Specific Heat of Liquid He³ /He⁴ Mixtures near the Junction of the λ and Phase-Separation Curves. II

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Measurements of the molar specific heat $c_{P,x}$ of liquid He³/He⁴ mixtures at saturated vapor pressure near the junction of the λ and phase-separation curves reported in an earlier paper have been used to calculate values of $(\partial s/\partial T)_{P,x} = c_{P,x}/T$, $(\partial \phi/\partial T)_{P,x} = -(\partial s/\partial x)_{P,T}$, s, and $\phi - \phi_0$ at saturated vapor pressure throughout the junction region. Here ϕ is the difference $\mu_3 - \mu_4$ between molar chemical potentials, x is the mole fraction of He³ present, and the subscript 0 denotes the value of a quantity at the junction. Comparisons of $(\partial s/\partial T)_{P,x}$ and $(\partial \phi/\partial T)_{P,x}$ with their respective upper bounds at the λ curve $(ds/dT)_{P,\lambda} + (d\phi/dT)_{P,\lambda}(dx/dT)_{P,\lambda}$ and $(d\phi/dT)_{P,\lambda}$ suggest but do not require that $(\partial s/\partial T)_{P,\phi} = c_{P,\phi}/T$ diverge all along the λ curve, as our results indicate that it does at the junction. Our results are consistent with the following asymptotic behaviors at the junction: $(\partial s/\partial T)_{P,x,0} - (\partial s/\partial T)_{P,x} \sim (T - T_0)^1$ at $x = x_0$ for $T > T_0$; $|\phi - \phi_0| \sim |x - x_0|^2$ at $T = T_0$ for $x \lessgtr x_0$; $(\partial s/\partial T)_{P,\phi} \sim |T - T_0|^{-1/2}$ at $\phi = \phi_0$ for $T \lessgtr T_0$.

I. INTRODUCTION

In an earlier paper bearing the same title (hereafter referred to as Paper I)[1] we presented the results of some measurements of the specific heat of liquid He³/He⁴ mixtures at saturated vapor pressure near the interesting junction of the λ and phase-separation curves which occurs at a temperature $T_0 \cong 0.87$ °K and a He³ mole fraction $x_0 \cong 0.67$. It is the purpose of this paper to continue the analysis of the data which was begun in Paper I. The reader is referred to that paper for the background of the present one and for the notation that we employ here.

Using the fact that, in principle, a rather complete thermodynamic picture of the junction region may be obtained almost entirely from measurements of the molar specific heat $c_{P,x}$ of the liquid alone, we calculate from our data the quantities $(\partial s/\partial T)_{P,x} = c_{P,x}/T$, $(\partial \phi/\partial T)_{P,x} = -(\partial s/\partial x)_{P,T}$, s, and $\phi - \phi_0$ in the junction region as functions of T and x at saturated vapor pressure. Here ϕ is the difference $\mu_3 - \mu_4$ between molar chemical potentials, and ϕ_0 is its value at the junction. We then make use of these calculations to discuss various aspects of the thermodynamic behavior of the mixtures near the λ curve and its junction with the phase-separation curves.

Our principal motivation in carrying out these calculations was the hope that they would aid the imagination in formulating explicit expressions to represent critical thermodynamic behavior near the junction and to describe how the second-order λ transition goes over into the first-order phase-separation transition with decreasing temperature.

Another motivation was the desire to provide explicit thermodynamic information about the junction region in a form which might be useful for other purposes and provide easily accessible points of comparison with other work.

II. CALCULATION OF THERMODYNAMIC PROPERTIES

Because of the occurrence of phase separation in the mixtures, it is possible, in principle, to determine a rather complete thermodynamic picture of the mixtures at saturated vapor pressure in the region of interest almost entirely from measurements of $c_{P,x}$ in that region alone. This remarkable state of affairs, which has also been made use of by de Bruyn Ouboter, Taconis, le Pair, and Beenakker in earlier work on the mixtures,[2] would not exist if the system remained homogeneous.

To be more specific, consider first the situation at constant pressure. In this case, from a knowledge of $c_{P,x}$ alone throughout the junction region one can determine $(\partial s/\partial T)_{P,x} = c_{P,x}/T$, $(\partial \phi/\partial T)_{P,x} = -(\partial s/\partial x)_{P,T}$, $(\partial \phi/\partial x)_{P,T}$, s, and ϕ throughout that region in terms of three undetermined constants. The situation at saturated vapor pressure is somewhat less ideal, in that here some knowledge of the vapor pressure as a function of T and x and of the liquid molar volume as a function of P, T, and x is also required. However, the correction terms necessitated by the nonconstancy of pressure are everywhere quite small, and the information needed to evaluate them is available. By making use of some supplementary information about the phase-separation region at low temperatures which was presented in Paper I, one can de-

TABLE I. Values of $(d\phi/dT)_\sigma$ and $x_0(d\mu_3/dT)_\sigma + (1-x_0)(d\mu_4/dT)_\sigma$.

T (°K)	$\left(\dfrac{d\phi}{dT}\right)_\sigma$ (J mole⁻¹ °K⁻¹)	$x_0\left(\dfrac{d\mu_3}{dT}\right)_\sigma + (1-x_0)\left(\dfrac{d\mu_4}{dT}\right)_\sigma$ (J mole⁻¹ °K⁻¹)
0.600	−7.16	−7.76
0.650	−7.61	−8.36
0.700	−8.05	−8.94
0.750	−8.46	−9.48
0.800	−8.86	−9.99
0.850	−9.22	−10.46
0.871	−9.38	−10.64

termine all but one of the three constants.

The main limitation in carrying out such determinations is the practical one arising from the limited resolution of the data. Considerable opportunity exists for error to accumulate in the numerical differentiations and integrations involved.

It was convenient for us to begin by taking the determinations of $(d^2\phi/dT^2)_\sigma$ and $x_0(d^2\mu_3/dT^2)_\sigma + (1-x_0)(d^2\mu_4/dT^2)_\sigma$ along the phase-separation curve at saturated vapor pressure displayed in Figs. 6 and 7 and in Table III of Paper I and integrating with respect to T from absolute zero to find $(d\phi/dT)_\sigma$ and $x_0(d\mu_3/dT)_\sigma + (1-x_0)(d\mu_4/dT)_\sigma$ as functions of T. Note that $(d\phi/dT)_\sigma$ and $x_0(d\mu_3/dT)_\sigma + (1-x_0)(d\mu_4/dT)_\sigma$ must vanish at $T=0$. Values for these quantities at selected values of T are presented in Table I. The integrations yield values of −9.38 J mole⁻¹ °K⁻¹ for $(d\phi/dT)_{\sigma;0}$ and −10.64 J mole⁻¹ °K⁻¹ for $x_0(d\mu_3/dT)_{\sigma;0} + (1-x_0)(d\mu_4/dT)_{\sigma;0}$, the values at the junction. Thus we have incorporated the results of outside data at low temperature right from the start. However, if one wants to avoid this dependence on outside data in what follows, the low-temperature parts of the integrations may be ignored and the high-temperature parts regarded as determining $(d\phi/dT)_\sigma$ and $x_0(d\mu_3/dT)_\sigma + (1-x_0) \times (d\mu_4/dT)_\sigma$ in the temperature region of interest relative to their values at the junction, which may be regarded as undetermined constants. The third constant needed for our determinations is ϕ_0, the value of ϕ at the junction. We have made no attempt to evaluate ϕ_0 but have merely carried it along explicitly.

