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VAPOR PRESSURE OF He^3—He^4 *MIXTURES IN THE* 0.7—1.3° K *TEMPERATURE RANGE*

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The vapor pressure of He^3—He^4 mixtures is measured at temperatures between 0.7 and 1.3°K for He^3 concentrations in the liquid up to 5% and for the complete range of He concentrations in the vapor. A dependence of the Henry law constant on temperature $a = 4.75\ (1/T - 0.17)$ is obtained between 0.7 and 2.0°K. A table listing the dependence of vapor pressure on temperature and concentration of gas phase is presented. The parameters of the excitation spectrum in dilute solutions of He^3 in He^4 are calculated: $\Delta = -2.65 \pm 0.1$°K and $m^*/m_3 = 2.8 \pm 0.2$.

IN connection with the extensive use of helium-isotope mixtures in physical experiments, it is necessary to have exact data on the liquid-vapor phase diagram of the He^3—He^4 system down to the lowest temperatures. The diagram was determined by a number of workers[1-4], but for temperatures below 1.2°K, down to the lamination region of the solutions, there are only the data of Sydoriak and Roberts on the vapor pressure over a liquid with concentration 10—90° He^3 (molar). In the lamination region, there are also the data of Goellner and Meyer[5] in a narrow concentration range near the junction of the λ line with the lamination curve.

The purpose of the present study was to determine the vapor line of the diagram, i.e., the dependence of the pressure on the gas-phase concentration, and also to determine the vapor pressure over a liquid with low concentration of He^3, where the pressure increases most rapidly with the concentration.

A diagram of the apparatus is shown in Fig. 1. The mixture chamber 1 and the coolant chamber 2 were machined from a solid piece of copper, and their surface was further enlarged by using posts of 2 × 2 mm. The mixture chamber had 50 mm diameter, 50 mm height, 23.7 cm^3 volume, and ≈ 200 cm^2 surface. The parasitic heat inflow at 0.7°K, determined from the temperature rise in the chamber in the course of time with the evacuation turned off, was 10^{-4} W. With such an enlarged surface, the unevenness in the temperature in the mixture chamber, due to the heat inflow, was less than 10^{-4} °K. The relative change of the concentration over the volume, as the result of thermo-osmosis[6] did not exceed 0.5% in this case. A temperature 0.7—1.3°K was obtained by pumping off He^3 or He^4, and could be maintained for an hour within ± 0.003% K. The temperature was measured with two phosphor-bronze thermometers of 30 μ diameter. One was suspended in the chamber and made contact with the liquid only, while the other was fastened to the chamber on the outside. The thermometers were calibrated in the chamber itself against the vapor pressure of He^3 (1962 scale) and He^4 (T_{58} scale). The calibration accuracy was ±0.002°K. Once equilibrium was reached, the readings of the thermometers in the course of the measurement were equal within (3—4) × 10^{-3} °K.

The mixture consisted of natural He^4 and He^3 with not more than 10^{-5} He^4. The relative error in the concentration of the mixture did not exceed 1% for small concentrations and 0.5% for intermediate ones.

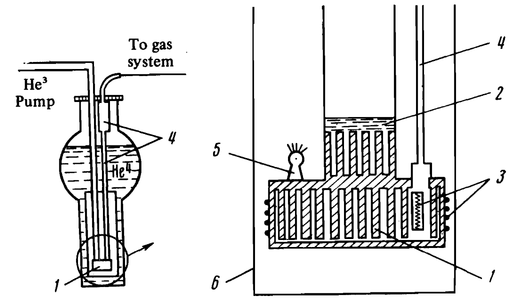

FIG. 1. Diagram of apparatus: 1—mixture chamber, 2—He^3 pumping chamber, 3—thermometers, 4—manometer tube, 5—electric leads, 6—vacuum jacket.

