II contains the calibration data for three runs using ferric ammonium alum. The calibration constants given are derived from the above provisional equation using the 55*E* scale coefficients. The data are given in sufficient detail to permit re-analysis should a new He^4 scale be adopted at some future time. The vapor pressure data obtained with iron alum are listed in Table III. After the lowest pressure was reached in run 1, the liquid was removed gradually and the readings were taken of pressure and temperature as a function of liquid level that are given in Table I. After the capsule was emptied, He^3 was recondensed and the data points 13–22 were obtained.

Figure 2 shows the differences between the temperatures observed with the susceptibility apparatus and temperatures calculated at the observed pressure from Eq. (8), an empirical equation fitting the data for both alums plus the Argonne data. The data from the two halves of run 1 agree within a millidegree, indicating that the salt calibration was not changed significantly by the removal and recondensation of liquid despite the loose packing of the salt. In run 3, the liquid was removed after point 8, calibration points *f*, *g*, and *h* were obtained and then data points 9 and 10 were observed. No significant difference in calibration was observed and all the calibration points were averaged together in the final analysis.

TABLE II. Iron ammonium alum calibration data.

	Run 1		Run 2		Run 3	
Point	p mm Hg at 0°C	θ mm/amp	p mm Hg at 0°C	θ mm/amp	p mm Hg at 0°C	θ mm/amp
a	362.19	−509.20	422.13	−520.13[a]	438.25	−524.23[a]
b	111.40	−358.70	119.78	−360.47	122.39	−364.67
c	47.41	−227.40	42.18	−198.40	42.48	−200.97
d	21.34	−88.17	21.81	−81.67	21.48	−80.00
e	9.91	+60.67	10.06	+69.47[a]	9.78	+73.33[a]
f					437.12	−523.87[a]
g					42.44	−199.53
h					9.86	+71.87[a]
Calibration constants, provisional T_E scale						
	k	θ_0	k	θ_0	k	θ_0
	989.50	−895.11	999.34	−892.56	996.83	−891.84

[a] These are averages of 20 readings, or twice the usual number, and are therefore weighted double in deriving the calibration constants.

The points above 1°K are the data of Abraham, Osborne, and Weinstock.[3] In their experiments a He^3 and a He^4 vapor pressure bulb were drilled in the same block. For the points above 1.7°K, designated by an asterisk, the observed temperatures were determined from the measured pressure in the He^4 bulb. Below 1.7°K, however, the Argonne workers could not obtain consistent results using the He^4 bulb pressures and had to determine T_{obs} from the measured He^4 cryostat pressure. Their lower temperature data points show appreciably more scatter and have been given less weight in deriving Eqs. (8) and (9).

TABLE III. Iron alum vapor pressure data.

Point	p (mm Hg at 0°C)	θ (mm/amp)
	Run 1	
1	5.951	163.50
2	3.487	276.73
3	2.332	365.73
4	1.512	462.87
5	0.9754	566.43
6	0.6446	666.73
7	0.4287	766.23
8	0.2870	865.47
9	0.1920	965.50
10	0.1310	1064.50
11.1	0.0900	1164.77
12	0.0654	1251.53
11.2–11.5	Liquid level studied at $p \sim 0.090$ mm	
13	4.559	219.77
14	2.909	317.67
15	1.856	415.77
16	1.210	515.00
17	0.7960	614.77
18	0.5249	715.07
19	0.3512	813.57
20	0.2310	916.67
21	0.1574	1013.27
22	0.1072	1111.40
	Run 2	
1	4.406	242.16
2	2.018	413.40
3	0.9798	582.00
4	0.5114	739.13
5	0.2633	904.50
6	0.1357	1066.53
7	0.0734	1244.42
	Run 3	
1	2.873	334.67
2	1.527	475.97
3	0.7212	652.80
4	0.3791	809.80
5	0.1948	978.50
6	0.1405	1063.20
7	0.1042	1143.40
8	0.0724	1240.60
Recondense and recalibrate		
9	1.004	573.17
10	0.1304	1076.07

Tables IV and V give the data for chrome methylamine alum. Figure 2 shows that the data scatter more than the iron alum data but are in good agreement. The greater scatter is due partly to the fact that the susceptibility of the chromium salt is about $\frac{1}{2}$ that of the iron salt. The points at about 0.75°K were the first points taken with the McLeod gauge in each run and

