Pressures on the Critical Isochore of He^4 †

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Measurements are reported of $(\partial P/\partial T)_{\rho_c}$ on the critical isochore of He^4 very close to the critical temperature. The measurements are well represented by an equation of the form $(\partial P/\partial T)_{\rho_c} = D + B^* t + A^* t \ln(t)$, where $t = (T - T_c)/T_c$ in the interval $-0.016 < t < 0.013$. They are used with Moldover's heat-capacity data to calculate $(\partial\mu/\partial T)_{\rho_c}$, which is found to be a linear function of temperature in the same temperature interval and to be analytic at the critical point. A comparison of the 1958 He^4 vapor-pressure temperature scale (T_{58}) with the NBS Provisional Scale 2-20 K (1965) indicates that T_{58} is a very unsuitable temperature scale for He^4 critical-point work.

INTRODUCTION

The demonstration by Moldover and Little[1] that the constant-volume heat capacity of He^4 is singular at the critical point, has raised the question of what other thermodynamic properties are singular.[2] In particular, since the heat capacity C_v is related to the pressure P and the chemical potential μ by the equation

$$\frac{\rho C_v}{T} = \left(\frac{\partial^2 P}{\partial T^2}\right)_\rho - \rho\left(\frac{\partial^2 \mu}{\partial T^2}\right)_\rho \quad , \qquad (1)$$

P and μ cannot both be analytic at the critical point. Several attractive schemes[3-6] for representing the thermodynamic properties of a fluid as homogeneous functions of the reduced density and temperature depend on the assumption that the chemical potential is analytic in temperature on the critical isochore. Hence, it is important to investigate the validity of that assumption. Since the chemical potential cannot be measured directly, it is necessary to calculate it from measurements of some other property. Moldover[1,7] has used the variation of the heat capacity with density, using the equation

$$\left(\frac{\partial(\rho C_v)}{\partial \rho}\right)_T = -T\left(\frac{\partial^2 \mu}{\partial T^2}\right)_\rho \quad , \qquad (2)$$

which can be derived from (1). This procedure works well in the two-phase region below the critical temperature, where ρC_v is linear in the density (since μ and P are independent of density). However, Eq. (2) is difficult to apply in the one-phase region, where μ is nonlinear in the density. A more direct approach is to combine pressure and heat-capacity measurements by means of Eq. (1). Since the second derivative of the pressure is needed, very high resolution is essential.

EXPERIMENTAL

The apparatus was designed to achieve the highest possible resolution in pressure and temperature, minimize gravitational effects, and maintain a reasonably short thermal time constant. The low-temperature part of the apparatus is shown in Fig. 1.

The sample space (K), 5.2027 cm^3 in volume, consisted of 192 slits, 0.25 mm wide and 1.0 mm deep, milled in a solid oxygen-free high-conductivity copper cell (L). It was surrounded on all sides by at least 1 cm of copper. The 0.5-mm-o.d. × 0.25-mm-i.d. 30% copper-nickel pressure-sensing capillary (E) was connected at the midplane of the 1-mm-high sample space and was horizontal for 2.0 cm before turning upwards. At the top of the vacuum can (D) it was connected to a vacuum-jacketed 2.1-mm-o.d. copper tube (A) which led out of the cryostat to the pressure gauge and filling manifold. The thermal conductivities of the two tubes were such that, when the cell was at the critical temperature, the bottom of the copper tube was within 10 K of room temperature and the high-temperature end of the horizontal part of the capillary was at 8 K. The total mass of helium in the capillary when the cell was at the critical point was calculated to be 55 μg, and the hydrostatic head was 0.035 Torr. The measured densities and pressures were corrected accordingly. At the point where the capillary entered the cell a 9 cm length of No. 30 copper wire was used to shunt most of the heat leak to the bath. The upper part of the capillary was surrounded by a copper radiation shield (not shown) to prevent it from radiating to the cell.

The temperature of the cell was controlled by means of a constantan wire electric heater (J) wound uniformly on the cylindrical surface of the cell and by a variable heat switch (B) inserted into one of the stainless-steel supporting tubes (H). The heat switch consisted of a copper rod which fitted snugly into H and partially shunted it. It could be moved vertically by means of a small stainless-steel tube which led to an O-ring seal at the top of the cryostat. When the heat switch was all the way in, the cell was held at about 4.23 K. When it was with-

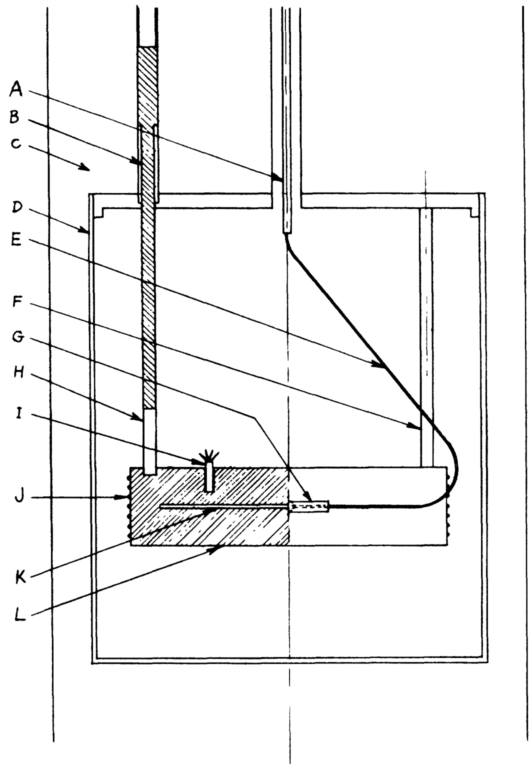

FIG. 1. The critical point cell shown in half-section. (A) 0.8-mm-i.d. ×2.1-mm-o.d. Cu vacuum-jacketed pressure-sensing tube; (B) heat-switch rod, OFHC Cu: (C) liquid-He bath; (D) brass vacuum can; (E) 0.3-mm-i.d. ×0.5-mm-o.d. 30% Cu-Ni capillary; (F) and (H) 3.2-mm-o.d. ×0.25-mm-wall stainless-steel support tubes; (G) brass fitting for pressure-sensing capillary at midplane of sample space; (I) germanium resistance thermometer; (J) manganin wire heater, 2 000 Ω; (K) sample space 1.0 mm high, 5.2027 cm^3 volume at 5 K; (L) OFHC Cu cell 10.2 cm o.d. ×2.9 cm high.

drawn all the way, the cell temperature rose to 5.36 K because of the residual heat leak from the capillary. It was normally inserted just far enough so that a small current in the heater could be used for fine temperature control.

