

DIAGRAM OF STATE FOR He^3-He^4 SOLUTIONS: PHASE STRATIFICATION AND SOLIDIFICATION CURVES

K. N. ZINOV'EVA

Institute for Physics Problems, Academy of Sciences, U.S.S.R.

Submitted to JETP editor January 17, 1963

J. Exptl. Theoret. Phys. (U.S.S.R.) 44, 1837-1846 (June, 1963)

Measurements have been made of the phase stratification curves for liquid He^3-He^4 solutions at elevated pressures, and of the solidification curves above the stratification point for various molar concentrations of He^3 . The general contours of the diagram of state $T(x)$ for $p = \text{const}$ have been constructed.

IN order to study the phase diagram of He^3-He^4 solutions we have extended our measurements on the stratification of mixtures^[1] into the region of elevated pressures, up to the crystallization pressure. The method of visual observation of the stratification which was used previously was again employed. The possibility of observing visually the process of crystallization made it feasible to study, not only the stratification, but also the solidification of the mixtures, both before and after their separation. It was of interest to compare these experimental data with the theoretical computations developed by I. Lifshitz and Sanikidze^[2].

The measurements were performed in an apparatus similar to that described in^[1]. The arrangement is shown in Fig. 1. A glass capsule 1, of 4 mm inside diameter and 20 mm in length, with

walls ~ 1 mm thick, was immersed in a Dewar containing He^3 . The capsule was soldered, via a ferrochrome seal, to a steel capillary 2, of 0.15 mm inside diameter and 0.5 mm outside diameter, through which the He^3-He^4 mixture could be condensed into the capsule. The inner seal was filled by a metal plug with a small clearance space for passage of the mixture. The volume of the capillary, together with this clearance space, amounted to ~ 1% of the volume of the capsule. This insured that the concentration of the mixture would remain essentially constant, even for large temperature gradients along the capillary. In certain of the experiments the capillary was enclosed in a vacuum jacket of German silver tubing. The capsule was provided with a capillary extension 3 at either its top or its bottom, depending upon the concentra-

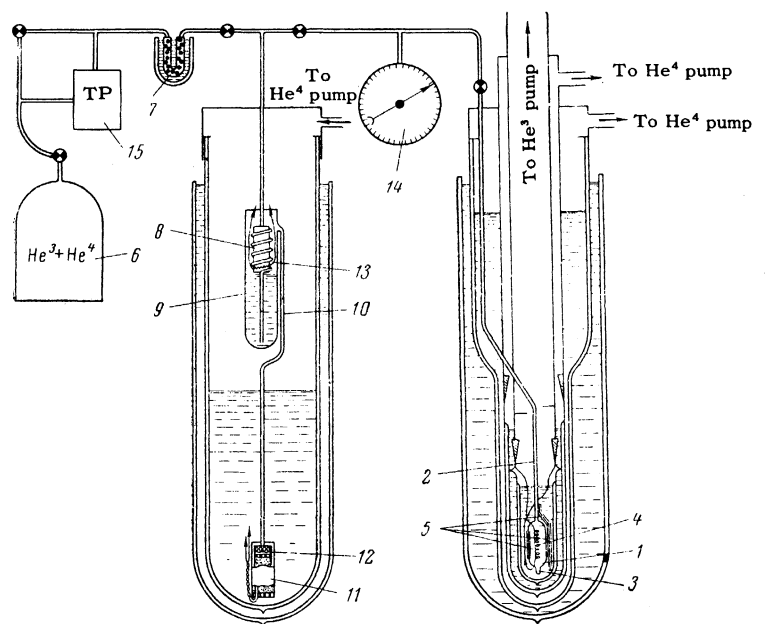


FIG. 1. Apparatus for measuring diagrams of state for He^3-He^4 mixtures at elevated pressures (see description in text).

tion of the mixture under study.

Reduction of the temperature was achieved by pumping on the He^3 vapor, making it possible to reach $\sim 0.35\text{--}0.4^\circ\text{K}$ within the capsule. The temperature of the mixture was measured with a resistance thermometer 4, of 35-micron phosphor bronze, sealed into the capsule and calibrated against the He^3 vapor pressure. In calibrating the thermometer the capsule was filled with He^4 ; the temperature scale of Sydoriak and Roberts^[3] was employed.

