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Study of the Specific Heat of a He^3-He^4 Mixture near Its Gas-Liquid Critical Point*

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We present measurements of the specific heat C_{vx} of a mixture of He^3 and He^4 with a nominal concentration of He^3, $X_3 = 0.80$. Data were taken with a flat calorimeter cell in the vicinity of the gas-liquid critical point of the mixture, which is characterized (at a given X_3) by its density ρ_c and temperature T_c. The data consist of nine isochores within the approximate density range $0.52 < \rho/\rho_c < 1.20$ and in the temperature range $-0.1 \leq t \leq 0.1$, where $t = (T - T_c)/T_c$. Data were taken to within 0.4 mK of the transition temperature on all but one of the isochores. We find that the behavior of the specific heat in the mixture for a given reduced density ρ/ρ_c is in general very similar to that seen in pure He^3. In particular, the behavior of C_{vx} along the critical isochore is the same as that for pure He^3 in the range $10^{-4} \leq t \leq 10^{-2}$. There the apparent weak divergence is characterized by an exponent $\alpha \approx 0.1$. From thermodynamic considerations of the upper bound of C_{vx} along a line of singularities in mixtures, the apparent weak divergence we observe does not, however, represent the asymptotic behavior. This question is discussed in the light of the paper by Griffiths and Wheeler and of new calculations by Leung and Griffiths for a binary fluid. The thermal-equilibrium times in the two-phase region were found to be much longer than in the pure He^3 fluid, and these are briefly discussed. The thermal diffusivity in this region is found to have a maximum at a density approximately 20% lower than ρ_c, in rough correspondence to the density of the temperature extremum of the two-phase-region boundary.

I. INTRODUCTION

The present work has been motivated by recent theoretical and experimental interest in generalizing the description of critical phenomena in one-component fluids[1,2] to multicomponent systems. Griffiths and Wheeler[3] were able to develop qualitative predictions about the forms taken by thermodynamic functions near the critical point in a binary-fluid system. These results were derived from a few simple postulates about the geometry of the critical line and the coexistence surface in the P-T-Δ field space, where $\Delta = \mu_i - \mu_j$, the difference in the respective chemical potentials of components i and j.

So far experimental data in the critical regions of most binary-fluid systems are rather meager. Chemical engineering work on industrial binary mixtures has concentrated on the determination of critical parameters such as T_c and V_c, and on excess free energies,[4] but such data are insufficient for the study of the asymptotic behavior of thermodynamic quantities. Wallace and Meyer (WM)[5] have recently presented a systematic investigation of P-V-T relations of He^3-He^4 solutions in the gas-liquid critical region, and the present work is complementary to that study.

The research described below consists of specific-heat measurements and their discussion along nine isochores in the vicinity of the gas-liquid critical point of an 80% He^3–20% He^4 mixture. The critical parameters of this mixture, as given by WM, are the density $\rho_c \approx 0.016$ mole/cm³, the temperature $T_c \approx 3.71$ K, and the pressure $P_c \approx 1050$ Torr. The isochores studied lie within the density range $0.52 < \rho/\rho_c < 1.20$ and are measured in the temperature range $0.9 \lesssim T/T_c \lesssim 1.1$. A complete tabulation of these data (approximately 800 points) is not given here, but will be included in a forthcoming technical report.[6]

Our discussion will be conducted in terms of the predictions by Griffiths and Wheeler for a binary fluid near its liquid-gas critical point. It is found that our results along the critical isochore indicate a weak divergence of C_{vx} as T_c is approached within the restricted temperature range given by $10^{-4} < |t| < 10^{-2}$, where $t = 1 - T/T_c$. However, general thermodynamic arguments, as demonstrated again most recently by Griffiths and Wheeler,[3] indicate that the true asymptotic behavior must show C_{vx} tending to a finite value at T_c. This disagreement can be resolved by the argument that the temperature region $t < t_{\text{cross}}$, within which the asymptotic behavior is obtained, is so small as to be experimentally inaccessible. Here t_{cross} is the "crossover temperature" that separates a region where C_{vx} is finite from a region farther from T_c where C_{vx} appears to be divergent. A very low value of t_{cross} is perhaps not unexpected if the slope $dT/d\Delta$ of the critical line in the P-T-Δ field space is very small.

II. EXPERIMENTAL PART

A. Apparatus

The apparatus used in this experiment is identical, except in one minor detail, with one used in work reported previously,[7] and the interested reader is referred to that paper for a detailed description. The only change that has been made for this work is that a Texas Instruments fused-quartz Bourdon gage has replaced the mercury manometer previously used to measure the filling pressure for the fluid samples. This allows convenient measurement of the pressure in the relevant range of 900–1200 Torr.

The important characteristics of the calorimeter are that the sample fluid is contained in a flat horizontal cell of vertical dimension 0.5 mm, thus reducing possible gravitational effects on the measurements, and a low-temperature valve is used to ensure that no changes in density or concentration of the fluid may occur after measurements have begun (see Fig. 1 of Ref. 7). This valve is at the same height as the sample cavity, and connected to it by a length of horizontal stainless-steel capillary. The volume between the valve seat and the sample cavity constitutes approximately 1% of the total volume of the cell. The calorimeter is thermally isolated by means of a thermal shield and a simple mechanical heat switch.

The thermometry system utilizes a specially doped germanium resistor as the temperature detector, and is capable of resolving temperature differences of 0.5 μK under the experimental conditions. The thermometer resistance is calibrated against the vapor pressure of He^4 in the range 3.4–4.0 K. We estimate the accuracy of our temperature scale to be within 0.5 mK of T_{58}.

The heat capacity of the empty calorimeter was measured in the same temperature interval to a precision of ± 1%. The contribution of this addenda to the total heat capacity never exceeded 23%, and was typically around 5% in the neighborhood of the transition.

