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¹²Note that ω_j , Eq. (4) refers to a chain $(M-1)$ -atoms long hooked up with springs at both ends to rigid supports, and that ω_j , Eq. (19), refers to internal vibrations of a segment of n atoms with both ends free; the form is still similar.

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Scaling of the Specific-Heat Singularity of He⁴ Near Its Critical Point*

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We have measured the specific heat at constant volume (C_v) of He⁴ near its critical temperature (T_c) and critical density (ρ_c). Tabulated data are given along seven isochores with densities in the range $-0.10 < \Delta\rho < +0.15$, where $\Delta\rho = (\rho - \rho_c)/\rho_c$, at temperatures in the range $-0.06 < t < +0.13$, where $t = (T - T_c)/T_c$. Density resolution was $0.001 \rho_c$ and the resolution of C_v measurements was $0.0003 T_c$ in temperature. Resulting values for the critical constants are $T_c = 5.1891 \pm 0.0007$ K and $\rho_c = 0.06958 \pm 0.00007$ g/cm³. The data in the one-phase region may be expressed as the sum of a nonsingular function of t and $\Delta\rho$ and a function of the form $|\Delta\rho|^{-\alpha/\beta} f(x)$, where α is the exponent describing the singularity in C_v at density ρ_c in the one-phase region, β is the exponent describing the coexistence curve, and x is the variable suggested in Griffith's discussion of homogeneous functions, $t |\Delta\rho|^{-1/\beta}$. In the two-phase region C_v diverges with an exponent α' with $\alpha' \approx \alpha \approx 0.15$. In the two-phase region the singularity in C_v seems to be dominated by d^2P/dT^2 where P is the vapor pressure. If μ is the chemical potential $d^2\mu/dT^2$ is less singular than d^2P/dT^2 and may even be constant in this temperature range. The singularity in d^2P/dT^2 implies the T_{58} helium vapor-pressure temperature scale is slightly in error. If T_{58} and its first derivative are assumed correct at 4.85 K, then T_{58} assigns a temperature 0.0007 K too high to pressures near the critical pressure. Where our C_v data may be compared to P - V - T data on He⁴ the agreement is generally good. The possibility now exists of making a complete model of the free energy near the critical point.

INTRODUCTION

In recent years an effort has been made to describe the thermodynamic behavior of both magnets and fluids near their critical temperatures in terms of scaling laws. These laws have been suggested by both the Ising model and the requirement that the thermodynamic functions be in some sense the

simplest of the class of functions which could possibly describe the singularities that experiments suggest are present at a critical point.¹⁻³ The scaling laws lead to an important prediction: The singular parts of all thermodynamic functions near a critical point, which ordinarily would be functions of two variables (say temperature and magnetization or temperature and pressure) are

in fact functions of a particular combination of these variables and thus essentially a function of a single variable. Some experimental confirmation that real systems obey scaling laws has been given by recent analyses of equation of state data for both magnets^{4,5} and fluids.⁶ We have attempted a direct test of the scaling of the thermal equation of state by measuring the specific heat at constant volume (C_v) of He⁴ along several isochores and correlating the resulting data using the variable suggested by scaling law ideas. Since P - V - T data have recently become available for He⁴ close to the critical point,^{7,8} the possibility now exists of making a complete model of the singularity in the free energy of He⁴.

DESCRIPTION OF APPARATUS

The design of our apparatus was dominated by efforts to avoid two problems frequently encountered in measurements near a liquid-gas critical point. To overcome the long thermal relaxation times found in fluids near their critical temperature (T_c) we attempted to keep thermal conduction paths through the helium in the calorimeter to a minimum. To avoid density gradients resulting from the pressure gradient in the fluid arising from its own weight we have restricted the height of our calorimeter.

The general design of the calorimeter and exchange-gas can was adopted for these measurements from the apparatus used by Fairbank, Buckingham, and Kellers^{9,10} for their measurements near the λ transition of He⁴. The calorimeter itself (see Fig. 1) consisted of two parts, both made of OFHC copper. The two parts were sealed together with an indium O ring. The slots in the lower part were 0.1-mm wide and 3-mm deep, and contained about $\frac{2}{3}$ of the helium. The rest of the helium was between the two parts of the calorimeter, thus extending over a range of 12 mm in height. The thermal relaxation time of the filled calorimeter was a few seconds far from the critical point, but became as long as several minutes close to the critical point.

The lower part of the calorimeter was wound with a heater and had a carbon resistor thermometer cemented in a hole through it. Superconducting leads were used to the heater and thermometer. The calorimeter was supported on nylon threads in an evacuated chamber. Thermal contact to the helium bath outside the chamber could be made by lifting the calorimeter until it contacted three copper fingers. A stainless-steel capillary led from the calorimeter to a needle valve. This arrangement allowed the quantity of helium in the calorimeter to be changed without warming it to room temperature. Helium gas was measured in a specially designed Toeppler pump and then condensed into the calo-