In order to accelerate the equalization of temperatures throughout the mixture, copper strips 5 were cemented along the capsule, both within and outside, in the He^3 bath.

Pressure was applied to the mixture by a helium gasifier of the type described by Tkachenko and Filimonov^[4].

The $\text{He}^3\text{--He}^4$ mixture was condensed from a storage container 6 (Fig. 1), through a charcoal trap 7 cooled with liquid nitrogen, into a thin-walled bulb 8. The bulb was of stainless steel, having a volume of $\sim 0.6\text{ cm}^3$, and was immersed in a vessel 9 filled with liquid helium. This vessel was suspended within a helium Dewar, and was filled with He II by means of the thermomechanical effect along a tube 10 communicating with a porous filter 11 and a heater 12. At the end of the condensation process, the helium was evaporated from the vessel by switching on a heater 13 wound onto the exterior of the bulb. By raising the temperature of the mixture trapped in the bulb, its pressure was raised to the required value, and the mixture was transferred by condensation into the capsule 1. The pressure was measured with a Bourdon manometer 14, accurate to ± 0.1 atm, which, to reduce the dead volume, was filled with mercury and calibrated against a standard manometer. At the end of the experiment, the $\text{He}^3\text{--He}^4$ mixture was pumped back into the storage container with the aid of a Toepler pump 15.

Measurement of the stratification curves was carried out in the following manner. A mixture of known concentration was condensed from the gasifier into the capsule at a temperature of $\sim 1.2^\circ\text{K}$, under a certain pressure p . Pumping was then started on the He^3 vapor, and the temperature of the solution was slowly reduced until the interphase boundary appeared within the capillary extension. The boundary was observed with the aid of a binocular microscope of low magnification. At the moment at which stratification of the solution occurred, pumping was stopped, and the disappearance of the boundary was observed. As a rule, the temperatures of appearance and disap-

pearance of the boundary failed at first to coincide by $0.01\text{--}0.02^\circ\text{K}$. When the measurements of T_c were repeated, however, with the temperature held constant near the stratification point for at least 30 min, this discrepancy virtually disappeared. A new pressure was then established, and the measurements were repeated. In this way, it was possible in one experiment to determine the pressure dependence of the stratification temperature for a solution of a given concentration right up to its crystallization point.

The experimental values of T_c as a function of pressure for eight solutions of different concentrations are shown in Fig. 2. The concentration x is expressed as the mole fraction $\text{He}^3/(\text{He}^3 + \text{He}^4)$. The curves terminate at the solidification pressure. Smoothed values from these curves are given in Table I.

A phase equilibrium diagram for liquid $\text{He}^3\text{--He}^4$ solutions at pressures of 1, 5, 10 and 20 atm, constructed on the basis of these experimental data, is presented in Fig. 3. The phase stratification curve for saturated vapor pressure ($p = 0$)^[1] is also given. The points plotted in the diagram are given in Table II.

The stratification curves for elevated pressures are displaced toward lower temperatures, remaining similar in form to the saturated vapor pressure curve. At a pressure $p = 23$ atm, near the crystallization point of the solutions $T_{c\text{max}} = 0.73 \pm 0.01^\circ\text{K}$ ($x = 64\%$). The largest value of $dT_c/dp = 0.04^\circ\text{K}/\text{atm}$ occurs at the peaks of the $T(x)$ curves, for small values of p .

In addition to stratification, we also made measurements on the solidification of the solutions in

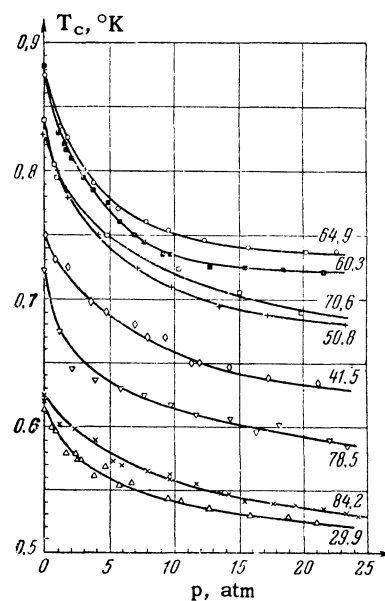


FIG. 2. Pressure dependence of solution stratification temperature for various concentrations. Numbers on curves indicate values of x in percent.