B. Sample Preparation

The He^3– He^4 mixture used in this experiment has a nominal concentration X of He^3 of 0.80. This sample was prepared in the same apparatus as was used to prepare the mixtures studied by WM, and is expected to have the same concentration as their $X = 0.800$ sample to within $\pm 0.5\%$ in X. We will consider the P-V-T-X data of WM on these mixtures as a standard. This is not only because these are the only presently available measurements on this system, but the possibility of systematic errors due to fractionation is smaller in the apparatus used by WM than is the case here.

During the filling of each isochore the calorimeter was held at a constant temperature T_f in the one-phase region for this concentration ($T_f = 3.750$ K), and the pressure was increased to a predetermined value in order to attain a desired final density, as calculated from the P-V-T-X data. This procedure is, in general, very similar to that used in filling the isochores in pure He^3, as reported in a previous paper.[7] An important difference, however, is that fractionation of the sample must be avoided during the filling process. This problem is not negligible in our apparatus, since the number of moles of gas in the vertical fill line above the low-temperature valve is comparable to that in the sample cavity volume. Since there exists a temperature gradient along this line, we could expect some concentration gradient at equilibrium.

We have avoided gross fractionation by vigorous mixing of the sample gas in the cryostat just prior to filling the cell to the desired pressure and closing the low-temperature valve. In this way it was hoped that the gas in the vertical fill line was not allowed to approach equilibrium. This procedure is based on the assumption, as a first approximation, that an effective temperature "equilibrium" is established in a much shorter time than is required for complete equilibrium with its attendant fractionation.

The transition temperature $T_{tr}(\rho, X)$ for each isochore was directly determined from our heat-capacity measurements (as explained below). In each case T_{tr} was found to lie about 10 mK below the temperature expected from the boiling- and dew-point curves[5(b)] given by WM for the $X = 0.800$ mixture. We note that a downward shift in $T_c(X)$ by 10 mK corresponds approximately to an increase in the mole fraction $\delta X \approx 0.005$. Then we can estimate that the mixtures finally enclosed within the sample cavity had a nominal concentration given by $X \approx 0.805$, and that fractionation during the filling process could not be too extensive.

C. Experimental Observations

During our measurement of the specific heat we could also observe the qualitative features of the time required for the system to reach thermal equilibrium after the administration of a heat pulse to the sample. The thermal-equilibrium time varied markedly within the temperature range studied. In the one-phase region the relaxation time was always so short (time to reach equilibrium $\lesssim 0.5$ min) as to be undetectable with our measuring technique, and this was true regardless of whether the single phase in the calorimeter was the gas or the liquid. On the other hand, the relaxation times in the two-phase region were very long, and increased dramatically as the transition temperature was approached from below.

This behavior is qualitatively similar to that seen[7,8] in pure He^3, where the interpretation is given that the boundary between the two phases is the primary bottleneck for thermal diffusion, i.e.,

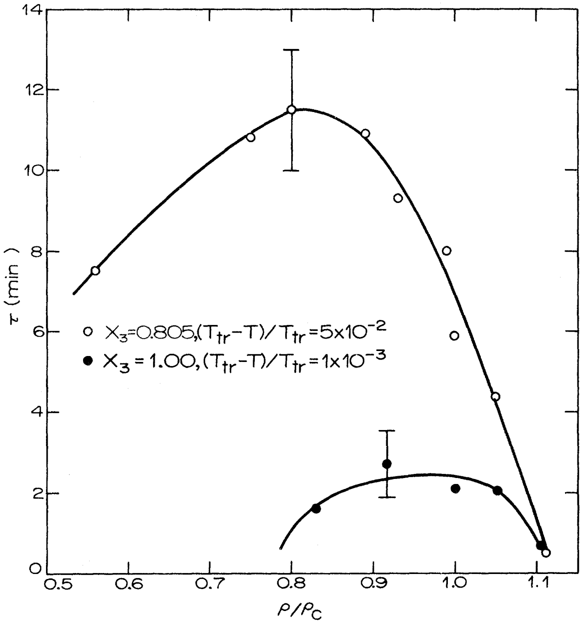

FIG. 1. Time τ to reach equilibrium in the two-phase region for the He^3-He^4 mixture $X=0.8$ and for pure He^3. The time τ is plotted as a function of the reduced density ρ/ρ_c and for constant reduced distances ϵ from the transition, $\epsilon=(T_{tr}-T)/T_{tr}$. A discussion of this figure is given in the text.

that mass transport between the liquid and gas phases takes place on a time scale large compared to that of thermal diffusion processes within either phase. We believe that this type of process is the source of the long relaxation times seen in the mixture. In this case, however, the mass transport processes are complicated by the presence of two isotopes, whose mole fractions are different in the two phases in equilibrium.[9] This complication probably explains our observation that the thermal equilibrium times in the mixture two-phase region are much longer than those of pure He^3 for a given distance $T_{tr}-T$ from the transition.

The magnitude of the thermal-equilibrium time is, of course, a function of density as well as temperature, and in a one-component system is found to be largest in the two-phase region at the critical density. From our observations this appears not to be the case in the mixture. Qualitatively, we observed the longest relaxation times (estimated to be of the order of 3–4 h) at densities approximately equal to the density at the temperature extremum of the phase separation curve, ρ_T, which is roughly 15% lower than ρ_c for $X=0.80$.[5(b)] Our density resolution is not quite accurate enough to make a firm distinction between ρ_T and ρ_P, the latter being the density at the pressure extremum of the phase-separation curve.[10] In Fig. 1 the time τ is shown at a representative reduced temperature $\epsilon\equiv(T_{tr}-T)/T_{tr}=5\times10^{-2}$ for the mixture $X=0.8$, and for pure He^3 at $(T_{tr}-T)/T_{tr}=1\times10^{-3}$. The choice of ϵ rather than $-t$ is justified by our observation that the relaxation time for a given isochore is better correlated with the distance $(T_{tr}-T)$ from the transition, rather than with T_c-T. It was not found possible to compare the τ for the mixture and for pure He^3 at the same ϵ, because of their vast difference in respective order of magnitude. For $\epsilon=5\times10^{-2}$, τ for He^3 is too small to be measured with our present techniques, while for $\epsilon=1\times10^{-3}$, τ for the $X=0.8$ mixture is too long to be estimated with a fair amount of accuracy. However, it is clear from Fig. 1 that the position of the maximum on the reduced density scale is markedly different. The possible significance of the maximum relaxation time being at ρ_T (or ρ_P) rather than ρ_c is unclear to us. We should point out that this does not necessarily involve any contradiction with the known behavior of the thermal diffusivity in the one-component system, since in that case ρ_c, ρ_P, and ρ_T are all identical.

