SOVIET PHYSICS JETP VOLUME 28, NUMBER 4 APRIL 1969

AN INVESTIGATION OF THE THERMODYNAMIC PROPERTIES OF He^3–He^4 *SOLUTIONS DURING THE* He I–He II *TRANSITION*

V. N. GRIGOR'EV, B. N. ESEL'SON, E. A. MASIMOV, G. A. MIKHAILOV, and P. O. NOVIKOV

Physico-technical Institute of Low Temperatures, Academy of Sciences, Ukrainian S.S.R.

Submitted April 12, 1968

Zh. Eksp. Teor. Fiz. 55, 1160–1167 (October, 1968)

The liquid-vapor phase diagram for He^3–He^4 solutions are investigated by the method of nuclear magnetic resonance (NMR). The temperature dependence of the distribution coefficient is measured for six solutions with different amounts of He^3. Singularities of the $\alpha(T)$ curves at T_λ predicted by the theory are found. Parts of the liquid-vapor phase diagram are studied in the vicinity of the λ points of the solutions. The form of the diagram is studied in greater detail. Breaks are detected on the $P(x_m)$ curves. Specific heat discontinuities at the λ points of the solutions are calculated on the basis of the data obtained. With increase in concentration, the specific heat jump for the He I–He II transition decreases. The heats of solution and vaporization discontinuities are calculated.

INTRODUCTION

In liquid solutions of helium isotopes singularities in the behavior of the thermodynamic properties of these solutions should take place, as is well known, in the He I–He II phase transition. Based on the experimentally observed fact[1, 2] that we are dealing with a second order phase transition in the given case, theoretical consideration of this problem has already been given in [3–6]. These have made it possible to establish the fact that discontinuities should be observed at T_λ for the temperature derivatives of the total (P) and partial pressures and of the distribution coefficient (c_v/c_l), and also discontinuities in the heats of fusion (q_3) and vaporization (λ_3):

$$\Delta\left(\frac{d\ln P}{dT}\right)_{x_l}=(x_v-x_l)\frac{\Delta C_P}{kT_\lambda^2}\frac{\partial T_\lambda}{\partial x_l}, \tag{1}$$

$$\Delta\frac{\partial}{\partial T}\ln\frac{c_v}{c_v}=\frac{\Delta C_P}{kT_\lambda^2}\frac{\partial T_\lambda}{\partial x_v}, \tag{2}$$

$$\Delta q_3=-(1-x_l)\Delta C_P\frac{\partial T_\lambda}{\partial x_l}, \tag{3}$$

$$\Delta\lambda_3=(x_v-x_l)\Delta C_P\frac{\partial T_\lambda}{\partial x_l}; \tag{4}$$

here ΔC_P is the jump in the heat capacity at constant pressure at the transition temperature, k the Boltzmann constant, x_v, x_l the molar concentration of the vapor and liquid phases, respectively.

$$c_v=\left(\frac{N_3}{N_4}\right)_v=\frac{x_v}{1-x_v},\quad c_l=\left(\frac{N_3}{N_4}\right)_l=\frac{x_l}{1-x_l}.$$

The experimental study of the properties of He^3–He^4 solutions[2, 7] made it possible to discover discontinuities in the temperature derivatives of the saturated vapor pressures; however, other features, of which we have spoken above, were not observed. In spite of the detailed study of the liquid-vapor phase diagram of He^3–He^4, the features associated with the phase transition were not reflected in it, inasmuch as the vicinity of T_λ was not specially studied. To obtain reliable data on the true character of the liquid-vapor diagram in the neighborhood of T_λ and of the distribution coefficient in He^3–He^4 solutions, it is most appropriate to make use of nuclear magnetic resonance (NMR). In this case, there is a possibility of the direct determination of the He^3 concentration in the vapor and in the liquid, in a state of equilibrium, without removal of material for analysis. The present research is devoted to the study of the singularities of thermodynamic quantities, by means of NMR, at the λ transition, and to a more precise determination of the liquid-vapor diagram of the He^3–He^4 system.