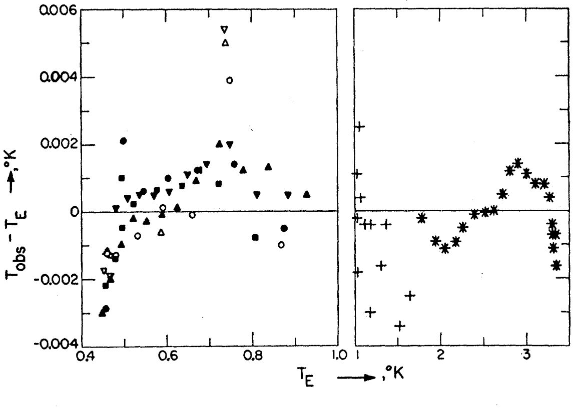

FIG. 2. Deviations of the vapor pressure data from Eq. (8), an empirical equation based on the 55*E* He^4 temperature scale. T_{obs} is the temperature observed with the susceptibility apparatus for temperatures below 1°K. The points above 1°K are the data of Abraham, Osborne, and Weinstock with T_{obs} determined for + points from the cryostat pressure and for * points from a He^4 vapor pressure bulb. The data points below 1°K correspond to those tabulated in Tables III and V: ▲, run 1 (points 1 to 12); ▼, run 1 (points 13 to 22); ●, run 2; ■, run 3; ○, run 4; △, run 5 ($i_p = 0.50$ amp); ▽, run 5 ($i_p = 0.25$ amp).

TABLE IV. Chrome methylamine alum calibration data.

	Run 4		Run 5	
	p	θ	p	θ
Point	(mm Hg at 0°C)	(mm/amp)	(mm Hg at 0°C)	(mm/amp)
a	476.33	−464.23	483.06	−464.33
b	132.97	−395.58	141.20	−399.09
c	57.67	−340.71	58.94	−341.89
d	23.83	−274.21	23.85	−274.07
e	9.980	−200.53	13.14	−224.81
	Calibration constants, provisional T_E scale			
	k	θ_0	k	θ_0
	434.84	−620.61	434.04	−619.85

were the only points taken at galvanometer deflections of less than 15 mm. The several observations involved in each tabulated point, however, showed no internal inconsistencies, so the points were included in the final equation fitting.

In run 5, i_p, the primary current in the susceptibility coils, was varied as shown (in Table V). The calibration data were obtained with a current of 0.50 amp. No effect was observed due to the lower current, within the limits of experimental accuracy. In all other runs i_p was about 0.30 amp.

The agreement of the results obtained with the two salts is interesting because of the uncertainty concerning the partition function and crystalline splitting factors for iron alum.[15,16] From specific heat measurements above 1°K, Kapadnis[17] finds a splitting factor of 0.192°K. The T^*-T values below 1°K found by Cooke, Meyer, and Wolf[18] differ very much from the values calculated from Eq. (1). Comparative values between 0.3 and 0.8°K are shown in Table VI. Since the values given by Cooke, Meyer, and Wolf approach the Eq. (1) values near 1°K, we have assumed that Eq. (1) T^* values are a valid extension of their scale above 1°K. Thus the same calibration equations would apply and hence absolute temperatures derived from magnetic measurements would be 20 millidegrees lower near 0.5°K if their T^*-T values were used. Our results for the two different salts agree to much better than 20 millidegrees. Therefore we have used the temperature values derived from Eqs. (1) and (2) pending further work on comparative T^*-T experimental measurements.

TABLE V. Chrome methylamine alum vapor pressure data.

Run No.	4		5		
Primary current	0.30 amp			0.25 amp	0.50 amp
Point	p (mm Hg at 0°C)	θ (mm/amp)	p	θ	θ
1	4.224	−121.04	1.694		−35.53
2	1.848	−43.10	1.694	−35.83	
3	0.9033	+34.16	0.4244	+114.87	
4	0.4190	116.73	0.4274		+115.00
5	0.2152	191.90	0.0857		297.94
6	0.1071	273.03	0.0866	297.92	
7	0.0763	312.71	0.0653	330.46	
8			0.0757		312.26

4. SEMIEMPIRICAL VAPOR PRESSURE EQUATION

Empirical relations frequently take the form of a power series because of the relative ease of fitting data to a power series by the method of least squares.

