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Pressure-Density-Temperature Relations of He^3-He^4 Mixtures near the Liquid-Vapor Critical Point*

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Measurements of the density ρ versus pressure P along isotherms for six He^3-He^4 solutions ($X_3 = 0.960$, 0.886, 0.800, 0.600, 0.400, and 0.200) near their liquid-vapor critical point are presented. For a given mole fraction X_3, it was found that the boiling and dew curves in the ρ-P plane could be represented by a relation similar to that for the coexistence curve of a pure fluid. Here the point at the extremity of the two-phase region, which we call the symmetry point with the parameters P_s, ρ_s, and T_s, takes the place of the critical point for a pure fluid. The dew curve is given by $(\rho_s - \rho) \propto (P_s - P)^{\beta'}$ with $\beta' = 0.375 \pm 0.02$, independent of X_3. The determination of the line of critical points in the P-T plane from the dew and boiling curves at various mole fractions is described. The pressure, density, and temperature for the critical and the symmetry points are presented and discussed. From the dew and boiling curves, the true coexistence curves were constructed in the ρ-P plane at constant T and in the ρ-T plane at constant P and could be described approximately by $(\rho_L - \rho_G) \propto (P_c - P)^{\beta_T}$ and $(\rho_L - \rho_G) \propto (T - T_c)^{\beta_P}$ with an average value for the various isotherms and isobars considered of $\beta_T = 0.42 \pm 0.06$ and $\beta_P = 0.39 \pm 0.05$. Here ρ_L and ρ_G are the densities along the coexistence curve on the liquid and the gas side, respectively. The measurements of the compressibility $k_{T,X}$ along the critical isochore in the one-phase region seem to exclude a "strong" divergence with $(T - T_c)$, but do not extend close enough to T_c to either support or disprove the "weak" divergence as predicted by Griffiths and Wheeler. These measurements are compared with those of the normalized compressibility $(\rho/\rho_s)^2 k_{T,X}$ along the dew and boiling curves. Comparisons are also made with the behavior of the compressibility for a pure fluid along the coexistence curve and above T_c. A brief addendum to the analysis for k_T in pure He^3 is presented.

I. INTRODUCTION

Recently there has been a great deal of theoretical and experimental work done on static and dynamic properties of pure fluids in the neighborhood of their liquid-vapor critical point.[1] One of the important results has been the verification of scaling laws for the critical exponents (at any rate for the static properties) and the proposal of several equations describing the static properties close to the critical point using the scaling relations.[2] So far, no such precise predictions have been made for binary mixtures near their liquid-gas critical point, but very recently their qualitative behavior was predicted by Griffiths and Wheeler[3] from a unified geometrical point of view. Much experimental work has been done by chemical engineers to determine the mole fraction of the liquid and vapor phases of industrial binary mixtures.[4] The critical parameters P_c, V_c, and T_c, the pressure, volume, and temperature at the critical point, were however obtained by rather long extrapolations, and in practice no work has been done in the critical region that could be of use to theorists interested in the modern aspects of critical phenomena.

We have attempted to fill this gap by carrying out a systematic investigation of the P-V-T relations of He^3-He^4 solutions in their gas-liquid critical region. This system offers a number of advantages for such a study. First, one would expect such an isotopic mixture to be "well behaved" and not to show critical azeotropy. It could, therefore, serve as a model for solutions where the behavior is close to being ideal. Second, the pressures involved are only of the order of 2 atm. This simplifies the design of the apparatus and it permits the use of high resolution commercial quartz pressure gauges. Third, the atomic polarizabilities α of liquid He^3 and He^4 are almost identical[5,6] and one can expect this to be nearly true in the critical region. Furthermore, α for fluid He^3 is almost independent of density near T_c,[6] and we can assume this to hold for mixtures. This reasonable assumption then leads to the convenient use of the dielectric constant method for density measurements.

II. EXPERIMENTAL PROCEDURES AND ERRORS

A. Cryostat and Experimental Considerations

The cryostat and other experimental arrangements used in this work are generally the same as those in a previous paper by the same authors[7] except for the density cell which is shown in Fig. 1 and the capillary leading to this cell. Therefore, we will give here only a brief discussion of the experimental details, emphasizing the changes necessary in studying He^3-He^4 mixtures rather than pure

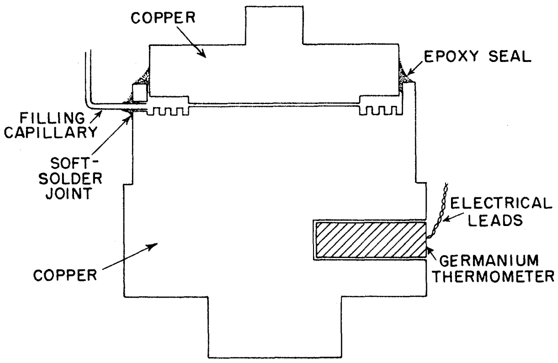

FIG. 1. Capacitor for measuring mixtures. Not shown are the copper wires which thermally anchor the filling capillary at the elbow to the 4.2 K bath. Horizontal temperature gradient is over a $1\frac{1}{2}$-in. length. The capacitor fits into the setting shown in Fig. 1 of Ref. 7.

He^3 and we refer the interested reader to the additional discussion of measuring techniques, errors, etc., given in Ref. 7.

The experiment consisted in measuring the molar volume of a sample of a He^3-He^4 mixture by means of a capacitive technique. The sample serves as the dielectric medium between the plates of a capacitor and the dielectric constant ϵ is determined by the Clausius-Mosotti relation

$$(\epsilon-1)/(\epsilon+2)=4\pi\mathcal{a}/3V\,, \tag{1}$$

where V is the molar volume and $\mathcal{a}$ is assumed to be constant and equal to 0.1234 cm^3/mole.[6] Although Kerr and Sherman[6] have shown that there is a small variation of $\mathcal{a}$ with density, the correction to the experimental data is less than 0.1% and comparable with the uncertainty of the experiment. For the analysis of properties near the critical temperature, the mass density $\rho=M/V$ (g/cm^3) or the particle density ρ/M (cm^{-3}) will be used instead of V. Here M is the molar mass of the mixture of composition X_3, where X_3 denotes the mole fraction of He^3.

It is well known[4] that for a mixture, the mole fractions of the components in the liquid and vapor phases in equilibrium are different, except at an azeotropic point. Since there was no convenient and reliable way to measure simultaneously the mole fractions for the two coexisting phases, it was decided to prepare gas mixtures of known composition and to determine the boiling- and dew-point curves for each composition.

For the P-ρ-T measurements, care must be taken to insure that the mole fraction X_3 of the fluid in the density cell is equal to the nominal one of the gas mixture at room temperature. Since, under equilibrium conditions, mole fraction gradients might be expected in the capillary leading to the cell, it is necessary to have the amount of helium in this capillary small in comparison with that in the cell.