METHOD OF MEASUREMENT AND THE RESULTS OBTAINED

The essence of the method used consisted in the measurement, by means of a pick-up coil, of NMR signals from the liquid and vapor phases, located in equilibrium. Inasmuch as the amplitude of the NMR signal at constant temperature depends only on the number of He^3 atoms in the volume of the coil,[8–10] it is easy to determine the corresponding concentrations from the measured amplitudes:[11]

$$\frac{x_v}{x_l}=\frac{A_v}{A_l}\frac{V_v}{V_l}; \tag{5}$$

Here A_v, A_l are the signal amplitudes from the vapor and the liquid, respectively, and V_v and V_l are the molar volumes.

For carrying out the NMR measurements, special apparatus was designed and constructed in which the method of differential approach was used. Inasmuch as the electronic part of the apparatus and the method of measurement have been discussed previously,[11] we shall limit ourselves to a short description of the instrument.

A glass ampoule 4 was placed in the part of a helium cryostat 1 located between the poles (Fig. 1) of a permanent magnet. The NMR pick-up coil 3 is wound around the ampoule. Inside it is placed a teflon plumb 2 which is connected by the quartz thread 5 to the core of a solenoid located outside the cryostat. This plumb can be

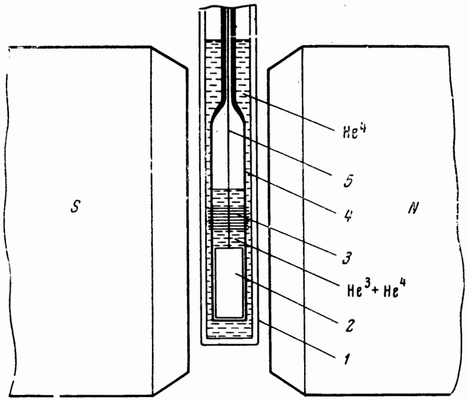

FIG. 1. Apparatus

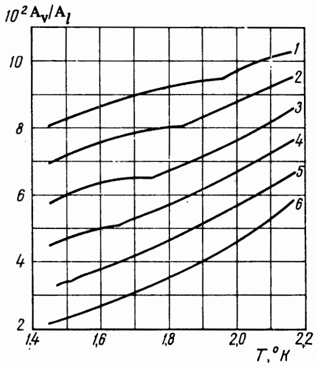

FIG. 2

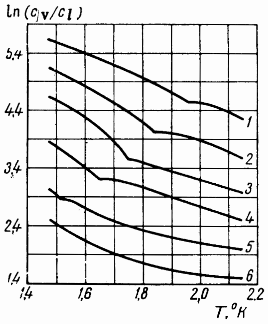

FIG. 3

FIG. 2. Dependences of the NMR amplitudes on temperature for different He^3 concentrations: 1–15.0, 2–21.6, 3–27.0, 4–31.8 5–38.5, 6–44.3 % He^3. The values of A_v/A_l shown on the ordinates correspond to curve 6. Each previous curve has been shifted relative to its predecessor by 10^{-2} upward.

FIG. 3. Dependence of the distribution coefficient c_v/c_l on the temperature for different concentrations of He^3: 1–15.0, 2–21.6, 3–27.0, 4–31.8, 5–38.5, 6–44.3% He^3. The values of c_v/c_l shown on the ordinates correspond to curve 6. Each of previous curve has been shifted relative to its predecessor by 0.5 upward.

moved along the length of the ampoule. The mixture to be studied is condensed in the ampoule. The amount condensed is so chosen that for the coil lowered below the plumb, the coil is completely filled with liquid, but when raised above the plumb, it is completely filled with vapor.

By means of this arrangement, measurements were made of the NMR signal amplitudes from the vapor and the liquid as a function of the temperature for solutions of various concentrations. The solutions of helium isotopes were obtained by the mixing of pure He^3 and He^4, while the concentration was obtained with accuracy no worse than 0.1%.

Figure 2 shows the experimental results for six solutions with He^3 content from 15.0% to 44.3%. Each curve is constructed by use of the results of many experiments, fitted by the least squares method by means of an M-20 computer. The mean square deviation of the points from the curves amounted to 1.5%. As follows from Fig. 2, the ratio of the amplitudes A of the signals for all the solutions studied increased smoothly with increase in temperature, undergoing breaks at the λ points.