Chen and London[19] have shown that if $\ln(p/T^{5/2})-i_0$ is equated to a power series in T, this should not contain a constant term nor terms involving lower powers than T^{-1}. The chemical constant, i_0, is numerically equal to 5.31733 for He^3 if p is expressed in mm Hg at 0°C. Using T powers of -1, 1, 2, 3 and 4, they obtained a good fit to data up to 340 mm Hg ($T=2.51°$), attributing deviations above 2.5°K to the increasing role of virial correction terms.

If, however, a T^0 term is included, a good fit to all the data is obtained,[3] even up to 889 mm Hg ($T=3.35$°K), with only three powers of T: -1, 0 and 3. Of course, being thermodynamically inconsistent in form, the equation cannot safely be extrapolated beyond the fitted range.

TABLE VI. Magnetic temperatures for iron ammonium alum.

T	0.3	0.4	0.5	0.6	0.7	0.8
T^* [Eq. (1)]	0.318	0.414	0.511	0.609	0.708	0.807
T^* (Cooke, Meyer, and Wolf[a])	0.342	0.437	0.532	0.628	0.722	0.812

[a] See reference 18.

We have attempted to fit the Argonne data plus our own to a five-term power series, excluding the T^0 term. This gave a poor fit to the data, deviations amounting to several millidegrees in various regions of temperature.

If the T^0 term is included we need fit only four coefficients to obtain much better agreement at low temperatures. However, much of the data above 1°K showed deviations of several millidegrees, an order of magnitude greater than the scatter in the data itself. We conclude that a power series is not an appropriate function for representing $\ln(p/T^{5/2})$ in the case of He^3. The reason for this was found to be that the effects of nuclear spin exchange forces on the vapor pressure are too great and are not adequately taken into account by a power series. The solution finally arrived at was to fit a power series to $\ln(p/T^{5/2})+Y$, where Y includes the chemical constant and a good approximation to the nuclear spin entropy term in the theoretical vapor pressure equation.

The usual statistical mechanical vapor pressure equation[3] is obtained from the equality of the free energies

---

[15] P. H. E. Meijer, Physica **17**, 899 (1951); Physica **18**, 723 (1952).

[16] Ubbink, Poulis, and Gorter, Physica **17**, 213 (1951).

[17] D. G. Kapadnis, Physica **22**, 159 (1956).

[18] Cooke, Meyer, and Wolf, Proc. Roy. Soc. (London) **A233**, 536 (1956).

[19] Tien Chi Chen and F. London, Phys. Rev. **89**, 1038 (1953).

of the saturated vapor and liquid. The equation can be written as

$$\ln\left(\frac{p}{T^{5/2}}\right)-i_0=-\frac{1}{RT}\int_0^T S_l dT-\frac{L_0}{T}+f(T), \tag{4}$$

where S_l is the liquid entropy, L_0 the heat of vaporization at absolute zero, and $f(T)$ a function of virial coefficients and variation of liquid density. Below 0.7°K, $f(T)$ is negligibly small.

In I we showed that between 0.4° and 2.5°K,

$$S_l=S_\sigma+0.88T. \tag{5}$$

Recent measurements[20] to 0.25°K are also consistent with this relation. Here S_σ is the entropy of spin disorder for an ideal Fermi-Dirac gas of particles of spin $\frac{1}{2}$ and with a degeneracy temperature of 0.45°K. Using the values tabulated by Goldstein,[21] we were unable to fit the function $(1/RT)\int_0^T S_\sigma dT$ to a short power series in T. Instead we find the S_σ term is fitted between 0.25° and 3.3°K to better than 1% in pressure by the empirical relation

$$\frac{1}{RT}\int_0^T S_\sigma dT=0.5020+0.1786\ln T-0.00912T^2, \qquad 0.25<T<3.3°\text{K}. \tag{6}$$

Since $\ln T$ is not representable by a short power series in T, this explains the failures encountered in fitting $\ln(p/T^{5/2})-i_0$ to a power series. Therefore we put this spin entropy term on the left side of Eq. (4) and fit a table of the sum of the three terms on the left to a power series in T, including in the fitted series a T^{-1} term but no constant term. Actually, in order that deviations in ΔT be minimized, it is better to multiply through by T, applying the least-squares analysis to the equation

$$X=a+bT^2+cT^3+dT^4, \tag{7}$$

where

$$X=T[\ln(p/T^{5/2})-i_0+0.5020+0.1786\ln T-0.00912T^2].$$

All of our 47-data points, as listed in Tables III and V, were weighted equally. The 12 low-temperature Argonne points determined from bath pressure readings were given the same weight as ours, while the remaining 20 Argonne points were given double weight.

