Molar Volume, Coefficient of Thermal Expansion, and Related Properties of Liquid He[4] under Pressure*

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From measurements of the dielectric constant, we have determined the molar volume of liquid He^4 along various isobars in the region 1.25 to 4.2°K and 0.5 to 28 atm. Tables of molar volume, thermal expansion coefficient α_P, entropy of compression, and isobaric change in the isothermal compressibility are presented for this region. Values of T_λ, P_λ, and V_λ are presented. Particular emphasis was put on the form of the expansion coefficient near the λ transition. We have found that the α_P singularity is logarithmic over the range of 2×10^{-5} to 10^{-2} °K displacement from the transition, and from the data that lead to this conclusion, we have been able to calculate various other properties of the fluid near the transition. These results are compared with those of other experiments wherever possible.

I. INTRODUCTION

We have made a detailed investigation of the molar volume of liquid He^4 along various isobars between 1.25 and 4.2°K, and from the results of this investigation we have obtained the thermal expansion coefficient, $\alpha_P=1/V(\partial V/\partial T)_P$, and thermodynamically related properties. In this study we have put particular emphasis on the region near the λ transition, and on the behavior of α_P as $|T-T_\lambda|$ decreases to 10^{-5}°K. Similar research has been done by several workers[1–4] along the vaporization curve with considerable resolution near the λ point, and α_P has been obtained by Grilly and Mills[5] along certain isobars near the melting curve but with limited resolution near the λ transition. We have improved on this work by a factor of 10 or more in temperature resolution, and have made the first systematic study of the variation of α_P with pressure in this temperature range.

Molar volumes are of fundamental importance in obtaining an equation of state for He^4. The fact that the molar volume decreases with increasing temperature ($\alpha_P<0$) over the entire range of our data below the λ line and, for part of the range above it, is most unusual and therefore worth studying in detail. In addition, such an isobaric study yields a particularly sensitive way of calculating changes in the isothermal compressibility, Δk_T, with temperature, and of calculating the entropy of compression. Our results of V and of α_P, and our calculations of $\Delta k_T=k_T(T)-k_T(T_0)$ and $S_{\mathrm{comp}}=S(T,P)-S(T,P_{\mathrm{SVP}})$ are presented in the first part of the results section, and are compared with existing data where possible.

Our study was undertaken primarily to determine the nature of the λ transition at elevated pressures. This requires quite high resolution in the independent variables, since previous studies near the transition have all shown that the various properties change rapidly. Fairbank, Buckingham, and Kellers[6,7] have shown that the singularity in the specific heat of the liquid under its saturated vapor is logarithmic over a wide range. Thermodynamic relations[7] indicate that α_P and C_P ought to display the same limiting behavior at T_λ. The thermal expansion α_P is more readily measurable at elevated pressures because the experiment, unlike that of C_P, does not involve thermal isolation from a bath. This isolation is difficult to achieve because of the heat leak through the pressure-transmitting capillary. Hence it was decided to make a systematic study of α_P close to the transition line.

A by-product of this research is a new determination of the λ line in which particular care has been taken to determine the limiting slope at the lower triple point, and we present the results of this determination expressed as $P_\lambda(T)$ and $V_\lambda(T)$. We present our expansion-coefficient results close to the transition at the various pressures where we have taken high-resolution data. From these results we have calculated by various means the specific heat C_P, the compressibility coefficient k_T, and the pressure coefficient $(\partial P/\partial T)_V$. All of these data are presented in the second section of results along with a discussion of internal consistency and a comparison with the results of previous workers. In general the agreement is quite good so that our results may be taken as giving a valid description of the shape of the volume surface near the λ line. Some of the results have already been reported in more concise form elsewhere.[8]

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[5] E. R. Grilly and R. L. Mills, Ann. Phys. (N. Y.) 18, 250 (1962).

[6] W. M. Fairbank, M. J. Buckingham, and C. F. Kellers, in *Proceedings of the Fifth International Conference on Low-Temperature Physics and Chemistry, Madison, Wisconsin, 1957*, edited by J. R. Dillinger (University of Wisconsin Press, Madison, 1958), p. 50; C. F. Kellers, thesis, Duke University, 1960 (unpublished).

[7] M. J. Buckingham and W. M. Fairbank, in *Progress in Low-Temperature Physics*, edited by C. J. Gorter (North-Holland Publishing Company, Amsterdam, 1960), Vol. III, p. 80.

