

SPECIFIC HEAT OF LIQUID  $\text{He}^3/\text{He}^4$  MIXTURES NEAR THE JUNCTION OF THE LAMBDA  
AND PHASE-SEPARATION CURVES

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The specific heat of liquid  $\text{He}^3/\text{He}^4$  mixtures has been measured at saturated vapor pressure for three values of the  $\text{He}^3$  mole fraction  $x$  near the junction of the lambda and phase-separation curves. The specific heat at the lambda peak appears to be finite, continuous, and cusped. Both the lambda peak and the anomaly in the specific heat as the system goes from the two-liquid-phase region to the one-liquid-phase region tend to disappear as the junction of phase boundaries is approached.

The nature of the lambda transition in liquid  $\text{He}^3/\text{He}^4$  mixtures and of the junction of the lambda and phase-separation curves are topics of growing interest. Recent measurements by Graf, Lee, and Reppy<sup>1</sup> based on the dielectric constant and thermal conduction of the liquid have indicated that in the  $T$  vs  $x$  plane at saturated vapor pressure the lambda curve meets the phase-separation curve in the manner shown by the lines in Fig. 1. Here  $T$  is the absolute temperature and  $x$  is the mole fraction of  $\text{He}^3$  present. As Rice has pointed out, the lambda transition and the phase separation seem to be intimately related, and the situation appears to be one in which a second-order phase transition goes over into a first-order transition with decreasing temperature.<sup>2</sup> In order to explore further the thermodynamics of this unusual junction of phase boundaries we undertook to measure the specific heat of the mixtures in this region, hoping to gain im-

proved resolution over the earlier measurements of de Bruyn Ouboter, Taconis, le Pair, and Beenakker.<sup>3</sup> This Letter is a report of our first results.

The measurements were made using a  $\text{He}^3$  refrigerator of conventional design. The calorimeter consisted principally of a 277-g, oxygen-free, high-conductivity copper cylinder. A 6.15-cm<sup>3</sup> cavity in this cylinder was filled with a compressed tangle of 0.07-mm-diam oxygen-free, high-conductivity copper wire to provide good thermal contact between liquid and calorimeter. The resulting sample space volume was approximately 2.8 cm<sup>3</sup>.

The mixtures were introduced into the calorimeter through a fill line which was closed with a valve only at the top of the cryostat. The lower part of this line consisted of a 0.25-mm-i.d. thin-wall cupro-nickel capillary partially filled with a 0.20-mm-o.d. stainless-steel wire. This section of capillary, whose overall length was approximately 60 cm, ran down from the main 4.2°K helium bath through pumped  $\text{He}^4$  and  $\text{He}^3$  pots, to each of which it was thermally anchored, and entered the calorimeter at the bottom. As a result some portion of the capillary between the calorimeter and the  $\text{He}^3$  pot was always filled with liquid, ensuring good thermal isolation between these two. For the measurements reported here, the sample space was between about 80 and 95% full of liquid.

Temperature measurements were made with a resolution of about  $10^{-5}$ °K using a germanium-doped resistance thermometer<sup>4</sup> calibrated against the 1962  $\text{He}^3$  vapor-pressure scale.<sup>5</sup> Specific-heat measurements were made by following the temperature drift of the calorimeter before and after short periods of electrical heating. In order to achieve a relative accuracy of a few tenths of a percent in specific heat, the smallest temperature interval spanned by a specific heat point was ~3 mdeg K. The temperature of the  $\text{He}^3$  pot

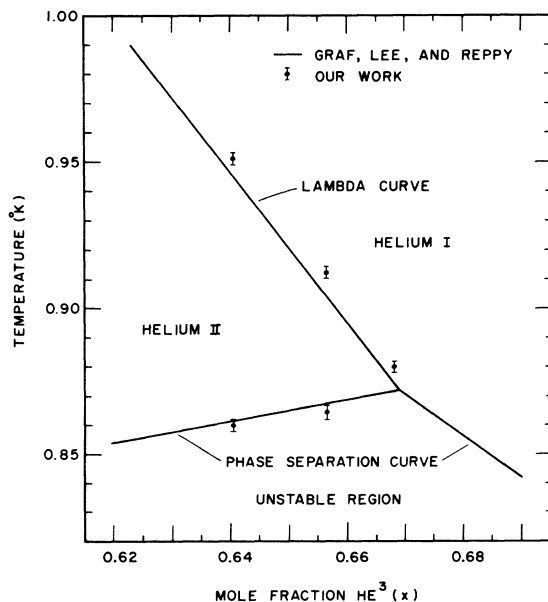


FIG. 1. Detail of the phase diagram for liquid  $\text{He}^3/\text{He}^4$  mixtures at saturated vapor pressure.

was normally held below that of the calorimeter, resulting in net negative heat leaks to the calorimeter of several erg/sec.