According to the measured values of A_v/A_l and the known concentration of the liquid (x_l), the equilibrium concentrations of He^3 in the vapor (x_v) were computed with the help of Eq. (5), in which the coefficient 1.08 appears, obtained as the result of control experiments with pure He^3. The values of V_v were calculated from the equation of state with the use of the values of the second virial coefficient.[12] The values of V_l were taken from [13]. The values of x_v thus found were used for the calculation of the distribution coefficient

$$\alpha = \frac{c_v}{c_l} = \frac{x_v(1 - x_{ж})}{x_l\,(1 - x_v)}. \tag{6}$$

The temperature dependence of the distribution coefficient for the solutions studied is shown in Fig. 3 and Table I. Errors in the determination of c_v/c_l ranged from 4% (for x_v = 0.50) to 8% (for x_v = 0.80). It is clearly evident that there is a sharp break in the curves $\alpha(T)$ at T_λ, the present of which confirms the deduction obtained from theoretical consideration of the question. With the exception of the vicinity of the λ points, the values of α agree very well with data obtained from the liquid-vapor diagram.[14]

Table I

x_l=0,150 T_λ=1,960°K		x_l=0.216 T_λ=1.839°K		x_l=0,270 T_λ=1.750°K		x_l=0.318 T_λ=1.648°K		x_l=0.385 T_λ=1.513°K		x_l=0,443 T_λ=1,420°K	
T, °K	c_v/c_l	T, °K	c_v/c_l	T, °K	c_v/c_l	T, °K	c_v/c_l	T, °K	c_v/c_l	T, °K	c_v/c_l
1.450	24,1	1,450	24,2	1.450	23.8	1,450	18.6	1,450	13,1	1,450	13,1
1.500	22,1	1.500	21.6	1,500	21,3	1,500	15,9	1,470	12.4	1,500	11,4
1,550	20,0	1,550	19.2	1,550	18.6	1.550	13.3	1,480	11,9	1,600	8,5
1,600	18,1	1,600	16.7	1,600	16.1	1,600	10,9	1,490	11,5	1.700	6,7
1.650	16.4	1,650	14.6	1,650	13,3	1,620	10,1	1,500	11,1	1,800	5,6
1,700	14,6	1,700	12.4	1,700	10,5	1,630	9,6	1.510	10.6	1,900	5,0
1,750	12,9	1.750	10.7	1,720	9,2	1,640	9,2	1,513	10,3	2,000	4,6
1,800	11,4	1.800	8,9	1,730	8,7	1,648	9.0	1,520	10.3	2,100	4,5
1,850	10,1	1.810	8,5	1,740	8.3	1,650	9.0	1,530	10,3	2,150	4,5
1,900	9,0	1.820	8.3	1,750	7,8	1.660	9,0	1,540	10,2		
1.920	8,5	1,830	7,9	1.760	7,7	1,670	9.0	1,550	10,1		
1,930	8,3	1,839	7,5	1,770	7,6	1,680	8,9	1,560	9.9		
1.940	8,1	1.850	7,5	1,780	7,4	1,690	8,9	1.570	9,6		
1,950	7,9	1,860	7,5	1,790	7.3	1,700	9,0	1.600	8,8		
1,960	7,7	1,870	7.5	1,800	7.1	1,720	8,8	1,650	7.8		
1,970	7,7	1.880	7,4	1,810	7,1	1.750	8,4	1,700	7.0		
1.980	7,7	1,890	7,4	1.820	6,9	1,800	7,7	1.800	6,2		
1,990	7.7	1,900	7,3	1,900	6,1	1,900	6,5	1,900	5,5		
2,000	7,7	2,000	6.4	2.000	5,3	2,000	5,6	2.000	4,9		
2.050	7.2	2,100	5,3	2,100	4,7	2,100	4,8	2,100	4,6		
2.100	6,5	2,150	4,7	2,150	4,3	2.150	4,4	2.150	4,4		
2.150	5,7										

Table II*

1,5°K		1,6°K		1,7°K		1,75°K		1,8°K	
x_l	P	x_l	P	x_l	P	x_l	P	x_l	P
0,385	27,98	0,334	33,45	0,270	37,05	0,260	39,84	0,216	41,17
0,392	28,10	0,344	33,7	0,279	37,46	0,264	40,10	0,221	41,45
0,399	28,21	0,354	33,75	0,288	37,84	0,268	40,34	0,225	41,67
0,406	28,17	0,362	34,05	0,296	37,92	0,274	40,40	0,230	42,03
0,414	28,31	0,370	34.40	0,301	38,05	0,280	40,55	0,241	42,21
0,422	28,50	0,378	34,65	0,307	38,35	0,286	40,85	0,250	42,67
0,448	29,05	0,386	34,90	0,314	38,65	0,2915	40,95	0,257	43,07
				0,320	38,94			0,264	43,50
				0,325	39,21			0,276	44,07

*Pressure given in mm Hg.