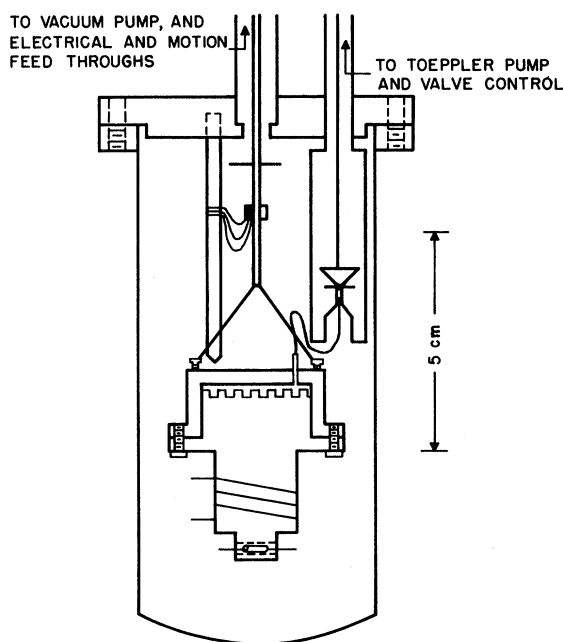


FIG. 1. Calorimeter and exchange gas can.

rimeter. The initial filling was measured as well as each subsequent addition or subtraction. At the conclusion of the experiment, the quantity of gas removed was measured. This differed by 0.07% of the total quantity measured from that expected and serves as an important check of many independent instrument readings.

To measure the volume of the calorimeter, enough helium was condensed to be sure it was full of liquid below the λ point. Then the valve was closed and the helium above it was pumped away. Next the valve was opened and the helium in the calorimeter was pumped out and measured as gas with the Toeppler pump. This procedure was reproducible to $\pm 0.05\%$ suggesting that the calorimeter did indeed fill. The liquid-density data of Kerr and Taylor¹¹ were used to convert these measurements to the calorimeter volume: 0.694 cm³. We believe our density measurements are accurate to within $\pm 0.1\%$.

At the conclusion of the experiment, helium gas was admitted to the vacuum space. The carbon resistor was calibrated in the range 4.37 to 5.17 K by measuring the pressure above the He⁴ bath and making hydrostatic head corrections. Pains were taken to assure that the bath was in temperature equilibrium. The T_{50} scale was used to convert pressures to temperatures. A resistance-temperature relation of the form

$$\frac{\log_{10}(\text{resistance})}{T} = \sum_{n=0}^N a_n \log_{10}(\text{resistance}) \quad (1)$$

was fitted to the calibration data. This relation

was extrapolated to measure temperatures as high as 5.27 K and it was differentiated to compute heat capacities. The derivative, particularly in the extrapolated region, depends sensitively on which algebraic form is fitted to the calibration data and probably leads to the largest systematic errors in the specific-heat measurements. A polynomial with three constants differed in derivative from one with four constants by 0.1% at 5.0 K; 0.7% at T_c ; and 1.2% at 5.27 K, the highest temperature at which data were taken. We have used the three constant polynomial which is equivalent to the widely used Clement-Quinnell formula.¹² The difference between these polynomials would not significantly alter our measurements of the temperature dependence of C_v near the critical point, only its absolute value.

On independent runs this calibrating procedure has yielded values of T_c of He⁴ (as observed by the specific-heat anomaly) differing by as much as 0.0005 K. Should a variation of comparable magnitude exist in the temperature calibration between one end of the calibrating interval and its center, a 0.1% variation in the temperature derivative and in the values of C_v would be introduced.

The capillary leading from the calorimeter to the needle valve probably led to the principal experimental difficulties in obtaining the data reported here. In preliminary experiments the needle valve was located above the calorimeter. The capillary connecting them was a stainless-steel tube about 5 in. long with an i. d. of 0.006 in. The volume beneath the seal of the needle valve, but above the calorimeter, was 0.8% of the volume of the calorimeter. It proved to be impossible, because of large irregular heat leaks, to take data close to the critical temperature unless the capillary was bent. Even with a U-shaped bend, a large decrease in the apparent heat leak between the calorimeter and the helium bath always occurred as the calorimeter was warmed through temperatures close to the temperature where the helium inside it became a single phase. This decrease in apparent thermal conductivity occurred whether the bath was only slightly below the critical temperature or as cold as 2.3 K. It is reasonable to assume the very effective convective heat transfer observed¹³ near the critical point was responsible for this effect. To take the data reported here the needle valve was redesigned and placed more nearly beside the calorimeter. In addition the capillary was shortened to 2 in. in length and a 0.004-in. stainless-steel wire was placed inside it. The volume between the valve seat and above the calorimeter was then 0.07% of the volume of the calorimeter. Large changes in apparent thermal conductivity still occurred. We then adopted the procedure of monitoring stray heat input to the calorimeter several minutes before and after each data point. At most 20 min

were used per point. The changes and irregularities in this heat input limited the precision of the data taken close to the phase boundary. When they were present, the normally abrupt drop in C_v at the phase boundary was rounded. On some occasions we have seen drops in C_v in a temperature interval 0.0003 K wide, but unfortunately in the data reported here the phase boundary is 0.001–0.002 K wide, hence this must be considered the limit of temperature resolution of the C_v data.