B. Density Measuring System

The sample fill capillary was surrounded by a vacuum space over its entire length through the cryostat. The top portion was copper of 0.020-in. i.d., which was then soldered to a 0.012-in. i.d. stainless-steel capillary 15 cm above the top of the vacuum can that surrounded the density cell and its temperature control system (see Fig. 1 of Ref. 7). The only thermal anchor to the main 4.2 K He^4 bath was by copper wires soldered to the elbow of the filling capillary. There was evidence that the temperature of the capillary was above 6 K everywhere except between this elbow and the cell. This arrangement had the purpose of keeping the capillary at a relatively high temperature, thereby filling it with as little gas as possible. Assuming a reasonable temperature profile in the copper and stainless-steel capillary, it was calculated that near the critical point of He^3, the amount of helium filling the capillary was less than 3% of that in the cell.

The density cell, shown in Fig. 1, was a compromise between the desirability of having a large amount of fluid in order to control X_3 accurately, and having a small height to lessen gravitational effects. The four grooves insured that the sample was no more than 0.4 mm from a copper wall and hence thermal equilibrium was rapidly obtained at least in the one-phase region. The sample covered a height of 1.5 mm and the density was measured at approximately the midplane. The effective area between the plates was 1.2 cm^2 and the total sample volume amounted to about 0.25 cm^3. The cell was calibrated with pure He^3 as before[7] and the calbration was checked by measuring the density of He^4 at several temperatures along the coexistence curve. Excellent agreement within the combined experimental uncertainty was found with the previous data.[8]

The uncertainty in the *absolute* value of the density was estimated to be less than approximately 0.2% in the region of the critical density. This estimate is based on considerations of the long-term stability in the dielectric-constant measurement and on possible systematic uncertainties in the calibration as well as those due to the slight density dependence of $\mathcal{a}$. Because of the difficulties inherent in the experiment, a density at a given T and P could only be reproduced to about 0.01% in the course of an experiment lasting several days.

C. Pressure Measurement

The pressure of the sample was measured by a Texas Instruments fused-quartz Bourdon gauge that had a stated resolution of 0.025 Torr. This gauge is expected to have very closely a linear read-out in terms of pressure, and this was indeed observed over the range of calibration (400–1400 Torr) against a mercury manometer.

Just as in earlier work,[7] a calculation was made to estimate the difference δP between the pressure inside the cell at low temperature and between that measured at room temperature. Using the calculated temperature profile along the copper capillary, we obtained $(\delta P)/P \approx 3\times 10^{-4}$.

D. Thermometry

The temperature of the density cell was measured by means of a germanium resistor thermally bonded to it by Apiezon *J* Oil and electrically connected to a 200-Hz Wheatstone bridge which could resolve temperature changes of 5 μK at 3.5 K. The phase sensitive detector of the bridge was connected to a heater circuit making possible the temperature regulation of the density cell to within 20 μK for the various isotherms. The thermometer was calibrated by the T_{58} He^4 vapor-pressure table. Below 4 K, the vapor pressure of the He^4 in the pot above the cell (Fig. 1 of Ref. 7) was read on a combination of mercury and oil manometers, using a cathetometer. The reading uncertainty of ± 0.1 Torr corresponds to a temperature uncertainty of 0.3 mK at 3.3 K. Between 4 and 5 K, the vapor pressure of He^4 in the density cell along the critical isochore was used to calibrate the germanium resistance thermometer. The temperature-vs-resistance readings were then fitted by a least-squares procedure to the equation

$$\ln(T - C_3) = C_1 \ln R + C_2 , \qquad (2)$$

where C_3 was determined by iteration. The deviations between the experimental points and the fit were random, giving a mean-square temperature deviation of 0.3 mK. The accuracy of the so obtained calibration is estimated to be within 0.5 mK of the T_{58} scale for $T < 4$ K and within 2 mK for T close to 5 K. The larger uncertainty results from possible inaccuracies in the absolute calibration of the quartz Bourdon gauge.

E. Experimental Procedure

All the data were taken along isotherms and the amount of fluid in the cell was changed by means of a movable piston at room temperature. The time that elapsed between two data points was usually of the order of 15 min, with the last 5 min spent insuring that the pressure and the dielectric constant had reached their equilibrium values. The possible uncertainty of representative isotherms due to inhomogeneities of the solution throughout the pressure system was carefully investigated by taking successive series of measurements with increasing and decreasing pressure. It was found that in the one-phase region, excellent consistency and reproducibility were obtained for the density along the same isotherm. Very close to the two-phase region, however, some irreproducibilities between the data taken by increasing and decreasing P were found. After some experimenting, it was concluded that such effects were kept at a minimum if the isotherms were taken in steps of always increasing pressure. This is to be expected since by increasing the pressure, a mixture of well-known composition is forced into the cell. On the other hand, withdrawing fluid from the cell can lead to some preferred enrichment of one of the components inside the cell for temperatures very close to and below T_c.

To determine the dew curve, the gas was compressed isothermally until the first droplet of liquid was formed, which was evidenced by a break in the P-vs-ρ plot. When the cell was being filled with liquid, the disappearance of the last bubble of gas was shown by another break in the P-ρ plot. The locus of these points determined the boiling curve. The dew point for a given isotherm was found to be clearly defined and well reproducible, just as for a pure fluid. However, the boiling curve was increasingly irreproducible as T_c was approached. The region in temperature $T_c - T$ over which such irreproducibilities occured increased to a maximum for X_3 near 0.5. For $X_3 = 0.8$, this region extended over 50 mK.

To insure that measurements were always carried out at the nominal mole fraction, all the fluid was removed from the cell after taking data along an isotherm, and the gas was thoroughly remixed inside a Toepler pump.

III. RESULTS AND DISCUSSION

Density measurements along isotherms at constant mole fraction were taken for six mixtures, namely, $X_3 = 0.960$, 0.886, 0.800, 0.600, 0.400, and 0.200. The amount of data, including approximately 3000 readings, is too large to be presented in this paper. A list of most of the measured P-V-T points is available on request from the authors in the form of a technical report.[9] The number of isotherms taken ranged from 16 for $X_3 = 0.960$ to 33 for $X_3 = 0.886$. Very close to T_c, isotherms were taken every 2 mK, and then progressively further apart as $|T - T_c|$ was increased. For the isotherms greater than the critical one, the measurements were taken at density intervals of about $7\times 10^{-4}\,\mathrm{g/cm^3}$, but for $T < T_c$, the data points near the dew and boiling curves were much more closely spaced. The mixtures $X_3 = 0.886$ and 0.800 were studied first and by far the most extensively. After the properties of the "symmetry point," to be discussed in Sec. III A, were realized, only limited data on the boiling curves were taken for the remaining solutions, the main effort being concentrated on the dew curves and on the homogeneous region above T_c.