Data on the equilibrium concentration in the vapor, together with parallel measurements of the saturated vapor pressure of the solutions were used for the construction of the diagram of state of the solutions shown in Fig. 4, where the data of [14] are also given. It is seen from Fig. 4 that the data obtained by the different methods are in excellent agreement with each other.

Special interest attaches to the portions of the diagram close to the λ transition, where, according to theoretical calculations,[6] there ought to be a jump in the derivatives $(\partial P/\partial x_l)_T$ and $(\partial^2 P/\partial x_v^2)_T$. For a detailed investigation of the form of the diagrams near T, special experiments were performed, in which the dependences of the saturated vapor pressure and the concentration in the vapor phase on the concentration in the liquid at constant temperature were measured directly. To obtain such data, a certain amount of pure He^3 was added in individual portions to the solution of known concentration in the ampoule (Fig. 1), all at constant temperature. Measurements were then made of the saturated vapor pressure and the ratio of amplitudes of the NMR signals. The NMR measurements served to determine the concentration in the vapor phase and as an additional control for establishment of equilibrium in the ampoule. The vapor pressure was measured by a mercury manometer with accuracy of 0.03 mm. The portions of the diagrams obtained in this fashion are shown in circles in enlarged scale at the upper left of Fig. 4 and in Table II. The breaks are clearly evident at the values of x_l corresponding to the λ points of the solutions.

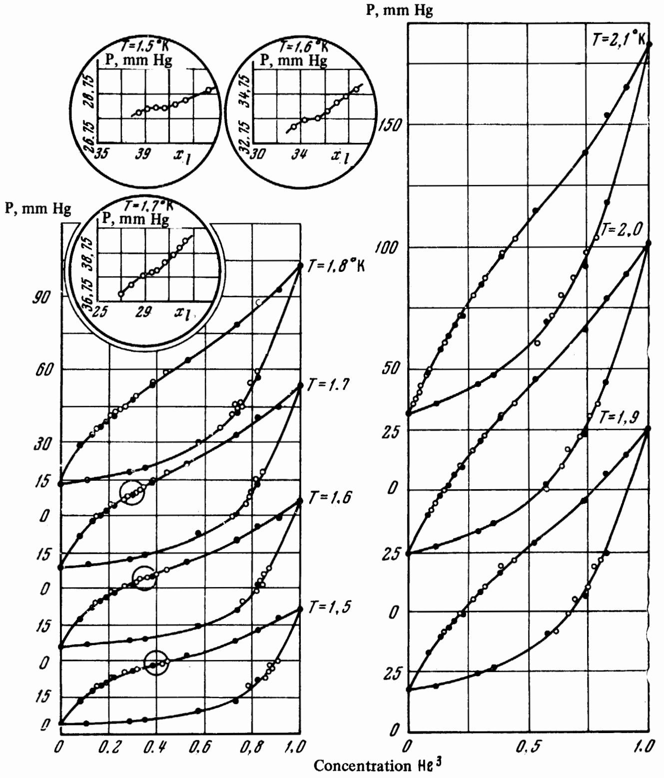

FIG. 4. Liquid-vapor state diagram for He^3—He^4 solutions: ○—data of [14], ●—data of present research (He^3 concentration given in units of $N_3/(N_3 + N_4)$).