Since it was impractical for us to attempt to wait longer than about 30 min for equilibrium to be established after the administration of a heat pulse to the sample, we were severely limited in our attempt to record accurate values of ρC_{vx} in the two-phase region near the transition. This practical limit of 30-min waiting time was always attained at temperatures such that $\epsilon\equiv(T_{tr}-T)/T_{tr}\approx10^{-2}$. For data in the region $0<\epsilon<10^{-2}$, we cannot guarantee that our measured specific heats were recorded under equilibrium conditions.

When equilibrium is not attained between measurements, the recorded values of ρC_{vx} will tend to be systematically lower than the true value. This is because of a small positive difference between the temperature of the copper calorimeter and the mean temperature of the enclosed fluid sample at the time when the "final" temperature is recorded, prior to another heat pulse. The possible error should be small ($\lesssim1\%$ of ρC_{vx}) for any one data point, but may accumulate as the temperature continues to be raised while remaining in the two-phase region. This accumulated systematic error in ρC_{vx} is counter balanced in the temperature interval of the data point spanning the transition temperature, since at T_{tr} the relaxation time drops by orders of magnitude, and a temperature difference between the walls of the calorimeter and the fluid sample can no longer be supported. Thus, except for the point spanning T_{tr}, this source of error does not affect our data in the one-phase region.

As the temperature of the samples is raised through the transition, a sharp decrease is noted in ρC_{vx} as well as in the thermal relaxation time. These two effects appear to be coincident in temperature and are taken as a direct measurement of $T_{tr}(\rho, X)$. The temperature interval in which these effects are seen varies from less than 0.5 mK for densities close to ρ_c to approximately 4.0 mK for the isochores with the largest and smallest densities. This broadening of the transition with increasing $|\rho - \rho_c|$ is also observed in the pure He^3 system.[7]

The extremely long thermal-equilibrium times seen near the transition in the two-phase region suggest that metastable super-cooled vapor states of the system might be observable in this region. To test this conjecture we performed several cooling runs through the transition on one of the isochores near the temperature extremum of the two-phase boundary; this is for $\rho < \rho_c$. During the cooling runs only the transition temperature was measured, and no attempt was made to record accurate values of ρC_{vx}. We find the measured transition temperature to be identical from both heating and cooling runs. Consequently, we have no evidence of any metastable states in this system.

D. Assignment of X and ρ

Although the measured $T_{tr}(X, \rho)$ indicate that all of our isochores have a mole fraction close to the nominal value of $X = 0.80$ for the mixture at room temperature before entering the cryostat, we would like to determine a precise assignment of X to each of the isochores. Given this knowledge of X, the density of each isochore could be determined with good precision, and a quantitative analysis of all our data would follow.

In principle, X and ρ for each isochore can be simultaneously determined from a knowledge of the equation of state and the measured values of the transition temperature, filling temperature, and filling pressure. Unfortunately, the available P-V-T-X data[5] are not extensive enough to allow this procedure to be done in an entirely satisfactory manner, although an indication of the possible range in X values for our data can be found. Independent estimations of this range can also be made by an examination of the scatter in ρC_{vx} values between different isochores at a constant temperature, and by the difference seen in $T_{tr}(\rho, X)$ for isochores with (nominally) nearly the same density.

By these criteria we estimate that all of our isochores have mole fractions within the range $X = 0.805 \pm 0.005$. Within this range in X, the assignment of density to any particular isochore is uncertain by approximately $\pm(2-5)\%$, depending on how close it may be to $\rho_c(X)$. In the discussion below we distinguish the isochores by numerical values of the label "ρ/ρ_c" and the numbers in question are uncertain by a few percent.

III. RESULTS AND DISCUSSION

Before we present the results, we comment briefly on the phase diagram in He^3-He^4 mixtures. This diagram, both in the ρ-P and P-T planes for a given mixture X, has been presented and discussed by WM.[5] We also refer the reader to the monograph by Rowlinson,[4] where phase diagrams of mixtures are discussed in their various thermodynamic aspects.

There are some rather striking changes in the diagram as one adds another component to a pure fluid. One of them is that in the two-phase region the isotherms in the ρ-P plane are no longer vertical. The boundary of the two-phase region for constant X does not therefore represent the coexistence curve in the sense it is understood for a pure fluid. The critical point is no longer at the extremum of the two-phase region in either ρ-P or ρ-T planes, but for He^3-He^4 it shifts gradually to a higher density as the composition tends to $X = \frac{1}{2}$. Unlike for a pure fluid, the slope of the isotherms in the one-phase region in the ρ-P plane does not appear to become infinite as the critical point is approached. Hence there is no experimental observation that k_{TX} diverges strongly along the critical isochore.

A. Relations between Isochores

In Fig. 2 we present a linear plot of our specific-heat data as a function of temperature for four of the isochores. The others have been omitted for the sake of clarity. The curve with the highest peak value of ρC_{vx} has been designated the "critical" isochore, and the other with a slightly higher transition temperature we believe to have a density close to ρ_T. The latter isochore was one exhibiting very long relaxation times in the two-phase region. For this reason we believe that the peak value of ρC_{vx} for data taken at true equilibrium would be higher than is indicated for this isochore in Fig. 2. Except for the well-established fact that the critical temperature for the mixture is lower than the extreme transition temperature, Fig. 2 is very similar in appearance to the corresponding plot of ρC_v vs T for the pure He^3 system.

