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PHASE DIAGRAM FOR LIQUID He^3-He^4 *SOLUTIONS*

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It is established that the critical point for phase separation in He^3-He^4 mixtures occurs at $T = 0.88°K$ and $x = 64\%$ He^3 molar concentration. At the point $T = 0.67°K$ and $x = 82\%$, the λ line intersects the phase separation curve. Above this temperature both phases are superfluid, while below, the He^3-rich phase is nonsuperfluid.

INTRODUCTION

EXPERIMENTS on the visual observation of separated He^3-He^4 mixtures[1] have shown that the boundary between the phases is clearly visible to the eye. The critical temperature at which a liquid of given concentration separates into phases may readily be deduced from the moment of appearance of the boundary. The critical point for phase separation in a He^3-He^4 solution having a concentration $He^3/(He^3 + He^4) = 51.1\%$ has already been determined by this method. The value of T^{cr} found for this concentration agreed to within the limits of error with the measurements of Walters and Fairbank.[2]

On the basis of a preliminary investigation into the character of the flow of the separated liquid, the suggestion was advanced in reference 1 that both phases were superfluid. It was essential that this hypothesis be confirmed by more direct observations. As we have previously noted,[1] the measurements of the λ line in solutions having high He^3 concentrations carried out by Daunt and Heer[3] indicate, rather, that the upper phase is in the normal state. These measurements, however, do not appear to be reliable. The data of Esel'son, Bereznyak and Kaganov,[4] as well as the data of Ptukha[5] and a number of other authors, were obtained with solutions having concentrations not exceeding 40%; thus the form of the λ line for concentrations above 40% has been in need of clarification.

In the present work we have set ourselves the task of investigating the temperature dependence of the λ transition curve simultaneously with the solution phase separation diagram. Direct determination of the temperature dependence of the λ line and the phase separation curve for solutions in the high-concentration region make it possible to reach a conclusion regarding the state of the liquid in the upper phase. In this work all measurements were performed using the visual method of observation.

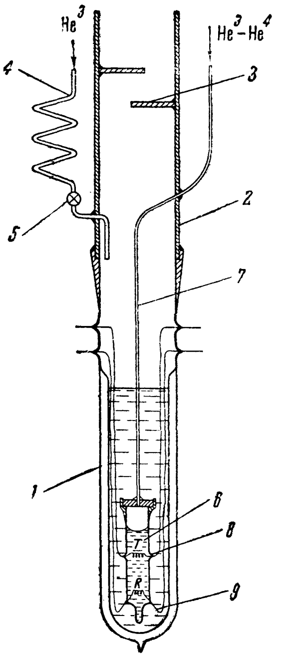

FIG. 1. Apparatus for measurements on the phase diagram of liquid He^3-He^4 solutions.

EXPERIMENTAL APPARATUS AND TECHNIQUE

The measurements were conducted with an apparatus whose interior is illustrated schematically in Fig. 1. A small transparent Dewar 1 filled with liquid He^3, 8 mm in diameter and 100 mm long, was placed within a double Dewar containing liquid He^4. A low temperature was produced within the small Dewar by pumping on the He^3 vapor with a mercury diffusion pump. The pumping was carried out through a 15-mm copper tube 2, joined farther up to one of steel. A copper screen 3 was fixed into the tube 2, in thermal contact with the liquid He^4, in order to reduce the heat transfer from above. The output side of the diffusion pump was connected to a coil 4, immersed in the helium bath, in which the He^3 vapor was re-condensed. Liquid He^3, cooled in the coil to bath temperature, ~ 1°K, was transferred into the inner Dewar as required through a bellows valve 5.

Within the He^3 Dewar there was submerged a glass capsule 6, 3.5 mm in diameter and 20-mm long, into which the He^3-He^4 mixture was condensed through a copper seal and a steel capillary 7. In order to increase the accuracy of determination of the moment at which phase separation occurred, the capsule was terminated at its lower end with a capillary extension 5 to 6 mm long and 0.5 mm in diameter.