Temperatures were measured by a Cryocal, Inc. germanium resistance thermometer (I) inserted into a close-fitting hole in the copper cell. Apiezon N grease was used to make good thermal contact. Its resistance was measured by an ac potentiometric method using a Gertsch model 1011R ratio transformer as the balancing element and a Princeton Applied Research Corporation model CR-4A preamplifier and model JB-4 lock-in amplifier as null detector. The detector output was displayed on a strip-chart recorder. The heater voltage was controlled by a retransmitting potentiometer mounted on the shaft of the recorder. With this simple control mechanism and occasional manual adjustment, the cell temperature could be maintained within a few microkelvin for many hours. As a check on the temperature scale, a second thermometer was mounted on the cell. At the end of the experiment the two thermometers were compared with each other and with the vapor pressure of helium. Then the apparatus was warmed to room temperature and both thermometers were sent to the National Bureau of Standards for calibration on the NBS Provisional Scale 2-20 K (1965) [8] (the acoustical thermometer scale). Except where noted below, all temperatures in this paper refer to that scale, which we will refer to as T_{NBS}. The two thermometers agreed with each other to better than 0.2 mdeg K.

Pressures were measured with Texas Instruments, Inc. fused-quartz Bourdon gauges. In order to achieve high resolution in $(\partial P/\partial T)_\rho$, pressure changes were measured on a differential gauge of 300-Torr range and 10^{-3}-Torr resolution. Its reference capsule was connected to a 1449-cm^3 reservoir of helium gas in an ice bath. A 2500-Torr gauge with a resolution of 10^{-2} Torr and a vacuum reference was used to measure the reference pressure. The reference pressure was kept constant to 10^{-3} Torr by small manual adjustments of the reference volume, using the null indicator of the 2500-Torr gauge as a pressure monitor. The sensitivity of the null indicator and the stability of the gauge at a constant dial setting were sufficient for this purpose, although the resolution of the counter dial was only 10^{-2} Torr and the absolute accuracy was about 0.1 Torr.

Both gauges were calibrated against a Ruska air-piston dead-weight tester at over 100 different pressures. Particular attention was paid to periodic errors caused by defects in the worm gear. The high-pressure gauge had only a small error (± 0.03 Torr), which was satisfactorily corrected by a sawtooth correction. The differential gauge had an error of ± 0.006 Torr which was not exactly periodic. Since it did not seem feasible to calibrate at every possible gauge setting, measurements were always made at the same position of the worm gear. This restriction set a lower limit on the measurement interval of about 3 Torr, which corresponds to about 2 mdeg K. The accuracy of the differential pressure measurements, considering the resolution of the Ruska gauge, irregularities in the main gear of the Bourdon gauge, and calibration errors, was about ± 0.006 Torr.

The He^4 was taken from a cylinder of 99.999% pure helium, passed through a trap cooled in liquid helium, and stored in the 1449-cm^3 reservoir where its pressure was measured with the high-pressure gauge. Then it was condensed into the evacuated cell. The mass of helium was calculated using 4.0023 for the atomic weight and the second virial coefficient given by Keesom.[9] Corrections were made for the volume of gas remaining in the part of the system at room temperature and in the cell capillary and for the measured diffusion rate of helium through the quartz Bourdon tubes. The volume of the reservoir was measured by weighing it filled with water after the experiment. The cell volume and all other volumes in the system were measured by displacing gas from a volumetric micrometer, with a capacity of 14 cm^3 and a resolution of 2×10^{-4} cm^3, which was also used for making small changes in the density of the sample. The true density in the cell decreased slightly with increasing pressure because the amount of helium gas in the dead volumes increased with pressure. The measured pressures were all corrected to the critical density using the scaling-law equation of state of Missoni, Sengers, and Green.[6] The correction was nowhere greater than 0.02 Torr. We believe the density measurements to be accurate to 0.02%.

With a constant amount of He^4 in the system and a constant reference pressure, measurements were made with the differential pressure gauge at a series of temperatures, and $(\partial P/\partial T)_\rho$ was calculated from the pressure and temperature increments. No curvature correction was made since it can be shown to be negligible. At each point the temperature was held constant until the system was in equilibrium. In the two-phase region the time constant was about 5 min. In the one-phase region the system came to equilibrium as fast as the temperature could be adjusted, but it was held at constant temperature for at least 5 min before readings were taken.

GRAVITY CORRECTION

Missoni, Sengers, and Green[6] have shown that for He^4, $\mu(\rho, T) - \mu(\rho_c, T)$ is an antisymmetric function of $\rho - \rho_c$ for $|\rho - \rho_c| \leq 0.5\rho_c$. In this case, in a cell of uniform cross section filled to a mean density equal to the critical density, the material at the midplane is at the critical density and its pressure is the pressure of the critical isochore. In the cell used in this work, the pressure was measured at the midplane so no gravitational correction was needed. In fact, the whole pressure difference in the cell was only 5×10^{-3} Torr (3×10^{-6} times the critical pressure).

Later we will have to use Moldover's[1,7] heat-capacity measurements, so we will consider the gravitational corrections in his cell. Because of a deformation of the cell caused by the force required to close the O-ring seal, $\frac{1}{3}$ of the cell volume was not in the main 3-mm-high sample space, but may have been as much as 10 mm below it. An approximate calculation indicates that the heat capacities and entropies may be seriously in error at temperatures within 2 mdeg K of the critical temperature, but they should be substantially correct outside that region.

CRITICAL CONSTANTS

The critical isochore was picked as the one for which there is no discontinuity in $(\partial P/\partial T)_\rho$ on passing from the two-phase to the one-phase region. Assuming that the size of the discontinuity is antisymmetric in $\rho - \rho_c$, at least near ρ_c, a study of the three isochores in Fig. 2, which differ by 1.0% in density, indicates that the central one is within 0.1% of the critical density. Therefore, the critical density is given by

$$\rho_c = 69.64 \pm 0.07 \text{ mg cm}^{-3} , \quad (3)$$

which is in good agreement with the values given by Moldover[1,7] (69.58 ± 0.07) and El Hadi[10] (69.76 ± 0.20), but is higher than those of Edwards[11] (69.323 ± 0.003) and of Roach[12] (68.5–69.0).

The critical temperature was determined by the following two methods:

(i) The thermal-equilibrium time was observed to be more than ten times greater when two phases were present in the cell than when there was only one phase present, presumably because of the time required for equilibrium between the two phases. This phenomenon provided a sensitive test of when the sample passed out of the two-phase region of the phase diagram. When the cell was filled to the critical density, the temperature at which this abrupt change in thermal behavior occurred was taken to be the critical temperature. It was found to be 5.19828 ± 0.00001 K on the temperature scale defined by our resistance thermometers.