Next we have determined $(\partial s/\partial T)_{P,x}$, $(\partial\phi/\partial T)_{P,x}$, $(\partial\phi/\partial x)_{P,T}$, s, and $\phi - \phi_0$ along both branches of the phase-separation curve as follows. The derivative $(\partial s/\partial T)_{P,x}$ is simply $c_{P,x}/T$ and was obtained directly from the specific-heat data. The derivative $(\partial\phi/\partial T)_{P,x}$ was determined along each branch of the phase-separation curve by means of the formula

$$\left(\frac{\partial\phi}{\partial T}\right)_{P,x} = \left(\frac{d\phi}{dT}\right)_\sigma - \left(\frac{\partial\phi}{\partial x}\right)_{P,T}\left(\frac{dx}{dT}\right)_\sigma$$
$$- \left(\frac{\partial v}{\partial x}\right)_{P,T}\left(\frac{dP}{dT}\right)_\sigma. \quad (1)$$

The derivative $(\partial\phi/\partial x)_{P,T}$, which is of interest in its own right as well as being needed here for evaluating $(\partial\phi/\partial T)_{P,x}$, was taken from Paper I, where it was determined from $\Delta c_{P,x}$ at the phase-separation curve and is displayed in Fig. 8 and Table IV. The derivative $(dx/dT)_\sigma$, which represents the inverse slope of the phase-separation curve in the T, x plane, was also determined in Paper I; its reciprocal is listed in Table IV of that paper. The last term on the right-hand side of Eq. (1) represents the correction due to the nonconstancy of saturated vapor pressure. As in other expressions to follow, these correction terms involve the molar volume of the liquid and its derivatives, which can be estimated from the molar-volume measurements of Kerr[3] and the speed-of-sound measurements of Roberts and Sydoriak,[4] and the derivatives of the vapor pressure, which can be estimated from the vapor-pressure measurements of Sydoriak and Roberts[5] in connection with the T_{62} He³ vapor-pressure scale of temperature.[6] In Eq. (1) the last term is estimated to equal 0.02 J mole⁻¹ °K⁻¹ in magnitude and thus to be < 0.4% of $(\partial\phi/\partial T)_{P,x}$ along the portion of the phase-separation curve of interest.

The molar entropy s along each branch of the phase-separation curve was determined using the relation

$$s = -\left[x_0\left(\frac{d\mu_3}{dT}\right)_\sigma + (1-x_0)\left(\frac{d\mu_4}{dT}\right)_\sigma\right]$$
$$- (x-x_0)\left(\frac{d\phi}{dT}\right)_\sigma + v\left(\frac{dP}{dT}\right)_\sigma. \quad (2)$$

Here the last term on the right-hand side never exceeds 0.08 J mole⁻¹ °K⁻¹ and thus remains < 1.0% of s along the portion of the phase-separation curve of interest. Finally, the difference $\phi - \phi_0$ along the phase-separation curve was evaluated simply by integrating $(d\phi/dT)_\sigma$ from the junction down to the temperature desired.

Having considered the determination of $(\partial s/\partial T)_{P,x}$, $(\partial\phi/\partial T)_{P,x}$, $(\partial\phi/\partial x)_{P,T}$, s, and $\phi - \phi_0$ along the two branches of the phase-separation curve, we may now turn to the evaluation of these same quantities for the liquid in the homogeneous region at saturated vapor pressure. Determinations of all but $(\partial\phi/\partial x)_{P,T}$ were carried out for ten evenly spaced values of x, and the phase-separation and λ temperatures for these values of x are listed in Table II.

The derivative $(\partial s/\partial T)_{P,x} = c_{P,x}/T$ in the homo-

TABLE II. Values of T_σ and T_λ at evenly spaced values of x.

x	T_σ (°K)	T_λ (°K)
0.540	0.812	1.198
0.560	0.823	1.149
0.580	0.833	1.100
0.600	0.842	1.051
0.620	0.850	1.002
0.640	0.858	0.953
0.660	0.866	0.904
0.680	0.861	···
0.700	0.830	···
0.720	0.802	···

geneous region at saturated vapor pressure was obtained directly from interpolations of smoothed data for $c_{P,x}/T$. Values of $(\partial s/\partial T)_{P,x}$ for selected values of T are given in Table III, and plots of $(\partial s/\partial T)_{P,x}$ for four representative evenly spaced values of x are displayed as solid curves in Fig. 1. A plot of $(\partial s/\partial T)_{P,x}$ for $x = x_0 = 0.6735$ is also included. The long-dashed curves in Fig. 1 show $(\partial s/\partial T)_{P,x}$ along the two branches of the phase-separation curve.

The derivative $(\partial \phi/\partial T)_{P,x} = -(\partial s/\partial x)_{P,T}$ in the homogeneous region at saturated vapor pressure was found by integrating the quantity

$$\left[\frac{d}{dT}\left(\frac{\partial \phi}{\partial T}\right)_{P,x}\right]_x = -\left[\frac{d}{dx}\left(\frac{\partial s}{\partial T}\right)_{P,x}\right]_T$$

$$-\left(\frac{\partial^2 v}{\partial T^2}\right)_{P,x}\left(\frac{dP}{dx}\right)_T + \left(\frac{\partial^2 v}{\partial x \partial T}\right)_P\left(\frac{dP}{dT}\right)_x \quad (3)$$

with respect to T along curves of constant x up from the phase-separation curve, where $(\partial \phi/\partial T)_{P,x}$ was already known. In the regions well away from the λ and phase-separation curves, $[d(\partial s/\partial T)_{P,x}/dx]_T$ could be evaluated by direct
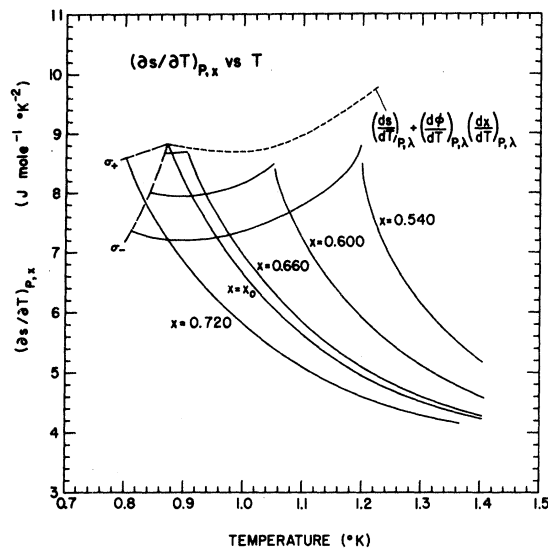