The resultant equation based on the 55E (Clement) scale is

$$\ln p_{\text{mm}}=2.3214\ln T_E-2.53853/T_E+4.8153-0.20644T_E+0.08640T_E^2-0.00919T_E^3. \tag{8}$$

When the entire analysis is repeated on the L55 (van Dijk and Durieux) scale, including (a) a recalculation of a provisional scale based on the Argonne data, and having the empirical form of Eq. (3), (b) recalculation of salt calibration equations using this provisional T_L scale, and (c) a calculation of a final T_L scale by Eq. (7), we find

$$\ln p_{\text{mm}}=2.3214\ln T_L-2.52608/T_L+4.8153-0.20046T_L+0.08183T_L^2-0.00850T_L^3. \tag{9}$$

Although these equations are based on direct measurements down to 0.45°K, we believe that they are fairly reliable to 0.25°K, because of the manner in which the large spin entropy term was handled in the fitting. Furthermore, the coefficients a, b, c, and d are not inconsistent in order of magnitude with theoretical expectations. Thus a is large because it represents mainly the internal energy at absolute zero. We find bT to be almost equal to the value expected from I for the contribution of the nonspin entropy, $-(1/RT)\int_0^T(S_l-S_\sigma)dT=-0.22T$. That the cT^2 and dT^3 terms are nearly negligible below 1°K is also gratifying because this is consistent with calculations of the terms in the theoretical expression for $f(T)$, as will be discussed in a paper on the theoretical vapor pressure equation. Finally, we believe that Eqs. (8) and (9) are not strongly dependent on the exact form of the S_σ expression used, since small deviations of this expression from reality are automatically compensated in the least-squares analysis.

Equations (8) and (9) cannot be extrapolated much below 0.25°K because Eq. (6) ceases to be a good approximation for the integral of the spin entropy. The sum of Eqs. (6) and (8), however, yields

$$\ln p_{\text{mm}}=2.5\ln T_E+i_0-(1/RT)\int_0^T S_\sigma dT-2.53853/T_E-0.20644T_E+0.07728T_E^2-0.00919T_E^3. \tag{10}$$

Vapor pressures calculated from this equation will approach zero properly at absolute zero. The latent heat at absolute zero by this equation is 5.044 cal/mole. The integral of the spin entropy may be approximately evaluated using the Fermic-Dirac functions as discussed by Goldstein.[21]

The boiling points calculated from the two equations are $T_E=3.189$°K and $T_L=3.190$°K.

The critical point has been determined by two methods. By a method based on the fact that at the critical point the densities of liquid and vapor are equal, critical vapor pressures of 875-mm Hg[2] and 890-mm Hg[3] have been determined. By the visual method of detecting disappearance of the liquid meniscus a value of 860-mm Hg was obtained.[3] Taking the average of all three measurements, 875-mm Hg, we find the critical temperatures on the two scales to be $T_E=3.327$°K and $T_L=3.329$°K.

The rms deviations of temperatures corresponding to all input pressure data is about 1.5 millidegrees on

---

[20] Abraham, Osborne, and Weinstock, Phys. Rev. **98**, 551 (1955).

[21] L. Goldstein, Phys. Rev. **96**, 1455 (1954); Phys. Rev. **102**, 1205 (1956).

TABLE VII. He^3 vapor pressures in mm Hg at 0°C in steps of 0.01°K; T_E scale.