DISCUSSION OF THE RESULTS

Data on singularities of thermodynamic quantities at the λ points of the solutions can be used for calculation of the jump in the heat capacity ΔC_P according to Eqs. (1)–(4). In the given case, the most reliable data on ΔC_P can be obtained in the treatment of the temperature dependence of the quantity A_v/A_l. Actually, by differentiating (5) at $T = T_\lambda$ and x_l = const, under the assumption of ideality of the vapor phase, it is easy to obtain the result

$$\Delta\left(\frac{\partial \ln x_v}{\partial T}\right) = \Delta\left[\frac{\partial \ln(A_v/A_l)}{\partial T}\right] - \Delta\left(\frac{\partial \ln P}{\partial T}\right) + \Delta\left(\frac{\partial \ln V_l}{\partial T}\right). \tag{7}$$

Using the value from (1) for $\Delta(\partial \ln P/\partial T)$, the value

$$\Delta\left(\frac{\partial x_v}{\partial T}\right) = x_v(1 - x_v)\frac{\Delta C_P}{kT_\lambda^2}\frac{\partial T_\lambda}{\partial x_l}, \tag{8}$$

for $\Delta(\partial \ln x/\partial T)$ obtained from [6], and the expression

$$\Delta\left(\frac{\partial \ln V_l}{\partial T}\right) = \frac{\Delta C_P}{V_l T_\lambda}\frac{\partial T_\lambda}{\partial P}, \tag{9}$$

we find

$$\Delta C_P = \left(\Delta\frac{\partial}{\partial T}\ln\frac{A_v}{A_l}\right)\Big/\left(\frac{1 - x_l}{kT_\lambda^2}\frac{\partial T_\lambda}{\partial x_l} - \frac{1}{V_l T_\lambda}\frac{\partial T_\lambda}{\partial P}\right). \tag{10}$$

Neglecting the second term in the denominator, inasmuch as it is much smaller than the first, we get

$$\Delta C_P = \frac{kT_\lambda^2}{(1 - x_l)\partial T_\lambda/\partial x_l}\Delta\frac{\partial}{\partial T}\ln\frac{A_v}{A_l}. \tag{11}$$

Formula (11) makes it possible to calculate ΔC_P for the solutions of different concentrations according to the experimental dependences of A_v/A_l on T with the help of formulas obtained in the treatment of these curves by the method of least squares. The results of such a calculation are given below (see also Fig. 5):

$x_l = \left(\frac{N_3}{N_3+N_4}\right)_l$:	0	0,150	0,216	0,270	0,318	0,385
ΔC_P, $\frac{\text{cal}}{\text{mole-deg}}$:	5,6	5,13	4,70	4,26	3,21	1,45

Errors in the determination of C_P amounted to 10%. For pure He^4, a value is used which was obtained in [15] for direct measurements of the heat capacity which, as is seen from Fig. 5, agrees excellently with the path of the curve $C_P(x_l)$. It is quite evident that the value of the jump in the heat capacity at T_λ depends essentially on the concentration and decreases with increase in x_l.

The quantity ΔC_P can be calculated also from the jumps in the derivatives $(\partial P/\partial x_l)_T$ found in the present work. However, these data are less detailed and the errors in ΔC_P are seen to be very large. Evidently, the values of ΔC_P obtained by Roberts and Swartz[16] in the treatment of data on the saturated vapor pressures with the help of relations similar to (1) are much less than ours for the same reason. It is interesting to note that the values of ΔC_P found in the first treatment of the same data, published in [17], are in good agreement with the results of the present work.

Using the found values of ΔC_P, we can calculate the jumps of a number of other thermodynamic quantity at the phase transition point, in particular, the heat of solution and the heat of vaporization, according to Eqs. (3) and (4).

The results obtained for Δq_3 and $\Delta\lambda_3$ as a function of concentration are shown in Fig. 6. As is seen from the drawing, for solutions with a content of He^3 of more than 25%, the dependences of both quantities on the concentration are similar: both Δq_3 and $\Delta\lambda_3$ fall off rapidly with increase in the concentration. At low concentrations, their behavior is different: $\Delta q_3(x)$ changes little, while $\Delta\lambda_3$ reaches a maximum and then decreases, approaching zero, in correspondence with the fact that for pure He^4 there is no jump in the heat of vaporization at the phase transition point He I–He II.

All the features of the transition He I–He II observed in our research on solutions of the helium isotopes, are described, within the limits of accuracy of measurement, by theoretical considerations obtained on the basis of the Landau theory. In the work of Sanikidze,[18] the effect, not considered by the Landau theory, of logarithmic singularities of the second derivatives of the thermodynamic potential on the results obtained in [3-6] was considered. It was shown[18] that the presence of logarithmic divergences should lead to a smoothing of the singularities of the thermodynamic properties of the solutions in the vicinity of the λ point. However, in the given research, such a smoothing was not observed. Evidently this smoothing, if it does exist, takes place in a very narrow region ($< 10^{-3}$ deg). One cannot also eliminate the possibility that for solutions, C_P does not go to infinity and in this case there is no basis for making more precise the formulas obtained in [3-6]. These problems require further investigation.