FIG. 1. Derivative $(\partial s/\partial T)_{P,x} = c_{P,x}/T$ at saturated vapor pressure. The solid curves show $(\partial s/\partial T)_{P,x}$ at five representative values of x including $x_0 = 0.6735$. The long-dashed curves show $(\partial s/\partial T)_{P,x}$ along the two arms of the phase-separation curve. The short-dashed curve shows $(ds/dT)_{P,\lambda} + (d\phi/dT)_{P,\lambda}(dx/dT)_{P,\lambda}$ along the λ curve (see Sec. III).

differentiation of smoothed data for $(\partial s/\partial T)_{P,x}$ at constant T. However, near the λ and phase-separation curves this procedure was not suitable. In these regions, $(\partial s/\partial T)_{P,x}$ was differentiated along lines parallel or nearly parallel to the curve in question in the T, x plane, using the relationship

$$\left[\frac{d}{dx}\left(\frac{\partial s}{\partial T}\right)_{P,x}\right]_T = \left[\frac{d}{dx}\left(\frac{\partial s}{\partial T}\right)_{P,x}\right]_\alpha$$

$$-\left[\frac{d}{dT}\left(\frac{\partial s}{\partial T}\right)_{P,x}\right]_x\left(\frac{dT}{dx}\right)_\alpha \quad (4)$$

TABLE III. The derivative $(\partial s/\partial T)_{P,x} = c_{P,x}/T$ at saturated vapor pressure.

| T (°K)			$\left(\dfrac{\partial s}{\partial T}\right)_{P,x}$ (J mole^{-1} °K^{-2})					
x	T_σ	T_λ	0.900	1.000	1.100	1.200	1.300	1.400
0.540	7.37	≥8.84	7.21	7.37	7.81	8.39	6.15	5.20
0.560	7.59	≥8.68	7.46	7.64	8.13	6.98	5.71	4.95
0.580	7.81	≥8.56	7.71	7.91		6.36	5.37	4.76
0.600	8.02	≥8.51	7.95	8.18	7.22	5.91	5.12	4.61
0.620	8.24	≥8.51	8.19	8.49	6.64	5.59	4.92	4.49
0.640	8.46	≥8.56	8.44	7.56	6.20	5.32	4.75	4.38
0.660	8.68	≥8.70	8.70	6.95	5.84	5.10	4.61	4.29
0.680	8.80	···	7.96	6.49	5.55	4.90	4.48	4.22
0.700	8.70	···	7.33	6.11	5.30	4.75	4.38	4.15
0.720	8.60	···	6.84	5.81	5.10	4.61	4.30	
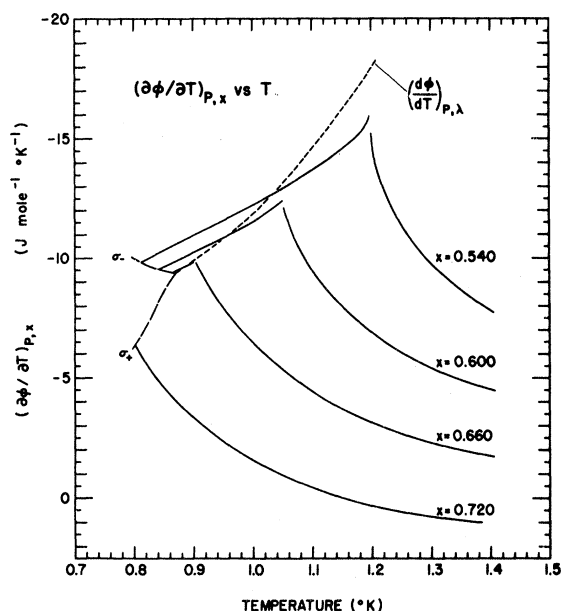
FIG. 2. Derivative $(\partial\phi/\partial T)_{P,x} = -(\partial s/\partial x)_{P,T}$ at saturated vapor pressure. The solid curves show $(\partial\phi/\partial T)_{P,x}$ at four representative values of x. The long-dashed curves show $(\partial\phi/\partial T)_{P,x}$ along the two arms of the phase-separation curve. The short-dashed curve shows $(d\phi/dT)_{P,\lambda}$ along the λ curve (see Sec. III).

to evaluate $[d(\partial s/\partial T)_{P,x}/dx]_T$. Here the subscript α is used to denote differentiation along the appropriate line at saturated vapor pressure. The magnitude of the sum of the last two terms on the right-hand side of Eq. (3), which arise from the nonconstancy of saturated vapor pressure, never exceeds 0.02 J mole⁻¹ °K⁻² and thus remains < 1% of the main term. Values of $(\partial\phi/\partial T)_{P,x}$ for

selected values of T are given in Table IV, and plots of $(\partial\phi/\partial T)_{P,x}$ for four representative evenly spaced values of x are displayed as solid curves in Fig. 2. The long-dashed curves in Fig. 2 show $(\partial\phi/\partial T)_{P,x}$ along the two branches of the phase-separation curve.

A comparison of our values of $(\partial\phi/\partial T)_{P,x}$ with those estimated at four points from the excess chemical potentials determined by Roberts and Swartz[7] yielded agreement to within 0.8 J mole⁻¹ °K⁻¹, with our values tending to be less negative than those derived from Roberts and Swartz. For comparison, those values have also been listed in Table IV.

The molar entropy s of the liquid in the homogeneous region at saturated vapor pressure was determined by integrating the quantity

$$\left(\frac{ds}{dT}\right)_x = \left(\frac{\partial s}{\partial T}\right)_{P,x} - \left(\frac{\partial v}{\partial T}\right)_{P,x}\left(\frac{dP}{dT}\right)_x \quad (5)$$

along lines of constant x up from the phase-separation curve, where s was already known. The magnitude of the last term on the right-hand side of Eq. (5), which arises from the nonconstancy of saturated vapor pressure, never exceeds 0.01 J mole⁻¹ °K⁻² and thus remains < 0.3% of $(\partial s/\partial T)_{P,x}$. Values of s for selected values of T are given in Table V, and plots of s for four representative evenly spaced values of x are displayed as solid curves in Fig. 3. The long-dashed curves in Fig. 3 show s along the two branches of the phase-spearation curve, while the short-dashed curve shows s along the λ curve.

Last, $\phi - \phi_0$ for the liquid in the homogeneous region at saturated vapor pressure was determined by integrating the quantity

TABLE IV. The derivative $(\partial\phi/\partial T)_{P,x} = -(\partial s/\partial x)_{P,T}$ at saturated vapor pressure. The main body of the table represents our determinations assuming $(d\phi/dT)_{\sigma;0} = -9.38$ J mole⁻¹°K⁻¹. The entries in the lower portion of the table were derived from the excess chemical potentials of Roberts and Swartz (Ref. 7).