[8] D. L. Elwell and H. Meyer, Bull. Am. Phys. Soc. 11, 175 (1966); D. L. Elwell and H. Meyer in Proceedings of the Tenth International Conference on Low-Temperature Physics, Moscow, 1966 (unpublished). In this report, the height of the mercury column measuring the vapor pressure of He^4 for calibration was erroneously not corrected to the height at 0°C and therefore the temperature scale is about 1.7 mdeg K too high near 2°K.

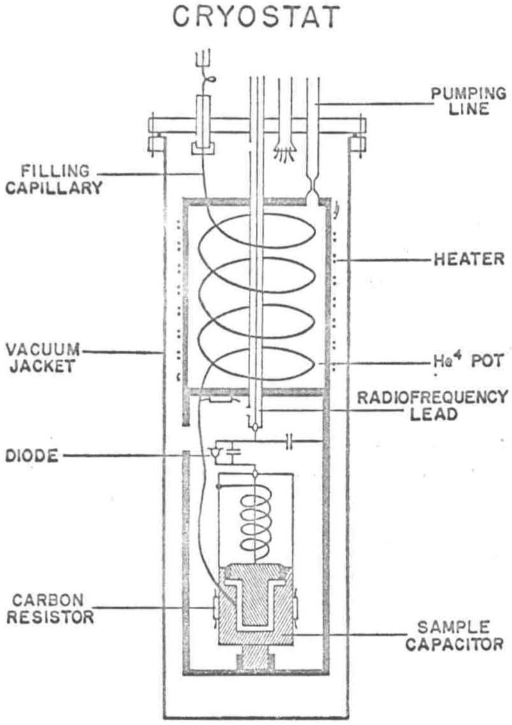

FIG. 1. Schematic diagram of the density cell and He^4 pot for the temperature range between 4.2 and 1.25°K. The vacuum jacket is surrounded by liquid He^4 at 4.2°K.

II. APPARATUS AND EXPERIMENTAL PROCEDURE

We have determined the molar volume of liquid He^4 by measuring the dielectric constant of a small sample of the liquid. This sample was contained in a capacitor which was part of an *LC* tank circuit, the resonance of which determined the frequency of a tunnel-diode oscillator. This circuit has been discussed previously,[9] where it was shown that

$$\epsilon=\{(\nu_0/\nu)^2+K[(\nu_0/\nu)^2-1]\}[1+B(P)]^{-1}, \qquad (1)$$

where ϵ is the dielectric constant of the sample, ν and ν_0 are the frequencies of the circuit with and without sample, respectively, and K and $B(P)$ are terms which correct for, respectively, part of the capacitive space being unavailable to the sample and pressure distortion of the capacitor. The molar volume V was then determined from the dielectric constant by using the Clausius-Mosotti relation

$$\frac{(\epsilon-1)}{(\epsilon+2)}=\frac{4\pi}{3}\left(\frac{A}{V}\right). \qquad (2)$$

A fundamental assumption that has been made in this work is that the molar polarizability A is a constant which we have taken to have the value[3] 0.1230. The justification for this assumption lies in the excellent agreement of the density data with the pycnometric data of Edeskuty and Sherman,[10] as will be described later.

The apparatus is very similar to those that have been described in detail elsewhere,[9] and is only discussed briefly here.[11] The heart of the cryostat is shown schematically in Fig. 1. It is an improvement over an original version in that the oscillator elements were close together (electrically as well as mechanically) and rigidly mounted with respect to each other so that the frequency was very stable. The operating frequency was about 14 MHz and did not change by more than ± 0.2 Hz over periods of about 1 h, as long as temperature and pressure were held constant. This made it possible to detect volume changes as small as 1 part in 10^6. This in turn made it meaningful to approach the λ line to a resolution of about 10 μ°K, since the molar volume changes by about 1 part in 10^6 in an interval of this size near the transition. The thermometers were $\frac{1}{10}$-W Allen Bradley carbon resistors, attached as shown in Fig. 1. A 110-Ω resistor attached to the capacitor was the main thermometer, while a 64-Ω resistor attached to the capacitor was used for work below 1.6°K, and a 64-Ω resistor attached to the pot was used to detect the presence of thermal gradients introduced by the sample in the superfluid phase. Resistances were measured on an ac Wheatstone bridge at a power level of about 10^{-8} W dissipated in the resistor; at 2.2°K this gave a resolution of about 5 μ°K on the main thermometer. The signal from the bridge was amplified and fed into a phase-sensitive detector, and this detector in turn fed a dc signal to a chart recorder to give a continuous display of the temperature change.