This similarity with the specific-heat data in pure He^3 is made more explicit in Figs. 3 and 4, where ρC_{vx} as a function of density at constant temperature is compared for the two cases. The particular temperatures given in the figure are chosen in order that isotherms with approximately the same reduced temperature difference $t = [T - T_c(X)]/T_c(X)$ are compared. [As found in previous experimental work, $T_c(X = 1.00) \approx 3.31$ K; see Refs. 5 and 7 and references cited therein.] For the mixture isotherms, we have indicated by heavy

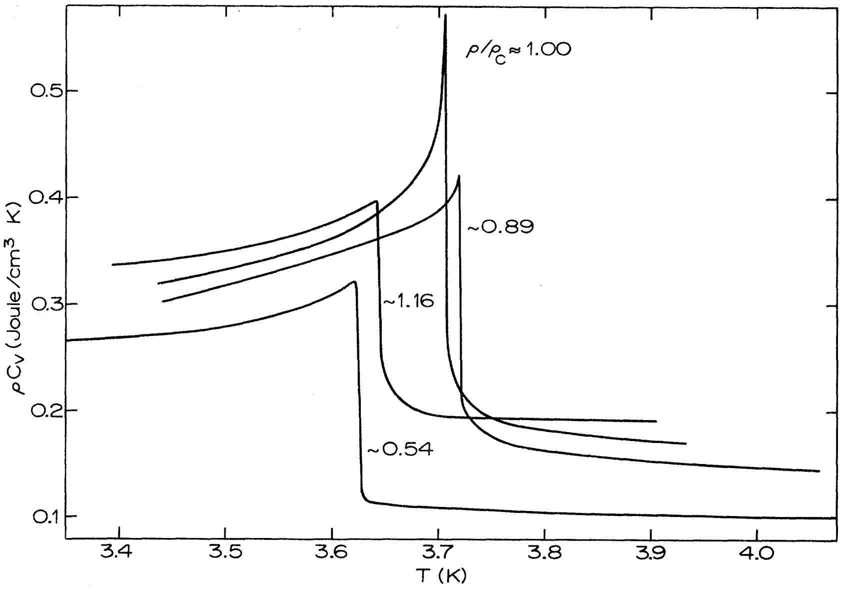

FIG. 2. Variation of ρC_{vx} with T for four representative isochores near the critical point. The numerical value associated with each isochore is its approximate reduced density ρ/ρ_c. Note that the maximum transition temperature occurs for an isochore with a density lower than the critical density. Aside from this feature, the figure is very similar to the analogous one for pure He^3.

curves the smooth behavior we believe to be appropriate to isotherms at a constant average mole fraction $X \approx 0.805$. We expect the scatter of our data from these smooth curves is due to slight differences in the mole fraction for the various isochores. This scatter increases near T_c, since the uncertainties in X and ρ become more important as the critical point is approached.

In Fig. 3 we present isotherms in the one-phase region. The purpose of this figure is simply to indicate the qualitative similarity in ρC_{vx} for $X = 0.805$ and $X = 1.00$ in this region. This same similarity also exists in the two-phase region, Fig. 4, where we point out in particular the fact that the mixture isotherms are parallel straight lines within experimental error.

This is a remarkable result in the two-phase region, for the following reason. For a pure fluid, the specific heat is given by the well-known expression

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

where μ is the chemical potential. In the two-phase region, the path in Gibbs space followed by the system is completely determined by the coexistence surface. Thus here the partial derivatives in Eq. (1) become total derivatives, and a plot of $(\rho C_v)_T$ vs ρ should be linear, with slope $= -T(d^2\mu/dT^2)$ and intercept $= T(d^2P/dT^2)$. Experimentally, the isotherms are also seen to be parallel, indicating that $-T(d^2\mu/dT^2)$ is practically a constant throughout the two-phase region.

For our two-component system, the analog to Eq. (1) is

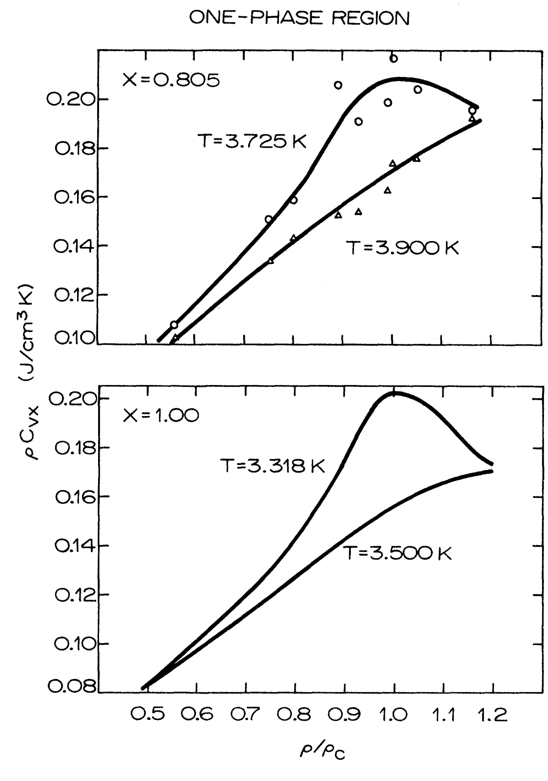

FIG. 3. Comparison of ρC_{vx} along isotherms between the 80% mixture and pure He^3 ($X = 1.00$), in the one-phase region. The curves for $X = 1.00$ are taken from Ref. 7. The smooth bold curves drawn through the mixture data are the authors' interpretation of the behavior appropriate to a constant average mole fraction $X \approx 0.805$. The authors believe the scatter of the data to be due to slight differences in the mole fraction for the various isochores (see text).