A. Symmetry Point (P_s, ρ_s, T_s)

The results for a few representative isotherms for $X_3 = 0.800$ are shown in Fig. 2. Two of the obvious differences between the boiling and dew curves at constant X shown here and the coexistence curve for a pure fluid are (i) the isotherms are not vertical in the mixed phase region, a well known property for solutions, and (ii) the critical point (CP) which marks the place where the liquid and gas densities become equal for each component does not occur at either the maximum pressure or maximum temperature of the two-phase region. The hatched areas connecting the ρ_L and ρ_G points are not tie lines, but binodals. The representation by hatched areas indicates that the shape of the binodals is somewhat uncertain and not necessarily a straight line. This is because of irreproducibility and drifts of the recorded density in the two-phase region—an experimental effect caused by the geometry of the cell. The phenomenon that an isotherm such as $T = 3.720$ K cuts the dew curve twice is known as retrograde condensation and has been discussed by Rowlinson,[4] for instance. The critical point cannot be determined from the measurements at one isolated isotopic composition, but is found from a graph that incorporates data from all other mixtures (see Sec. III B). It is obvious that as X_3 tends to unity or to zero, the critical point moves to the maximum pressure of the mixed-phase region. At the same time, the isotherms in this region become vertical.

For an arbitrary composition X it was found that the point at the extremity of the two-phase region, which we call the "symmetry point," could be used in several critical point-type relations similar to those for a pure fluid. The symmetry parameters (P_s, ρ_s, and T_s) could be determined rather precisely by several methods that were simply extensions of those used for pure fluids. In He^3 for instance, it was found[7] that the maximum of $M(\partial\rho/\partial\mu)_T = \rho^2 k_T$ occured at ρ_c for all isotherms with $T > T_c$. Here μ and k_T are, respectively, the chemical potential and the compressibility. For the mixtures, the same relationship for $\rho^2 k_{T,X}$ was found around the value ρ_s as is shown in Fig. 3. In pure He^3 the rectilinear diameter $\bar{\rho} = \frac{1}{2}(\rho_L + \rho_G)$ was found to be almost constant and equal to ρ_c at a given T and P. For the mixtures, it was found empirically

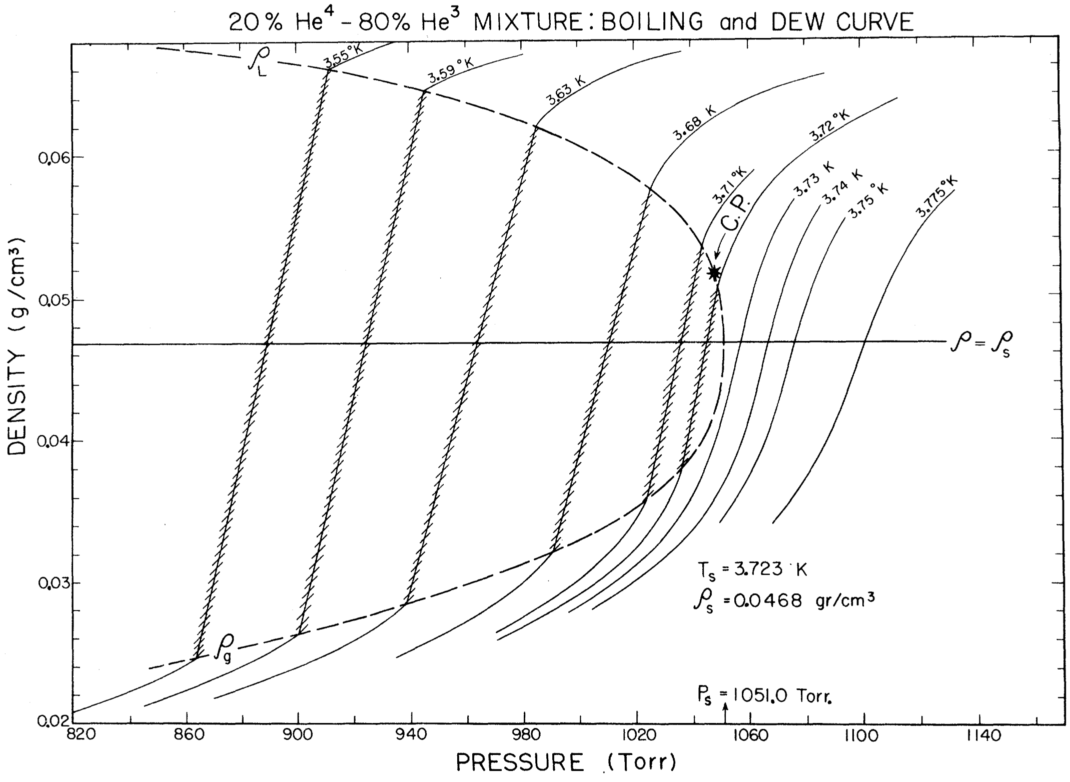

FIG. 2. Boiling and dew curve for $X_3 = 0.800$. Solid lines are part of the 33 isotherms taken. To avoid confusion, several isotherms near T_s have not been plotted. Lines connecting the ρ_L and ρ_G points are not tie-lines, but binodals. Because of some irreproducibility in these lines, they are hatched, and are not necessarily exactly straight.

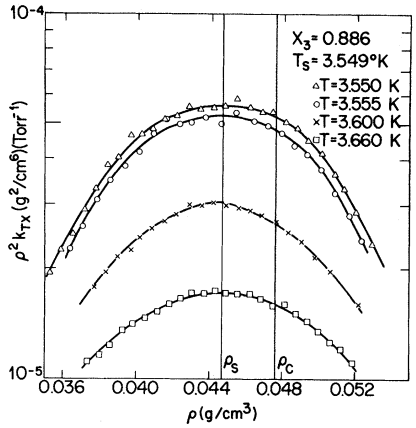

FIG. 3. Determination of symmetry density ρ_s. Values of $\rho^2 k_{T,X}$ vs ρ are plotted for four representative isotherms to show that this quantity has its maximum value at ρ_s, not at ρ_c.

that

$$\tfrac{1}{2}\left[\rho_L(P)+\rho_G(P)\right]=\rho_s+A\,(P_s-P)/P_s\cdots \qquad (X_3=\text{const}) \qquad (3)$$

from the lowest temperature 2 K up to the region close to T_c where irreproducibilities on the boiling curve became significant.

The parameter A that characterizes the effective slope of the "rectilinear diameter" in Eq. (3) was found to vary, with X_3 taking values intermediate between those observed for the pure fluids. From recent work,[7–11] A is $\approx -3\times10^{-4}$ g/cm^3 for He^3, while for He^4, $A\approx 1\times10^{-3}$ g/cm^3. For the helium isotopes the slope A is unusually small compared with other fluids.