			$\left(\dfrac{\partial\phi}{\partial T}\right)_{P,x}$ (J mole⁻¹°K⁻¹)					
T (°K) x	T_σ	T_λ	0.900	1.000	1.100	1.200	1.300	1.400
0.540	−9.83	≤ −16.05	−10.95	−12.22	−13.69	−15.00	−9.76	−7.82
0.560	−9.70	≤ −14.68	−10.68	−11.96	−13.45	−10.68	−8.04	−6.59
0.580	−9.60	≤ −13.47	−10.44	−11.71		−8.51	−6.59	−5.48
0.600	−9.52	≤ −12.42	−10.23	−11.52	−9.48	−6.89	−5.40	−4.52
0.620	−9.46	≤ −11.48	−10.07	−11.45	−7.51	−5.59	−4.38	−3.66
0.640	−9.42	≤ −10.61	−9.92	−8.51	−5.89	−4.35	−3.36	−2.75
0.660	−9.40	≤ −9.87	−9.82	−6.48	−4.44	−3.13	−2.29	−1.75
0.680	−9.04	···	−7.54	−4.82	−3.11	−2.01	−1.30	−0.83
0.700	−7.60	···	−5.20	−3.05	−1.66	−0.76	−0.18	0.19
0.720	−6.39	···	−3.34	−1.59	−0.45	0.31	0.78	
0.600				−9.47			−6.14	
0.700				−2.04			−0.71	

TABLE V. The molar entropy s at saturated vapor pressure assuming $(d\phi/dT)_{\sigma;0} = -9.38$ J mole^{-1}°K^{-1} and $x_0(d\mu_3/dT)_{\sigma;0}$ $+ (1-x_0)(d\mu_4/dT)_{\sigma;0} = -10.64$ J mole^{-1}°K^{-1}.

T (°K)			$s(T,x)$ (J mole^{-1}°K^{-1})					
x	T_σ	T_λ	0.900	1.000	1.100	1.200	1.300	1.400
0.540	8.97	11.89	9.61	10.33	11.09	11.91	12.61	13.17
0.560	9.25	11.77	9.83	10.58	11.36	12.16	12.79	13.32
0.580	9.52	11.63	10.04	10.82	11.63	12.35	12.93	13.44
0.600	9.78	11.47	10.24	11.05	11.85	12.50	13.05	13.54
0.620	10.04	11.30	10.45	11.28	12.02	12.63	13.15	13.62
0.640	10.30	11.10	10.65	11.48	12.16	12.74	13.24	13.69
0.660	10.55	10.88	10.85	11.62	12.26	12.80	13.29	13.73
0.680	10.69	...	11.02	11.73	12.33	12.85	13.32	13.75
0.700	10.59	...	11.15	11.82	12.38	12.88	13.34	13.76
0.720	10.48	...	11.23	11.85	12.40	12.88	13.33	

$$\left(\frac{d\phi}{dT}\right)_x = \left(\frac{\partial\phi}{\partial T}\right)_{P,x} + \left(\frac{\partial v}{\partial x}\right)_{P,T}\left(\frac{dP}{dT}\right)_x \qquad (6)$$

along lines of constant x up from the phase-separation curve, where $\phi - \phi_0$ was already known. The magnitude of the last term on the right-hand side of Eq. (6), which arises from the nonconstancy of saturated vapor pressure, varies between 0.02 and 0.13 Jmole^{-1}°K^{-1}. Values of $\phi - \phi_0$ for selected values of T are given in Table VI, and plots of $\phi - \phi_0$ for four representative evenly spaced values of x are displayed as solid curves in Fig. 4. The long-dashed curve in Fig. 4 shows $\phi - \phi_0$ along the phase-separation curve, while the short-dashed curve shows $\phi - \phi_0$ along the λ curve.

It would have been of considerable interest to complete the picture by obtaining the derivative $(\partial\phi/\partial x)_{P,T}$ in the homogeneous region at saturated vapor pressure. In principle, it could be determined either by differentiation of $\phi - \phi_0$ with respect to x or by differentiation of $(\partial\phi/\partial T)_{P,x}$ with respect to x followed by integration with respect to T. However, because of the accumulation of error involved in the succession of differentiations and integrations of the data involved, it did not seem likely that enough detail could be preserved to make the process worthwhile.

A rather coarse-grained determination of $(d\phi/dx)_T$ was in fact carried out by direct differentiation of $\phi - \phi_0$, and although the scatter was rather large, the values obtained compared well with a determination of $(d\phi/dx)_T$ obtained rather
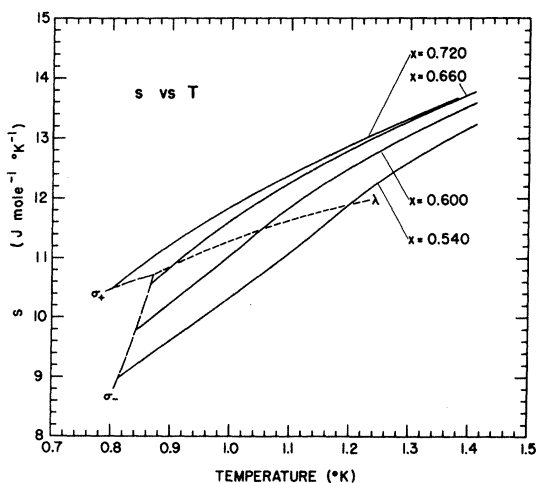

FIG. 3. Molar entropy s at saturated vapor pressure. The solid curves show s at four representative values of x. The long-dashed curves show s along the two arms of the phase-separation curve. The short-dashed curve shows s along the λ curve.
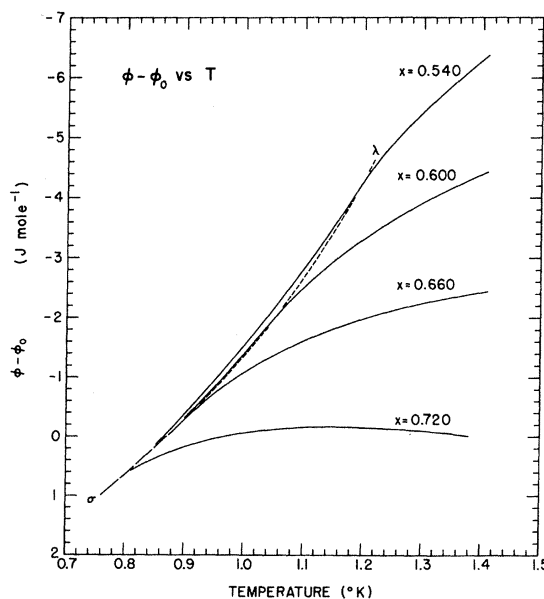

FIG. 4. Quantity $\phi - \phi_0$ at saturated vapor pressure. The solid curves show $\phi - \phi_0$ at four representative values of x. The long-dashed curve shows $\phi - \phi_0$ along the phase-separation curve. The short-dashed curve shows $\phi - \phi_0$ along the λ curve.