In order to compare the data taken at different densities the stability of the thermometer resistor must be examined. Earlier experience¹⁴ with this particular thermometer, using the critical temperature of He⁴ as a fixed point, showed that it drifted towards higher resistance at an initial rate exceeding 0.001 K/week, but this drift rapidly decreased. We assumed the same drift occurs in the present data. Strong support for this assumption comes from the data itself. The adjustment of the temperature scale required to make the data at $\rho = 0.0690$ g/cm³ coincide with the data taken at $\rho = 0.0694$ g/cm³ is exactly that suggested by the assumption the thermometer drifts in a reproducible way upon being cooled to liquid helium temperatures. This assumption has led to Table I in which we suggest temperature corrections to be applied to the specific-heat data on each isochore. We have used these corrections in our own analysis of the data, but they have not been applied in Table II. Drifts in carbon resistors of a similar nature have been observed by others¹⁵; however, no explanation has been offered.

ANALYSIS OF DATA

The problem of interpretation of published data is particularly acute in the case of experiments seeking to observe asymptotic behavior of various phenomena near critical points. One set of measurements of the index of refraction of He⁴ near its critical point has been the principal subject of five papers.¹⁶ Questions such as: What should be considered a parameter determined by this

TABLE I. Temperature drift of thermometer.

Density (g/cm ³)	Estimated drift, to be subtracted from temperatures in Table III (mK)
0.0694	1.4
0.0766	1.0
0.0623	0.4
0.0660	0.3
0.0690	0.2
0.0732	0.2
0.0805	0.1

TABLE II. Experimental values of (density) × (specific heat) at various temperatures along seven isochores of He⁴. Temperatures are on T_{58} scale and not corrected for thermometer drift.

Temp (K)	Sp Heat (J/cm ³ K)
$\rho = 0.0694 \text{ g/cm}^3$	
4.9129	0.549
4.9771	0.572
5.0392	0.601
5.0934	0.636
5.1585	0.724
5.1661	0.745
5.1708	0.764
5.1754	0.788
5.1794	0.816
5.1822	0.845
5.1842	0.870
5.1859	0.908
5.1874	0.950
5.1884	1.006
5.1890	0.977
5.1892	1.013
5.1896	1.049
5.1897	1.041
5.1899	1.011
5.1900	1.011
5.1901	0.859
5.1903	0.753
5.1905	0.653
5.1907	0.556
5.1910	0.528
5.1913	0.483
5.1918	0.451
5.1926	0.419
5.1936	0.396
5.1952	0.375
5.1978	0.353
5.2013	0.333
5.2063	0.316
5.2185	0.293
5.2383	0.272
5.2572	0.261
$\rho = 0.0766 \text{ g/cm}^3$	
5.1833	0.876
5.1841	0.895
5.1850	0.917
5.1855	0.905
5.1858	0.915
5.1859	0.858
5.1861	0.904
5.1862	0.884
5.1864	0.863
5.1866	0.750
4.9894	0.592
4.9912	0.592
5.0323	0.611

TABLE II. (cont.)

Temp (K)	Sp Heat (J/cm ³ K)
5.0708	0.635
5.1111	0.667
5.1438	0.708
5.1613	0.747
5.1690	0.773
5.1748	0.801
5.1784	0.822
5.1806	0.853
5.1822	0.864
5.1843	0.889
5.1849	0.912
5.1853	0.919
5.1857	0.922
5.1860	0.916
5.1862	0.905
5.1864	0.909
5.1867	0.921
5.1870	0.690
5.1877	0.368
5.1885	0.353
5.1898	0.354
5.1916	0.337
5.1944	0.330
5.1986	0.318
5.2051	0.305
5.2137	0.294
5.2270	0.283
5.2526	0.270
$\rho = 0.0623 \text{ g/cm}^3$	
4.8544	0.514
4.8929	0.526
4.9334	0.539
4.9766	0.557
5.0217	0.578
5.0665	0.600
5.0935	0.620
5.1094	0.635
5.1318	0.660
5.1398	0.672
5.1520	0.694
5.1546	0.700
5.1622	0.721
5.1699	0.750
5.1763	0.784
5.1805	0.815
5.1815	0.831
5.1819	0.834
5.1827	0.840
5.1829	0.832
5.1836	0.852
5.1837	0.885
5.1842	0.811
5.1846	0.714
5.1850	0.722

TABLE II. (cont.)

Temp (K)	Sp Heat (J/cm ³ K)
5.1854	0.599
5.1858	0.737
5.1860	0.584
5.1864	0.523
5.1866	0.459
5.1872	0.329
5.1878	0.323
5.1881	0.319
5.1893	0.312
5.1911	0.303
5.1940	0.293
5.1974	0.285
5.2018	0.276
5.2086	0.267
5.2188	0.257
5.2330	0.246
$\rho = 0.0660 \text{ g/cm}^3$	
4.8334	0.516
4.8825	0.531
4.9344	0.549
4.9892	0.570
5.0461	0.598
5.0925	0.629
5.1166	0.650
5.1308	0.673
5.1426	0.686
5.1513	0.703
5.1607	0.726
5.1696	0.758
5.1758	0.790
5.1801	0.830
5.1824	0.862
5.1839	0.881
5.1849	0.908
5.1857	0.910
5.1857	0.915
5.1863	0.942
5.1868	0.951
5.1868	0.972
5.1873	0.961
5.1876	0.945
5.1878	0.993
5.1881	0.954
5.1884	0.917
5.1884	0.744
5.1887	0.834
5.1891	0.529
5.1892	0.538
5.1899	0.447
5.1910	0.383
5.1927	0.353
5.1953	0.339
5.1991	0.320
5.2056	0.300

TABLE II. (cont.)