A resistance thermometer 8 of 30-μ phosphor bronze and a heater 9 of constantan wire were sealed into the capsule containing the mixture. The temperature of the mixture was measured with the thermometer 8, which had previously been calibrated against the He^3 vapor pressure with the capsule unsealed. The vapor pressure was measured with a MacLeod gage. For determination of the temperature we employed the scale of Sydoriak and Roberts.[6]

The measurements were carried out in the following manner. The previously prepared mixture was condensed into the capsule at a temperature known to be above the λ point. The level of the liquid mixture was always kept below the copper-glass seal. Simultaneously with the initiation of pumping on the He^3 vapor, a small current was passed through the heater 9, causing the mixture to boil. Illumination was provided by a daylight lamp. When the meniscus of the solution was observed through a cathetometer, bubbles of gas were clearly visible, rising through the liquid to the surface. The boiling of the solution stopped immediately as the temperature reached the λ point. The meniscus, at the λ point, became quiet and immobile. We recorded the temperature at which the boiling of the solution suddenly ceased at the λ transition point. In order to repeat the λ point observation during a single experiment, it was necessary each time to stir the solution carefully, since radiation of heat within the superfluid phase led to a nonuniform volume distribution of concentrations. Stirring was accomplished by boiling the mixture above the λ point.

A determination of the solution phase separation temperature was made together with the λ point determination during one and the same experiment. To accomplish this, the power supply to the heater was shut off, and, as the temperature was reduced smoothly, the moment of appearance of the interphase boundary was recorded. The interphase boundary appeared within the capsule from below or above, accordingly as the concentration of the mixture was greater or less than 64% (the concentration corresponding to the peak of the phase separation diagram). Only for concentrations close to 64% did the boundary appear, practically instantaneously, in the central part of the capsule. The critical phase-separation temperature for each concentration was determined from a series of repeated observations of the appearance and disappearance of the boundary, as the system was cooled and heated slightly. For cooling and heating under quasi-stationary conditions, the appearance and disappearance of the boundary occurred at the same temperature. The results of individual measurements, both during the course of a single experiment and from experiment to experiment, agree well with one another. We should note that for all concentrations the reproducibility of the critical points for phase separation of the solutions was appreciably better than that of the λ points.

We recorded the phase separation diagram for the solutions in the absence of a thermal current. Control experiments showed, however, that the dissipation of a small amount of power in the heater caused only an insignificant shift in the critical phase separation temperature.

We were able to obtain the λ point and phase separation temperature for a mixture of one concentration during the course of a single experiment. Each individual experiment was carried out with a new mixture, prepared from the preceding one by the addition of He^4. The mixture was condensed into the capsule through a miniature charcoal trap, containing 1 g of charcoal cooled to liquid nitrogen temperature.

RESULTS OF THE MEASUREMENTS

The results of the measurements of the λ line and the phase separation diagram for He^3 - He^4 solutions are presented in Fig. 2. The two sets of

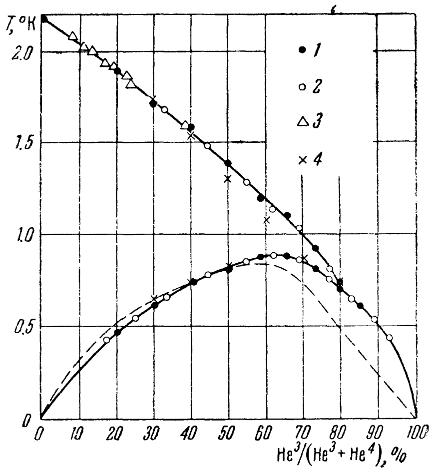

FIG. 2. Phase diagram for liquid He^3-He^4 mixtures. 1, 2 – present work (apparatus 1 and 2); 3 – data of Esel'son, Bereznyak, and Kaganov;[4] 4 – data of Roberts and Sydoriak;[7] dashed curve – from the data of Walters and Fairbank.[3]

points represented by the closed and open circles correspond to measurements made using two different systems having different diameters for the capillary 7 and different dimensions for the capsule 6 (Fig. 1). In view of the fact that the concentration of a solution might be altered due to enrichment of the vapor in the lighter isotope, we attempted to keep to a minimum the volume occupied by the gaseous phase. In the second apparatus (open circles), the volume of the capsule was increased slightly, while the volume of the gaseous phase was reduced by more than four times, as compared with the first system. Calculation showed, however, that the mass of the vapor did not exceed 2% of the total condensed mass under the least favorable conditions, and that, as a consequence, there must have been virtually no variation in the liquid concentration due to enrichment of the vapor in He^3. It is clearly evident from the figure that the two sets of results do, in fact, agree with each other.