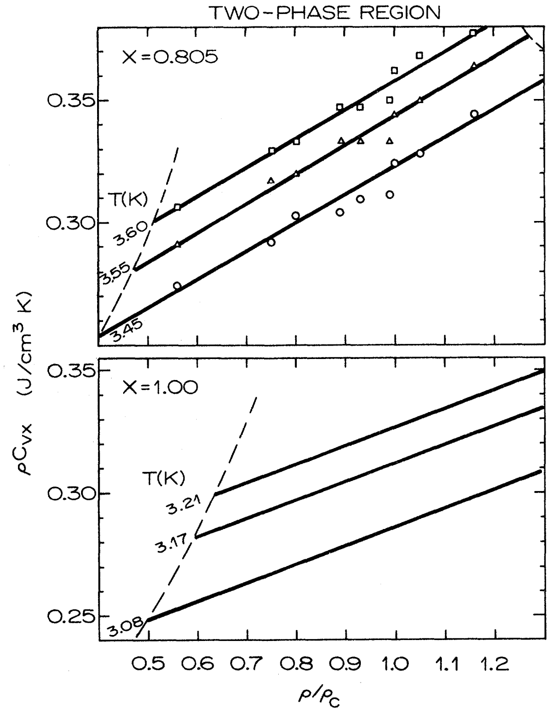

FIG. 4. Comparison of ρC_{vx} along isotherms for $X=0.805$ and $X=1.00$ in the two-phase region. The curves for pure He^3 are taken from Ref. 7. The solid heavy lines have the same meaning as the bold curves in Fig. 2. The dashed curves are the projection of the boundary of the two-phase region. Not shown are isotherms closer to T_c, where the parallel straight lines drawn for the mixture are still consistent with the data but the scatter is much greater due to the very long relaxation times in this region.

$$\rho C_{vx} = -\rho T\left[X\left(\frac{\partial^2\mu_3}{\partial T^2}\right)_{\rho,x} + (1-X)\left(\frac{\partial^2\mu_4}{\partial T^2}\right)_{\rho,x}\right] + T\left(\frac{\partial^2 P}{\partial T^2}\right)_{\rho,x}, \quad (2)$$

where μ_3 and μ_4 are the respective molar chemical potentials of the He^3 and He^4 species. Equation (2) has been given by Barieau,[11] and applied to the He^3-He^4 superfluid-normal-liquid phase separation by Alvesalo *et al.*[12] The partial derivatives in Eq. (2) become independent of ρ and X only when three phases coexist in the system (from the Gibbs phase rule), and thus they can be expected in general to depend on ρ and X in the two-phase region of the gas-liquid transition.

The parallel straight lines given by the isotherms in Fig. 4 indicate that the quantity

$$\mathcal{R} = -T\left[X\left(\frac{\partial^2\mu_3}{\partial T^2}\right)_{\rho,x} + (1-X)\left(\frac{\partial^2\mu_4}{\partial T^2}\right)_{\rho,x}\right]$$

depends only weakly on both the density and temperature. At least this appears to be true within the temperature range in which we have determined the isotherm slopes. Thus to a good approximation, $\mathcal{R} = \mathcal{R}(X)$ in the two-phase region, and at constant mole fraction, $\mathcal{R}$ behaves in the same way as does $-T(d^2\mu/dT^2) = \mathcal{R}(X=0 \text{ or } 1)$ for the pure fluid in a comparable range of t. Measurement of the isotherm slopes in Fig. 3 give $\mathcal{R}(X=0.805) = 3.1 \pm 0.3$ in reduced units of P_cV_c/T_c. (These units are weakly dependent on X.) This value is approximately 20% larger than is found by linear interpolation between the values for the pure substances, respectively, $-T\, d^2\mu/dT^2 = 2.2 \pm 0.2$ for[7] He^3 and 3.5 ± 0.4 for[2,13–15] He^4.

The long relaxation times encountered during the experiment preclude an accurate determination from our data of the jump in the specific heat at the transition, $\delta(\rho C_{vx})$, as a function of ρ and T. We can state, however, that $\delta(\rho C_{vx})$ in the solution is not very different from that for pure He^3.

B. Critical Isochore

Although we cannot guarantee that any of the isochores we have investigated in this system is at precisely the critical density $\rho_c(X)$, we believe at least four of the nine isochores are "close" to the critical one. We have designated the one with the highest recorded values of ρC_{vx} as the critical one, and present in this section an analysis of its temperature behavior near the transition.

Our data on the critical isochore are exhibited in a plot of $\log_{10}\rho_c(X)C_{vx}$ versus $\log_{10}|t|$ in Fig. 5, where we also show the behavior for pure He^3 as taken from Ref. 7. This figure strongly suggests that over the region $10^{-4} \leq |t| \leq 10^{-2}$, $\rho(X)C_{vx}$ for the 80% mixture behaves as if there were a weak divergence at $T_c(X)$, and we proceed with an analysis in terms of the expression

$$\rho_c C_{vx} = A^{\pm}|t|^{-\alpha^{\pm}} + B^{\pm}. \quad (3)$$

Here $A^{\pm}$ and $B^{\pm}$ are constants, the ± superscript referring to temperatures below (−) or above (+) T_c. This equation was shown to be appropriate to the pure He^3 fluid, where the exponent $\alpha^{\pm}$ is positive and $\alpha^{+} \approx \alpha^{-} = 0.105 \pm 0.015$.