(ii) In the two-phase region $(\partial P/\partial T)_\rho$ is, of course, independent of density, but this is not the case in the one-phase region. On an expanded plot of Fig. 2 the temperature at which the three isochores diverge from each other was determined to be 5.1983 ± 0.0005 K. Calculations using the equation for the coexistence curve given, for example, by Missoni, Sengers, and Green[6] showed that all three isochores pass through the coexistence curve within μdeg K of the critical temperature.

Both methods are based on the classical definition of the critical temperature as the temperature at which the two-phase region disappears. Method (i) is more precise, and $T_c = 5.19828$ was used in the reduction of our data, but it depends on the use of a nonthermodynamic concept. Method (ii) uses only established thermodynamic principles applied to the data. Fortunately, it gives the same result but with less precision. In any event there is a ± 2 medg K uncertainty in the Bureau of Standards calibration of our thermometers. Therefore

$$T_c = 5.1983 \pm 0.0021 \text{ K} (T_{\text{NBS}}) . \quad (4)$$

In the same experiment we determined the critical pressure to be

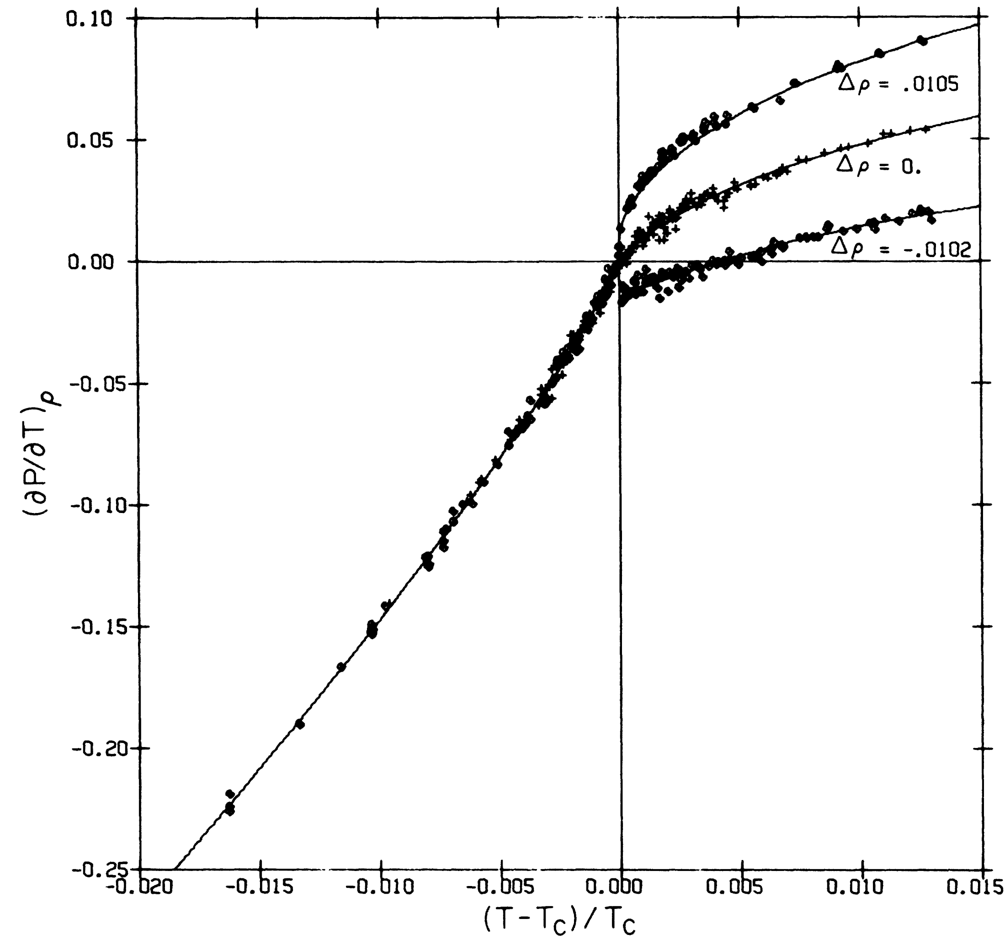

FIG. 2. $(\partial P/\partial T)_\rho$ in units of P_c/T_c, relative to its value at T_c, for three isochores close to $\rho_c = 69.64$ mg/cm^3. The curve for the critical isochore was calculated using Eq. (9). For the other two isochores an asymptotic expansion of the scaling-law equation of state of Missoni, Sengers, and Green (Ref. 6) was used.

$$P_c = 1706.12 \pm 0.10 \text{ Torr} \quad , \tag{5}$$

where the uncertainty is due to the calibration of the Bourdon gauge. The corresponding temperature on the 1958 vapor-pressure-temperature scale scale[13] is

$$T_c = 5.189\,92 \pm 0.000\,10 \text{ K}(T_{58}) \quad , \tag{6}$$

in excellent agreement with the value 5.189 88 ± 0.000 02 K reported by Edwards.[11]

These results are summarized in Table I, along with recent determinations by other workers.

In discussing critical phenomena it is customary to express the thermodynamic functions in reduced or dimensionless form by dividing by the appropriate combination of the critical temperature, pressure, and density. From the above measurements we find that the unit of dP/dT, entropy per unit volume, and heat capacity per unit volume (P_c/T_c) is 328.209 Torr/K or 0.0437 577 J/cm^3 K. The unit of chemical potential (P_c/ρ_c) is 3.266 030 J/g. In the following we will also use the reduced temperature

$$t = (T - T_c)/T_c \tag{7}$$

and reduced density

$$\Delta\rho = (\rho - \rho_c)/\rho_c \quad . \tag{8}$$

SLOPE OF CRITICAL ISOCHORE

The slope $(\partial P/\partial T)_{\rho_c}$ of the critical isochore is plotted against temperature in Fig. 2, along with the isochores for $\rho = 68.926$ mg/cm^2 $(\Delta\rho = -0.010\,25)$ and 70.373 mg/cm^2 $(\Delta\rho = +0.010\,52)$. The measurements are tabulated in Table III. The data for the critical isochore were fitted by the method of least squares (unweighted) to the equation, suggested by Moldover and Little's[1] equation for C_v:

$$\left(\frac{\partial P}{\partial T}\right)_{\rho_c} = D + B^* t + A^* t \ln|t| \quad , \quad -0.016 < t < 0.013 \tag{9}$$

where

TABLE I. The critical constants. Except for the first entry, all temperatures are on the T_{58} scale.[a]