Table I. Pressure dependence of He³-He⁴ solution stratification temperature

$x, \%$	$p, \text{ atm}$	$T_c, \text{ }^\circ\text{K}$	$x, \%$	$p, \text{ atm}$	$T_c, \text{ }^\circ\text{K}$	$x, \%$	$p, \text{ atm}$	$T_c, \text{ }^\circ\text{K}$
29.9	0	0.620	60.3	0	0.875	78.5	0	0.725
	2	0.582		2	0.810		2	0.662
	4	0.564		4	0.780		4	0.641
	6	0.554		6	0.759		6	0.630
	9	0.543		9	0.738		9	0.618
	12	0.537		12	0.728		12	0.610
	15	0.532		15	0.724		15	0.602
	18	0.528		18	0.722		18	0.597
	21	0.524		21	0.721		21	0.591
	24	0.520		23	0.720		24	0.586
41.5	0	0.750	64.9	0	0.880	84.2	0	0.625
	2	0.714		2	0.819		2	0.600
	4	0.695		4	0.789		4	0.585
	6	0.680		6	0.770		6	0.576
	9	0.664		9	0.754		9	0.561
	12	0.651		12	0.745		12	0.552
	15	0.642		15	0.741		15	0.544
	18	0.637		18	0.738		18	0.539
	21	0.632		21	0.736		21	0.534
	23.7	0.629		23	0.735		25	0.530
50.8	0	0.830	70.6	0	0.840			
	2	0.777		2	0.781			
	4	0.749		4	0.756			
	6	0.732		6	0.740			
	9	0.713		9	0.724			
	12	0.700		12	0.712			
	15	0.692		15	0.703			
	18	0.687		18	0.695			
	21	0.683		21	0.689			
	22.9	0.680		23	0.687			

Table II. Phase equilibrium curves for liquid He³-He⁴ solutions at elevated pressures

$x, \%$	$T_c, \text{ }^\circ\text{K}$				
	$p = 0$	1 atm	5 atm	10 atm	20 atm
29.9	0.615	0.595	0.558	0.541	0.525
41.5	0.750	0.728	0.687	0.659	0.634
50.8	0.827	0.800	0.740	0.708	0.684
60.3	0.875	0.835	0.769	0.734	0.722
64.9	0.880	0.840	0.778	0.751	0.736
70.6	0.840	0.797	0.747	0.720	0.691
78.5	0.725	0.678	0.735	0.615	0.693
84.2	0.625	0.610	0.579	0.558	0.536

the temperature range above their stratification points. The method of measurement consisted of the following: at a constant temperature, the pressure was increased at an extremely slow rate up to the point at which crystals first began to form in the solution. At this point the heat of crystallization was liberated, the process being accompanied by a temperature jump. The latter was recorded as a sharp deflection on a galvanometer and on the chart of an ÉPP-09 automatic potentiometer connected in parallel with it. Besides this objective record of the solidification, the presence of crystals was always verified visually: the solid

solution is turbid, and the boundary between the liquid and solid phases is clearly visible.

The results of such measurements for ten different concentrations, including pure He³ and He⁴, are presented in Fig. 4. Except for the case of He³, the solid curves are drawn through the points whose coordinates are given in Table III. For He³ the solid curve above T_{min} is drawn according to the data of Mills, Grilly, and Sydoriak^[5], and below T_{min} , from the results of Baum, Brewer, Daunt, and Edwards^[6]. As is evident from Fig. 4, our results for He³ agree well with the values given by the former authors. The dashed curves