The ρC_{vx} data in the two-phase region are rather sparse for such an analysis and in addition might be slightly systematically lower than the true specific heat on account of the long relaxation times. Still, even this lower bound on ρC_{vx} appears to diverge weakly. The reduced precision is the reason why we restrict our attention to the one-phase region, dispense with the ± symbol, and arbitrarily choose the range $10^{-4} \leq t \leq 10^{-2}$ for our fitting procedure. The exponents α and $T_c(X)$ are made free parameters in our fit to Eq. (3). For negative values of α [in which case Eq. (3) expresses a finite cusp at $t=0$] the least-squares fit of the data to Eq.

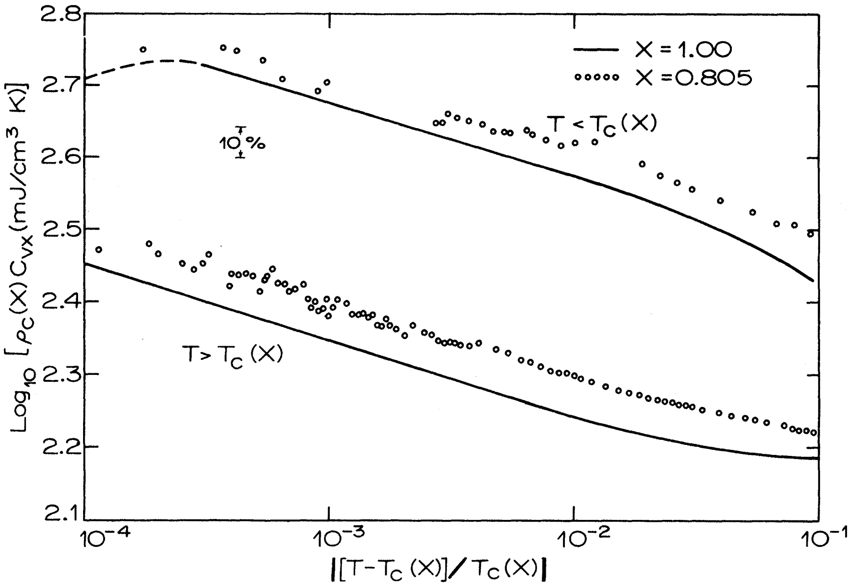

FIG. 5. Comparison of the specific heat along the critical isochore between the 80% mixture and pure He^3. The pure He^3 curves are taken from Ref. 7. The data for $X = 0.805$ in the two-phase region $[T < T_c(X)]$ might be affected by long relaxation times for $|[T - T_c(X)]/T_c(X)| < 10^{-2}$. The long relaxation times tend to make the observed ρC_{vx} smaller than the true value. The dashed curve indicates the effect of long equilibrium times in a much smaller region in the pure He^3 system (Ref. 7).

(3) did not converge to finite values of A and B. For $\alpha > 0$, a shallow minimum was found in the mean-square deviation of the fit, with the nominal best-fit values $\alpha = 0.1$, $T_c = 3.7072$ K, $A = 0.11$ J/cm K, and $B = 0.00$. The transition temperature chosen by the fit was always in good agreement with our direct determination of $T_{tr} = 3.7071 \pm 0.0003$ K for this isochore. However, the other parameters were poorly determined; fits lying within one standard deviation of the "best fit" were found with parameter values within the ranges $0.01 \leq \alpha \leq 0.2$, $0.03 \leq A \leq 0.4$ J/cm K, and $-0.3 \lesssim B \lesssim 0.1$ J/cm K.

The nominal best-fit value $B = 0$ is suggestive of the case of pure He^3, where as reported earlier[7] this constant term is found to be indistinguishable from zero. If we then enforce $B = 0$ as a constraint on our fit to Eq. (3), a satisfactory convergence is found to the values $\alpha = 0.09 \pm 0.02$, $A = 0.12 \pm 0.02$ J/cm K, and $T_c = 3.7073 \pm 0.0003$ K. This additional constraint increases the mean-square deviation of the fit by about two standard deviations.

Our fitting procedure thus confirms the apparent weak divergence and is in remarkably good agreement with the result for the pure He^3 system. From the results over the range $10^{-4} < |t| < 10^{-2}$ there is hence no evidence that C_{vx} tends to a finite value. This conclusion is qualitatively unaltered if we choose any of the other isochores that are apparently "close to the critical" one. This is shown in Fig. 6 where the data in the one-phase region of these four isochores are compared. This figure suggests that a weakly divergent behavior in the mixture may be found over a fairly extended range of densities near $T_c(X)$.

Before proceeding to a discussion of the results in terms of the theoretical predictions, we find it useful to make some remarks concerning the region about the critical point within which various asymptotic forms of thermodynamic functions can be expected to apply. We will also refer to the results of related experiments.

In pure substances, certain thermodynamic functions near critical points are assumed to have the form of a sum of a singular term plus nonsingular terms, the latter contributing a smooth background. The critical exponents are defined for the singular part, and the experimental determination of the exponent requires measurement of the quantity in question within some region (the "asymptotic region") about the critical point in which the singular term is the dominant contribution to the total. Thus one may define a "crossover temperature," t^p_{cross} (p for pure substance), such that for $|t| < |t^p_{\mathrm{cross}}|$ the asymptotic behavior of the singular term is apparent experimentally, while for $|t| > |t^p_{\mathrm{cross}}|$, nonsingular background terms become more significant. This crossover temperature is usually of the order of 10^{-1}–10^{-2}, and present day experiments often resolve two or more decades in t within the asymptotic region of pure substances.