Temp (K)	Sp Heat (J/cm ³ K)
5.2154	0.283
5.2307	0.267
5.2583	0.250
$\rho = 0.0690 \text{ g/cm}^3$	
5.1748	0.775
5.1773	0.808
5.1809	0.852
5.1835	0.885
5.1854	0.927
5.1866	0.971
5.1874	0.978
5.1880	1.016
5.1884	1.052
5.1888	1.043
5.1894	0.660
5.1902	0.496
5.1913	0.423
5.1931	0.382
$\rho = 0.0732 \text{ g/cm}^3$	
4.8458	0.541
4.9057	0.554
4.9680	0.577
5.0284	0.604
5.0754	0.631
5.1090	0.659
5.1344	0.688
5.1500	0.714
5.1586	0.734
5.1639	0.750
5.1691	0.773
5.1742	0.796
5.1781	0.822
5.1813	0.858
5.1835	0.895
5.1851	0.931
5.1862	0.956
5.1866	0.966
5.1868	0.985
5.1872	0.983
5.1875	1.000
5.1876	0.968
5.1879	1.027
5.1883	0.927
5.1883	0.948
5.1887	0.555
5.1890	0.500
5.1894	0.432
5.1898	0.400
5.1909	0.399
5.1909	0.392
5.1931	0.368
5.1967	0.346
5.2020	0.325
5.2096	0.307

TABLE II. (cont.)

Temp (K)	Sp Heat (J/cm ³ K)
5.2219	0.291
5.2396	0.276
5.2656	0.263
$\rho = 0.0805 \text{ g/cm}^3$	
4.8512	0.552
4.9128	0.582
4.9722	0.594
5.0295	0.624
5.0797	0.650
5.1151	0.681
5.1354	0.705
5.1482	0.727
5.1594	0.753
5.1664	0.779
5.1738	0.805
5.1756	0.818
5.1768	0.815
5.1770	0.867
5.1774	0.831
5.1781	0.735
5.1781	0.847
5.1783	0.737
5.1788	0.464
5.1793	0.355
5.1797	0.383
5.1815	0.324
5.1844	0.310
5.1888	0.305
5.1952	0.298
5.2213	0.280

experiment and what should be used from other experiments? How should the data close to the critical point which are more representative of asymptotic behavior, but more scattered, be weighted relative to other data? What are the limits of resolution of the experiment?, do not have unambiguous answers. Hence we consider the table of data (Table II) with the suggested temperature corrections (Table I) to be the only unbiased presentation of our results. Also we are careful to state our assumptions in the analysis below.

Our primary effort has been to find a relatively simple algebraic form meeting "reasonable" criteria with a limited number of parameters which could be adjusted to fit all the data at once. Such a form would be a useful summary of the data even if it had no fundamental significance. Since all the data are to be fit at once we are assured there will be unique values for T_c and ρ_c . The drop in C_v at the coexistence curve is on the order of 0.001–0.002 K wide; therefore, the data in

this region could not be used. It is still reasonable to require that these drops fall on a smooth curve of the form $t|\Delta\rho|^{-1/\beta} = x_0$ since both dielectric constant⁷ and index of refraction⁸ measurements on He⁴ have led to this result. Here t is the reduced temperature measured from the critical temperature, $t = (T - T_c)/T_c$; and $\Delta\rho$ is the reduced density measured from the critical density, $\Delta\rho = (\rho - \rho_c)/\rho_c$. We also did not use the data at $\rho = 1.16 \rho_c$ in the analysis of the one-phase region, assuming it was too far from ρ_c to be useful. However we do show it in the results.

It is frequently assumed that sufficiently near the critical point the free energy may be represented by a constant plus some simple singularity located at the critical point alone. This singularity reflects itself quite weakly in the specific heat. The largest value of C_v we observed (see Fig. 2) is about 5 times the ideal-gas value. This occurs within a few tenths of a percent of ρ_c and a few hundredths of a percent of T_c . In contrast, the analysis of Roach suggests the isothermal compressibility is about 60 times the ideal-gas value where the isochore $\rho = 1.16 \rho_c$ crosses the coexistence curve. This isochore is our most distant from ρ_c and crosses the coexistence curve about 0.002 T_c below T_c . The weakness of the singularity requires that we assume C_v has nonsingular terms including an additive constant (B' in the two-phase region and B in the one-phase region). We have also included terms linear in the temperature and density for reasons stated below. We have considered the critical region to be defined by $|t| \lesssim 0.015$ since it is in this temperature range that the coexistence curve of He⁴ is well described by a power law. To fit out data at temperatures below these, we have included a term proportional to the temperature (the constant of proportionality is called E). The introduction of this term slight-

