

*Research supported by a grant from the National Science Foundation.

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⁷B. A. Wallace and H. Meyer, Phys. Rev. A **2**, 1563 (1970). We wish to correct the following errors we noticed in this paper: (a) Reference 29 should be to E. C. Kerr and R. D. Taylor, Ann. Phys. **26**, 292 (1964) instead of Atkins and Edwards. (b) In the caption of Fig. 3, the vertical scale and first line should read $M(\partial\rho/\partial\mu)_T$ instead of $(\partial\rho/\partial\mu)_T$. (c) The caption of Fig. 7, line 3, should read isotherm instead of isobar. Also in this paper it was mentioned that the direct analysis of $(\partial\rho/\partial\mu)_T$ data indicate a tendency for γ' to be smaller than γ . We have carried out a more complete analysis of the compressibility on the critical isochore and along the coexistence curve and that included in addition data from He³ with 10 ppm He⁴. This analysis showed that within experimental error $\gamma = \gamma' = 1.17 \pm 0.05$ for $|t| \lesssim 0.02$ and over this range,

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

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 ρ_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 $X=t(\Delta\rho)^{1/\beta} = \text{constant}$. 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 He³-He⁴ Mixtures[†]

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Pressure and density measurements along the boiling and dew curves for He³-He⁴ 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 Ouboter¹ give a review of the most recent measurements which are used to define the P - T - X_3 phase diagram of He³-He⁴ mixtures below 2 K, where X_3 is the mole fraction of

He³. The most extensive are the data of Sydoriak and Roberts² (SR), who determined the boiling curve at 10% steps in the mole fraction over the temperature range 0.6–2.0 K. Sreedhar and Daunt³ have

taken vapor-pressure measurements for $X_3 \leq 0.12$ and temperatures between 1.4 and 2.6 K which are consistent with those of SR. Sommers⁴ has determined the dew curve for $X_3 < 0.80$ and the boiling curve for $X_3 < 0.13$ for the temperature interval 1.3–2.18 K. The only previous research that investigated both the boiling and dew curves over the entire concentration range is that given by Eselson and Berezniak⁵ (EB), who measured 20 solutions with $0.004 \leq X_3 \leq 0.908$ and $1.32 < T < 3.22$ K. However, the boiling and dew curves of EB were found to be thermodynamically inconsistent when submitted to a consistency test originating from thermodynamic considerations.^{1,6}

We have extended the range over which both the complete boiling and dew curves have been measured and report here recent pressure and density data along these curves at 2.00, 2.50, 3.00, and 3.31 K (the data on the last isotherm being obtained by interpolation), which were found to be thermodynamically consistent.

The apparatus and experimental procedures are being discussed in detail elsewhere.⁷ The temperature was measured by a germanium thermometer, the pressure by a Texas Instruments fused-quartz Bourdon gauge and the density by the dielectric-constant technique. The boiling and dew curves were determined for samples with $X_3 = 0.886, 0.800, 0.600, 0.400,$ and 0.200 . The vapor pressures of pure He³ and He⁴ were taken from the T_{62} and T_{58} temperature scales, respectively.⁸

As discussed previously,⁷ the pressures and densities on the boiling and dew curves, respectively, P_L and ρ_L , and P_V and ρ_V were found from the abrupt change in the slope of a ρ - P plot for a given isotherm at constant X_3 . Here the subscripts L and V are for "liquid" and "vapor," respectively. The other experimenters mostly reported only P_L , the value of the saturated vapor pressure of the liquid. Eselson and Berezniak⁵ found P_V by increasing the amount of sample until there was a break in the graph of the pressure versus the amount of sample.

The thermodynamic formulas which are used to define the liquid-vapor equilibrium have been given by a number of authors. We follow here in a general way the treatment of De Bruyn Ouboter, Beenakker, and Taconis (DBT).⁶ From their paper, it follows that the excess chemical potential of the i th component μ_i^E is given by the relation

$$\mu_i^E = RT \ln[P_i^*/(X_{iL}P_i^{0*})], \quad (1)$$

where R is the gas constant, P_i^* and P_i^{0*} are the partial fugacities given by

$$\ln P_i^* = \ln P_i + B_{ii}P_L/(RT), \quad (2)$$

$$\ln P_i^{0*} = \ln P_i^0 + B_{ii}P_i^0/(RT).$$

Here P_L is the total pressure on the boiling curve,

P_i^0 is the vapor pressure of the pure component i , and B_{ii} is the second virial coefficient of the pure component i . The partial pressure P_i is given by $P_i = X_{iV}P_L$. It is then possible in principle to calculate μ_i^E if one knows the total pressure as a function of X_i along the boiling and dew curves.

From the Gibbs-Duhem relation,¹ Redlich and Kister⁹ have derived a simple thermodynamic consistency test for the boiling- and dew-curve data for a given isotherm. The significant terms in the test equation are

$$\int_0^1 \ln([X_{3V}(1-X_{3L})]/[(1-X_{3V})X_{3L}])dX_{3L} \\ = \ln(P_3^0/P_4^0) + (B_{33} + B_{44} - V_{3L}^0 - V_{3L}^4)(P_3^0 - P_4^0)/(2RT), \quad (3)$$

which is a necessary but not sufficient test for consistency of the data.¹⁰ The additional terms account for only a fraction of a percent of the value of the left-hand side of Eq. (3) and are neglected.