Precision measurements of low pressures were made with an oil manometer, the second bend of which was connected with a carbon adsorber in liquid nitrogen. The calibration was against a mercury manometer, and the ratio of the mercury and oil columns was 15.4 ± 0.1. The null of the manometer was regularly verified by evacuation to a pressure below 10^{-3} mm Hg. The shift did not exceed 2 μHg. The pressure was read with a cathetometer accurate to 3 μ. Such a system made is possible to measure low pressures with the accuracy needed to observe very small kinks on the filling isotherm when determining the dew point for a gas with a large He^3 concentration.

The manometer tube 4 leading to the chamber consisted of two parts. A thin tube of 1.6 mm diameter in the helium-temperature region, up to the top of the copper spherical He^4 container, was followed by a thick tube of 20 mm diameter in the region of the transition to room temperature. Such a geometry made the thermomolecular pressure difference negligible in the measurement range, less than 0.5% according to Roberts and Sydoriak[7]. The main source of error was distortion of the pressure by the evaporating superfluid film. A control experiment has shown that the error due to the evaporation of the film did not exceed the measurement error down to a pressure 0.3 mm Hg, but increased catastrophically with further decrease of pressure. It was this circumstance which determined the lower limit of the measurement range.

Table I. Vapor pressure over a liquid He^3—He^4 mixture for different He^3 contents in the gas phase

T, °K	P, mm Hg	T, °K	P, mm Hg
x = 33.2%		x = 95.44%	
0.984	0.176±0.006	0.906	1.11±0.07
1.117	0.512±0.005	x = 97.60%	
1.153	0.660±0.007	0.886	1.57±0.07
1.301	1.845±0.015	0.923	1.93±0.07
x = 66.8%		0.963	2.75±0.07
0.978	0.337±0.01	x = 98.59%	
1.085	0.78±0.03	0.869	2.22±0.07
1.104	0.88±0.02	0.915	3.17±0.23
x = 91.3%		x = 98.55%	
0.914	0.485±0.04	0.908	3.11±0.17
0.943	0.83±0.045	1.036	6.90±0.15
1.007	1.37±0.13	1.065	7.6±0.4
1.128	3.60±0.20		

Table II. Vapor pressure over a liquid with different He^3 contents

T, °K	P, mm Hg	T, °K	P, mm Hg	T, °K	P, mm Hg	T, °K	P, mm Hg	T, °K	P, mm Hg	T, °K	P, mm Hg
x = 0.50%		x = 0.98%		x = 1.92%		x = 2.88%		x = 2.88%		x = 4.79%	
1.415	2.84	1.404	3.23	1.331	3.22	1.367	4.54	0.861	0.598	1.334	5.77
1.353	2.19	1.395	3.13	1.328	3.18	1.349	4.29	0.849	0.567	1.289	5.00
1.286	1.56	1.357	2.65	1.310	2.97	1.340	4.13	0.829	0.513	1.252	4.37
1.197	0.978	1.336	2.44	1.294	2.78	1.311	3.79	0.818	0.485	1.208	3.82
1.146	0.737	1.296	2.05	1.270	2.51	1.296	3.56	0.777	0.385	1.159	3.23
1.098	0.563	1.262	1.73	1.229	2.18	1.266	3.20	0.751	0.329	1.128	2.87
1.065	0.483	1.242	1.58	1.194	1.88	1.232	2.83	0.959	0.921	1.100	2.60
1.028	0.365	1.211	1.38	1.146	1.53	1.223	2.76	0.964	0.947	1.060	2.21
0.982	0.280	1.166	1.114	1.116	1.35	1.190	2.44	0.943	0.862	1.033	1.98
1.131	0.644	1.132	0.937	1.070	1.091	1.148	2.09	0.893	0.683	1.006	1.76
1.132	0.658	1.105	0.820	1.033	0.918	1.116	1.82			0.813	0.752
0.997	0.299	1.073	0.692	1.004	0.800	1.086	1.61			0.761	0.555
0.989	0.290	1.049	0.612	0.907	0.515	1.060	1.44			0.714	0.418
		1.018	0.524	0.935	0.576	1.032	1.27			0.682	0.327
		1.006	0.490	0.952	0.627	1.003	1.12				
		0.976	0.418	0.923	0.545						
		1.064	0.660	0.830	0.352						
		1.071	0.679								
		0.931	0.324								
		0.923	0.316								