The sample pressure was held constant to ± 0.1 mm of Hg throughout a pressure run. The absolute accuracy to which the pressure was known varied with the measuring device. It was ± 0.2 mm Hg for pressures up to 1 atm, where a mercury manometer was used. In runs I and II a bourdon gauge was used with a pressure resolution of ± 0.05 atm. In run III, a Heise bourdon gauge with a resolution of about ± 0.01 atm was used. Both Bourdon gauges were calibrated against a dead weight tester and were accurate to the resolution to which they could be read. Hysteresis of the gauges was found to be negligible. The external pressure control system was connected to the sample capacitor by a 0.010-in. i.d. stainless-steel capillary that had an 0.008-in. wire in it between a thermal anchor at 4.2°K and the He^4 pot. This reduced the heat influx along the pressure line considerably but, for pressures below 1 atm lead to a small lag (2 or 3 sec) between pressure adjustment and frequency equilibrium. Thus there was

[9] C. Boghosian, H. Meyer, and J. E. Rives, Phys. Rev. 146, 110 (1966).

[10] F. J. Edeskuty and R. H. Sherman, in *Proceedings of the Fifth International Conference on Low Temperature Physics, Madison, Wisconsin, 1957*, edited by J. R. Dillinger (University of Wisconsin Press, Madison, 1958), p. 102.

[11] A detailed description of the apparatus and tabulation of all the results can be found in the Ph.D. thesis by D. L. Elwell, Duke University, 1967 (unpublished).

somewhat more scatter in the high resolution data at low pressures than elsewhere.

Resistance and sample frequency were recorded automatically on IBM punch cards. The 14 MHz signal was amplified and mixed with a 10-MHz standard (from the counter) and the resultant beat frequency was counted on a Hewlett-Packard 5245L solid-state scaler. The reading of this counter fed on command directly to the key punch. Resistance values were read both as dial settings on the standard decade box which was one arm of the Wheatstone bridge, and as the voltage imbalance from the phase-sensitive detector. This recording system was designed and built by Dr. J. Jarvis of this laboratory and has been described by him in detail elsewhere.[12]

At the beginning of an experimental run the empty-cell frequency of the oscillator and the resistance of the thermometers were measured as a function of the vapor pressure of the He^4 in the pot and thus of temperature on the T_{58} scale. The resistance calibration showed a scatter of ± 0.5 mdeg, and in addition there was a small drift in the resistance of the thermometers over periods of several days which introduced other uncertainties, so that we estimate the total uncertainty in the absolute temperature to be ± 1 mdeg on the T_{58} scale. The empty-cell frequency calibration scattered by about ± 2 Hz. Additional shifts as large as ± 50 Hz (over a total range of 400 Hz) were often induced by shaking the apparatus while filling the helium pot and were compensated for by maintaining reference points at various pressures. It should be noted that these shifts were avoided during the data-taking periods, and therefore the high-resolution data were not affected.

Once helium was introduced into the density cell, the calibration constants in Eq. (1) were determined from a fitting of our frequency results to the densities given by Lounasmaa[13] along the 1.75°K isotherm. The uncertainty in Lounasmaa's data and hence in the absolute value at our molar volumes was estimated to be about 0.1%. Relative values along a given isobar are of course known to a much greater precision. After calibration of the apparatus, volume measurements were made at constant pressure over the whole temperature range available to us, and in this process the approximate location of the transition was determined. Successively higher resolution passes were then made over decreasing intervals of temperature both while warming and cooling the density cell through the transition. The last three to five such passes would cover an interval of about 2 mdeg and take around 2 h with readings punched every 20 sec. The data for one such pass at 13 atm are shown in Fig. 2, and we emphasize that most of the other passes were parallel and of similar quality. We take this parallelism to indicate that thermal equilibrium was maintained in the sample. This is of course important, because even a small disequilibrium would smear the transition badly. The cell was particularly suitable from this point of view, since the sample was always within 0.05 mm of a copper wall and since there was a large surface-to-volume ratio and heat could be exchanged rapidly. A further potential source of broadening was the hydrostatic pressure head in the sample. However the 1-cm height of our sample corresponded to a shift in T_λ of only about 10^{-7}°K and since this was considerably less than the available resolution it did not effect the validity of the results.