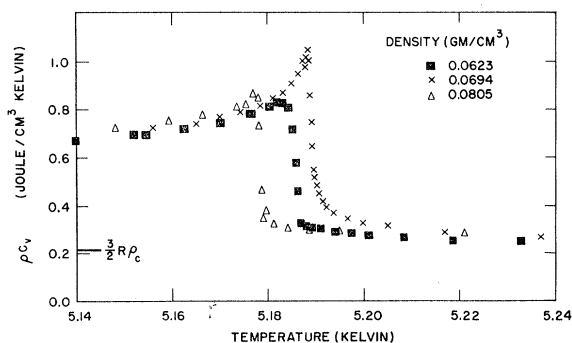


FIG. 2. The specific-heat anomaly of He⁴ near its critical temperature. Data are shown near the critical density, 10% below the critical density and 16% above the critical density. The ideal-gas value of ρC_v at the critical density is also indicated.

ly improves the fits to the data above T_c , but does not significantly change results for the critical parameters or exponents.

Yang and Yang¹⁷ have emphasized that everywhere in the two-phase region the pressure and chemical potential are functions of temperature alone (and not volume). Then

$$SdT = -Nd\mu + VdP$$

leads to

$$\rho C_v = NT \frac{d^2P}{dT^2} - NT\rho \frac{d^2\mu}{dT^2}. \quad (2)$$

Thus in the two-phase region ρC_v is proportional to ρ . This is evident in Fig. 3, where we have plotted $\rho C_v / \rho_c R$ for three densities as a function of the reduced temperature $t = (T - T_c) / T_c$ measured from the critical temperature in the two-phase region. An examination of the "constant" of proportionality, $NT(d^2\mu/dT^2)$ as determined by this data, relatively far from the critical temperature indicates the temperature dependence of $NT(d^2\mu/dT^2)$ is certainly weaker than that of C_v itself. Accordingly we have assumed a term $D\Delta\rho$ ($D = \text{a constant}$) to be part of ρC_v in the two-phase region. If this term with the same value of D is assumed to be present in the one-phase region, the remainder of ρC_v in the one-phase region has a symmetrical density dependence about $\rho = \rho_c$. This is illustrated for our data in Fig. 4. A similar observation has been made earlier about data taken on argon.¹⁸ Thus we are led to assume $D\Delta\rho$ is present in the one-phase region as well. We emphasize that a *weak* temperature dependence of D (e. g., $D \propto T$) is not excluded by our data.

We have chosen to state our results in terms of ρC_v rather than C_v itself, primarily because ρC_v

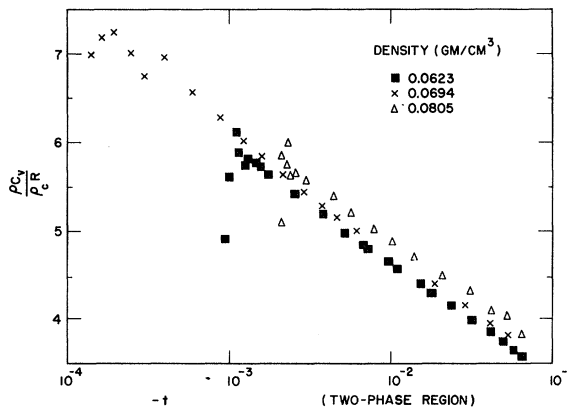


FIG. 3. Normalized specific heat in the two-phase region at three densities versus the reduced temperature, measured from the critical temperature. The linear dependence of ρC_v on ρ is evident. The weak power law divergence as $-t \rightarrow 0$ is also evident.

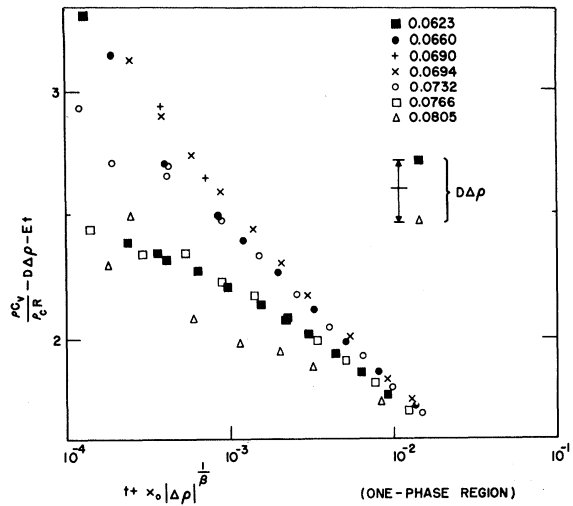


FIG. 4. Normalized specific-heat data in the one-phase region versus reduced temperature measured from the coexistence curve. The linear dependences of ρC_v , on ρ and t have been removed. The size of the linear dependence on ρ is indicated by the sketch showing how far the data points at two densities have been displaced. The data are now symmetrical about $\rho = 0.0696$ gm/cm³.

is more commonly compared with results of calculations on lattice gases. It is also true that ρC_v comes from the raw data in a slightly more direct way than C_v itself.