In conclusion, we note that the singularities on the curves $(\partial P/\partial x_V)_T$, theoretically predicted by Sanikidze,[6] were not discovered by us. Evidently, it is necessary to increase considerably the accuracy of the measurements for the observation of these singularities.

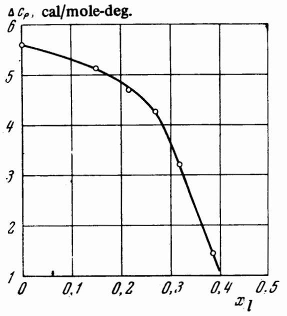

FIG. 5

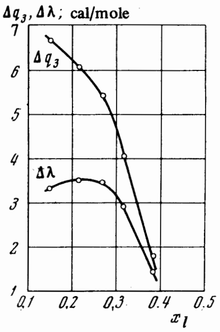

FIG. 6

FIG. 5. Dependence of the jump in the heat capacity at the λ transition on the He^3 concentration. The value of ΔC_P for pure He^4 was taken from [15].

FIG. 6. Dependence of the heat of vaporization $\Delta\lambda_3$ and of solution Δq_3 on the He^3 concentration at the λ points of the solutions.

The authors thank A. A. Besruk for writing the program for treatment of the data on the computer and V. V. Shapovalenko for help in the measurements.

---

[1] B. N. Esel'son, B. G. Lazarev, and N. A. Alekseevskiĭ, Zh. Eksp. Teor. Fiz. **20**, 1055 (1950).

[2] B. N. Esel'son, Zh. Eksp. Teor. Fiz. **26**, 744 (1954).

[3] B. N. Esel'son, B. G. Lazarev, and I. M. Lifshitz, Zh. Eksp. Teor. Fiz. **20**, 748 (1950).

[4] B. N. Esel'son, M. I. Kaganov, and I. M. Lifshitz, Zh. Eksp. Teor. Fiz. **33**, 936 (1957) [Sov. Phys.-JETP **6**, 719 (1958)].

[5] J. de Boer and C. J. Gorter, Physica **18**, 565 (1952).

[6] D. G. Sanikidze, Candidate's Dissertation, Physicotechnical Institute, Academy of Sciences, Ukr. SSR, Kharkov, 1959.

[7] S. G. Sydoriak and T. R. Roberts, Phys. Rev. **118**, 801 (1960).

[8] G. K. Walters and W. M. Fairbank, Phys. Rev. **103**, 263 (1956).

[9] J. E. Opfer, K. Luszczynski, and R. E. Norberg, Phys. Rev. **140A**, 100 (1965).

[10] B. T. Beal and J. Hatton, Phys. Rev. **139A**, 1751 (1965).

[11] V. N. Grigor'ev, B. N. Esel'son, E. A. Masimov, G. A. Mikhailov, and P. S. Novikov, Ukr. Fiz. Zh. **12**, 1786 (1967).

[12] W. E. Keller, Phys. Rev. **98**, 1571 (1955).

[13] E. C. Kerr, Proc. Fifth Intern. Conf. on Low Temp. Phys. **3**, 80 (1961).

[14] B. N. Esel'son and N. G. Beresnyak, Zh. Eksp. Teor. Fiz. **27**, 648 (1954); Dokl. Akad. Nauk SSSR **105**, 454 (1955).

[15] M. J. Buckingham and W. M. Fairbank, Progr. in Low Temp. Phys. **3**, 80 (1961).

[16] T. R. Roberts and B. K. Swartz, Symposium on Liquid and Solid He^3, Ohio State Univ. Press, 1960, p. 158.

[17] R. de Bruyn Ouboter, J. J. M. Beenakker and K. W. Taconis, Physica **25**, 1162 (1959).

[18] D. G. Sanikidze, Zh. Eksp. Teor. Fiz. **42**, 1330 (1962) [Sov. Phys.-JETP **15**, 922 (1962)].

Translated by R. T. Beyer
129