	Temperature (K)	Pressure (Torr)	Density (mg/cm^3)
This work (T_{NBS})	5.1983 ± 0.0020	1706.12 ± 0.10	69.64 ± 0.07
This work (T_{58})	5.189 92 ± 0.000 10		
Edwards[b]	5.189 88 ± 0.000 02	1706.07 ± 0.02	69.323 ± 0.003
Edwards[c]	5.1897 ± 0.0007	1705.84 ± 0.86	
Moldover[d]	5.1891 ± 0.0007	1705.04 ± 0.9	69.58 ± 0.07
el Hadi[e]			69.76 ± 0.20
Roach[f]	5.191 ± 0.002	1707.5 ± 2.5	68.75 ± 0.25
van Dijk *et al.*[a]	5.1994	1718	

[a]Reference 13.
[b]Reference 11. From least-squares fit to the coexistence curve.
[c]Reference 11. Direct determination (meniscus disappearance).
[d]Reference 7.
[e]Reference 10.
[f]Reference 12.

$$D = 1289.18 \pm 0.30 \text{ Torr/K}$$

$$= 3.92793 \pm 0.00100 \quad \text{(reduced)}, \tag{10}$$

$$A^* = -664 \pm 20 \text{ Torr/K}$$

$$= -2.022 \pm 0.060 \; ; \tag{11}$$

for $t < 0$,

$$B^* = B_-^* = 1764 \pm 100 \text{ Torr/K}$$

$$= 5.376 \pm 0.300 \; , \tag{12}$$

and for $t > 0$,

$$B^* = B_+^* = -1496 \pm 100 \text{ Torr/K}$$

$$= 04.560 \pm 0.300 \; . \tag{13}$$

The root-mean-square deviation of the measured points from the curve was 0.85 Torr/K. The large error limits on A^* and B^* result from correlation between the constants (98% between A^* and each B^*, 95% between B_+^* and B_-^*). D is very little correlated with the other constants, and its error results mainly from the error of the pressure measurements. The logarithmic term in (9) corresponds to a critical exponent[14] α^* of zero in the equation

$$\left(\frac{\partial P}{\partial T}\right)_{\rho_c} = D + B^* t + A_\alpha^* t \, | t |^{-\alpha^*} \; . \tag{14}$$

Since in the accessible temperature range the constant and linear terms dominate, the data are not very sensitive to α^* and acceptable fits are obtained with values of α^* in the range -0.2 to $+0.2$. We have preferred to use the form (9), which has fewer adjustable constants.

CHEMICAL POTENTIAL

Integration of Eq. (1) at constant density yields

$$\rho\left(\frac{\partial \mu}{\partial T}\right)_\rho = \left(\frac{\partial P}{\partial T}\right)_\rho - \rho S \; , \tag{15}$$

where S, the entropy, can be obtained by integrating the heat capacity

$$S = S_c + \int_{T_c}^{T} \frac{C_v}{T} \, dT \; . \tag{16}$$

We have calculated $(\partial\mu/\partial T)_{\rho_c}$ from our $(\partial P/\partial T)_{\rho_c}$ measurements and a table of entropies obtained by integrating Moldover's[7] heat-capacity data. For this integration we used the equation given by Moldover,[7] which fits his data quite well except within 2 mK of the critical temperature, where the effect of gravity is quite pronounced. At the critical isochore his equation reduces to

$$C_v = A_\alpha \, | \, t \, |^{-\alpha} + B_\alpha + Et \; , \tag{17}$$

with different values of A_α, B_α, and α above and below T_c. Where the equation does not fit Moldover's data we used graphical integration of the data.

Below T_c Moldover used the T_{58} temperature scale, and above T_c he used an arbitrary scale based on an extrapolation of his carbon thermometer. We could have corrected his temperature scale below T_c, but there is no way to do it above T_c. Since the absolute temperature is only of secondary importance, we have used Moldover's value of T_c (5.1891 K) in reducing his data to dimensionless form. However, in a calculation like this one in which data from two different experiments are used, it is crucially important that the data points to be subtracted from one another correspond to the same temperature. This would be a simple matter if the critical temperature could be used as a fixed point to tie the two scales together as is commonly done, for example, at the λ point. But in these two experiments the critical temperatures were determined by very different methods. Our critical temperature was determined by a thermodynamic criterion (the disappearance of the two-phase region), while Moldover's was based on a least-squares fit of his data to an assumed equation of state. Fortunately, the calculated values of $(\partial\mu/\partial T)_{\rho_c}$ themselves afford a means of relating the two temperature scales, as will be seen below.

In Fig. 3 are plotted values of $(\partial\mu/\partial T)_{\rho_c}$ calculated using Moldover's T_c with his data and our T_c with ours. Points within 2 mK of T_c are not plotted because they are affected by gravity. The points appear to fall within experimental error on two