TABLE VI. The quantity $\phi - \phi_0$ at saturated vapor pressure assuming $(d\phi/dT)_{\sigma,0} = -9.38$ J mole^{-1}°K^{-1}.

T (°K) \ x	T_σ	T_λ	$\phi(T,x) - \phi_0$ (J mole^{-1})					
			0.900	1.000	1.100	1.200	1.300	1.400
0.540	0.54	−4.24	−0.37	−1.53	−2.82	−4.27	−5.43	−6.29
0.560	0.44	−3.41	−0.34	−1.47	−2.73	−4.02	−4.94	−5.65
0.580	0.35	−2.67	−0.32	−1.42	−2.67	−3.69	−4.43	−5.01
0.600	0.27	−1.99	−0.30	−1.39	−2.51	−3.31	−3.91	−4.39
0.620	0.20	−1.38	−0.29	−1.36	−2.27	−2.91	−3.40	−3.79
0.640	0.12	−0.83	−0.28	−1.27	−1.97	−2.47	−2.84	−3.14
0.660	0.05	−0.32	−0.28	−1.08	−1.61	−1.98	−2.24	−2.43
0.680	0.09	···	−0.23	−0.83	−1.22	−1.46	−1.62	−1.71
0.700	0.38	···	−0.06	−0.46	−0.69	−0.80	−0.83	−0.82
0.720	0.63	···	0.18	−0.06	−0.15	−0.15	−0.09	

directly from the vapor-pressure data of Sydoriak and Roberts[5] using an approximate form of the appropriate generalization of the Clapeyron equation for the mixtures in equilibrium with the vapor.[8,9]

III. THE λ TRANSITION

On rather general grounds it is attractive to suppose that the basic nature of the λ transition in He³/He⁴ mixtures is the same as in pure He⁴. In accord with suggestions by Rice[10] and by Fisher,[11] the specific heat $c_{P,\phi}$, which for stability reasons must always be $\geq c_{P,x}$, might then be expected to diverge in a manner similar to c_P for pure He⁴ while $c_{P,x}$ shows a "renormalized" nondivergent critical behavior. It should be mentioned that Wheeler and Griffiths have given rather general arguments which show that if $c_{P,x}$ diverges at all at the λ curve it must do so only at isolated points.[12]

In order to discuss the relation between $(\partial s/\partial T)_{P,\phi} = c_{P,\phi}/T$, $(\partial s/\partial T)_{P,x} = c_{P,x}/T$, and other thermodynamic derivatives of the same order near the λ curve, it is helpful to apply to the mixtures in ϕ, x, T space (at constant P) the same arguments which have been applied by Buckingham and Fairbank[13] and by Lipa and Buckingham[14] to pure He⁴ in P, v, T space, utilizing the analogy developed in Sec. II of Paper I. In particular, one may derive the following relations between $(\partial\phi/\partial x)_{P,T}$, $(\partial s/\partial T)_{P,\phi}$, $(\partial s/\partial T)_{P,x}$, and $(\partial\phi/\partial T)_{P,x}$ at an arbitrary point in T, x (or T, ϕ) space:

$$\left(\frac{\partial\phi}{\partial x}\right)_{P,T} = \left(\frac{d\phi}{dT}\right)_{P,\alpha}^2 \Bigg/ \left[\left[\left(\frac{\partial s}{\partial T}\right)_{P,\phi} - \left(\frac{ds}{dT}\right)_{P,\alpha}\right]\right.$$
$$\left. + \left(\frac{d\phi}{dT}\right)_{P,\alpha}\left(\frac{dx}{dT}\right)_{P,\alpha}\right], \quad (7)$$

$$\left(\frac{\partial\phi}{\partial x}\right)_{P,T} = \left[\left(\frac{ds}{dT}\right)_{P,\alpha} + \left(\frac{d\phi}{dT}\right)_{P,\alpha}\left(\frac{dx}{dT}\right)_{P,\alpha}\right]$$

$$- \left(\frac{\partial s}{\partial T}\right)_{P,x}\Bigg] \Bigg/ \left(\frac{dx}{dT}\right)_{P,\alpha}^2, \quad (8)$$

$$\left(\frac{\partial\phi}{\partial x}\right)_{P,T} = \left[\left(\frac{d\phi}{dT}\right)_{P,\alpha} - \left(\frac{\partial\phi}{\partial T}\right)_{P,x}\right] \Bigg/ \left(\frac{dx}{dT}\right)_{P,\alpha}. \quad (9)$$

Here the derivatives ( )$_{P,\alpha}$ are evaluated along some arbitrary curve α in T, x (or T, ϕ) space (at constant P) passing through the point in question. A number of other similar expressions can also be derived, each relating a pair of partial derivatives of the same order as $(\partial\phi/\partial x)_{P,T}$, $(\partial s/\partial T)_{P,\phi}$, $(\partial s/\partial T)_{P,x}$, and $(\partial\phi/\partial T)_{P,x}$. Some closely related expressions have recently been presented by Rice and Chang.[15]

Let us apply these relations in the limit as the λ curve is approached from either side, choosing curve α to become the λ curve in the limit. We may expect the derivatives $(ds/dT)_{P,\lambda}$, $(d\phi/dT)_{P,\lambda}$, and $(dx/dT)_{P,\lambda}$ all to be well defined and finite. Assuming that these derivatives are all nonzero, we then see immediately that the following four statements are either all true or all false together at the λ curve: (i) $(\partial\phi/\partial x)_{P,T}$ vanishes; (ii) $(\partial s/\partial T)_{P,\phi} = c_{P,\phi}/T$ diverges; (iii) $(\partial s/\partial T)_{P,x} = c_{P,x}/T$ attains its upper bound of $(ds/dT)_{P,\lambda} + (d\phi/dT)_{P,\lambda}(dx/dT)_{P,\lambda}$; (iv) $(\partial\phi/\partial T)_{P,x}$ attains its upper bound of $(d\phi/dT)_{P,\lambda}$.

From (i) and (ii) we see that the conclusion that $(\partial\phi/\partial x)_{P,T}$ vanishes at the junction reached in Paper I implies immediately that $(\partial s/\partial T)_{P,\phi}$ diverges there. In regard to the more general question of whether the above statements hold all along the λ curve we may turn to (iii) and (iv).