For pure He^3 and He^4, the coexistence curve near T_c is given by

$$\Delta\rho=B\,(-t)^{\beta}\,, \qquad (4)$$

where $\Delta\rho=(\rho-\rho_c)/\rho_c$ and $t=(T-T_c)/T_c$. Since close to T_c one has

$$T_c-T=\left(\frac{\partial T}{\partial P}\right)_{\rho_c}(P_c-P)+\cdots\,, \qquad (5)$$

one can rewrite Eq. (4) in the limit $|P-P_c|\to 0$ as

$$\Delta\rho\propto(-\Delta P)^{\beta}\,, \qquad (6)$$

where $\Delta P=(P-P_c)/P_c$. Over a larger range of ΔP, where the higher-order terms in Eq. (5) become important, one expects the same relation, but with an "effective" index β' not very different from β. Such a plot is shown in Fig. 4. This representation of the data is extended to the mixtures, where, however, ρ_s and P_s are substituted for ρ_c and P_c and this is also shown in Fig. 4. Note that only the dew-curve data are being used for this analysis, and no assumption of symmetry of the two-phase region around ρ_s is being made. It can be seen that all the data seem to scale, the effective slope of the lines for all compositions being $\beta'=0.375$. As stated before, however, the limiting slope for $(T_s-T)\to 0$ must tend to β for the pure fluids. The index β' for the mixtures is obviously in good agreement with that for pure fluids, and this is also found to be true for the three solutions not presented in Fig. 4. It is found that ρ_s as determined from the fit to Eq. (6) is the same as that from the other two determinations to within an experimental error of 0.5%. The P_s value chosen is that giving the best fit to Eq. (6) and, finally, the T_s value is that corresponding to ρ_s and P_s.

Table I shows the results for the "symmetry parameters" for the mixtures, along with the values[10] for pure He^3 and He^4 where these parameters are identical with the critical ones. Within the 0.5% uncertainty in its determination, $\rho_s(X)$ was found to agree with the linear interpolation formula $\rho_{\text{lin}}=X_3\rho_c(\text{He}^3)+(1-X_3)\,\rho_c(\text{He}^4)$.

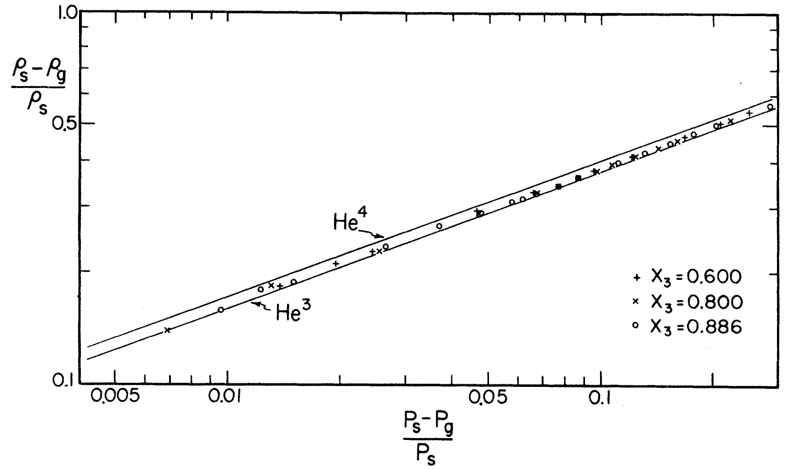

FIG. 4. Dew-point curve in He^3–He^4 mixtures. To avoid overcrowding, we have not shown the data for $X_3=0.960$, 0.400, and 0.200, which also lie between the pure He^3 and pure He^4 curves. Slope is the index β' as defined in Eq. (6).

TABLE I. Critical and symmetry parameters for He^3-He^4 mixtures.

X_3	P_c(Torr)	T_c(K)	V_c(cm^3/mole)	P_cV_c/RT_c
1.000	860	3.310	72.87	0.304
0.960	898.5	3.393	68.84	0.292
0.886	968	3.545	65.74	0.288
0.800	1049.5	3.717	63.65	0.288
0.600	1229	4.100	59.75	0.287
0.400	1406	4.487	57.65	0.290
0.200	1558.5	4.837	56.64	0.293
0.000	1708	5.193	57.78	0.305
X_3	P_s(Torr)	T_s(K)	V_s(cm^3/mole)	P_sV_s/RT_s
1.000	860	3.310	72.87	0.304
0.960	899	3.395	71.74	0.305
0.886	969	3.549	70.32	0.308
0.800	1051	3.723	68.68	0.311
0.600	1231.5	4.109	65.23	0.313
0.400	1408	4.495	62.17	0.312
0.200	1559.5	4.841	59.71	0.308
0.000	1708	5.193	57.78	0.305

B. Critical Parameters P_c, ρ_c, T_c

The thermodynamic conditions that define the critical point in a mixture, $\partial g/\partial X_3 = \partial^2 g/\partial X_3^2 = 0$ and $\partial^3 g/\partial X_3^3 > 0$, where g is the molar Gibbs function, have been derived in a number of textbooks (see for instance, Ref. 4) but are not straightforward to apply. Therefore, it was decided to determine the critical parameters by a graphical technique such as pictured in Ref. 4, p. 194. The first step is to construct large graphs for all the mixtures similar to Fig. 2, and which include all of the isotherms taken. We then make the assumption that if the boiling and dew curves are symmetric about ρ_s over a large temperature range (see Sec. III A), they continue to be so all the way to the symmetry point, except possibly for a small region around the critical point. Hence, missing parts of the boiling curve that were not well located because of experimental difficulties can be constructed from the dew curve. This method is only intended as a first approximation to locate T_c. Then, interpolating temperatures in 0.1 K steps far away from T_s and in 2 mK steps close to T_s, the P, T values necessary to construct accurately Fig. 5 for the six mixtures are obtained. The line of critical points is then just the envelope of these curves. The results of this interpolation may also be used to construct Figs. 6 and 7 which show a succession of constant-T and constant-P planes, respectively, together with the relevant critical line.[11] This line is determined by $(dP/dX)_{T,\text{coex curve}} = 0$ and $(dT/dX)_{P,\text{coex curve}} = 0$ for each composition.[4]

From Fig. 5, the P_c and T_c values for a given X are determined. Finally, using them together with the boiling curve, the value of ρ_c is obtained, and the results are given in Table I. We note that the ratio $P_c V_c/RT_c$ only changes by a few percent as