The most interesting features of our results are shown in Fig. 2. Each specific-heat point plotted there is simply the measured total specific heat minus the relatively small background specific heat of the calorimeter divided by the number of moles of sample present. For  $x=0.641$  the cell was approximately 81% full of liquid, for  $x=0.657$  approximately 94% full, and for  $x=0.668$  approximately 89% full. Although it is believed that the specific heat plotted is rather closely related to the molar specific heat of the liquid  $c_{P,x}$  at constant pressure  $P$  and mole fraction  $x$ , it must be kept in mind that in fact it was measured for a liquid-vapor system in which evaporation was taking place with increasing temperature and in which small pressure and mole fraction changes were taking place in both the liquid and vapor phases. A clear understanding of the relation between this specific heat and  $c_{P,x}$  awaits further analysis.

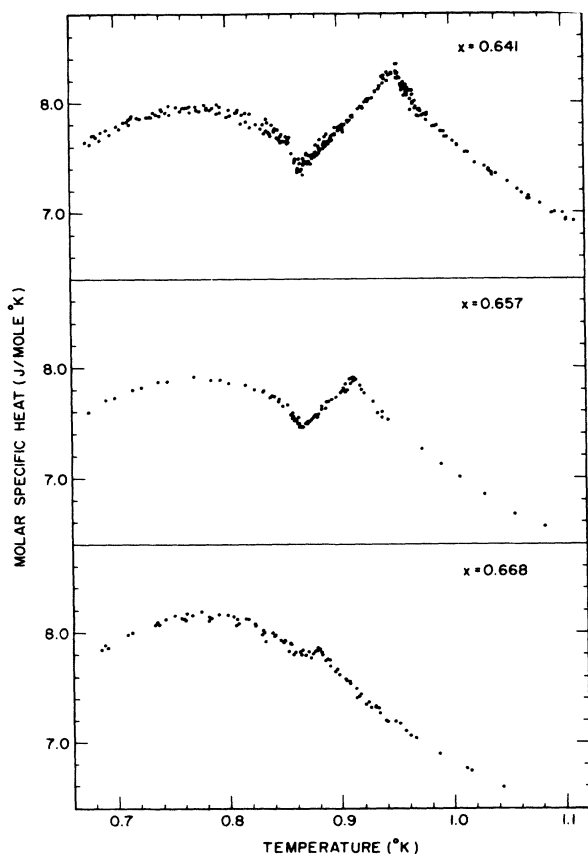


FIG. 2. Molar specific heats of liquid  $\text{He}^3/\text{He}^4$  mixtures at saturated vapor pressure for three different values of the  $\text{He}^3$  mole fraction  $x$ .

In the upper curve in Fig. 2 we believe there to be a discontinuity in both the specific heat and its first derivative at about  $0.860^\circ\text{K}$  separating the two-liquid-phase region from the one-liquid-phase region, and there occurs a peak at  $0.951^\circ\text{K}$  marking the lambda transition. Specific-heat points whose initial and final temperatures unambiguously spanned either the division between the two-liquid-phase and one-liquid-phase region or the lambda peak have not been plotted. However, a number of ambiguous cases in which these features may well have been spanned have been included in the plots, such as for example the points in the upper curve lying within a millidegree or so of  $0.860^\circ\text{K}$ . In the middle curve the discontinuity in the specific heat separating the two-liquid-phase region from the one-liquid-phase region, if present, is less pronounced, and the lambda peak is considerably diminished in size. In the lower curve, measured at a concentration close to the junction of the lambda and phase-separation curves, only a small bump remains. The locations of the features just described have been plotted in Fig. 1 as solid circles, where the error bars simply represent estimates of the temperature limits of these features as determined from Fig. 2. Our results are in rather good agreement with the results of Graf, Lee, and Reppy,<sup>1</sup> except perhaps for an overall positive displacement in  $x$  of about 0.003, which is within their stated experimental error for the absolute value of  $x$ .