As terms singular at the critical point we have chosen

$$\rho C_v / \rho_c R = A'(-t)^{-\alpha'} \quad (3)$$

in the two-phase region and

$$\rho C_v / \rho_c R = A |\Delta\rho|^{-\alpha/\beta} (1 + \text{sgn}x |x|^N)^{-\alpha/N} \quad (4)$$

in the one-phase region with $x = t |\Delta\rho|^{-1/\beta}$. Equation (3) is appropriate for the two-phase region since the assumption $D = \text{constant}$ leads in the same temperature dependence on all isochores. The data reported here are not significantly different from those we reported earlier at the critical isochore.^{19,20} Then we stated C_v was well approximated by a singularity of the form $-A' \ln(-t) + B'$ in the two-phase region although small ($\sim 1\%$) systematic deviations were evident in the center of the temperature range considered. Now, since the same deviations occur on each isochore, and they cannot be ascribed to a slight modification of the temperature scale we are forced to abandon the idea that the function $-A' \ln(-t) + B' + Et$ describes the data in this temperature region although such a function might be adequate for data still closer to the critical point. Our choice of Eq. (4) in the one-phase region was

suggested by the proposal of Widom² and Griffiths³ that the thermodynamic function belong to a particular class of homogeneous functions, although Eq. (4) is not completely consistent with their ideas. For example its expansion in density about the critical isochore starts with the term $|\Delta\rho|^{N/\beta}$ ($N/\beta \approx 2.4$ in our case), not $(\Delta\rho)^2$ which would be expected from a function analytic in the one-phase region. Equation (4) is useful because it reduces to $At^{-\alpha}$ on the critical isochore, has few parameters, and fits the data.

RESULTS

The results stated below are based on a fit of selected data to Eqs. (3) and (4) with the addition of the nonsingular terms described above. The constants in Table III resulted from this fit and were used for plotting the deviations for all data on Fig. 5. The fact that many significant figures are given is not intended to imply the constants are uniquely determined to high precision, but only that this combination of constants will lead to Fig. 5.

TABLE III. Critical constants resulting from a fit of selected data to Eqs. (3) and (4), with the extra terms $B' + D\Delta\rho + Et$ added to the right-hand side of Eq. (3) and the extra terms $B + D\Delta\rho + Et$ added to the right hand side of Eq. (4). This is the combination of constants which leads to Fig. 5.

ρ_c	0.06958 g/cm ³	A'	1.546
T_c	5.1891 K	α'	0.159
D	1.05	B'	1.563
E	4.3	A	1.197
β	0.3724	α	0.127
x_0	0.30	B	-0.330
N	0.891		

1. Critical Constants

Our estimates for the critical constants are $T_c = 5.1891 \pm 0.0007$ K and $\rho_c = 0.06958 \pm 0.00007$ g/cm³. These error estimates are based on the accuracy of our temperature and density measurements. They do not include statistical uncertainties arising from the multiparameter fit to the formulas listed in Table III. Such "statistical" errors are often misleadingly small. Both critical constants were sharply determined by the various functions we tried fitting to the data; the values gotten by various choices always fell within the ranges given. The value of T_c agrees with that we stated earlier^{19,20} and with the more recent results of Edwards⁷ and of Roach.⁶ The value of T_c occurs 0.0009 K above the temperature of the specific-heat maximum at densities near ρ_c . This is consistent with the idea that the C_v

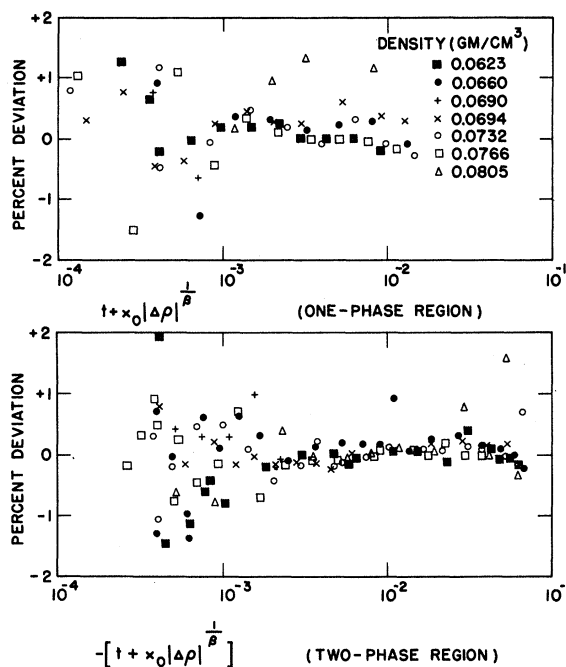


FIG. 5. The percentage deviation of the data from the equations summarized in Table III are plotted against the reduced temperature measured from the coexistence curve. All data except a few points close to the coexistence curve which fell off the graph are plotted.

data have an inherent resolution slightly greater than 0.002 K. The value of ρ_c is equal within combined experimental error to that found by Edwards. It falls outside the range of values Roach used in the analysis of his data; however, he did not estimate the absolute accuracy of his density measurements.