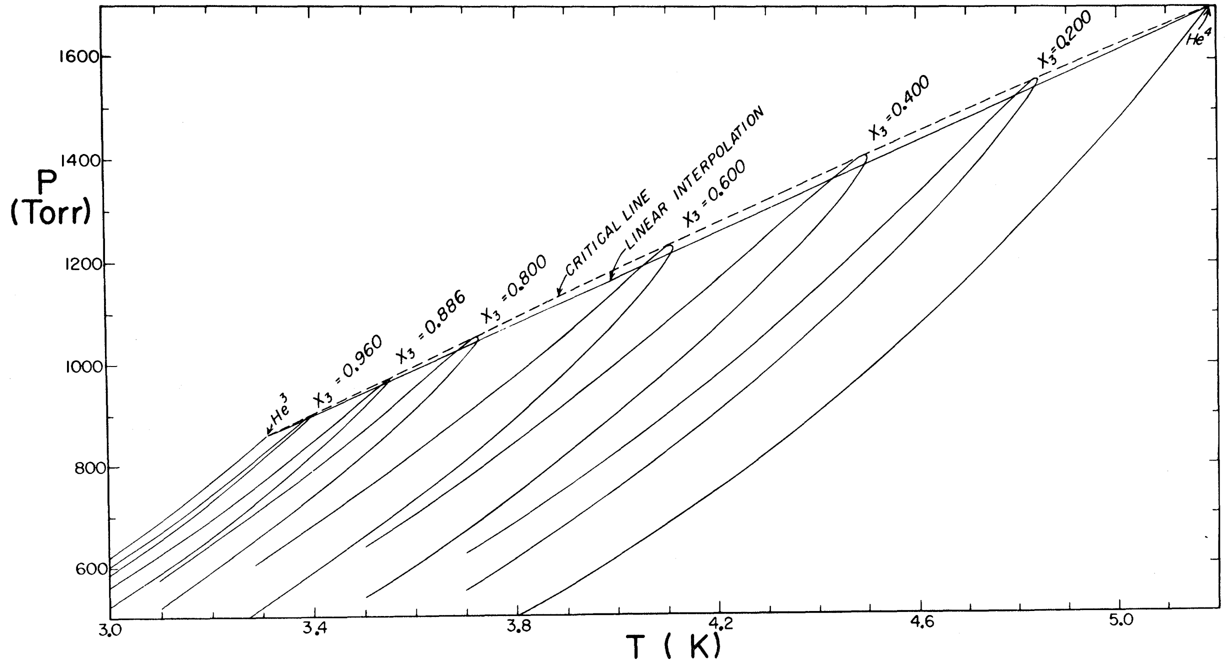

FIG. 5. P vs T for He^3-He^4 mixtures. These loops were interpolated from the six large graphs similar to Fig. 2 as discussed in the text. Critical line is the envelope of the tangent points.

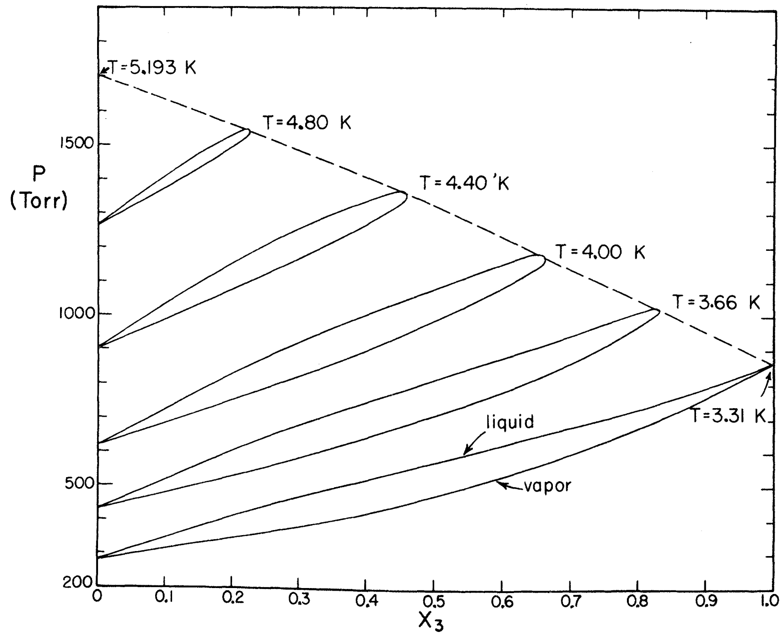

FIG. 6. Phase diagram for constant-temperature projections. Critical line intersects the P-X loops at the maximum pressure as given by the equation $(dP/dX)_{T,\,\text{coex curve}}=0$.

a function of X_3. For mixtures such as Ar-N_2 [12] and CH_4-N_2, [13] this ratio can change by the order of 50%. In Figs. 8 and 9, the departure from a linear interpolation for the critical and symmetry parameters is shown as a function of X_3. A review of theories that calculate this departure from a linear interpolation for solutions has been presented by Prigogine. [14] These theories apply to solutions where the critical parameters of the pure components are almost the same, and cannot apparently be used for He^3-He^4 solutions, where the ratios for the critical pressures, temperatures and volumes are very different from unity.

C. Isothermal Compressibility k_{TX}

Griffiths and Wheeler[3] have predicted the diver-

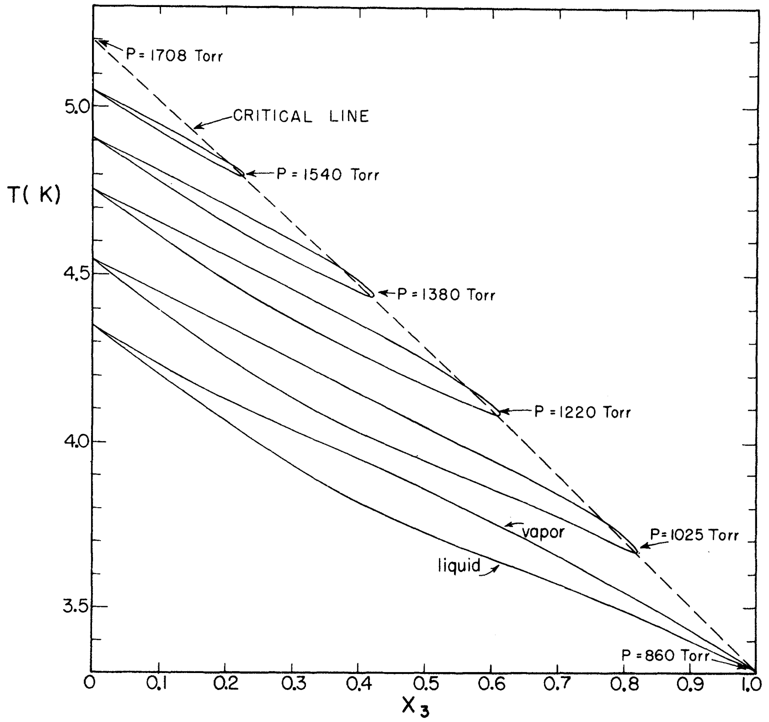

FIG. 7. Phase diagram for constant-pressure projections. Critical line intersects the T-X loops at the minimum temperature as given by the equation $(dT/dX)_{P,\,\text{coex curve}}=0$.

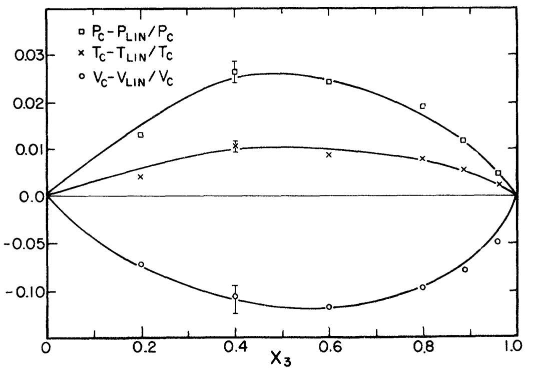

FIG. 8. Deviation of the critical parameters from a linear interpolation between the pure He^3 and pure He^4 values given in Ref. 10.