T	0.01	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09
0.3	0.00150	0.00213	0.00296	0.00404	0.00542	0.00717	0.00935	0.01205	0.01533	0.01930
0.4	0.02405	0.02969	0.03634	0.04411	0.05314	0.06355	0.07551	0.08915	0.10462	0.12210
0.5	0.1418	0.1638	0.1883	0.2155	0.2456	0.2789	0.3154	0.3554	0.3991	0.4468
0.6	0.4985	0.5546	0.6152	0.6806	0.7510	0.8267	0.9077	0.9945	1.0872	1.1860
0.7	1.291	1.403	1.522	1.647	1.780	1.921	2.069	2.225	2.390	2.563
0.8	2.744	2.935	3.135	3.344	3.563	3.792	4.031	4.280	4.540	4.810
0.9	5.092	5.385	5.689	6.005	6.333	6.673	7.026	7.391	7.769	8.160
1.0	8.564	8.981	9.413	9.858	10.318	10.792	11.280	11.783	12.301	12.835
1.1	13.384	13.948	14.528	15.124	15.737	16.366	17.012	17.674	18.354	19.051
1.2	19.765	20.497	21.247	22.015	22.801	23.606	24.429	25.271	26.132	27.013
1.3	27.913	28.833	29.772	30.732	31.711	32.711	33.732	34.774	35.837	36.920
1.4	38.03	39.15	40.30	41.47	42.66	43.88	45.12	46.38	47.66	48.97
1.5	50.30	51.65	53.03	54.43	55.85	57.30	58.77	60.27	61.79	63.34
1.6	64.91	66.51	68.13	69.78	71.46	73.16	74.88	76.64	78.42	80.23
1.7	82.06	83.92	85.81	87.73	89.67	91.64	93.64	95.67	97.73	99.81
1.8	101.93	104.07	106.24	108.44	110.67	112.94	115.23	117.55	119.90	122.28
1.9	124.69	127.14	129.61	132.12	134.66	137.23	139.83	142.46	145.12	147.82
2.0	150.55	153.31	156.11	158.94	161.80	164.70	167.63	170.59	173.59	176.62
2.1	179.68	182.78	185.92	189.09	192.30	195.54	198.81	202.13	205.47	208.86
2.2	212.28	215.74	219.23	222.76	226.33	229.93	233.58	237.26	240.97	244.73
2.3	248.52	252.36	256.23	260.14	264.08	268.07	272.10	276.17	280.27	284.42
2.4	288.60	292.83	297.10	301.41	305.75	310.14	314.57	319.04	323.56	328.11
2.5	332.71	337.35	342.03	346.75	351.52	356.33	361.18	366.08	371.02	376.00
2.6	381.02	386.09	391.21	396.37	401.57	406.82	412.11	417.45	422.83	428.26
2.7	433.73	439.25	444.81	450.42	456.08	461.78	467.53	473.33	479.17	485.06
2.8	491.00	496.99	503.02	509.10	515.23	521.40	527.63	533.90	540.22	546.59
2.9	553.01	559.48	566.00	572.56	579.18	585.84	592.56	599.32	606.13	613.00
3.0	619.92	626.89	633.90	640.97	648.09	655.26	662.48	669.76	677.08	684.46
3.1	691.88	699.36	706.89	714.48	722.11	729.80	737.54	745.34	753.18	761.08
3.2	769.04	777.04	785.10	793.21	801.38	809.60	817.87	826.20	834.58	843.01
3.3	851.50	860.05	868.64	877.30	886.00					

either scale; hence the He^3 data do not indicate a choice between the two scales. Figure 2 shows the data compared to Eq. (8).

A table of pressure every ten millidegrees on the 55E scale is presented in Table VII. Linear interpolation fits Eq. (8) to 0.1 millidegree or better everywhere above 0.6°K. At the lowest temperatures linear interpolation between tabulated pressure points gives temperatures up to 0.3 millidegree too high.

These results supersede tentative results[22] based on part of the data given here. The earlier results were analyzed on the basis of the Kistemaker correction to the 1948 scale given in reference 3. Furthermore, because of difficulties in equation fitting which were resolved in the manner described above, the equation given in reference 22 should no longer be used.

ACKNOWLEDGMENTS

We are indebted to Dr. Clement for the use of 55E scale equations which have been sent to us prior to publication by Keller in reference 13. The scale was calculated by us and found to be the same, within 0.0002°K or closer, as the scale distributed at the Baton Rouge, Louisiana, Conference on Low Temperature Physics and Chemistry, December 28–30, 1955. We wish to thank Dr. van Dijk for sending us a copy of the final T_{L55} scale prior to publication. We gratefully acknowledge the help of Max Goldstein, Ralph Anderson, and Sandra Swan Larson in the equation fitting and the calculation of the various vapor pressure tables.

---

[22] C. J. Gorter, *Progress in Low Temperature Physics* (Interscience Publishers, Inc., New York, 1955), Vol. I, pp. 83–89.