Table III. Values of $1000P_x/P_3$ as functions of the temperature (in the interval 0.6—1.2° K) and of the molar concentration of He^3

x	T, °K						
	0.6	0.7	0.8	0.9	1.0	1.10	1.2
0.00	0.5/0.5	1.6/1.6	4.0/4.0	7.8/7.8	14/14	22/22	31/31
0.02	143/0.5	121/1.6	106/4.0	97/7.9	92/14	91/22	94/31
0.04	276/0.5	233/1.7	202/4.1	184/8.1	162/14	159/23	156/32
0.06	389/0.5	330/1.7	289/4.2	263/8.3	239/14	223/23	214/32
0.08	482/0.5	414/1.8	365/4.3	333/8.5	302/15	281/24	267/33
0.10	560/0.5	487/1.8	432/4.4	394/8.7	359/15	333/24	315/34
0.20	805/0.6	726/2.0	654/5.0	597/9.8	551/17	513/27	482/39
0.30	P/0.7	824/2.3	757/5.7	703/11	656/19	616/30	581/44
0.40	P/0.8	P/2.7	807/6.6	757/13	713/23	673/35	638/52
0.50	P/1.0	P/3.3	821/7.9	777/16	738/27	701/43	666/62
0.60	P/1.3	P/4.1	P/9.9	783/20	747/34	717/53	699/77
0.70	P/1.7	P/5.5	P/13	793/26	779/45	767/71	761/103
0.80	P/2.6	861/8.2	849/20	841/39	835/68	831/106	829/155
0.90	930/5.2	918/16	912/40	910/78	908/136	908/212	908/300
0.92	942/6.5	933/20	928/50	927/98	925/170	925/263	926/365
0.94	956/8.6	947/27	943/66	942/131	941/225	942/338	944/454
0.96	970/13	964/41	961/99	960/196	959/325	960/465	962/588
0.98	983/26	981/82	980/197	979/368	980/546	980/685	980/780
0.99	991/52	990/165	990/372	990/592	990/752	990/840	990/890
1.00 **	0.5460	1.3855	2.9004	5.6191	8.8661	13.762	20.218

*The first value is for the liquid and the second for the vapor. P—two-phase region in the liquid.

**The absolute values of the pressures in mm Hg are indicated for unity He^3 concentration.

Table IV. Values of $1000\,P_x/P_3$ as functions of temperature (in the interval 1.3—2.0°K) and the molar concentration of He^3

x	T, °K							
	1.3	1.4	1.5	1.6	1.7	1.8	1.9	2.0
0.00	43/43	56/56	71/71	87/87	104/104	122/122	140/140	157/157
0.05	175/45	177/59	183/75	191/91	197/109	206/128	215/147	222/165
0.10	296/47	287/62	281/79	279/96	277/115	277/135	278/155	279/175
0.15	387/50	371/66	358/84	348/102	339/122	333/143	327/164	328/185
0.20	456/53	434/70	416/89	401/109	387/130	375/152	369/174	373/197
0.25	510/57	485/75	463/94	445/116	425/139	410/162	412/186	415/210
0.30	551/61	524/80	500/101	477/124	454/149	451/174	452/199	455/225
0.35	579/66	555/86	528/109	500/134	494/160	491/187	492/214	495/242
0.40	606/71	577/93	547/118	536/145	530/173	530/202	532/231	536/260
0.45	623/77	593/101	578/129	571/158	568/189	570/220	571/251	575/280
0.50	634/85	618/111	610/142	607/174	607/208	608/241	609/274	612/304
0.55	660/95	650/124	645/157	643/193	646/230	646/265	647/301	649/333
0.60	689/106	683/140	681/177	681/217	682/257	682/294	683/333	684/369
0.65	722/121	719/160	719/202	719/246	719/289	720/332	721/372	722/411
0.70	756/142	755/186	755/234	756/282	756/331	757/377	758/421	759/461
0.75	793/170	791/222	792/277	792/332	794/386	794/435	795/481	796/521
0.80	829/212	829/274	831/338	831/400	832/458	833/510	834/555	834/594
0.85	868/353	868/353	870/426	871/494	871/553	871/604	872/648	873/682
0.90	909/394	909/482	910/560	911/626	912/679	912/723	913/758	914/784
0.95	954/620	954/700	955/760	955/804	955/838	955/860	955/879	955/892
1.00	28.437	38.621	50.960	65.645	82.863	102.79	125.62	151.52