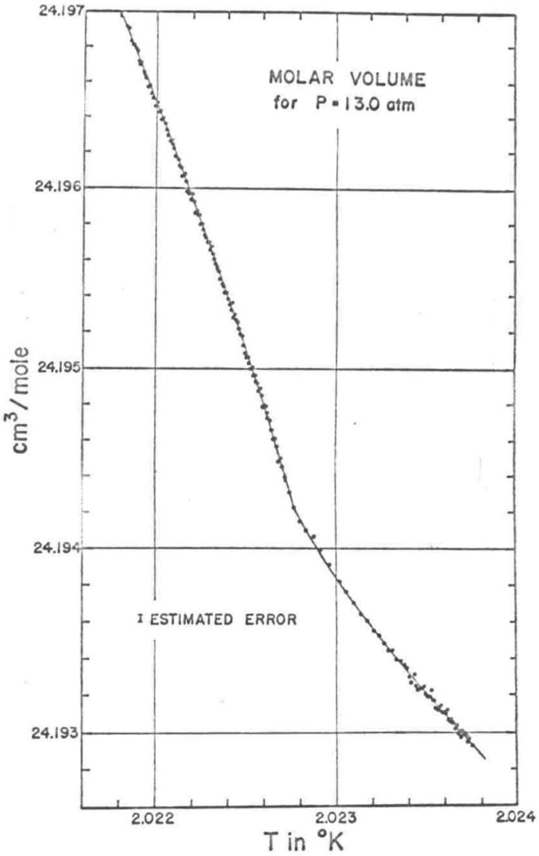

FIG. 2. High-resolution data at 13.0 atm in the neighborhood of the λ transition.

Finally, the raw data were converted by computer, without smoothing or fitting, into molar volume-versus-temperature points, and these were plotted on large graphs. Curves were drawn through the data by hand and slopes obtained graphically. In this way we have avoided prejudicing the shape of the α_P singularity in favor of any particular mathematical form and consider that the data we present in the next section give a good representation of the equation of state near the λ transition.

III. RESULTS AND DISCUSSION

For convenience we divide this section into two parts; the first one gives our data over the broad temperature range and a comparison with other such data, and the

[12] J. F. Jarvis, thesis, Duke University, 1967 (unpublished).
[13] O. V. Lounasmaa, Cryogenics 1, 1 (1961).

TABLE I. Molar volume of He^4 (cm^3/mole).