Our results for the isotherms are presented in Table I. Figure 1 shows a P -vs- X plot of the results along with the data of EB. Since the integral in Eq. (3) contains the ratios of the molefractions in the liquid and vapor phases and since X_{3V} rapidly approaches unity at the lower temperatures for a given X_{3L} one sees that Eq. (3) is a severe test of the consistency of the data, as small errors in X_{3V} result in large errors for the value of the integral. Figure 2 shows the results of applying Eq. (3) to both the present data and those of EB. For consistency, the area above the line [which equals the right-hand side of Eq. (3)] must be equal to the area below this line, and this test shows the present data to be consistent. Similar results are obtained for our 2.00- and 3.00-K isotherms. From Fig. 1, we note that the boiling curves as determined by EB and in the present research agree closely, but that the dew curves do not agree too well except at 2.00 K. To avoid overcrowding in Fig. 1, the boiling-curve measurements of SR are not shown.

TABLE I. Boiling- and dew-curve data. On the average, the absolute pressure and the density are determined to within about 0.5 Torr and 0.5%, respectively.

	X_3	P_L (Torr)	P_V (Torr)	ρ_L (g/cm ³)	ρ_V (g/cm ³)
$T = 2.000$ K	0.200	56.0	29.5	0.1318	0.00085
	0.400	80.5	38.0	0.1176	0.00122
	0.600	140.0	54.0	0.1033	0.00164
	0.800	127.0	83.0	0.0904	0.00261
	0.886	137.0	106.5	0.0850	0.00318
$T = 2.500$ K	0.200	133.5	93.0	0.1295	0.00254
	0.400	185.5	116.5	0.1148	0.00311
	0.600	232.5	151.0	0.1003	0.00390
	0.800	279.0	220.0	0.0867	0.00580
	0.886	301.0	262.0	0.0810	0.00700
$T = 3.000$ K	0.200	277.0	217.0	0.1256	0.00529
	0.400	360.0	268.0	0.1105	0.00638
	0.600	438.5	344.0	0.0953	0.00828
	0.800	518.5	456.0	0.0802	0.01135
	0.886	562.0	516.0	0.0740	0.01380

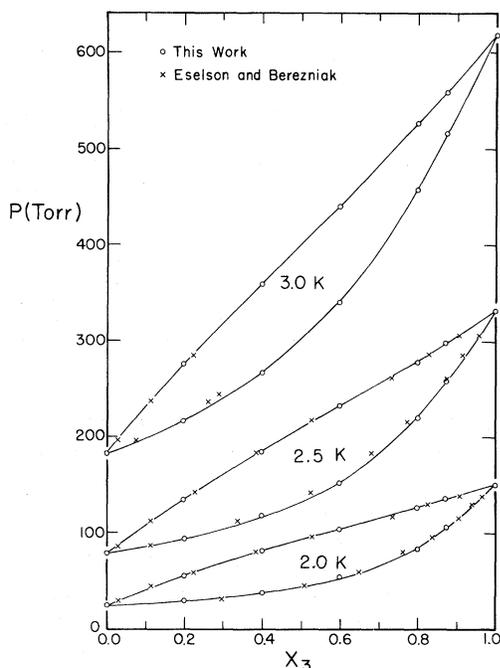


FIG. 1. Phase diagram for 2, 2.5, and 3 K. Points for EB were interpolated from their 1956 data. Vapor pressures of pure He³ and pure He⁴ were taken from the T_{62} He³ and T_{58} He⁴ thermodynamic vapor-pressure tables.

For the 2K isotherm, our boiling curve agrees to better than 1 Torr (<1%) with the boiling curve found by SR and within 5 Torr (<5%) with that found by EB. Possibly one reason that the present data are more consistent than those of EB is that concentrations of the mixtures were known to within 0.1%, while EB only knew their concentration to 1.5–4.0%.

To minimize certain problems associated with uncertainties in the mole fraction X_3 , a procedure used by DBT was followed to determine the excess Gibbs free energy $G^E = \mu_3^E X_{3L} + \mu_4^E (1 - X_{3L})$. These authors knew that EB's data were not consistent, so they used the more accurate boiling curve of SR along with EB's dew curve in an iterative procedure. The idea behind this procedure is that (i) one can determine the boiling curve more accurately than the dew curve, and (ii) an error in the boiling curve does not cause as large a change in G^E as does a similar error in the dew curve.