Fisher[16] has shown that with the addition of an impurity concentration, assumed small, into the previously pure system, a second crossover temperature, t^x_{cross}, enters the description. For $|t| < |t^x_{\mathrm{cross}}|$, Fisher's theory indicates that the critical exponents are "renormalized" to new values. For $|t^x_{\mathrm{cross}}| < |t| < |t^p_{\mathrm{cross}}|$, the observable behavior may be characterized by power laws with exponents predicted by this theory to have the same values as the critical exponents of the pure

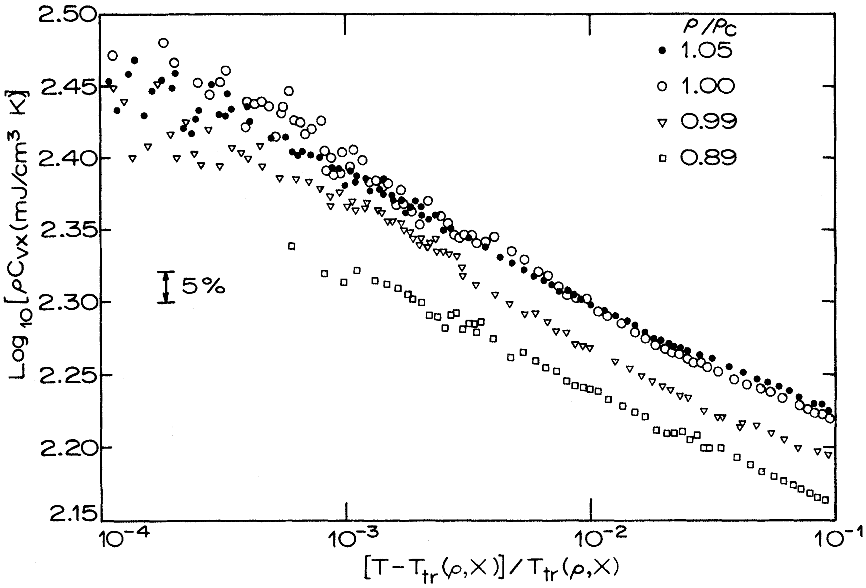

FIG. 6. Comparison of the specific heat in the one-phase region between four isochores in the "critical region." The apparently divergent behavior is very similar for all of these isochores. Here, $T_{tr}(\rho, X)$ is the transition temperature, which is slightly different for each of the isochores.

system. Furthermore, t^{x}_{cross} should increase with increasing impurity concentration. This type of behavior is qualitatively seen in the C_{Px} data of Gasparini and Moldover[17] and Alvesalo *et al.*[12] for a He^3-He^4 mixture undergoing the superfluid transition. There C_{Px} shows very clearly a different asymptotic behavior from that of the pure fluid, even for an impurity concentration as low as 10%.[17] This is in contrast to the behavior of C_{vx} at the liquid-gas transition, as described in the present paper.

An experiment closely related to this one is the measurement of the compressibility k_{Tx} for He^3-He^4 mixtures in the one-phase region near the liquid-gas transition.[5] Although the asymptotic behavior has not been determined for $t < 10^{-3}$, k_{Tx} appears to be either finite or at most weakly divergent at $T_c(X)$. The behavior of k_{Tx} is clearly different from that of the pure fluid (where k_T diverges strongly with the exponent $\gamma \approx 1.2$) for $t \lesssim 10^{-2}$, which is roughly the same figure as t^{p}_{cross}.

The qualitative aspects of the observed behavior of both C_{vx} and k_{Tx} in the liquid-gas system may be explained theoretically from either of two viewpoints, described below.

Griffiths and Wheeler[3] consider the geometrical behavior of "coexistence" and "critical" surfaces in the field space P-T-Δ, where $\Delta = \mu_3 - \mu_4$. Their postulates lead to the following theoretical predictions for a binary mixture at the critical point. For the general case where there is no special relationship between the axes of the P-T-Δ field space and the coexistence surface along the critical line, C_{vx} is finite and k_{Tx} diverges weakly. An exceptional situation takes place when T_c passes through an extremum as a function of X (and hence of Δ) at some point r on the critical line. Then the critical line $T_c(\Delta)$ at r will be parallel to the P-Δ plane in the field space. The postulates then predict that C_{vx} will diverge weakly and k_{Tx} will be finite upon approaching r. No evidence of such an extremum in T_c exists in the P-V-T-X data of Ref. 5. However, in an intermediate situation, where the variation rate of T_c with Δ is very slow, but without necessarily showing an extremum in T_c, the authors carefully point out that while their "theory predicts in principle a finite value for C_{vx} (and a divergence for k_{Tx}) in practice the situation may resemble that in which T_c passes through an extremum." They also point out that "the difference between a weak divergence and a sharp cusp may be extremely difficult to observe in practice." This difficulty in liquid-gas transitions is of course compounded by gravity effects[18] and the long relaxation times we mentioned before.

In light of the Griffiths-Wheeler postulates, and in view of the experimental results that tend to favor a weakly divergent behavior of C_{vx} and perhaps a finite k_{Tx} (at least for $t > 10^{-4}$), we are led to believe that the variation of T_c with Δ must be very slow indeed, at least for $X = 0.8$. One might expect that at $X = 0.5$ the slope $dT_c/d\Delta$ will be somewhat larger so that a cusped behavior for C_{vx} might become more evident. However, the k_{Tx} data at $X = 0.6$ and 0.4, imperfect as they are, do not seem to indicate a more divergent trend than for $X = 0.8$. Hence, conversely, we feel that the cusped behavior for C_{vx} will be difficult to see, even at $X = 0.5$. Additional support for this is given below.