We have estimated the derivatives $(ds/dT)_{P,\lambda}$ and $(d\phi/dT)_{P,\lambda}$ by direct differentiation of our values for s and $\phi - \phi_0$ along the λ curve at saturated vapor pressure using the formulas

$$\left(\frac{ds}{dT}\right)_{P,\lambda} = \left(\frac{ds}{dT}\right)_{\lambda} + \left(\frac{\partial v}{\partial T}\right)_{P,x}\left(\frac{dP}{dT}\right)_{\lambda} - \left(\frac{\partial \phi}{\partial T}\right)_{P,x}\left(\frac{dx}{dT}\right)_{\lambda}\left(\frac{dP}{dT}\right)_{\lambda}\Big/\left[\left(\frac{dP}{dT}\right)_{x,\lambda} - \left(\frac{dP}{dT}\right)_{\lambda}\right], \quad (10)$$

$$\left(\frac{d\phi}{dT}\right)_{P,\lambda} = \left[\left(\frac{d\phi}{dT}\right)_{\lambda} - \left(\frac{\partial v}{\partial x}\right)_{P,T}\left(\frac{dP}{dT}\right)_{\lambda} - \left(\frac{\partial \phi}{\partial T}\right)_{P,x}\left(\frac{dP}{dT}\right)_{\lambda}\left(\frac{dP}{dT}\right)_{x,\lambda}^{-1}\right]\Big/\left[1 - \left(\frac{dP}{dT}\right)_{\lambda}\left(\frac{dP}{dT}\right)_{x,\lambda}^{-1}\right]. \quad (11)$$

The derivative $(dx/dT)_{P,\lambda}$ was estimated from the inverse slope of the λ curve in the T, x plane at saturated vapor pressure by means of the formula

$$\left(\frac{dx}{dT}\right)_{P,\lambda} = \left(\frac{dx}{dT}\right)_{\lambda}\Big/\left[1 - \left(\frac{dP}{dT}\right)_{\lambda}\left(\frac{dP}{dT}\right)_{x,\lambda}^{-1}\right]. \quad (12)$$

In all three of the above formulas the terms on the right-hand side due to the nonconstancy of saturated vapor pressure bring in a correction of less than 0.3% to the main term. In calculating the magnitudes of the correction terms use was made of an estimate of ~ -100 atm $^\circ$K^{-1} for $(dP/dT)_{x,\lambda}$.[16,17] Our estimates of the three derivatives $(ds/dT)_{P,\lambda}$, $(d\phi/dT)_{P,\lambda}$, and $(dx/dT)_{P,\lambda}$ at selected values of T are presented in Table VII.

In order to make the comparison that is of interest in (iii), the quantity $(ds/dT)_{P,\lambda} + (d\phi/dT)_{P,\lambda} \times (dx/dT)_{P,\lambda}$ has been plotted in Fig. 1 as the short-dashed curve. In this plot the solid curves for $(\partial s/\partial T)_{P,x}$ end at a distance of 1 m $^\circ$K from the λ transition on each side. At the lowest concentration the maximum value of $(\partial s/\partial T)_{P,x}$ plotted falls below its calculated upper bound by ~ 0.8 J mole^{-1} $^\circ$K^{-2}. However, in view of the limited resolution of the data it is quite possible, although by no means established, that $(\partial s/\partial T)_{P,x}$ does in fact attain its upper bound all along the λ curve and that thus all four statements are true there. A similar conclusion was reached by Gasparini and Moldover at lower values of x.[18]

With regard to (iv), the derivative $(d\phi/dT)_{P,\lambda}$ has been plotted in Fig. 2 as the short-dashed curve for comparison with $(\partial \phi/\partial T)_{P,x}$ near the λ transition. A conclusion similar to that above is reached here. It seems entirely possible although by no means certain that $(\partial \phi/\partial T)_{P,x}$ attains its upper bound $(d\phi/dT)_{P,\lambda}$ all along the λ curve.

The estimates made here for $(ds/dT)_{P,\lambda}$ and $(d\phi/dT)_{P,\lambda}$ each depend on the value determined

for $(d\phi/dT)_{\sigma;0}$ and thus on our integration of $(d^2\phi/dT^2)_\sigma$ up from $T = 0$, which was based in part on outside data. However, this dependence cancels out in the quantity $(ds/dT)_{P,\lambda} + (d\phi/dT)_{P,\lambda}(dx/dT)_{P,\lambda}$. Further, the value of $(d\phi/dT)_{\sigma;0}$ is an additive component of both $(d\phi/dT)_{P,\lambda}$ and $(\partial \phi/\partial T)_{P,x}$ and thus cancels out in the comparison of these two quantities. Thus both of the comparisons between maximum values and upper bounds discussed above are based entirely on our measurements of $c_{P,x}$, except for the rather small vapor-pressure corrections.

A firmer conclusion about the validity of the four statements along the λ curve awaits some combination of more detailed measurements of thermodynamic quantities near the λ curve and more accurate determinations of the derivatives $(ds/dT)_{P,\lambda}$, $(d\phi/dT)_{P,\lambda}$, and $(dx/dT)_{P,\lambda}$ along the λ curve.

IV. CRITICAL BEHAVIOR NEAR THE JUNCTION

The most direct and detailed information contained in our data about critical behavior near the junction concerns the behavior of $(\partial s/\partial T)_{P,x} = c_{P,x}/T$ at saturated vapor pressure along the curve $x = x_0$ for $T \geq T_0$. The most probable form for this behavior was constructed by extrapolation and interpolation of our smoothed data for $(\partial s/\partial T)_{P,x}$ and is presented in Table VIII. The data in this table have been included in Fig. 1, and within the resolution available our curve appears to have finite slope at T_0. A more sensitive test of this question is provided in Fig. 5, where $\ln[(\partial s/\partial T)_{P,x;0} - (\partial s/\partial T)_{P,x}]$ for these same data is plotted against

TABLE VII. Derivatives along the λ curve.

T ($^\circ$K)	$\left(\dfrac{ds}{dT}\right)_{P,\lambda}$ (J mole^{-1} $^\circ$K^{-2})	$\left(\dfrac{d\phi}{dT}\right)_{P,\lambda}$ (J mole^{-1} $^\circ$K^{-1})	$\left(\dfrac{dx}{dT}\right)_{P,\lambda}$ ($^\circ$K^{-1})
0.871	4.99	-9.40	-0.409
0.900	4.73	-9.88	-0.409
1.000	3.86	-11.86	-0.409
1.100	3.03	-14.56	-0.409

TABLE VIII. The derivative $(\partial s/\partial T)_{P,x} = c_{P,x}/T$ at saturated vapor pressure along the curve $x = x_0 = 0.6735$ for $T \geq T_0$.