Applied to our data the technique is as follows. As a zeroth approximation the dew-point measurements are used and from these the partial pressure $P_3 = X_{3v} P_L$ is calculated. With the second virial coefficients calculated by Kilpatrick *et al.*¹¹ we determine the partial fugacity P_3^* from Eq. (2). Hence μ_3^E is known from Eq. (1) to a zeroth ap-

proximation at different concentrations. By graphically integrating the Gibbs-Duhem equation we find μ_4^E to a first approximation, and then P_4 , using Eq. (1). Then one obtains $X_{3v} = (1 - P_4/P_L)$ in a first approximation. The whole procedure is repeated until μ_3^E and μ_4^E converge. Chandra and Nanda¹² have also used the same procedure to evaluate μ_3^E and μ_4^E for the data of Sreedhar and Daunt.³ We used a computer for the above work and evaluated the excess chemical potentials and G^E for our four isotherms at every 10% change in concentration. We found convergence after two or three iterations and our results are given in Table II.

As the temperature increases, one notices that μ_3^E becomes increasingly negative at the higher X_3 values. This is due to the negative deviations from Raoult's law. The present results at 2K are in good agreement with the calculation of Roberts and Swartz,¹³ who used the data of SR. The small discrepancies between the present results and those of Roberts and Swartz are due first to a small difference ($\approx 1\%$) in vapor pressure and second to a slightly different technique for evaluating the VdP term in the Gibbs-Duhem equation. Furthermore, we used the actual $V(X)$ measurements while Roberts and Swartz used a linear interpolation between $V(X=0)$ and $V(X=1)$. The results for small X_3 at 2.5 K appear to merge smoothly with the analysis by Chandra and Nanda¹² of the data by Sreedhar and Daunt,³ which was for

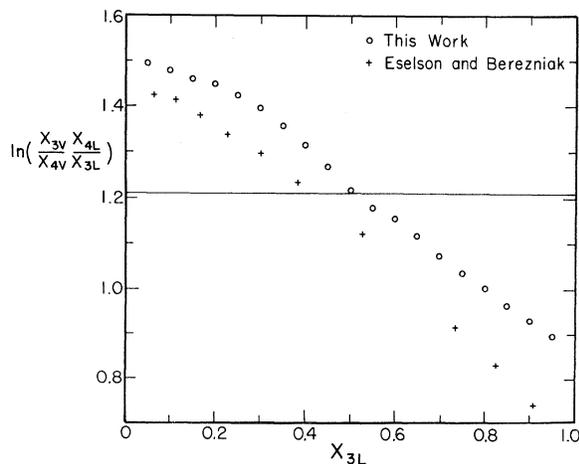


FIG. 2. Consistency test for the 2.5 K Data. The straight line has the value

$$\ln \frac{P_3^0/P_4^0 + (B_{33} + B_{44} - V_{3L}^0 - V_{4L}^0)(P_3^0 - P_4^0)}{2RT}$$

For consistency, the area above this line must equal the area below the line [see Eq. (3)].

TABLE II. The calculated excess chemical potentials, μ_3^E and μ_4^E , and the excess Gibbs free energy G^E as a function of the mole fraction X_3 and temperature.

X_{3L}	T(K)	μ_3^E/R				μ_4^E/R				G^E/R			
		2.00	2.50	3.00	3.31	2.00	2.50	3.00	3.31	2.00	2.50	3.00	3.31
0.1	0.755	0.435	0.390	0.433	0.032	0.019	0.031	0.033	0.104	0.061	0.067	0.073	
0.2	0.509	0.324	0.327	0.292	0.084	0.054	0.071	0.092	0.169	0.108	0.122	0.132	
0.3	0.351	0.273	0.210	0.174	0.143	0.089	0.139	0.170	0.206	0.144	0.160	0.171	
0.4	0.226	0.193	0.099	0.082	0.219	0.151	0.231	0.265	0.222	0.168	0.178	0.192	
0.5	0.160	0.130	0.030	0.000	0.287	0.225	0.329	0.386	0.223	0.178	0.180	0.193	
0.6	0.102	0.056	-0.031	-0.082	0.372	0.345	0.452	0.552	0.210	0.171	0.162	0.172	
0.7	0.060	0.003	-0.070	-0.107	0.470	0.482	0.585	0.691	0.183	0.146	0.126	0.132	
0.8	0.026	-0.029	-0.073	-0.097	0.599	0.633	0.693	0.811	0.141	0.104	0.080	0.085	
0.9	0.007	-0.012	-0.014	-0.049	0.758	0.655	0.596	0.900	0.082	0.054	0.047	0.046	

$0.02 \leq X_3 \leq 0.12$. The 3.31 K critical isotherm for pure He³ was obtained by interpolating the data presented in Ref. 7. In this reference a P - X plot of this isotherm is shown in Fig. 6. DBT and most of the earlier workers¹ who calculated the excess chemical potentials for $T \lesssim 2$ K neglected the VdP term in the Gibbs-Duhem equation. This will result in a G^E value too low by $\sim 8\%$ at 2 K and $\sim 30\%$ at 3 K. As had been found previously,^{6,11,12} we also observed that G^E could not be adequately expressed

by the predictions of regular solution theory⁶ which give $G^E = X(1-X)W$, where W depends only on temperature.

In conclusion, it is hoped that the values of G^E for the various temperatures will be useful to theorists interested in the behavior of solutions with small variations from ideal solution theory.

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