The agreement between the critical temperature determined from C_v measurements and that determined from P - V - T measurements is much better in the case of He⁴ than in the cases of O₂, Ar, and one set of measurements on Xe. It has been suggested the discrepancies result from large gravitational gradients in the C_v apparatus.²¹ Recently additional C_v measurements have been made on Xe with a calorimeter of height comparable to ours. Reassuringly, T_c determined from these C_v measurements agrees with T_c determined from P - V - T measurements about as well as it does for helium.²²

2. The Critical Isochore

The isochore $\rho = 0.0694$ g/cm³ is within 0.3% of ρ_c . This isochore and the data taken as a whole in the range $0.013 > |t| > 0.0004$ are consistent with a power law divergence of ρC_v on the critical isochore with the exponents $\alpha \approx \alpha' \approx 0.15$ giving the best fit. If one is committed to a power law and

this temperature range, α and α' will vary about 25% with different reasonable choices of E . These exponents are very sensitive to the choice of T_c . If for some reason the optimum value is not chosen, much wider variations will result with one exponent increasing and the other decreasing.

If data closest to T_c were excluded, the remaining data would be best fit by values of α and α' smaller than 0.15. This fact might suggest that our values for these exponents are smaller than asymptotic values at $T \rightarrow T_c$. On the other hand, the data which are closest to T_c are most subject to the effects of limited resolution; therefore we have assumed this dependence of α and α' on the choice of data is not significant.

3. Scaling of Data in One-Phase Region

In Fig. 4 we have plotted ρC_v in the one-phase region after two nonsingular functions were subtracted. The symmetry about ρ_c is evident as well as the effects of limited resolution very close to the coexistence curve. In Fig. 6 the data in Fig. 4 at the five highest densities (the rest are omitted for clarity) have been reduced by a constant B , and have been multiplied by $|\Delta\rho|^\alpha/\beta$. To the extent that the data at different densities now fall on a single smooth curve when plotted against the variable x one may say the data "scale" experimentally. In principle this graph could have been made without any prior knowledge of the function of x to which the data scale. This is our major experimental result. As a practical matter we have chosen a particular $f(x)$ to approxi-

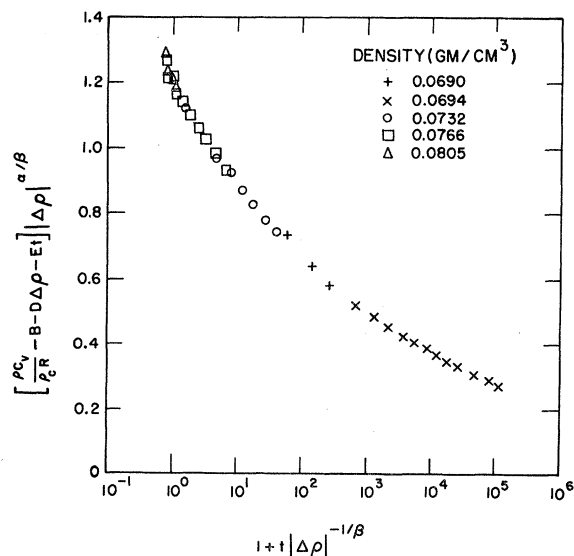


FIG. 6. Scaled specific-heat data versus "scaling law" variable. 1.00 has been arbitrarily added to the variable x to permit use of semilog paper. Coexistence curve occurs at $1.00 + x = 0.70$.

mate this curve so we could numerically separate out the nonsingular contribution to ρC_v . The fact that our approximate $f(x)$ does not satisfy all of the conditions of Widom and Griffiths does not weaken the conclusion. To examine in greater detail how well the data fall on a single curve we have plotted in Fig. 5 the deviations of the data on all seven isochores from our choice of $f(x)$. Most of the data fall within a few tenths of a percent of this particular $f(x)$. The most notable exceptions are the data at $\rho = 1.16 \rho_c$ which were not used to find the parameters in $f(x)$.

4. The Coexistence Curve

The parameters α_0 and β which determine the coexistence curve are found from both the location of the jump in ρC_v and the scaling factor $|\Delta\rho|^\alpha/\beta$. Values of β with different choices for $f(x)$ (for example requiring $N=1.0$) differ from the one cited by as much as 4%. The coexistence curve indicated by this data falls between that of Edwards and that of Roach in most of the temperature range, although our value of β is about 4% greater than the β 's they get.

5. The Isothermal Compressibility

The slope of the isotherms where they intersect the coexistence curve is related to the jump in C_v at the coexistence curve by

$$\Delta C_v = \frac{T}{\rho^2} \left(\frac{\partial P}{\partial \rho} \right)_T \left(\frac{d\rho}{dT} \right)^2. \quad (5)$$

Thus we may compare ρC_v data with the compressibilities (χ_T) derived from P - V - T measurements. To extract ΔC_v from our data it is necessary to extrapolate approximately 0.001 K to coexistence curve itself. This may be done with excellent reliability in the two-phase region with the help of Table III or a graph like Fig. 3. The temperature dependence of ρC_v is similar on each isochore, hence information from the critical isochore may be used on the other isochores until the temperature gets to within the temperature resolution of the ρC_v measurements from T_c . In the one-phase region the extrapolation problem is more complex. Figure 4 suggests the approach of ρC_v to its maximum value in the one-phase region may be well resolved on the isochores $\rho = 0.0623 \text{ g/cm}^3$ and $\rho = 0.0766 \text{ g/cm}^3$. We would expect the isochore $\rho = 0.0805$ to be even more clearly resolved, but apparently it is not. The other isochores cross the coexistence curve within 0.001 K of T_c , hence are not expected to be resolved. We have used the functions and constants in Table III to estimate $\rho \Delta C_v$ on the three isochores furthest from ρ_c and then have calculated $(\partial P / \partial \rho)_T$. The errors cited are based on estimates of the extrapolation errors in the one-phase

region. They do not allow for the effects of errors in x_0 , β , and ρ_c which enter into the calculation of $(\partial P/\partial \rho)_T$. Our results are:

Density (g/cm ³)	$(\partial P/\partial \rho)_T$ (Torr cm ³ /g)
0.0805	431 ± 40
0.0766	101 ± 10
0.0623	93 ± 10

We may use our coexistence curve to convert ρ to t and then plot

$$\chi_T = (P/\rho_c^2)(\rho \partial \rho / \partial P)_T$$

versus t . If we neglect nonsingular terms and assume

$$\chi_T = G(-t)^{-\gamma'}$$

we estimate from these three points $\gamma' = 1.15$ in this temperature range.

To derive χ_T from ΔC_v we had to use values of β and x_0 to calculate $(d\rho/dT)^2$. It seemed reasonable that P - V - T measurements which look at the coexistence curve itself at many points would yield more reliable values of $(d\rho/dT)^2$ than our C_v measurements which cross the coexistence curve at seven points. However, at the three densities in question $(d\rho/dT)^2$ derived from Edwards' and Roach's data differ from each other by about as much as they differ from our values (up to 20%). Thus we do not have a clear reason to prefer P - V - T derived values, and have used our own.

Our values for χ_T agree with those of Roach. Our estimated error is much smaller, even if the uncertainty in $(d\rho/dT)^2$ were included. Our value of γ' is midway between the values Roach gets from his $\rho > \rho_c$ and $\rho < \rho_c$ data. Our values of χ_T

are about one-half those Edwards' data indicates at the same densities. Our value of γ' would equal his (1.26) within combined error limits.

6. Implications for the T_{58} Temperature Scale

The T_{58} temperature²³ scale relates the vapor pressure of liquid He⁴ to the absolute temperature. This scale is the internationally accepted scale in the range where vapor-pressure measurements of He⁴ are possible. The singularity in C_v at the critical point implies a singularity in the second derivative of the vapor pressure [Eq. (2)] which was not considered in the preparation of T_{58} . To estimate the importance of the singularity we assumed that at 4.85 K (near the lowest temperature at which we have data) T_{58} gives the true vapor pressure and that the derivative of T_{58} gives the true value of dP/dT . We assumed the values of d^2P/dT^2 derived from our C_v data were correct and integrated them to find a new temperature scale $P^*(T)$. We used the $P^*(T)$ scale to re-evaluate our resistor calibration and recalculate our C_v data. This process was iterated until it converged. The net effect was to assign to pressures near the critical pressure (1705 Torr) temperatures 0.0007 K below those listed in T_{58} . An effect of the same magnitude would result if dP/dT in T_{58} were in error by 0.3% at 4.85 K. It is interesting to note that d^2P/dT^2 at 4.85 K on T_{58} is 1.6% larger than our value.

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Thermodynamics of the Isentropic Sound Velocity Near the Superfluid Transition in He⁴

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A thermodynamic relation between the isentropic velocity of sound u in the zero frequency limit and the heat capacity for He⁴ near the superfluid transition temperature T_λ is presented. The validity of the calculation depends upon the logarithmic temperature dependence of the heat capacity. The effect of the gravitational field on u in samples of finite height is calculated. The minimum measurable velocity in real samples exceeds the velocity at T_λ by at least 48 cm/sec. The major contribution to the velocity arises from a term whose temperature dependence is C_p^{-1} . However, there are additional appreciable contributions whose temperature dependence is $T_\lambda - T$ and $(T_\lambda - T) \ln|T_\lambda - T|$. Comparison with the measurements of Barmatz and Rudnick shows that the present treatment quantitatively explains all the features of the experimental data. The calculation can be used to determine the contribution from dispersion to measured velocities at nonzero frequencies.

I. INTRODUCTION

In this paper a thermodynamic relation between the isentropic sound velocity u in the zero-frequency limit and the heat capacity at constant pressure C_p for liquid helium in the gravitational field and near the superfluid transition temperature T_λ will be derived. The calculation will be based on the assumption that C_p depends logarithmically on $T_\lambda - T$, and will be restricted to the temperature range $T_\lambda \pm 5 \times 10^{-3}$ °K over which this dependence is experimentally verified.¹ Detailed calculations of u for isobars and general expressions for isochores will be presented. Comparison of these predictions with the measured low-frequency velocity² at saturated vapor pressure is very in-

structive. The sound velocity has been measured with sufficient precision to reveal interesting details of the thermodynamics of the superfluid transition, and the agreement with the present prediction indicates that these details can be understood on the basis of thermodynamics as presented here. The general results of the calculation also are applicable to other systems with λ -lines and logarithmic specific-heat singularities. The method used here can be applied equally well to the calculation of other thermodynamic properties.

In addition to explaining the behavior of the sound velocity near T_λ , the present results can be used also to extract the dispersion contributions from measured sound velocities at nonzero frequencies.