There are two aspects of these results that are of particular interest. The first is that to the temperature resolution of our specific-heat measurements of  $\sim 3$  mdeg K the lambda peak at these concentrations appears to be finite (in accord with the stability arguments of Rice<sup>2</sup> and of Wheeler and Griffiths<sup>6</sup>), continuous, and cusped. It would, of course, be extremely desirable to pursue this question with increased temperature resolution. If the true asymptotic behavior of  $c_{P,x}$  at the lambda point for these mixtures is indeed correctly represented by this apparent behavior, it contrasts strongly to the apparent logarithmic plus discontinuous behavior of  $c_{P,x}$  for  $x=0$  (pure  $\text{He}^4$ ),<sup>7</sup> and it is of considerable interest to inquire how the latter behavior goes over into the former as  $x$  is increased from 0. It is also of interest to inquire whether for these mixtures the complementary but experimentally less accessible specific heat  $c_{P,\varphi}$  at constant pressure  $P$  and relative chemical potential per mole  $\varphi$  is infinite at the lambda point, even though

$c_{P,x}$  is finite.<sup>8</sup> Here  $\varphi$  is defined as  $\mu_3 - \mu_4$ , where  $\mu_3$  and  $\mu_4$  are the chemical potentials per mole of the He<sup>3</sup> and He<sup>4</sup> components, respectively.

The second aspect of interest is that as the value of  $x$  approaches that of the junction of the lambda and phase-separation curves, both the lambda anomaly and the discontinuities separating the two-liquid-phase region from the one-liquid-phase region tend to disappear, presumably leaving a smooth specific heat at the He<sup>3</sup> mole fraction of the junction.

The disappearance of the discontinuity in the specific heat separating the two-liquid-phase region from the one-liquid-phase region can be understood in terms of the nonzero slopes of the two arms of the phase-separation curve as they meet at the junction with the lambda curve. The present case differs from that of an ordinary upper critical point of a binary mixture which exhibits phase separation, where the slope of the phase-separation curve goes to zero at the critical temperature.<sup>9</sup> If we consider  $c_{P,x}$  of the liquid, it can be shown thermodynamically that the discontinuity  $\Delta c_{P,x}$  which occurs in going from the two-phase region to the one-phase region is always negative and is given by

$$\Delta c_{P,x} = -T \left( \frac{\partial \varphi}{\partial x} \right)_{P,T} \left( \frac{dx}{dT} \right)_{p.s.}^2. \quad (1)$$

The derivative  $(\partial \varphi / \partial x)_{P,T}$  is to be evaluated at the mean value of  $x$  for the mixture just inside the one-phase region, and  $(dx/dT)_{p.s.}$  is the reciprocal of the slope of the phase-separation curve at constant pressure at the same value of  $x$ . The separation into two phases requires that, in effect,  $(\partial \varphi / \partial x)_{P,T}$  be  $< 0$  in the unstable region immediately below the top of the phase-separation curve, whereas the stability against phase separation above the top requires that  $(\partial \varphi / \partial x)_{P,T}$  be  $\geq 0$  in that region. Thus  $(\partial \varphi / \partial x)_{P,T}$

may be expected to be zero at the top of the curve. This condition, together with the finiteness of  $(dx/dT)_{p.s.}$  as the top of the phase-separation curve is approached, implies that  $\Delta c_{P,x}$  may be expected to disappear at the top of the curve.

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<sup>1</sup>E. H. Graf, D. M. Lee, and J. D. Reppy, *Phys. Rev. Letters* **19**, 417 (1967).

<sup>2</sup>O. K. Rice, *Phys. Rev. Letters* **19**, 295 (1967).

<sup>3</sup>R. de Bruyn Ouboter, K. W. Taconis, C. le Pair, and J. J. M. Beenakker, *Physica* **26**, 853 (1960).

<sup>4</sup>Model CG-4, Radiation Research Corporation, Westbury, N. Y.

<sup>5</sup>R. H. Sherman, S. G. Sydorik, and T. R. Roberts, *J. Res. Natl. Bur. Std. (U.S.)* **68A**, 579 (1964).

<sup>6</sup>J. C. Wheeler and R. B. Griffiths, *Phys. Rev.* **170**, 249 (1968).

<sup>7</sup>M. J. Buckingham and W. M. Fairbank, in *Progress in Low Temperature Physics*, edited by C. J. Gorter (North-Holland Publishing Company, Amsterdam, The Netherlands, 1961), Vol. III, Chap. 3.

<sup>8</sup>For a suggestion as to how  $c_{P,\varphi}$  and  $c_{P,x}$  may be related in the asymptotic region, see M. E. Fisher, *Phys. Rev.* **176**, 257 (1968).

<sup>9</sup>J. S. Rowlinson, *Liquids and Liquid Mixtures* (Butterworths Scientific Publications, Ltd., London, England, 1959).