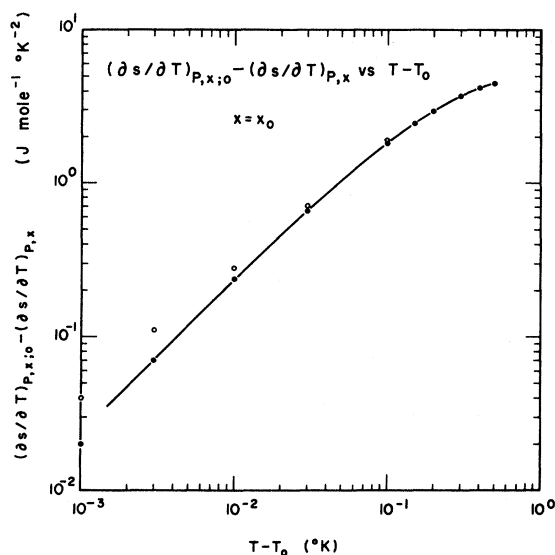| T ($^\circ$K)	$(\partial s/\partial T)_{P,x}$ (J mole^{-1} $^\circ$K^{-2})
0.871	8.83
0.872	8.81
0.874	8.76
0.881	8.59
0.901	8.17
0.971	7.01
1.021	6.39
1.071	5.88
1.171	5.12
1.271	4.63
1.371	4.31

FIG. 5. Quantity $\ln[(\partial s/\partial T)_{P,x;0} - (\partial s/\partial T)_{P,x}]$ = $\ln[(c_{P,x}/T)_0 - (c_{P,x}/T)]$ at saturated vapor pressure vs $\ln(T - T_0)$ for $x = x_0 = 0.6735$. The solid circles represent the set of most-probable values. The open circles represent a somewhat unlikely but possible alternative set of values.
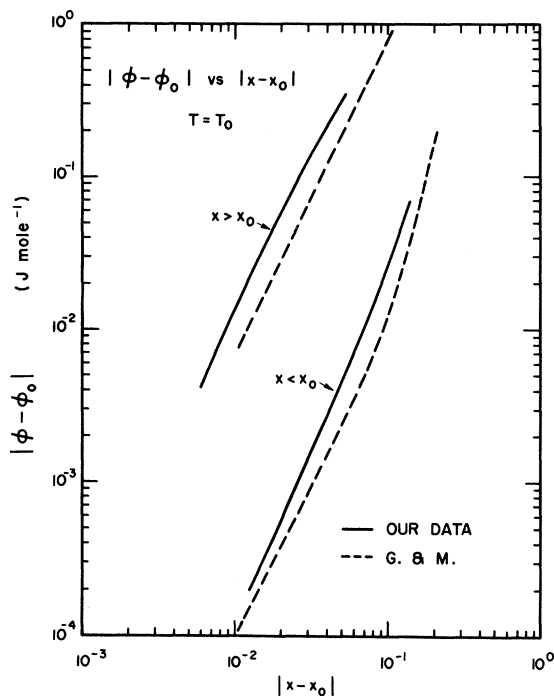

FIG. 6. Quantity $\ln|\phi - \phi_0|$ at saturated vapor pressure vs $\ln|x - x_0|$ for $T = T_0 = 0.871$ °K. The solid curves show our results, while the dashed curves show the results of Goellner and Meyer (Ref. 9).

$\ln(T - T_0)$ as solid circles. The open circles in Fig. 5 represent a somewhat unlikely but possible alternative set of values for $\ln[(\partial s/\partial T)_{P,x;0} - (\partial s/\partial T)_{P,x}]$, and the difference between the two sets is representative of the uncertainties involved. The most probable values are consistent with a curve whose limiting slope as $T - T_0$ goes to zero is unity. Thus our data are consistent with an asymptotic behavior for $(\partial s/\partial T)_{P,x}$ at $x = x_0$ described by the expression

$$\left(\frac{\partial s}{\partial T}\right)_{P,x;0} - \left(\frac{\partial s}{\partial T}\right)_{P,x} \sim (T - T_0)^1. \qquad (13)$$

In Paper I evidence was presented for the vanishing of $(\partial\phi/\partial x)_{P,T}$ at the junction along both arms of the phase-separation curve, with asymptotic temperature dependences characterized by the expression

$$\left(\frac{\partial\phi}{\partial x}\right)_{P,T} \sim (T_0 - T)^{\gamma'_\pm}, \qquad (14)$$

with $\gamma'_\pm$ both $\cong 1$. Here $\pm$ refer to the He³-rich and He³-poor branches, respectively. We may now use our determination of $\phi - \phi_0$ to investigate the behavior of the integral of $(\partial\phi/\partial x)_{P,T}$ along the critical isotherm $T = T_0$. Values of $\phi - \phi_0$ at saturated vapor pressure along the critical isotherm are presented in Table IX, and Fig. 6 shows a plot of $\ln|\phi - \phi_0|$ vs $\ln|x - x_0|$ for x both less than and greater than x_0. The solid curves show our determinations, while the dashed curves

show the determinations of Goellner and Meyer based on a combination of their vapor-pressure measurements and our determination of $(\partial\phi/\partial x)_{P,T}$ at the phase-separation curve.[9] It appears that both our data and those of Goellner and Meyer are consistent with asymptotic behaviors for $\phi-\phi_0$ along the critical isotherm given by the expression

$$|\phi - \phi_0| \sim |x - x_0|^{\delta_\pm}, \qquad (15)$$

in which, with some uncertainty, both $\delta_\pm = 2$. However, our values of $|\phi - \phi_0|$ are consistently larger than theirs by a factor of up to 2. Note that

TABLE IX. The quantity $\phi - \phi_0$ at saturated vapor pressure for $T = T_0 = 0.871$ °K.

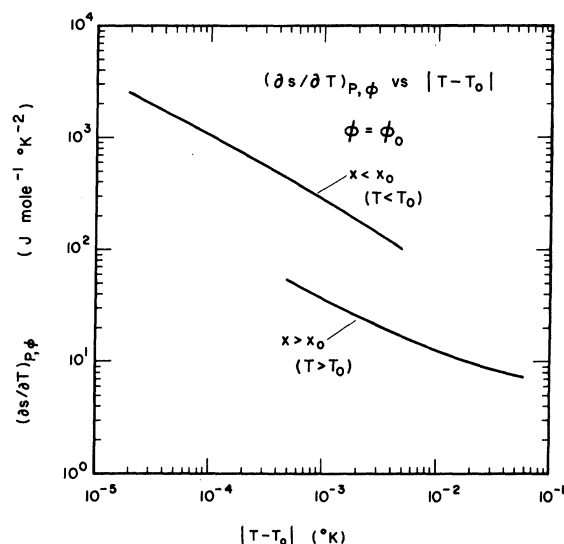| x	$\phi - \phi_0$ (J mole⁻¹)
0.540	− 0.0604
0.560	− 0.0378
0.580	− 0.0221
0.600	− 0.0117
0.620	− 0.00551
0.640	− 0.00186
0.660	− 0.00024
0.680	0.00522
0.700	0.101
0.720	0.281

FIG. 7. Quantity $\ln(\partial s/\partial T)_{P,\phi} = \ln(c_{P,\phi}/T)$ at saturated vapor pressure vs $\ln|T - T_0|$ for $\phi = \phi_0$. The condition $x < x_0$ corresponds to $T < T_0$ while $x > x_0$ corresponds to $T > T_0$.