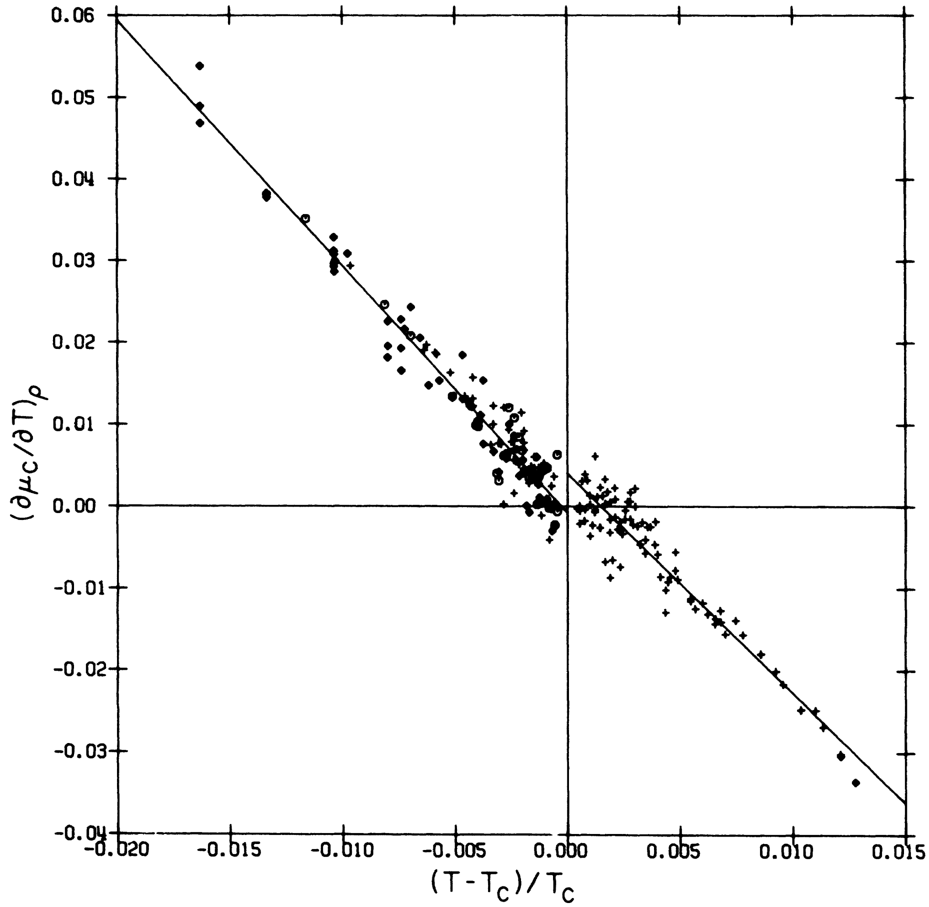

FIG. 3. $(\partial\mu/\partial T)_{\rho_c}$ in units of $P_c/(\rho_c T_c)$, relative to its value at T_c, calculated using the critical temperature reported by Moldover (Ref. 7).

straight lines which do not meet at the critical point. The points above and below T_c were fitted separately to straight lines by the method of least squares. These lines are shown in Fig. 3. Their slopes are -2.677 ± 0.093 above T_c and -3.013 ± 0.061 below T_c; $(\partial\mu/\partial T)_{\rho_c}$ has a discontinuity at T_c of $(4.81\pm0.57)\times10^{-3}$. This displacement of the high-temperature points relative to the low-temperature ones cannot be correct, since it would imply that a phase with $\rho=\rho_c$ would be stable below T_c. Therefore we repeated the calculation, displacing Moldover's T_c downward in steps of 0.52 mdeg K (increasing the value of t for all his points in steps of 1×10^{-4}). As T_c decreased the discontinuity decreased and the slopes became more nearly equal. When Moldover's T_c was decreased by 2.1 mdeg K (to 5.187 K), the discontinuity was reduced to $(0.38\pm0.57)\times10^{-3}$ and the slopes were -2.799 ± 0.091 and -2.848 ± 0.061. In fact, the data were equally well fitted by a single line of slope -2.801 ± 0.033, which is shown in Fig. 4. A further reduction of 0.52 mK in Moldover's T_c caused both discontinuities to reappear with opposite signs. The fact that the discontinuities in $(\partial\mu/\partial T)_{\rho_c}$ and $(\partial^2\mu/\partial T^2)_{\rho_c}$ disappeared for the same decrease in Moldover's T_c is a strong indication that both derivatives are in fact continuous and that either Moldover's T_c or ours is in error by 2.1 ± 0.5 mdeg K, and we will assume this to be the case. The standard deviations given in this paragraph are based solely on the fitting errors and are cited only for comparative purposes. When we allow for systematic errors in the heat-capacity and pressure measurements and uncertainty in the critical temperature correction, we have

$$\left(\frac{\partial^2\mu}{\partial T^2}\right)_{\rho_c}=-2.80\pm0.25,\quad -0.016<t<0.013\ . \qquad (18)$$

Hill and Lounasmaa[15] tabulated the entropy of He^4 at 5.25 K and at ρ_c. Their value was combined with Moldover's heat-capacity data to calculate the entropy at T_c. A small correction was made because Hill and Lounasmaa's assumed critical density was smaller than ours. We find

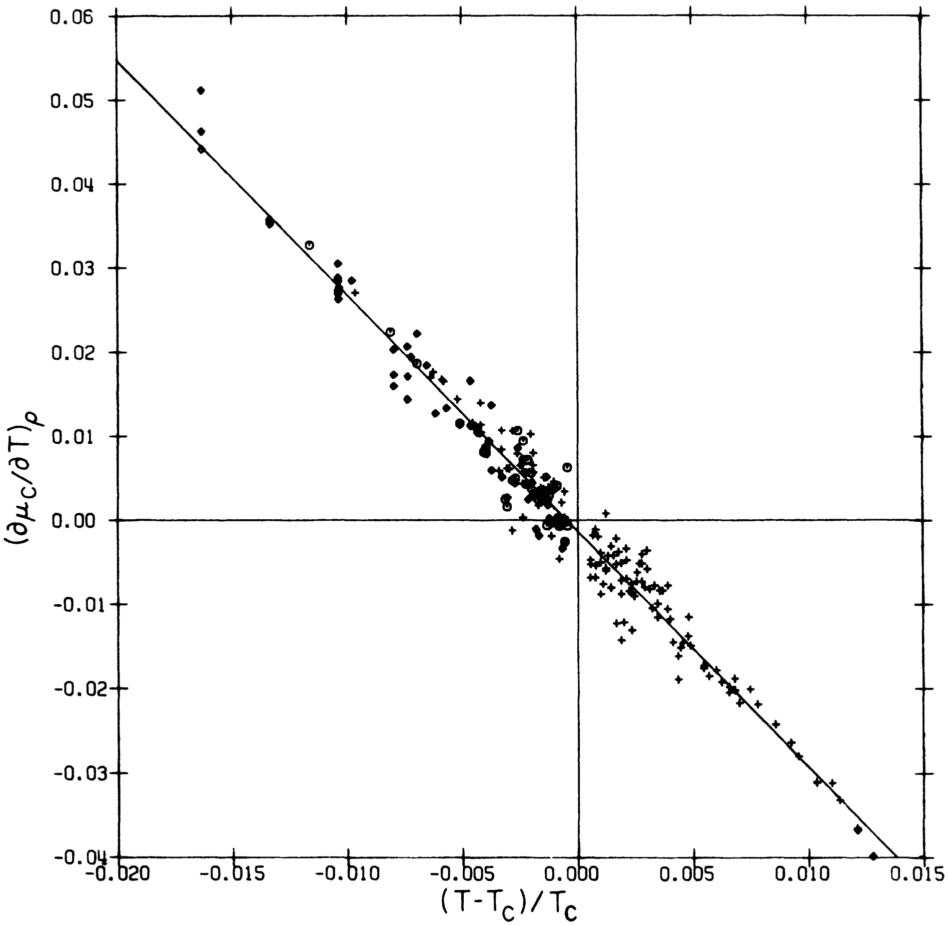

FIG. 4. $(\partial\mu/\partial T)_{\rho_c}$ in units of $P_c/(\rho_c T_c)$, relative to its value at T_c, calculated with Moldover's critical temperature decreased by 2.1 mdeg K.

$$\rho_c S_c = 8.977 \pm 0.08 \quad . \tag{19}$$

Combining this value with our value for $(\partial P/\partial T)_{\rho_c}$ (Eq. 10), and with Eq. (18), we find

$$\left(\frac{\partial\mu}{\partial T}\right)_{\rho_c} = D_\mu + B_\mu t \ , \quad -0.016 < t < 0.013 \tag{20}$$

TABLE II. Coefficients of equations for $(\partial P/\partial T)_{\rho_c}$ [Eq. (9)], $(\partial\mu/\partial T)_{\rho_c}$ [Eq. (25)], and $T_{NBS} - T_{58}$[Eq. (28)].