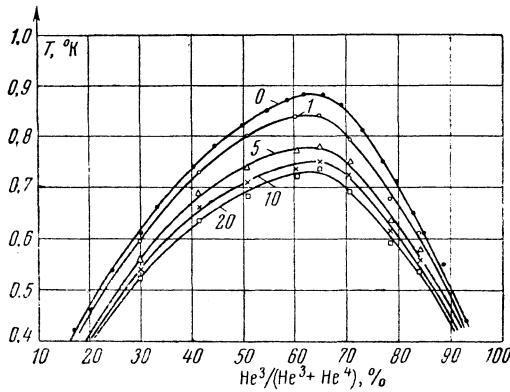


FIG. 3. Phase diagrams for liquid He³-He⁴ solutions for pressures of 0-20 atm. Numbers on curves indicate pressure in atm.

in Fig. 4 represent the results of the measurements by Lepair, Taconis, Ouboter, and Das^[7] which lie somewhat higher than our data. In absolute magnitude, our results agree well with the measurements by Weinstock, Lipschultz, Kellers, Tedrow, and Lee^[8], Esel'son and Lazarev^[9],

Bereznyak, Bogoyavlenskii, and Esel'son^[10], and Swenson^[11].

It is interesting to note that up to a concentration $x = 84\%$ the minimum crystallization pressures for the solutions lie below that for pure He⁴. This circumstance has also been reported in ^[7,8].

The solidification curves for solutions of concentrations 20.2, 29.9 and 41.5% show minima at temperatures of 0.87, 0.79 and 0.76°K, respectively, above their stratification points. The existence of minima for similar concentrations (25 and 38%) has also been observed by Weinstock et al.^[8]. The locations of the minima were determined in our case from the change in sign of the heat of fusion—below T_{\min} crystallization of the solution is accompanied by cooling, and the galvanometer deflection, as well as that on the chart of the automatic potentiometer, changes sign. In order to avoid blockage of the capillary below T_{\min} it was surrounded by a vacuum jacket and the He³ level was held below the glass-to-ferrochrome seal. Thus, the drop between the lowest temperature and T_{\min}

Table III. Solidification curves for He³-He⁴ solutions

$x, \%$	$T, ^\circ\text{K}$	p, atm	$x, \%$	$T, ^\circ\text{K}$	p, atm	$x, \%$	$T, ^\circ\text{K}$	p, atm				
He ⁴	0.5	25.0	He ⁴	0.79	22.9	He ⁴	60.3	0.72	22.05			
	0.6	25.0		0.8	22.9		0.8	23.0				
	0.7	25.0		0.9	23.0		0.9	23.45				
	0.8	25.0		1.0	23.4		1.0	25.1				
	0.9	25.0		1.1	24.0		1.1	27.6				
	1.0	25.05		1.2	24.7		1.2	30.5				
	1.1	25.1		1.3	25.8		1.3	33.8				
	1.2	25.2		1.4	27.7		1.4	37.5				
	1.3	25.4		1.5	30.9		1.5	41.5				
	1.4	25.7		1.6	34.6		He ⁴	78.5	0.59	24.0		
	1.5	26.2		1.7	38.1				0.7	25.3		
	1.6	27.1		1.8	41.8				0.8	26.9		
	1.7	28.3		He ⁴	41.5				0.63	23.6	0.9	28.9
	1.8	30.3							0.7	23.2	1.0	31.4
1.9	33.0	0.76	23.0			1.1			34.2			
2.0	36.3	0.8	23.0			1.2			37.5			
2.1	40.0	0.9	23.1			1.3			41.3			
2.2	43.8	1.0	23.5			He ⁴			84.2	0.53	24.9	
20.2	0.58	23.9	1.1							24.2	0.6	25.4
	0.6	23.8	1.2							25.3	0.7	26.7
	0.7	23.3	1.3							27.7	0.8	28.7
	0.8	23.2	1.4							31.5	0.9	31.0
	0.87	23.2	1.5							35.4	1.0	33.6
	0.9	23.2	1.6				39.3	1.1		36.5		
	1.0	23.3	1.7				43.1	1.2		39.8		
	1.1	23.8	He ⁴				50.8	0.69		22.9	He ⁴	91.8
	1.2	24.4		0.8	23.0			0.5		27.1		
	1.3	25.2		0.9	23.3			0.6		28.3		
	1.4	26.3		1.0	23.7			0.7		29.9		
	1.5	28.3		1.1	25.0			0.8		31.7		
	1.6	31.9		1.2	27.7			0.9		34.0		
	1.7	35.4		1.3	30.7	1.0		36.7				
1.8	39.0	1.4		34.1	1.1	39.6						
1.9	42.6	1.5		37.9	1.2	42.7						
29.9	0.55	23.7		1.6	39.4	He ⁴		29.9	0.55	23.7		
	0.6	23.3		1.65	43.6				0.6	23.3		
	0.7	22.95							0.7	22.95		