*The notation is the same as in Table III.

lamination region, where, in view of the jump of the concentration of the liquid, a kink should appear on the $P(x_{4V})$ curve according to (1). This, however, takes place at very high He^3 concentrations. An estimate shows that the He^4 concentration at the kink point is less than 0.5, 0.2, and 0.1% for 0.8, 0.7, and 0.6°, respectively.

We have also measured the vapor pressure over liquids with small concentrations of He^3 in He^4, namely 0.98, 1.92, 2.88, and 4.79% He^3. The results are given in Table II. The obtained data enable us to calculate the Henry-law constant a (Fig. 4)

$$P_x = P_4(1 - x_{3L}) + aP_3x_{3L}, \tag{4}$$

where x_{3L} is the He^3 concentration in the liquid. The plot shows good agreement with the data for high temperatures (1) and (2), and with the interpolation proposed by Sydoriak and Roberts[4] from the 10% concentration. It turned out that the Henry-law constant depends linearly on the reciprocal temperature in the 0.7—2.0° K range:

$$a = 4.75(1/T - 0.17) \tag{5}$$

(it is represented by the solid line in Fig. 4).

Tables III and IV were constructed on the basis of the derived formulas (3) and (5) and on the basis of the data of Sydoriak and Roberts[4]. Notice should be taken of the good agreement between the vapor line of the diagram described by formula (3) and the previously calculated[10] vapor line.

The results can be used to calculate the constants Δ and m* in the law of excitation dispersion in a weak solution of He^3 in He^4[11]:

$$E = \Delta + p^2/2m^*, \tag{6}$$

where E is the energy and p is the excitation momentum. The chemical potential of He^3 in the solution is

$$\mu = \Delta - T\ln\left[\frac{2}{x_{3L}\,n_4}\left(\frac{m^*T}{2\pi\hbar^2}\right)^{3/2}\right], \tag{7}$$

where n_4 is the number of He^4 atoms per cm^3. Equating it to the chemical potential of the He^3 in the gas[9], we obtain

$$\ln\frac{N_V}{N_L} = \frac{\Delta}{T} - \frac{3}{2}\ln\frac{m^*}{m_3}, \tag{8}$$

To prevent evaporation of the He^3 from altering the low He^3 concentration, the chamber was filled in such a way that the low-temperature gas volume was small (less than 1 cm^3), not more than 2% of the He^3 in the liquid turned into gas at pressures below 4 mm Hg and at the minimum concentration. This was done by condensing in a chamber of known volume (23.7 cm^3) a strictly determined amount of gas from a flask of known volume (25.00 liters), as monitored by the pressure in the flask. The volume of the liquid mixture was calculated by using the data of Ptukha[8] on the density of liquid solutions of He^3 in He^4.

We measured the dew points down to 0.85° K for concentrations 32.2, 66.8, 91.3, 95.44, 97.60, 98.59, and 98.55% He^3 in the vapor. The results are listed in Table I. The indicated error is the error in the determination of the position of the kink in the gas amount—pressure isotherm in each individual experiment.