The phase separation diagram for the solutions, as can easily be seen, conforms in its general features to the results of the measurements of Walters and Fairbank,[2] represented in Fig. 2 by the dashed curve. According to our data, however, the maximum and the right-hand branch lie considerably higher. At the conclusion of the present work we were informed of the measurements of Roberts and Sydoriak.[7] Their data on the measurement of the phase separation diagram for solutions with concentrations from 30 to 80%, represented in Fig. 2 by the crosses, lie quite well on our curve.

In Fig. 2, the results of the measurements of the λ line are represented by the closed and open circles on the upper curve. For comparison, the data of Esel'son, Bereznyak, and Kaganov[4] obtained by a different method for solutions with concentrations less than 40%, are indicated by triangles. It is evident that our results agree well with their data. As regards the values of Roberts and Sydoriak (crosses), their λ temperatures in the concentration region above 40% lie appreciably lower than the λ points obtained by us. The discrepancy is evidently to be explained by experimental errors in the work of these authors.[7] We note that the values for the λ temperatures obtained by us are well represented for all concentrations by the empirical formula proposed by Kerr.[8]

$$T_{\lambda s} = T_{\lambda 4} x_4^{2/3},$$

where $T_{\lambda s}$ is the solution λ temperature, $T_{\lambda 4}$ is the λ temperature for pure He^4, and x_4 is the concentration of He^4 in the solution.

Values for the λ points and critical phase separation temperatures for mixtures of various concentrations obtained with the two different systems are given in the table. The phase separation temperatures are determined to an accuracy of ± 0.02°K.

Apparatus No. 1			Apparatus No. 2		
x, %	T^{cr}, °K	T_λ, °K	x, %	T^{cr}, °K	T_λ, °K
84.99	0.61	—	93.22	0.44	—
79.84	0.71	0.73	88.90	0.55	—
73.17	0.81	0.92	83.11	0.65	—
66.06	0.88	1.10	77.14	0.75	—
58.78	0.87	1.19	69.23	0.86	1.03
50.08	0.82	1.38	61.93	0.88	1.13
40.34	0.74	1.58	54.85	0.85	1.28
30.28	0.61	1.71	44.76	0.78	1.48
20.37	0.46	1.89	33.35	0.66	1.68
0	—	2.17	24.85	0.54	—
			17.2	0.42	—

From Fig. 2 it can quite clearly be seen that the λ line intersects the solution phase separation curve a substantial distance to the right of its maximum, which corresponds to a temperature T^{cr}_{max} = 0.88 ± 0.01°K and a molar concentration x = 64 ± 1%. The point of intersection of the λ line with the phase separation curve has, according to our measurements, the coordinates T^{cr}_{λ} = 0.67 ± 0.02°K and x = 81 ± 1%.

In addition to direct measurements of the λ line and the phase separation curve, we performed experiments which further confirmed the superfluidity of the upper phase near T^{cr}_{max}. The first experiment was as follows: a beaker, open at the top, 8 mm long and 1 mm inside diameter, was suspended within the capsule 6 (Fig. 1). The isotope mixture was condensed into the capsule at T = 0.5°K in such a way that only the upper phase was introduced into the beaker, while the liquid level was stopped 1 mm above its top. We then elevated the temperature by such an amount that the boundary outside the beaker rose upward, but did not reach the top of the beaker. As the temperature was raised, a boundary appeared at the bottom of the beaker and rose upward. If the upper phase had not been superfluid, the transfer within the beaker by diffusion of a quantity of He^4 sufficient for the appearance of the lower phase would have required tens of hours, while in our case the entire process was completed within ten minutes.