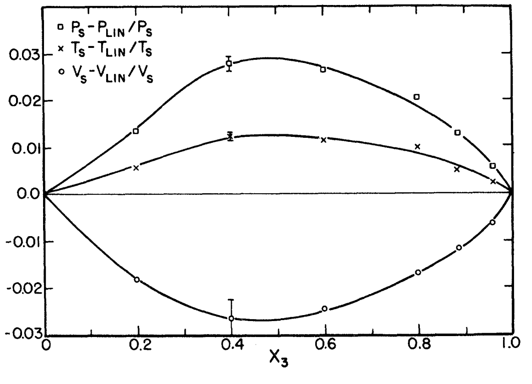

FIG. 9. Deviation of the symmetry parameters from a linear interpolation between the pure He^3 and He^4 values given in Ref. 10.

gence of k_{TX}, the isothermal compressibility at constant composition for a binary liquid mixture, and their arguments should be applicable to the He^3-He^4 mixtures near their liquid-gas critical point.[15]

The compressibility along the critical isochore for a pure fluid is usually given by

$$\rho^{-1}\left(\frac{\partial \rho}{\partial P}\right)_T = k_T = \Gamma t^{-\gamma} \quad \text{for } T > T_c\,,\ \rho = \rho_c \tag{7a}$$

and

$$\left(\frac{\rho}{\rho_c}\right)^2 k_T = \Gamma' t^{-\gamma'} \quad \text{for } T < T_c \tag{7b}$$

along the coexistence curve, where for the helium isotopes $\gamma \approx \gamma' \approx 1.2$. Griffiths and Wheeler suggest that for a mixture, k_{TX} for $T > T_c$ diverges "weakly" with an exponent α characterizing the divergence of C_v for a pure fluid. For He^3 and He^4, this exponent[16,17] is of the order of 0.1. In Fig. 10, the compressibility k_{TX} for $T > T_c$ has been plotted along the critical isochore as well as for $\rho = \rho_s$ since the magnitude of k_{TX} is larger along ρ_s. The results for several mixtures are shown in Fig. 10 together with those for He^3 and He^4. Clearly the asymptotic divergence of k_{TX}, if any, is weak. Because of the difficulties in achieving reproducible measurements of k_{TX} very close to T_c, especially at temperatures where the phenomenon of retrograde condensation is observed, the limiting be-

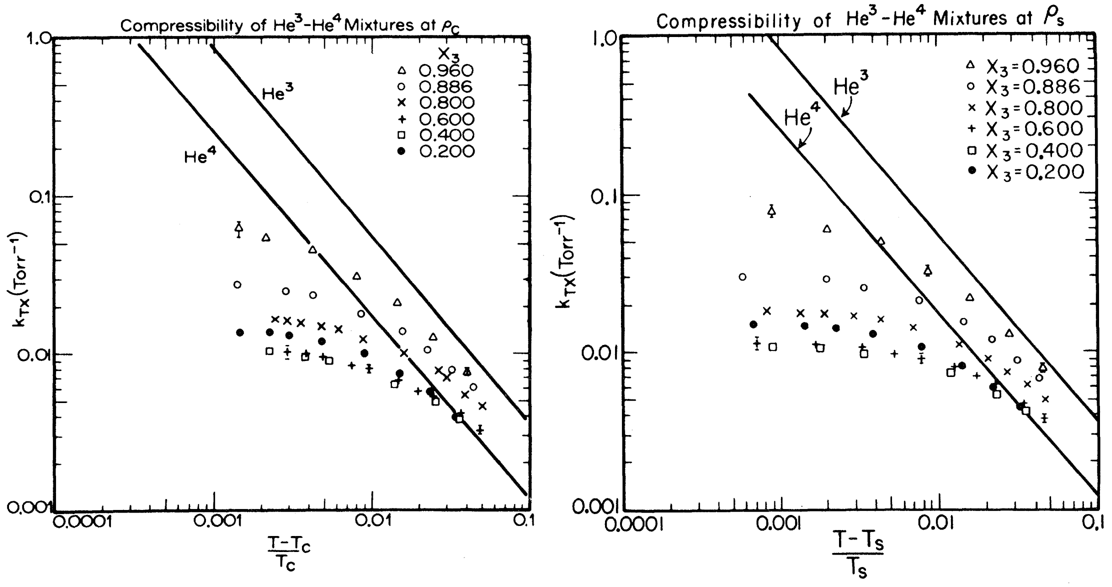

FIG. 10. Isothermal compressibility, $k_{T,X}(\rho_c)$ and $k_{T,X}(\rho_s)$, for He^3-He^4 mixtures. Pure He^3 and He^4 values were taken as stated in Ref. 10.

havior of k_{TX} is difficult to assess. However, the results are not inconsistent with the divergence predicted by Griffiths and Wheeler.[3]

It will be noted that for the pure fluids,[7,10] the compressibility follows approximately the asymptotic behavior [Eq. (7)] already for $t = 0.05$. At this reduced temperature, k_{TX} for mixtures is intermediate between the k_T for pure He^3 and He^4. But as t becomes smaller, a "crossover region" $10^{-3} \lesssim t < 5\times10^{-2}$ shows the transition to the possibly weakly diverging behavior. As the composition of the mixtures tends to that of a pure fluid, the crossover region tends to shift to lower values of t, as evidenced best by the results for $X_3 = 0.96$. This is in agreement with the parameter scaling theory of Riedel and Wegner,[18] applied to mixtures in the neighborhood of the liquid-gas critical point.

We point out here the absence of any observable behavior that distinguishes k_{TX} along ρ_c from that along the symmetric isochore on the vapor side, namely, $\rho = \rho_s - (\rho_c - \rho_s)$. Hence it is only very close to T_c, say $t < 10^{-4}$, that k_{TX} is expected to reach values larger than those shown in Fig. 10.

As mentioned before, density measurements along isotherms became irreproducible below T_s on the side of the boiling curve for temperatures close to T_c. Therefore only the compressibility data $\rho^2 k_{T,X}$ along the dew curve extended from the lowest temperatures up to T_s. Over the temperature region where both the dew and the boiling curves were well defined, it was found that for a given pressure, $\rho^2 k_{T,X}$ on both the boiling and the dew curve were equal, just as for a pure fluid. Note that here again, just as for the density relation [Eq. (3)], the equality is for a given pressure rather than temperature. This equality can then presumably be assumed to extend until not too far from T_c, at which point, however, $k_{T,X}$ along the critical isochore should become infinite according to Griffiths and Wheeler.

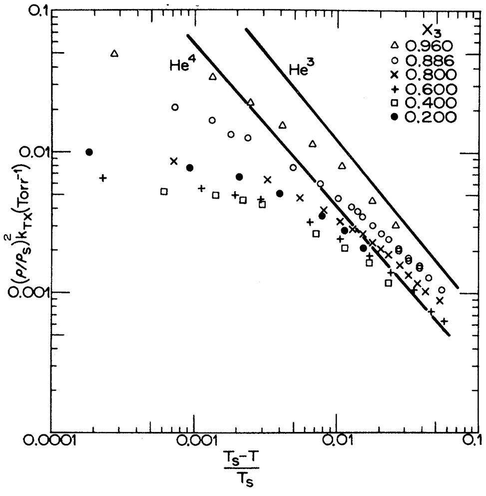

FIG. 11. Isothermal compressibility $(\rho/\rho_s)^2 k_{T,X}$, at the dew curve for He^3-He^4 mixtures. Pure He^3 and He^4 values were taken as stated in Ref. 10.