Speaking strictly in terms of the field-space picture, we can illustrate the different behavior of

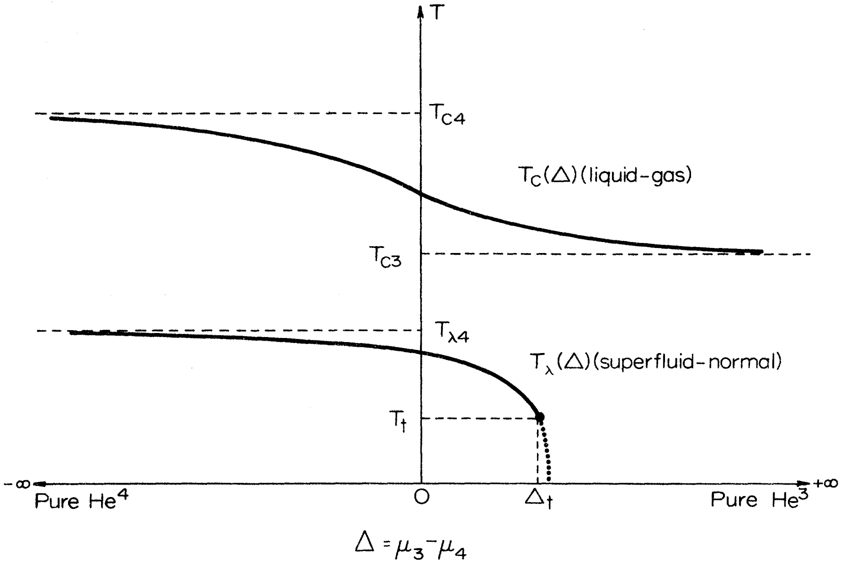

FIG. 7. Schematic diagram of projections of the liquid-gas critical line and the λ line in the T-Δ plane. The point at (Δ_t, T_t) is the tricritical point.

He^3-He^4 mixtures at the liquid-gas transition and at the λ line (under saturated vapor conditions), respectively. Figure 7 shows a schematic projection of the critical line on the T-Δ plane. For the liquid-gas transition, where $T_c(X)$ varies monotonically between the T_c of the pure components, only a small slope $dT_c/d\Delta$ is expected. For the λ line, which terminates at the tricritical point T_t, $dT_\lambda/d\Delta$ becomes progressively larger as T_t is approached.[19] It is clear that the cusped nature of C_{vx} must become progressively more evident along this path. This is evidenced by the recent results of Alvesalo *et al.*[12]

The alternative explanation is given by preliminary results of calculations by Leung and Griffiths[20] for the He^3-He^4 mixture system near the liquid-gas critical point. These authors find that the behavior of the product of C_{vx} and k_{Tx} is weakly divergent everywhere in the neighborhood of the critical point, except for X approaching 0 or 1, in agreement with Griffiths and Wheeler. They find, however, that the behavior of C_{vx} and k_{Tx}, considered individually, differs according to whether t is greater than or less than a crossover temperature t^x_{cross}. For $|t| > |t^x_{\text{cross}}|$ they find C_{vx} to be dominated by a weakly divergent term, and k_{Tx} by a term that tends to a finite value, in qualitative agreement with the available data. For $|t| < |t^x_{\text{cross}}|$, a cancellation of weakly divergent terms in C_{vx} leaves only a contribution which is finite at $T_c(X)$, while k_{Tx} becomes dominated by a weakly divergent term. Leung and Griffiths have calculated t^x_{cross} for the case $X = 0.5$, where t^x_{cross} is expected to be a maximum. They estimate in this case that t^x_{cross} is of the order 10^{-12}–10^{-15}. This small value is experimentally inaccessible, and thus leads to a qualitative explanation of the experimental observations.

We strongly suspect that the two explanations outlined above are in fact closely related. Comparison of the behavior of the specific heat near the superfluid and liquid-gas critical point for He^3-He^4 mixtures suggests that the larger the slope $d\Delta/dT$ of the critical line, the larger is t^x_{cross}. Thus, referring again to Fig. 7, the predicted asymptotic behavior of some thermodynamic quantities near the λ line can be more clearly observed near the λ line than near the liquid-gas critical line.

IV. CONCLUSIONS

We find that, generally speaking, the specific heat of the 80% He^3–20% He^4 mixture near its gas-liquid critical point is remarkably similar to that of the pure He^3 system. Within our experimental error and temperature resolution, the similarities may be enumerated as follows:

(i) Over the range $10^{-4} < |t|$, $\rho_c(X)C_{vx}$ appears to diverge as $T_c(X)$ is approached, and with an exponent nearly identical to that found in pure He^3.

(ii) Isotherms of ρC_{vx} have the same general shape as those of ρC_v for $X = 1.00$ (pure He^3).

(iii) As a consequence of (ii), the quantity

$$T\left[X\left(\frac{\partial^2\mu_3}{\partial T^2}\right)_{\rho,x} + (1-X)\left(\frac{\partial^2\mu_4}{\partial T^2}\right)_{\rho,x}\right]$$

in the two-phase region is, to a good approximation, independent of ρ and T at a constant X.

Since the critical density of the mixture is not at the extremum of the two-phase boundary in either the ρ-T or ρ-P projections, most contemporary techniques do not determine $\rho_c(X)$ with the same precision that is found in the pure substances. Our measurements suggest that this is somewhat compensated for by an increase in the relative size of the "critical region" in the mixture.

The apparent divergence of ρC_{vx} along the critical isochore is interpreted from the Griffiths-Wheeler theory as the result of a small slope $dT_c/d\Delta$ of the critical line in the field space P-T-Δ for mixtures. (Δ is the difference of the respective chemical potentials for the two components, $\Delta = \mu_3 - \mu_4$.) This must at this time remain a reasonable conjecture awaiting confirmation by experimental determination of the critical line in the P-T-Δ space. From a complementary viewpoint, the asymptotically finite behavior predicted by Griffiths and Wheeler may simply be experimentally inaccessible in this particular system, which is the implication of the calculation of Leung and Griffiths. We feel that these alternative explanations for the observed behavior are probably closely related and we have suggested a plausible connection. From either viewpoint it is clear that our results do not determine the *critical exponent* for C_{vx} in the mixture, since we must conclude that the *asymptotic* behavior is not observed in this experiment.

Thermal-equilibrium times in the one-phase region of the mixture were unobservably small in this experiment. Our observations of the thermal equilibrium times in the two-phase region indicate that relaxation takes a much longer time in this system than is the case in the one-component fluid. The relaxation time appears to have a maximum (in the two-phase region) at a density different from the critical density.

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