$|\phi - \phi_0|$ is two orders of magnitude smaller on the He³-poor side of the junction than on the He³-rich side. This asymmetry implies much smaller values of $(\partial\phi/\partial x)_{P,T}$ on the He³-poor side than on the He³-rich side, an asymmetry which has already been noted along the phase-separation curve. [1]

We can also use our determinations of $\phi - \phi_0$ to construct at saturated vapor pressure the curve $\phi = \phi_0$. Further, one can construct along this curve the derivative $(\partial s/\partial T)_{P,\phi} = c_{P,\phi}/T$ as a function of temperature using the formula

$$\left(\frac{\partial s}{\partial T}\right)_{P,\phi} = \left(\frac{\partial s}{\partial T}\right)_{P,x} - \left(\frac{\partial\phi}{\partial T}\right)_{P,x}\left(\frac{\partial x}{\partial T}\right)_{P,\phi} , \qquad (16)$$

where $(\partial x/\partial T)_{P,\phi}$ is given in terms of $(dx/dT)_\phi$, the inverse slope of the curve $\phi = \phi_0$ in the T, x plane, by the expression

$$\left(\frac{\partial x}{\partial T}\right)_{P,\phi} = \left(\frac{dx}{dT}\right)_\phi \left\{1 + \left(\frac{\partial v}{\partial x}\right)_{P,T}\left[\frac{v_v - v}{x_v - x} - \left(\frac{\partial v}{\partial x}\right)_{P,T}\right]^{-1}\right\} \Big/$$
$$\left[1 + \left(\frac{\partial v}{\partial x}\right)_{P,T}\left(\frac{dP}{dT}\right)_x\left(\frac{\partial\phi}{\partial T}\right)_{P,x}^{-1}\right]. \qquad (17)$$

Here the subscript v denotes vapor terms; all the remaining unmarked terms are liquid terms as in the rest of this paper. In deriving this formula use was made of the appropriate generalization of the Clapeyron equation for the mixtures in equilibrium with the vapor. [8] The difference between $(\partial x/\partial T)_{P,\phi}$ and $(dx/dT)_\phi$ amounts to less than 2% over the region of interest. A plot of $\ln(\partial s/\partial T)_{P,\phi}$ at saturated vapor pressure vs $\ln|T - T_0|$ along the curve $\phi = \phi_0$ is shown in Fig. 7 for T both be-

low and above T_0. Hence $(\partial s/\partial T)_{P,\phi}$ along the curve $\phi = \phi_0$ is seen to diverge at T_0 with asymptotic behaviors consistent with the expression

$$\left(\frac{\partial s}{\partial T}\right)_{P,\phi} \sim |T - T_0|^{-1/2} \qquad (18)$$

both below and above T_0, with some uncertainty in the exponent. Note that the magnitude of $(\partial s/\partial T)_{P,\phi}$ is quite asymmetrical about T_0 and that it reaches very large values for $T < T_0$ $(x < x_0)$.

We see then that at least within the resolution available, the asymptotic behavior of $(\partial s/\partial T)_{P,\phi}$ along a curve of constant ϕ at the low-temperature end of the λ curve is quite different from the very nearly logarithmic behavior of $(\partial s/\partial T)_P$ for pure He⁴ at the high-temperature end. Therefore, even if $(\partial s/\partial T)_{P,\phi}$ diverges all along the λ curve, there remains the question of how the relatively weak divergence of $(\partial s/\partial T)_P$ for pure He⁴ goes over into the rather stronger, approximately minus one-half power divergence of $(\partial s/\partial T)_{P,\phi}$ at the junction. A suggestion related to this question is made in Sec. V.

It is interesting to note that a minus one-half power divergence of $(\partial s/\partial T)_{P,\phi}$ vs T along the curve $\phi = \phi_0$ for $T > T_0$ is consistent with a linear behavior of $(\partial s/\partial T)_{P,x}$ vs T along the curve $x = x_0$ for $T > T_0$, according to the exponent renormalization scheme proposed by Fisher. [11]

V. CONCLUDING DISCUSSION

We turn now briefly to the subject of whether there is some simple functional form for the appropriate free energy which yields a good representation of the data for $(\partial s/\partial T)_{P,x}$ over the range of measurement. Such a form would not only provide a convenient description of the thermodynamics of the junction region but might also suggest a way to understand the region theoretically.

One such form, which includes a number of the distinctive qualitative features of the junction, has been proposed by Griffiths. [19] Another, rather general scaling form has recently been proposed by Riedel. [20] The initial disadvantage of these forms for our purpose is that their natural independent variables are T and ϕ rather than T and x. Although as suggested by Secs. III and IV there may be reasons to prefer the "field" ϕ over the "density" x as an independent variable, [21] our experimental results are obtained as a function of T and x. Of course, we have shown in Sec. II that it is possible to obtain the form of $\phi(T, x)$ from our measurements and thus to convert from T and x as independent variables to T and ϕ. Nevertheless, $\phi(T, x)$ is removed from $(\partial s/\partial T)_{P,x}$ by one differentiation and two integrations in which considerable error and loss of resolution may occur. One additional disadvantage of the Griffiths form for

fitting our results over a wide region is the absence of a provision for nonzero $d^2\phi/dT^2$ along the λ and phase-separation curves.

At the same time, the data at saturated vapor pressure do appear to have a certain simplicity in T, x space which suggests a rather simple representation. First, throughout the region of measurement the λ curve in T, x space is remarkably straight. Further, the two branches of the phase-separation curve approach the junction with smooth and apparently linear asymptotic forms in T, x space. Moreover, when plotted along straight lines radiating from the junction in T, x space, $(\partial s/\partial T)_{P,x}$ and the other thermodynamic functions determined from it in Sec. II appear to behave rather smoothly, with no indication along an individual line of a nonanalytic approach to the junction. As a result, we propose to attempt to represent the free energy $g(T, x)$ by the form

$$g(T,x)=\sum_{n=0}^{n(\max)} r^n g_n(\theta) \ , \qquad (19)$$

where r and θ are simply circular polar coordinates in T, x space with origin at the junction, and where $n(\max)$ is taken to be 4 or 5. For simplicity here we are neglecting variations of pressure. The nonanalyticity of the λ curve and junction are carried by the functions $g_n(\theta)$. It is conceivable that nonintegral powers of r might eventually be of use in such an expansion, but our data do not indicate such a need at present. It is true, of course, that this form is not invariant under linear changes in the T scale relative to the x scale. However, since such changes carry radial lines into new radial lines, it does not appear that this lack of invariance will cause any essential difficulty.

If we consider the use of the expression for $(\partial s/\partial T)_{P,x}$ derived from this form for g to represent our data, we can anticipate that the term involving $g_3(\theta)$ will express the behavior of $(\partial s/\partial T)_{P,x}$ close to the λ curve which is dominant near the junction, namely, a continuous behavior with discontinuous but finite slope. The more sharply peaked infinite-slope behavior seen farther away from the junction will be expressed by the term involving $g_4(\theta)$ and any higher-order terms which have been included. Thus in this representation the diminishing importance of the fourth- and higher-order terms relative to the third as the junction is approached provides a natural characterization of the way in which the critical behavior at the λ curve at lower concentrations goes over into the rather different critical behavior displayed at the junction discussed in Sec. IV. We intend to analyze our data using this form for g in a future paper.

ACKNOWLEDGMENTS

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