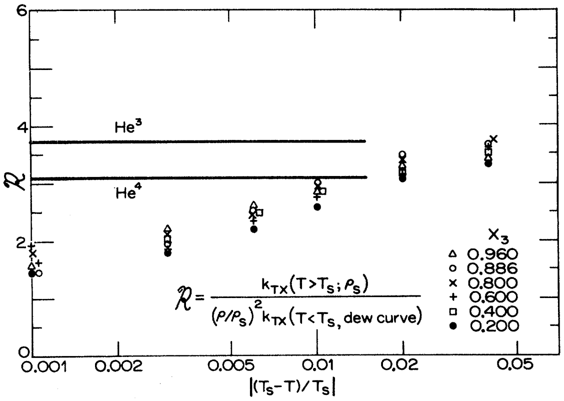

FIG. 12. The ratio $\mathcal{R} = k_{T,X}(\rho_s,\ T > T_s)/[(\rho/\rho_s)^2 k_{T,X}(\text{dew curve},\ T < T_s)]$ for a given value of $|(T_s - T)/T_s|$.

Along the dew line, the compressibility $(\rho/\rho_c)^2 k_{T,X}$ for $T < T_c$ stays finite at T_c on the "gas side," but continues to increase with T for $T_c < T < T_s$, which is in the region of retrograde condensation. The normalized compressibility $(\rho/\rho_s)^2 k_T$ is plotted in Fig. 11 against $(T_s - T)/T_s$. In Fig. 12, the role of the symmetry point is again illustrated by plotting the ratio of the normalized compressibilities along the dew line and for $\rho = \rho_s$ $(T > T_s)$ at equal values of $|(T_s - T)/T_s|$. For comparison, this ratio is also plotted for pure He^3 and He^4. At high values of $(T - T_s)/T_s$, the results for the mixture tend to an intermediate value between He^3 and He^4, but as $(T - T_s)/T_s$ becomes smaller, there is a gradual drop of this ratio. Pure He^3 and He^4 have, at least for $|t| \lesssim 0.03$, a temperature independent ratio $\mathcal{R}$ shown on Fig. 12, which indicates the equality of the critical exponents γ and γ'. These exponents have the value of 1.17[7] and 1.24[2,8] for He^3 and He^4, respectively.

D. Coexistence Curves for Constant-*P* and Constant-*T* Planes

The exponent β is usually taken as relating to the vanishing difference $\rho_L - \rho_G$ along the coexistence curve for a pure fluid. Here the subscripts L and G denote the density on the liquid and the gas side of the coexistence curve. We used Eq. (6) to attempt to describe the boiling and dew curves (Sec. III A) at constant X. These curves, of course, do not represent coexistent phases, since at a given pressure and composition, the dew point and boiling point do not occur at the same temperature. By in-

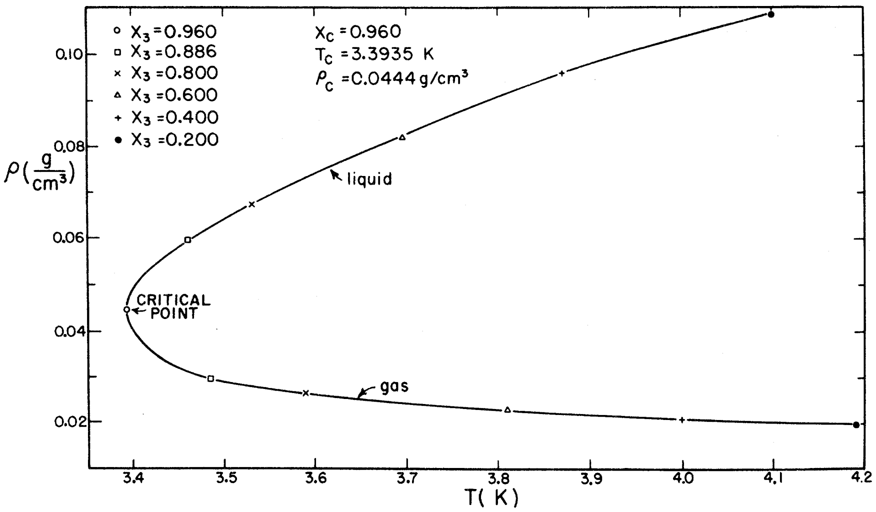

FIG. 13. Coexistence curve for $P=898.5$ Torr. This curve was found by interpolation on the ρ-vs-P isothermal data for each concentration as discussed in the text.

terpolation on the large boiling- and dew-curve graphs, several plots such as "density vs temperature at constant pressure" and "density vs pressure at constant temperature" were generated. For these two coexistence-curve plots, one can foresee relationships of the type

$$(\rho_L - \rho_G) \propto (T - T_c)^{\beta_P} \quad (P = \text{const}) , \tag{8}$$

$$(\rho_L - \rho_G) \propto (P_c - P)^{\beta_T} \quad (T = \text{const}) . \tag{9}$$

Figure 13 shows a density-vs-temperature plot for the coexistence curve at $P = 898.5$ Torr. The critical point occurs at the minimum temperature as expected from Fig. 7 and vertical lines joining the liquid and the vapor sides are true "tie lines" as for a pure fluid. Not shown is a "ρ vs P at constant T" plot, which from Fig. 6 has its critical point at the maximum pressure and therefore is similar to the usual ρ-vs-P plot for a pure fluid. We remind the reader that the coexistence curve plots and consequently the exponents β_P and β_T are affected by the symmetry assumption of the boiling and dew curves close to T_c (Sec. III B).

Equations (8) and (9) were used to fit the curves just mentioned, and the results for several pressures are shown in Fig. 14. Comparison with the analogous curve[7] for pure He^3 shows that there is more scatter in the mixture data, probably caused by interpolation errors and the difficulties in measuring accurately the boiling curve close to the critical point. It is felt, however, that there is no systematic tendency for β to change over the measured P, T, or X_3 intervals.