Coefficient	Value	Units	Reduced
D	1289.18 ± 0.30	Torr/K	3.92793 ± 0.00100
A^*	-664 ± 20	Torr/K	-2.022 ± 0.060
B^*_-	1764 ± 100	Torr/K	5.376 ± 0.300
B^*_+	-1496 ± 100	Torr/K	-4.560 ± 0.300
D_μ	-0.2209 ± 0.004	$J/cm^3 K$	-5.049 ± 0.09
B_μ	-0.123 ± 0.008	$J/cm^3 K$	-2.80 ± 0.20
c_1	8.45745	mK	
c_2	61.7795	mK	
c_3	122.121	mK	
c_4	34.0113	mK	

where

$$D_\mu = 5.049 \pm 0.09 = -0.2209 \pm 0.004 \ J/cm^3 K \ , \tag{21}$$

$$B_\mu = -2.80 \pm 0.20 = 0.123 \pm 0.008 \ J/cm^3 K \ . \tag{22}$$

Our value for B_μ is substantially less in magnitude than Moldover's[7] (-3.47). However, it is a relatively small correction in his analysis, and it has to be determined by comparing data from different isochores. Since Moldover had difficulties with thermometer stability and had to adjust the temperature scales for the different isochores empirically, we feel that his value may be in error by this much. Missoni, Sengers, and Green[6] give an even higher value (-3.9) calculated from Hill and Lounasmaa's[15] C_v measurements. However, those data were taken so far from critical, in both temperature and density, that they can hardly be considered to represent the critical region. Equation

(20) implies that the third and all higher derivatives of μ are negligible at T_c and, therefore, that μ is analytic at T_c within the experimental error.

1958 He^4 TEMPERATURE SCALE

The 1958 He^4 temperature scale[12] (T_{58}), based on He^4 vapor pressures, is used almost universally by workers studying the properties of He^4, but it has two serious drawbacks for work at the critical point. In the first place, it does not exist above the critical temperature so that measurements above T_c are based on the individual experimenter's idea of what is a "suitable" extrapolation of T_{58}. Such scales will differ from laboratory to laboratory, especially since all secondary thermometers sufficiently sensitive for critical-point work are notoriously nonlinear. The second drawback is that T_{58} behaves anomalously, compared to the thermodynamic temperature, as the critical temperature is approached. This happens because T_{58} is defined by a vapor-pressure table in which d^2P/dT^2 approaches zero as T approaches T_c, whereas, in fact, d^2P/dT^2 approaches infinity as T approaches T_c. For these reasons we have used the NBS Provisional Scale 2-20 K (1965)[8] in spite of the obvious disadvantages of having to send thermometers to another laboratory for calibration. The two scales differ by as much as 12 mK, and in order to compare measurements on different scales it is necessary to have a correction curve. No such curve is available for the range 4.2–5.2 K, aside from two points published by Cataland and Plumb.[16] Therefore, we have calculated $T_{NBS} - T_{58}$ from some of our vapor-pressure measurements and plotted them in Fig. 5. The rapid decrease of $T_{NBS} - T_{58}$ near T_c should be noted. The curve in Fig. 4 is plotted from the empirical equation

$$T_{NBS} - T_{58} = c_1 + c_2 t + c_3 t^2 + c_4 t \ln(-t) , \qquad (23)$$

with coefficients c_n given in Table II.

It should be noted that unfortunately the Bureau of Standards provides no calibration points between 4.2 and 5.0 K. However, the eight-parameter interpolation equation is fitted to 20 calibration points in the range 2.3–20 K, so the interpolation should be reasonably smooth. Our measurements of $T_{NBS} - T_{58}$ at 4.2 and 5.0 K (11.9 and 10.5 mK, respectively) do not agree very well with those published by Cataland and Plumb[16] (10 and 12 mdeg K, respectively). We know of no reason for this, except that the NBS calibration of our thermometers is only guaranteed to ± 2 mdeg K. Cetas and Swenson[17] have

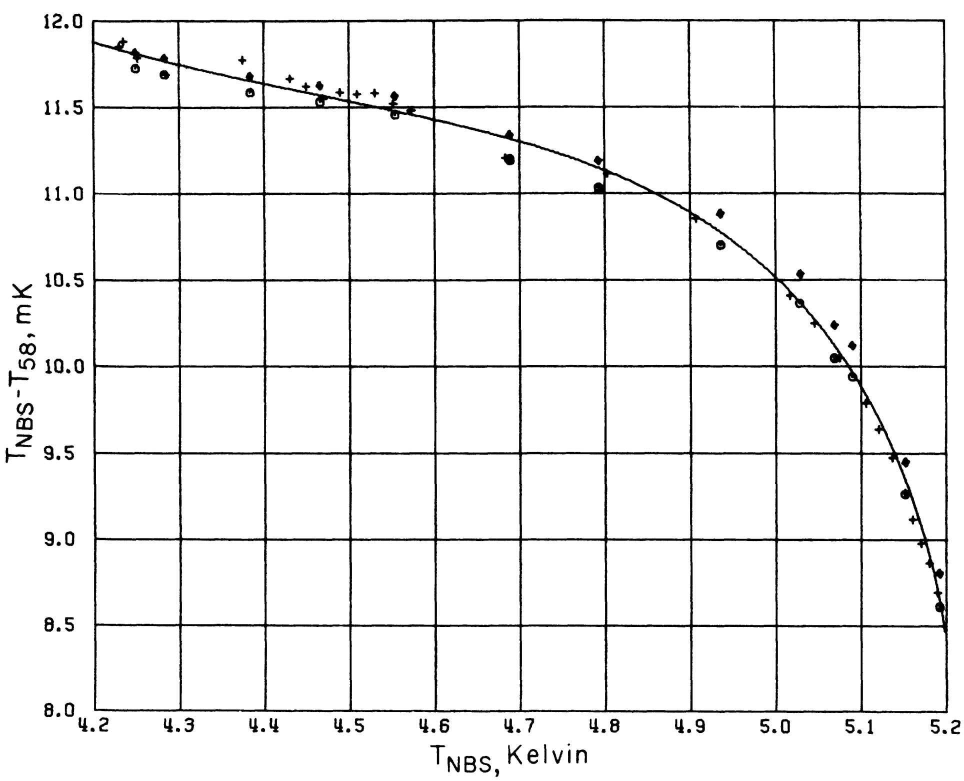

FIG. 5. Difference between the NBS Provisional Scale 2-20 K (1965) and the 1958 He^4 vapor-pressure temperature scales. The curve was calculated using Eq. (28).