For a solution, assuming the vapor to be ideal, we have the thermodynamic equation[9]

$$1-\frac{x_{3L}}{x_{3V}}=-\frac{\partial \ln P}{\partial \ln x_{4V}}, \qquad (1)$$

where x_{3L} and x_{3V} are the molar concentrations of the He^3 in the liquid and in the vapor, and $x_{4V} = 1 - x_{3V}$. At temperatures below 1.3° the vapor can be regarded as ideal. In addition, in a large range of He^3 concentrations in the vapor (up to $x_{3V} \lesssim 0.9$ at 1°), we have $x_{3L}/x_{3V} \ll 1$, so that the following expression is valid in this range:

$$P = P_4 / x_{4V}, \qquad (2)$$

where P_4 is the pressure of pure He^4 at the same temperature.

For high He^3 concentrations in the vapor, close to 100%, our data together with the data by others[1,2] enable us to determine the dependence of $(P_3 - P_X)/P_3x_{4V}$ on the reciprocal temperature, where P_X is the pressure of the mixture and P_3 is the pressure of pure He^3 at the same temperature, approximately equal to the value of $\partial \ln P/\partial x_{4V}$ at $x_{4V} = 0$ (Fig. 2). This dependence coincides with the dependence of $0.3P_3/P_4$ on the reciprocal temperature, where P_4 and P_3 are the pressures of pure He^4 and He^3.

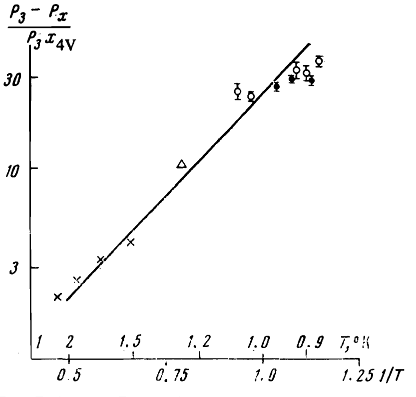

FIG. 2. $(P_3-P_X)-x_{4V}P_3$ vs the reciprocal temperature at high He^3 concentrations: ○—1.45 and 1.41% He^4, ●—2.4% He^4, △—data of [1]; ×—data of [2]; the straight line is a plot of $0.3\ P_3/P_4$ against the reciprocal temperature.

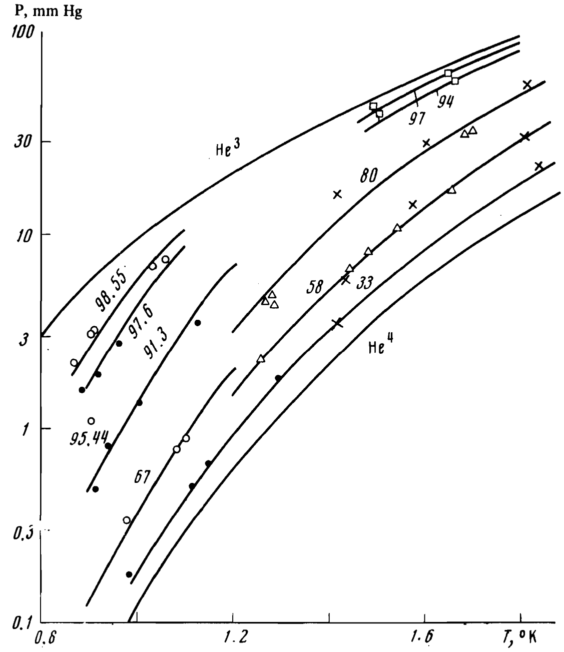

FIG. 3. Temperature dependence of the pressure for different concentrations of the gas phase. ●, ○—present work, △—data of [1], He^3 concentrations 58 and 78%; ×—[2]. He^3 concentrations 35.4, 57.6, and 82.4%; □—[3], He^3 concentrations 94 and 97%. Solid lines—calculated from formula (3).