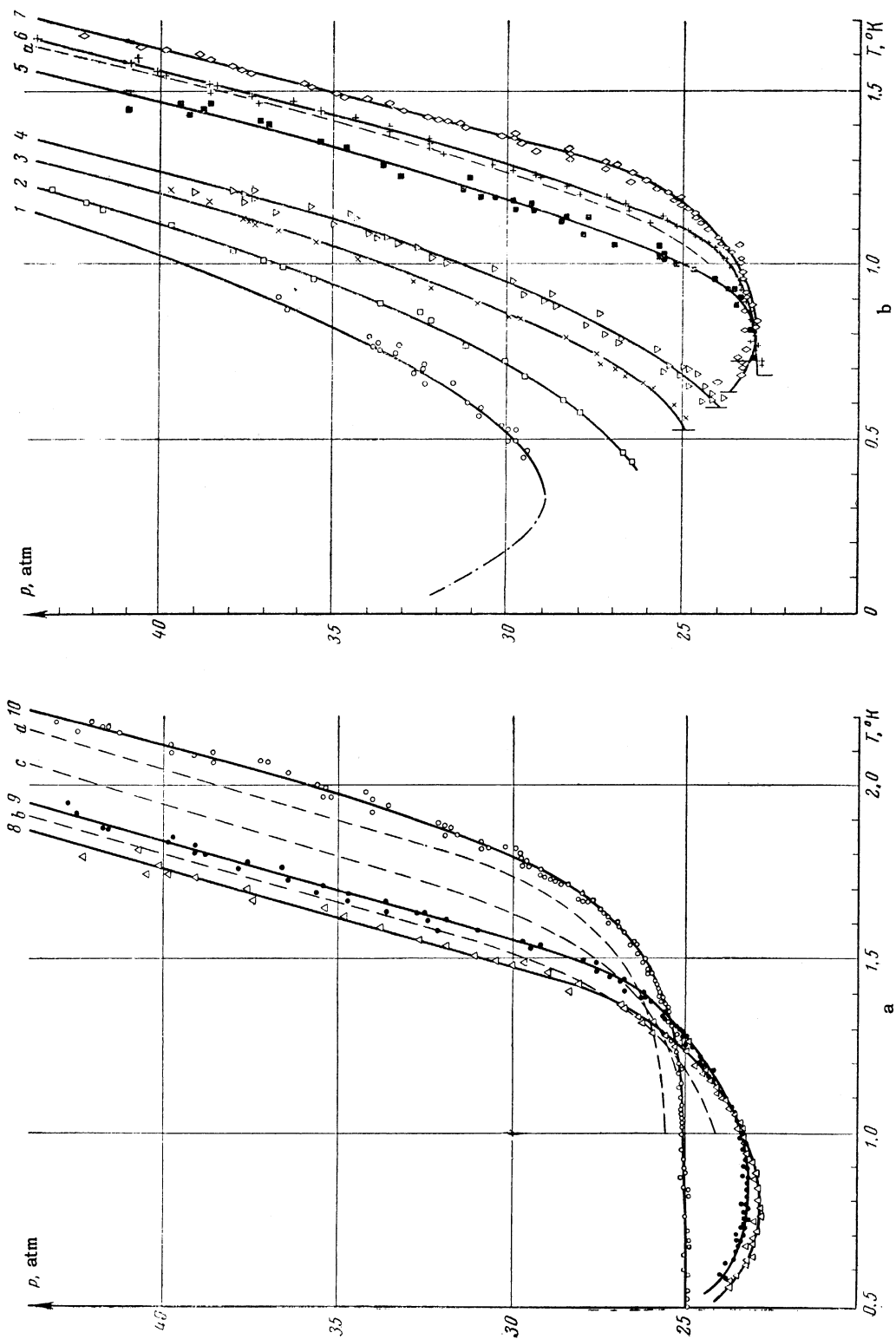


FIG. 4. Curves for onset of solidification in He³-He⁴ solutions at the following concentrations: Curve 1-He³, 2-91.8, 3-84.2, 4-78.5, 5-60.3, 6-50.8, 7-41.5, 8-29.9, 9-20.2%, 10-He⁴. Dashed curves from [7] for concentrations: a-51, b-25, c-8%, d-He³; dot-dash curve, from [6], for He³.

was confined to the large-diameter portion of the capsule. This made it possible to extend the measurements to temperatures somewhat below T_{\min} . For the greatest such temperature drop, $\Delta T \approx 0.2^\circ\text{K}$, an order-of-magnitude estimate of the maximum concentration gradient ∇x in the solution can be made using the formula $kTm_3^{-1}\nabla x = -\sigma_0\nabla T$, with m_3 the mass of the He^3 atom, σ_0 the entropy per unit mass of pure He^4 at $T \sim 0.8^\circ\text{K}$ and $p \sim 23$ atm, and k the Boltzmann constant. This yields $\nabla x \approx 0.1\%$ per cm, which for concentrations of 20 and 30% is negligible. The solidification of the solution in the capsule below T_{\min} was observed visually. Thus, the Pomeranchuk effect occurs in solutions at substantially higher temperatures than in pure He^3 .

For solutions of high concentration stratification occurs at temperatures higher than that at which the fusion curves reach their minima. The stratification temperatures for solutions with concentrations between 50.8 and 84.2% are indicated in Fig. 4 by vertical line segments. Solidification of the solutions below their stratification temperatures is not shown in Fig. 4, although it was observed visually.

With two liquid phases present, solidification

takes place, at different pressures, first in the lower, and then in the upper phase, the boundary being displaced slightly. Initially, the boundary between the two solid phases is clearly visible. The crystallization process in a stratified solution is indicated on the recorder chart by two deflections. The first deflection occurs upon solidification of the lower phase, and represents a drop in temperature, since crystallization of the He^4 -rich lower phase takes place at a temperature below its T_{\min} . The second deflection corresponds to crystallization of the upper phase and can be of either sign, according to the situation relative to the T_{\min} for the He^3 -rich solution.

The observations of the crystallization of solutions below their stratification temperatures in the present work were of a qualitative nature. The concentration of the solution changes continuously during the solidification process. In order to obtain fusion curves below the stratification temperature it would be necessary to measure the concentration of the solution as well as its temperature and pressure. For the same reason, melting curves for solid solutions were not measured during this experiment.