also compared T_{58} with T_{NBS} by means of germanium thermometers calibrated by the NBS. They find $T_{NBS} - T_{58}$ to be 11 and 10 mK, respectively, at the same two temperatures.

CONCLUSION

Experimental evidence that the chemical potential

TABLE III. Isochores of He^4.

Temp (K)	$(\partial P/\partial T)_\rho$ (Torr/K)	Temp (K)	$(\partial P/\partial T)_\rho$ (Torr/K)	Temp (K)	$(\partial P/\partial T)_\rho$ (Torr/K)
Density = 68.93 mg/cm^3					
5.113 56	1215.7	5.191 87	1280.9	5.212 92	1287.8
5.113 57	1215.1	5.192 30	1281.3	5.213 49	1286.9
5.113 57	1217.4	5.192 48	1281.5	5.214 07	1288.6
5.128 87	1226.7	5.193 03	1283.5	5.215 26	1288.5
5.128 88	1226.9	5.193 59	1283.1	5.215 83	1288.0
5.128 88	1226.8	5.194 64	1284.1	5.216 40	1287.0
5.144 33	1239.2	5.194 78	1284.4	5.217 59	1288.4
5.144 33	1240.3	5.194 82	1283.5	5.218 73	1289.2
5.144 34	1239.6	5.195 37	1286.8	5.219 33	1288.7
5.144 34	1239.1	5.195 94	1286.5	5.219 92	1289.1
5.144 34	1239.7	5.196 56	1286.0	5.221 07	1288.6
5.144 34	1239.2	5.196 98	1287.2	5.221 15	1289.2
5.144 42	1239.0	5.197 16	1287.8	5.221 18	1289.3
5.144 60	1239.6	5.198 27	1288.7	5.222 25	1289.3
5.147 44	1242.7	5.198 90	1283.6	5.222 29	1290.4
5.156 79	1248.0	5.199 32	1285.3	5.223 40	1289.2
5.156 80	1249.4	5.199 40	1285.8	5.223 99	1288.7
5.156 80	1248.4	5.199 47	1285.5	5.224 72	1289.6
5.159 94	1250.7	5.199 50	1284.0	5.226 89	1289.6
5.159 95	1251.6	5.200 05	1285.2	5.227 85	1289.9
5.159 95	1252.7	5.200 61	1284.7	5.228 08	1289.7
5.160 70	1253.1	5.201 24	1284.9	5.229 02	1289.1
5.162 17	1255.5	5.201 66	1286.5	5.229 04	1290.4
5.164 26	1256.5	5.201 81	1284.6	5.230 98	1290.7
5.166 22	1256.6	5.201 84	1286.2	5.231 34	1290.2
5.168 73	1259.4	5.202 37	1287.3	5.231 35	1291.0
5.171 74	1262.0	5.202 95	1285.0	5.231 79	1291.7
5.174 11	1266.2	5.206 33	1285.7	5.233 70	1291.3
5.174 12	1264.5	5.206 48	1286.7	5.233 71	1291.0
5.175 68	1266.0	5.206 52	1285.5	5.233 72	1291.0
5.175 71	1265.9	5.207 06	1284.1	5.233 88	1291.1
5.175 71	1266.0	5.207 62	1287.0	5.237 39	1292.3
5.176 24	1266.5	5.207 69	1287.1	5.238 80	1292.2
5.178 25	1268.4	5.207 69	1287.6	5.238 80	1292.3
5.178 87	1270.4	5.208 25	1287.4	5.240 29	1292.4
5.178 88	1267.9	5.203 58	1285.0	5.241 42	1292.4
5.181 24	1270.3	5.203 99	1287.0	5.243 18	1293.4
5.182 44	1270.8	5.204 14	1286.2	5.243 59	1294.0
5.184 18	1273.3	5.204 18	1288.0	5.243 59	1294.0
5.184 80	1275.4	5.204 73	1286.3	5.246 69	1293.2
5.185 98	1276.3	5.205 29	1286.9	5.249 59	1293.4
5.186 54	1276.0	5.205 92	1287.1	5.252 47	1294.2
5.186 59	1276.5	5.206 07	1286.6	5.253 52	1293.4
5.187 16	1276.1	5.208 82	1285.0	5.253 52	1294.3
5.188 03	1277.8	5.209 39	1287.6	5.255 98	1294.9
5.188 40	1277.7	5.209 96	1287.0	5.258 88	1294.5
5.188 90	1277.0	5.210 59	1287.7	5.261 76	1295.5
5.189 51	1279.1	5.210 90	1288.2	5.263 50	1296.0
5.189 52	1277.4	5.211 16	1285.5	5.263 51	1295.9
5.191 25	1281.8	5.211 50	1287.6	5.263 52	1295.7
5.191 60	1281.3	5.211 51	1287.9	5.265 26	1295.8
5.191 62	1281.2	5.211 73	1286.7	5.265 84	1294.6
5.191 62	1281.2	5.211 87	1287.6		

TABLE III. (*continued*)