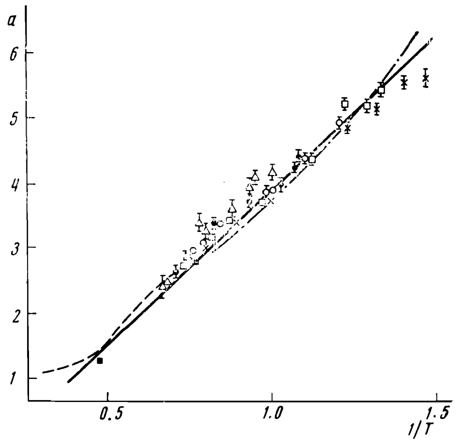

FIG. 4. Temperature dependence of the Henry-law constant. Data for the following He^3 concentrations: △—0.5%; ●—1.0%; ○—1.9%, □—2.9%, ×—4.8%; ■—data of [1], dashed—data of [2], dash-dot—[4].

Knowledge of the behavior of the curve in the two mentioned regions enables us to propose an interpolation formula for the vapor line on the liquid-vapor diagram of He^3-He^4 mixtures:

$$P=P_4\Big/\left[x_{4V}+\frac{P_4}{P_3}\exp\left(-0.7x_{4V}\frac{P_3}{P_4}\right)\right]. \qquad (3)$$

The curves calculated by means of this formula for different concentrations are shown in Fig. 3. The experimental data of the present paper and the data of[1-3] agree well with the calculated curve up to 1.8°, where the gas ceases to be ideal and formula (1) no longer holds[2].

The interpolation curve proposed for the vapor phase diagram differs qualitatively from the real curve in the

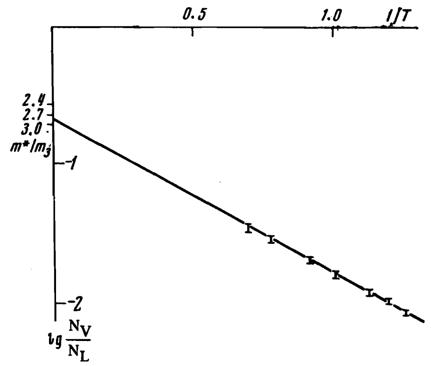

FIG. 5. Determination of the excitation parameters m^*/m_3 and $\Delta = d\ln(N_V/N_L)/d(1/T)$ in weak He^3 solutions.

where N_V is the number of He^3 atoms per cm^3 of gas, $N_L = x_{3L}n_4$ is the number of He^3 atoms per cm^3 of liquid, and m_3 is the mass of the He^3 atom. From the data on the density[12], $n_4 = 0.22 \times 10^{23}$ cm^{-3} at a temperature below 2°K

$$N_V = 0.97 \cdot 10^{19}\, P_{\text{part}} / T,$$

where P_{part} is the partial pressure of the He^3 determined on the basis of data on the vapor line of the diagram. Figure 5 shows a plot of $\log(N_V/N_L)$ against the reciprocal temperature, from which we get

$$\Delta = -2.65 \pm 0.1°, \qquad m^* / m_3 = 2.8 \pm 0.2.$$

This value of Δ agrees with the value −2.68°K for concentrations smaller than 4% He^3 and temperatures 0.6–1.0°K, calculated in[13] on the basis of the vapor-pressure data of Sydoriak and Roberts[4].

The effective mass averaged over the range 0.7–1.4°K exceeds the values obtained for temperatures below 0.6°K ($m^*/m_3 = 2.2$–2.5)[14-16]. This can be attributed to the increase of m* with increasing temperature, as indicated in[16,17]. It must be noted, however, that there are appreciable discrepancies between the values of m* given by different authors[18].

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