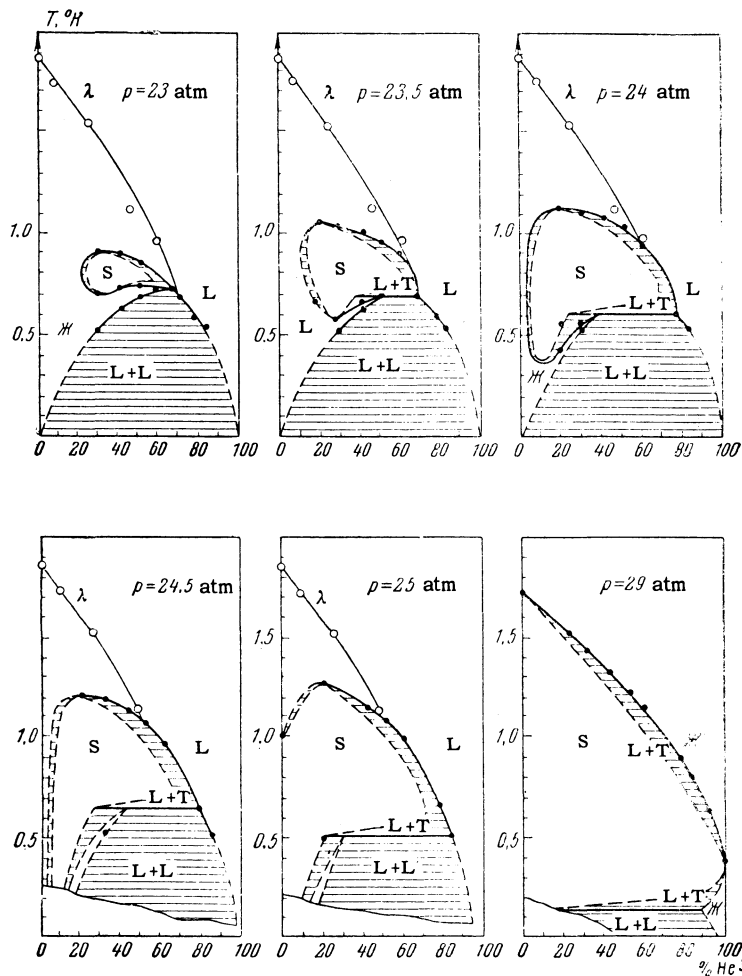


FIG. 5. Diagrams of state for He^3 - He^4 solutions for pressures of 23-29 atm.

Owing to the incompleteness of the experimental data it is unfortunately impossible as yet to construct exact diagrams of state for He³-He⁴ solutions at high pressures. From the data on hand, however, an attempt can be made to construct the general outlines of such a diagram. In addition to the diagrams of state presented in Fig. 3 for pressures of 0-20 atm, Fig. 5 shows the evolution of the state diagrams as the solid phase comes into existence for pressures $p = 23-29$ atm. In constructing these diagrams we have assumed limited solubility in the liquid solutions at low temperatures, right up to the crystallization pressure. The points in the diagrams correspond to the experimental data. The solid solution region is enclosed by an arbitrarily-drawn curve. The possibility is not excluded that within this region there may exist sub-regions of limited solubility. The diagrams also include λ -lines from the measurements of Lepair, Taconis, Ouboter, and Das^[7].

In one of the experiments a special check of the solution diagram of state was made for a concentration $x = 20\%$. At constant pressures of 24 and 25 atm the temperature was gradually reduced from 1.5°K to the lowest attainable, $\sim 0.32^\circ\text{K}$. It was then possible to observe directly by eye all of the stages in the transition of the solution from the liquid state to the solid, then to the solid + liquid, and finally to the liquid state. Unfortunately, it proved impossible to observe stratification for $x = 20\%$ at these pressures, since this process evidently occurs below 0.32°K . The points for 24 and 25 atm pressure obtained in this experiment are plotted on the state diagrams. It should be emphasized, however, that after melting occurs at the lower point, the pressure within the capsule may somewhat exceed the initial value due to possible blockage of the capillary, and that the true value of the lower solidification temperature for $p = 24$ atm may therefore lie somewhat higher. At $p = 25$ atm it was not possible to obtain pure liquid at the lower point; only three-quarters of the crystal melted.

Further experiments will be needed to establish the exact form of the state diagrams, especially at extremely low temperatures.

In conclusion, I am deeply grateful to Professor V. P. Peshkov for advice and for discussing these results, to Academician P. L. Kapitsa for his constant attention to and interest in the work, to Professor A. S. Kompaneets for discussions of the state diagrams, and to V. N. Krutikhin, who aided in assembling the apparatus and making the measurements.

Note added in proof (May 4, 1963). At the time this article went to press we secured additional data confirming the occurrence of stratification of solutions into two liquid phases at low temperatures and at pressures $p > 25$ atm, for which pure He⁴ has already become solid. At $T = 0.35$ and 0.3°K , and $p = 26$ atm, we observed the stratification of a mixture of initial concentration $x = 86.3\%$ into two liquid phases having volume ratios, respectively, of $\sim 1:10$ and $1:15$. The fact that both phases were liquid was evident from motion of the interphase boundary when the apparatus was gently shaken.

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