Temp (K)	$(\partial P/\partial T)_\rho$ (Torr/K)	Temp (K)	$(\partial P/\partial T)_\rho$ (Torr/K)	Temp (K)	$(\partial P/\partial T)_\rho$ (Torr/K)
		Density = 69.64 mg/cm³			
5.148 19	1243.0	5.197 06	1287.7	5.211 64	1296.3
5.165 10	1256.8	5.197 64	1288.7	5.212 18	1296.9
5.165 77	1257.7	5.197 66	1287.5	5.212 75	1297.2
5.167 70	1259.5	5.198 24	1280.0	5.212 77	1297.5
5.168 09	1259.8	5.198 82	1288.7	5.212 78	1296.5
5.171 25	1262.4	5.198 83	1288.7	5.213 34	1296.5
5.174 65	1265.2	5.198 83	1289.9	5.213 94	1298.2
5.175 31	1265.7	5.199 39	1289.1	5.213 96	1297.5
5.176 43	1267.9	5.199 97	1288.8	5.214 50	1297.0
5.176 44	1267.0	5.200 00	1289.8	5.215 09	1296.5
5.176 46	1266.8	5.200 02	1289.6	5.215 10	1296.5
5.180 59	1269.8	5.200 57	1290.7	5.215 65	1297.6
5.181 18	1272.0	5.201 15	1290.5	5.216 26	1296.7
5.181 21	1271.3	5.201 16	1291.2	5.216 27	1297.2
5.181 25	1270.2	5.201 16	1291.0	5.216 82	1298.0
5.182 38	1271.9	5.201 72	1292.5	5.217 42	1298.2
5.182 96	1272.5	5.202 30	1291.2	5.218 57	1298.0
5.183 54	1270.7	5.202 33	1291.7	5.218 59	1299.0
5.183 57	1274.7	5.202 35	1293.1	5.219 13	1297.9
5.184 74	1275.1	5.202 90	1293.2	5.219 73	1297.3
5.185 32	1275.3	5.203 48	1292.9	5.220 89	1296.3
5.185 91	1276.0	5.203 49	1292.5	5.220 90	1297.2
5.185 91	1273.9	5.203 49	1291.3	5.221 45	1297.8
5.185 93	1275.3	5.204 05	1292.0	5.222 05	1298.3
5.185 97	1275.8	5.204 63	1292.8	5.223 21	1299.0
5.187 10	1276.5	5.204 65	1292.9	5.223 22	1299.8
5.187 68	1279.2	5.204 68	1295.1	5.223 76	1298.9
5.188 26	1278.7	5.205 22	1293.7	5.226 68	1299.2
5.188 29	1279.2	5.205 80	1292.8	5.226 69	1299.3
5.188 32	1278.5	5.205 81	1292.8	5.227 83	1299.4
5.189 45	1278.5	5.205 81	1294.4	5.229 54	1300.3
5.190 03	1279.9	5.206 37	1294.3	5.230 61	1300.3
5.190 62	1280.4	5.206 95	1295.3	5.232 35	1300.7
5.190 64	1280.6	5.206 98	1292.0	5.232 37	1300.9
5.190 67	1281.1	5.207 00	1294.3	5.233 61	1301.7
5.191 79	1282.1	5.207 54	1295.1	5.233 62	1301.3
5.191 80	1281.9	5.208 12	1293.7	5.234 66	1301.2
5.192 38	1280.9	5.208 13	1295.0	5.237 07	1302.7
5.192 96	1283.7	5.208 13	1294.3	5.238 78	1302.8
5.192 98	1283.5	5.208 14	1291.9	5.242 83	1303.6
5.193 02	1283.7	5.208 69	1292.9	5.242 85	1303.6
5.194 14	1283.6	5.209 27	1296.1	5.246 29	1304.3
5.194 15	1282.2	5.209 30	1295.6	5.248 00	1304.4
5.194 72	1285.1	5.209 32	1294.9	5.252 05	1305.0
5.195 30	1286.3	5.209 86	1294.7	5.252 07	1305.0
5.195 33	1284.3	5.210 45	1295.3	5.255 51	1306.3
5.195 36	1285.4	5.210 46	1294.9	5.257 21	1306.2
5.195 90	1286.0	5.210 46	1293.5	5.261 26	1306.7
5.196 48	1285.7	5.211 02	1295.1	5.261 27	1306.6
5.196 49	1285.0	5.211 62	1295.9	5.264 71	1306.9

is an analytic function of temperature on the critical isochore clears up, at least for He^4, a previously unanswered question which affects the validity of scaling-law formulations of the equation of state near the critical point, since these theories always assume the analyticity of $\mu(\rho_c, t)$. On the other hand, observation of the logarithmic anomaly in the pressure serves to emphasize the need for a revision of the 1958 He^4 temperature scale.

Numerical constants reported in this paper are

TABLE III. *(continued)*

Temp (K)	$(\partial P/\partial T)_\rho$ (Torr/K)	Temp (K)	$(\partial P/\partial T)_\rho$ (Torr/K)	Temp (K)	$(\partial P/\partial T)_\rho$ (Torr/K)
		Density = 70.37 mg/cm^3			
5.13784	1234.6	5.19836	1289.9	5.21222	1305.9
5.15606	1249.3	5.19880	1293.5	5.21222	1305.3
5.16204	1254.2	5.19880	1291.2	5.21266	1305.9
5.17169	1262.0	5.20006	1296.2	5.21452	1305.6
5.17715	1266.7	5.20067	1296.6	5.21453	1306.3
5.17761	1267.4	5.20068	1297.1	5.21496	1305.4
5.17765	1267.3	5.20112	1297.7	5.21682	1306.6
5.18190	1270.1	5.20113	1296.8	5.21683	1307.2
5.18235	1270.3	5.20237	1299.2	5.21726	1307.9
5.18360	1272.8	5.20300	1299.4	5.21912	1308.6
5.18426	1273.6	5.20343	1300.7	5.21912	1307.7
5.18472	1276.0	5.20344	1300.0	5.21956	1307.3
5.18596	1277.0	5.20414	1300.0	5.22142	1307.6
5.18707	1277.5	5.20469	1300.7	5.22142	1307.6
5.18780	1277.9	5.20531	1301.3	5.22186	1308.7
5.18831	1277.7	5.20574	1301.4	5.22716	1310.0
5.18943	1278.7	5.20576	1301.0	5.22760	1309.8
5.19067	1280.2	5.20700	1301.9	5.23318	1310.8
5.19133	1280.0	5.20761	1303.1	5.23633	1313.1
5.19178	1281.7	5.20762	1303.8	5.23676	1313.1
5.19367	1284.5	5.20805	1304.0	5.24548	1315.1
5.19412	1283.4	5.20806	1302.7	5.24591	1315.6
5.19539	1284.5	5.20930	1303.3	5.24658	1315.2
5.19601	1285.9	5.20991	1303.8	5.25461	1317.2
5.19602	1288.2	5.20992	1304.4	5.25504	1317.1
5.19646	1286.2	5.21036	1303.4	5.26373	1318.8
5.19773	1288.5	5.21161	1305.2	5.26416	1318.7
5.19835	1291.1				

summarized in Tables I and II, and the experimental data are listed in Table III.

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