In a second experiment analogous to the first, the beaker, which had a blackened spot, was again completely submerged in the liquid and filled with the upper phase alone; when it was illuminated with a directed light beam, a boundary appeared immediately at the bottom, bearing witness to the filling of the beaker with He^4 by superflow from the upper phase outside the beaker.

A third experiment, testifying graphically to the occurrence of a λ transition in the upper phase, consisted of the following: a quantity of a He^3 - He^4 mixture of initial concentration 63.1% was condensed into the capsule 6 at a temperature $\lesssim$ 0.5°K, such that the heater was situated in the vicinity of the phase separation boundary in the mixture, lying principally in the upper phase. The volume ratio of the lower and upper phases in this case was ~ 1:2, and the meniscus of the mixture was somewhat lower than the thermometer. The temperature of the liquid was determined approximately with the thermometer, in the vapor region, as well as from the vapor pressure of the He^3 surrounding the capsule. (The difference between the true temperature of the liquid and the thermometer temperature did not exceed 0.01- 0.02°K, as was established by observation above the mixture phase separation point.) Upon passage of a current $I = 1$ ma through the heater, $R = 10\Omega$, at a temperature $T \lesssim 0.5$°K, the upper phase boiled vigorously while the lower remained immobile, as could be clearly observed through the cathetometer telescope. As the temperature was raised farther, there came a moment at which the boiling of the upper phase with the heater turned on ceased instantaneously, becoming just as quiet and stationary as the lower phase. The λ transition temperature for the upper phase found in these observations agreed to within the limits of accuracy of the experiment with the value we had found previously, $T_\lambda^{cr} = 0.67 \pm 0.02$°K.

The experiments just described thus leave no doubt that the He^3-rich phase undergoes a λ transition. Above the λ transition temperature the upper phase is superfluid, just as the lower is. Below the transition temperature the He^3 - rich phase becomes normal.

With the object of verifying the data on phase separation in He^3 - He^4 solutions, we performed control experiments with a mixture of initial concentration $x_0 = 63.1\%$. In these experiments the dependence of the volumes of the upper and lower phases of the solution upon temperature was measured. Using the well-known "lever rule," as written for a presumed linear dependence of the solution density upon concentration:

$$(x_2 - x_0) V_2 = (x_0 - x_1) V_1,$$

where x_1 and x_2 are the He^3 concentrations in the upper and lower phases, whose volumes are, respectively, V_1 and V_2, it is possible from the temperature dependences of V_1 and V_2 and the initial concentration x_0 to compute one branch of the curve when the other branch is given, i.e., $x_1(T)$ for a curve $x_2(T)$. (The assumption of a linear dependence of density upon concentration is made on the basis of the measurements of Ptukha,[5] extrapolated to lower temperatures.) This check showed that to within the accuracy of the measurements of the volumes V_1 and V_2 (~ 2%), the "lever rule" yields the same curve as the direct measurements.

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[1] V. P. Peshkov and K. N. Zinov'eva, J. Exptl. Theoret. Phys. (U.S.S.R.) **32**, 1256 (1957), Soviet Phys. JETP **5**, 1024 (1957).

[2] G. K. Walters and W. M. Fairbank, Phys. Rev. **103**, 262 (1956).

[3] J. G. Daunt and C. V. Heer, Phys. Rev. **79**, 46 (1950).

[4] Esel'son, Bereznyak and Kaganov, Dokl. Akad. Nauk SSSR **111**, 568 (1956); Soviet Phys. "Doklady" **1**, 683 (1956).

[5] T. P. Ptukha, J. Exptl. Theoret. Phys. (U.S.S.R.) **34**, 33 (1958); Soviet Phys. JETP **34**, 22 (1958).

[6] S. G. Sydoriak and T. R. Roberts, Phys. Rev. **106**, 175 (1957).

[7] T. R. Roberts and S. G. Sydoriak, Proc. Fifth Internat. Conf. on Low Temp. Physics and Chemistry, Univ. of Wisconsin, 1958, p. 170 (preprint).

[8] E. C. Kerr, Proc. Fifth Internat. Conf. on Low Temp. Physics and Chemistry, Univ. of Wisconsin, 1958, p. 158.

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