We have also made similar plots where the number density (1/cm³) was used instead of the mass density (g/cm³). The effective exponents β_T and β_P were not significantly changed and in summary, the coexistence curves are described by the critical exponents

$$\beta_P = 0.39 \pm 0.05 , \quad 0.002 \leq t \leq 0.2 \tag{10}$$

$$\beta_T = 0.42 \pm 0.06 , \quad 0.003 \leq \Delta P \leq 0.3 . \tag{11}$$

It is obvious from Fig. 13 that the coexistence curve

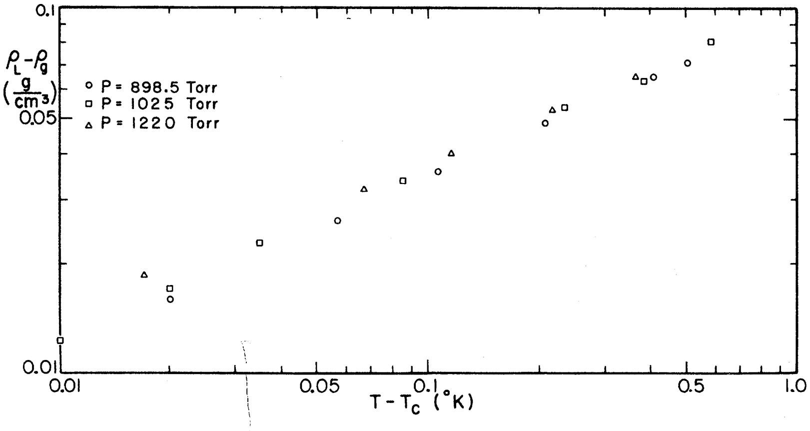

FIG. 14. Coexistence curve for three constant-pressure curves. Slope is the index β_P as given in Eq. (8) and for all constant-P curves was 0.39 ±0.05.

at constant P is not symmetric about ρ_c, and that the equation of the "rectilinear diameter" is given by

$$\bar{\rho} = \tfrac{1}{2}(\rho_L + \rho_G) = \rho_c + A_P\,[(T - T_c)/T_c] + \cdots \;, \qquad (12)$$

with $A_P \simeq 0.1\ \mathrm{g/cm^3}$ Similarly for the coexistence curve at constant T one has

$$\bar{\rho} = \rho_c + A_T\,[(P_c - P)/P_c] + \cdots\ (\mathrm{g/cm^3})\;, \qquad (13)$$

with $A_T \simeq 0.05\ \mathrm{g/cm^3}$. This is to be compared with the situation in pure He^3 and He^4 where $\bar{\rho} - \rho_c \approx 0$. This is also to be contrasted with the "rectilinear diameter" $\bar{\rho} = \frac{1}{2}[\rho_L(P, X) + \rho_G(P, X)]$ defined from the boiling and dew curves, which appears to be nearly independent of P, as discussed in Sec. II A. Perhaps this implies that the β' defined by Eq. (6) may be more directly related to the β found from the shape of the coexistence curve for a pure fluid [Eq. (4)] that may be β_P and β_T defined by Eqs. (8) and (9). It might be mentioned at this point that measurements of the particle density of each component in both phases along the critical isochore in the two-phase region would be the logical extension of the density measurements along the coexistence curve for the pure fluids. One could then expect a similar asymptotic behavior near the critical point, with the critical exponent not too different from that in pure He^3 and He^4. Unfortunately, such an experiment is not feasible with the equipment described here.

IV. CONCLUSIONS

The study of the pressure-density-temperature relationship near the critical line for He^3-He^4 mixtures has led to the following observations:

(i) For each mixture of composition X, the point at the maximum pressure of the dew curve in the density-pressure plane which we call the "symmetry point" seems to deserve special attention. The properties around this symmetry point, characterized by the parameters P_s, ρ_s, and T_s, are similar in some respects to those of the critical point of a pure fluid. Except in the close vicinity of the critical point, where irreproducibilities made the experiments difficult, these properties can be summarized as follows for any given composition X_3: (a) $(\rho_s - \rho(P)_{\text{dew line}}) \simeq (\rho(P)_{\text{boiling line}} - \rho_s) \propto (P_s - P)^{0.37}$; (b) $\rho^2 k_{T,X}$ at P along dew line $\simeq \rho^2 k_{T,X}$ at P along boiling line; (c) $\rho^2 k_{T,X}$ is maximum at $\rho = \rho_s$ for $T > T_s$. However $\rho^2 k_{T,X}$ does not diverge at $T = T_s$.

(ii) The critical point for a mixture of given composition occurs at a lower temperature, pressure, and molar volume than the symmetry point. The critical parameters are smoothly varying functions of X with T_c and P_c always higher than the values given by a linear interpolation between the values for pure He^3 and He^4, while V_c is always lower than the linearly interpolated value. The ratio $P_c V_c / RT_c$ is nearly independent of X.

(iii) It was not possible in this work to investigate the isothermal compressibility close enough to the critical locus either to support or disprove the predictions of Griffiths and Wheeler that it should diverge weakly there.

(iv) The exponent β describing the coexistence curves for constant-P and constant-T planes was found to be somewhat higher than the β for pure He^3 and He^4.

Throughout this work, the tendency has been to explore the similarities between mixtures and pure fluids. The "symmetry point," which is more precisely located than the critical point, seems to have some attractive properties for scaling among the mixtures. The properties of the critical point in terms of scaling and divergences are less evident experimentally than for a pure liquid.

The theoretical as well as the experimental problem for liquid-gas transition in mixtures is much more complicated than for pure liquids, since fluctuations in both density and composition near T_c have to be considered, and these fluctuations are not independent. Their relative importance is a function of the average composition and of P and T as well. For a complete study of the phase diagram, one would need a systematic set of data for a number of closely spaced compositions in order to be able to express variables such as $P_G - P_c$ as a function of $(X_G - X_c)$ at constant T along the true coexistence curve. Under the described experimental conditions, it is not possible to measure simultaneously the composition of both coexisting phases.

So far, then, only a beginning has been made in the study of this complex problem, and although one would like to have more data on several different mixtures, we believe that the analysis of the data presented above is a useful first step and we hope that it will stimulate further work, both experimental and theoretical. It is also hoped that these experiments will encourage a new theoretical effort to calculate the critical parameters P_c, V_c and T_c for the helium mixtures.

ACKNOWLEDGMENTS

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$$\frac{(\partial\rho/\partial\mu)_T(t>0,\ \rho=\rho_c)}{(\partial\rho/\partial\mu)_T(\text{coexistence curve})}=3.7=\frac{\Gamma}{\Gamma'}.$$

The analysis leading to γ' was improved by using the values of $(\partial\rho/\partial\mu)_T$ at densities $[\rho_c+a(\rho_L-\rho_c)]$ and $\rho_c-a(\rho_c-\rho_G)$, where a was taken to be 1.05, 1.10, 1.15, and 1.20. When $a=1.00$, the data are along the coexistence curve. This technique corresponds to using $(\partial\rho/\partial\mu)_T$ along curves in the $\rho-T$ plane with $X=t(\Delta\rho)^{1/\beta}=$ constant. This method was recently suggested by M. H. Edwards, in *Proceedings of the Eleventh International Conference on Low Temperature Physics* (University of St. Andrews Printing Dept., St. Andrews, Scotland, 1969), p. 231.

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Boiling and Dew Curves of He^3-He^4 Mixtures[†]

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Pressure and density measurements along the boiling and dew curves for He^3-He^4 mixtures for several temperatures above 2 K are presented. From these data, the excess chemical potentials and the excess Gibbs energy are calculated.

Taconis and De Bruyn Ouboter[1] give a review of the most recent measurements which are used to define the P-T-X_3 phase diagram of He^3-He^4 mixtures below 2 K, where X_3 is the mole fraction of He^3. The most extensive are the data of Sydoriak and Roberts[2] (SR), who determined the boiling curve at 10% steps in the mole fraction over the temperature range 0.6–2.0K. Sreedhar and Daunt[3] have