T(°K) \ P(atm)	0.493	0.996	2.70 ±0.05	5.06 ±0.01	8.00 ±0.05	10.01 ±0.01	13.00 ±0.05	15.01 ±0.01	17.97 ±0.01	20.10 ±0.05	22.08 ±0.01	24.93 ±0.01	27.10 ±0.05	28.00 ±0.01
1.250	(27.3942)	(27.2494)	(26.753)	26.137	25.486	25.124	24.598	24.313	23.900	23.645	23.397	23.078	···	···
1.300	27.3933	27.2480	26.751	26.134	25.482	25.120	24.593	24.308	23.894	23.638	23.389	23.070	···	···
1.350	27.392	27.246	26.748	26.130	25.477	25.114	24.587	24.301	23.886	23.629	23.380	23.059	···	···
1.400	27.390	27.243	26.745	26.125	25.471	25.108	24.579	24.293	23.876	23.619	23.368	23.047	···	···
1.450	27.387	27.240	26.740	26.120	25.464	25.100	24.570	24.283	23.865	23.606	23.355	23.031	···	···
1.500	27.383	27.237	26.735	26.113	25.456	25.090	24.559	24.271	23.852	23.591	23.338	23.011	···	···
1.550	27.379	27.232	26.729	26.105	25.445	25.079	24.546	24.256	23.835	23.572	23.318	22.988	in solid	···
1.600	27.374	27.226	26.721	26.095	25.434	25.066	24.531	24.239	23.816	23.550	23.294	22.958	(22.759)	···
1.650	27.369	27.220	26.712	26.084	25.420	25.050	24.512	24.218	23.792	23.524	23.264	22.923	22.714	in solid
1.700	27.362	27.212	26.702	26.071	25.403	25.032	24.490	24.195	23.764	23.493	23.228	22.878	22.660	22.512
1.750	27.354	27.203	26.690	26.056	25.384	25.010	24.467	24.166	23.731	23.454	23.182	22.821	22.589	22.430
1.800	27.345	27.193	26.676	26.038	25.361	24.987	24.435	24.133	23.691	23.406	23.128	22.749	22.485	22.318
1.850	27.335	27.181	26.661	26.018	25.336	24.957	24.400	24.093	23.641	23.345	23.053	22.639	22.437	22.303
1.900	27.322	27.168	26.643	25.994	25.307	24.922	24.358	24.044	23.578	23.269	22.957	22.624	22.436	22.303
1.950	27.308	27.152	26.622	25.967	25.272	24.881	24.304	23.981	23.492	23.203	22.947	22.626	22.440	22.308
2.000	27.293	27.135	26.597	25.935	25.229	24.831	24.238	23.898	23.463	23.200	22.949	22.631	22.447	22.316
2.050	27.273	27.112	26.568	25.897	25.178	24.764	24.183	23.886	23.463	23.203	22.955	22.639	22.456	22.326
2.100	27.251	27.088	26.532	25.846	25.114	24.727	24.182	23.889	23.469	23.212	22.964	22.648	22.466	22.337
2.150	27.222	27.051	26.478	25.804	25.111	24.731	24.188	23.898	23.480	23.223	22.976	22.660	22.477	22.348
2.200	27.203	27.035	26.481	25.812	25.121	24.741	24.199	23.910	23.491	23.236	22.988	22.672	22.490	22.361
2.250	27.226	27.059	26.500	25.828	25.136	24.756	24.213	23.923	23.504	23.250	23.002	22.686	22.503	22.375
2.300	27.259	27.090	26.525	25.850	25.153	24.774	24.229	23.938	23.519	23.264	23.017	22.701	22.517	22.388
2.400	27.343	27.170	26.590	25.905	25.201	24.816	24.268	23.973	23.552	23.296	23.049	22.731	22.546	22.418
2.500	27.442	27.263	26.670	25.969	25.254	24.866	24.310	24.015	23.591	23.333	23.084	22.763	22.579	22.450
2.600	27.559	27.372	26.761	26.042	25.315	24.921	24.357	24.062	23.633	23.372	23.121	22.797	22.613	22.484
2.700	27.694	27.495	26.862	26.125	25.382	24.981	24.410	24.111	23.678	23.413	23.159	22.833	22.648	22.520
2.800	27.839	27.631	26.974	26.216	25.456	25.045	24.466	24.163	23.725	23.457	23.201	22.871	22.686	22.556
2.900	27.999	27.782	27.095	26.312	25.534	25.115	24.527	24.218	23.775	23.503	23.245	22.912	22.725	22.594
3.000	28.173	27.946	27.225	26.417	25.618	25.189	24.590	24.276	23.826	23.552	23.292	22.954	22.767	22.634
3.100	28.366	28.121	27.369	26.527	25.707	25.266	24.656	24.336	23.881	23.602	23.340	22.999	22.810	22.675
3.200	28.581	28.315	27.521	26.646	25.801	25.348	24.727	24.400	23.938	23.656	23.389	23.045	22.854	22.717
3.300	28.815	28.533[a]	27.686	26.773	25.902	25.436	24.801	24.467	23.998	23.712	23.440	23.093	22.900	22.761
3.400	29.071	28.759[a]	27.864	26.909	26.009	25.529	24.880	24.538	24.060	23.770	23.494	23.142	22.946	22.806
3.500	29.352	29.013[a]	28.053	27.050	26.119	25.625	24.960	24.612	24.124	23.830	23.550	23.193	22.994	22.853
3.600	in gas	29.292[a]	28.262	27.200	26.233	25.727	25.045	24.690	24.193	23.892	23.609	23.246	23.045	22.903
3.700	···	29.602[a]	28.487	27.361	26.353	25.832	25.133	24.770	24.263	23.956	23.668	23.301	23.095	22.954
3.800	···	29.940[a]	28.719[a]	27.533	26.480	25.942	25.226	24.853	24.337	24.024	23.731	23.358	23.147	23.006
3.900	···	30.324[a]	28.976[a]	27.720	26.612	26.060	25.323	24.941	24.412	24.093	23.795	23.417	23.202	23.060
4.000	···	30.751[a]	29.258[a]	27.911	26.753	26.182	25.422	25.031	24.491	24.162	23.861	23.478	23.256	23.115
4.200	···	31.839[a]	···	28.349	27.049	26.445	···	25.222	24.657	24.304	24.002	23.607	23.372	23.232

[a] Indicates reading uncertainty of more than ±0.001.

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TABLE II. Thermal expansion coefficient of He^4 (10^{-3}°K^{-1}).

3.900	...	30.324[a]	28.976[a]	27.720	26.612	26.060	25.323	24.941	24.412	24.093	23.795	23.417	23.202	23.060
4.000	...	30.751[a]	29.258[a]	27.911	26.753	26.182	25.422	25.031	24.491	24.162	23.861	23.478	23.256	23.115
4.200	...	31.839[a]	...	28.349	27.049	26.445	...	25.222	24.657	24.304	24.002	23.607	23.372	23.232

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T(°K) \ P(atm)	0.493	0.996	2.70	5.06	8.00	10.01	13.00	15.01	17.97	20.10	22.08	24.93	27.10	28.00
1.25	...	...	...	...	...	−3.00	−3.63	−4.18	−4.73	−5.53	−5.73	−6.13	in solid	in solid
1.30	−0.88	−1.15	−1.79	−2.69	−3.39	−3.79	−4.64	−5.09	−5.90	−6.40	−7.39	−8.70	in solid	in solid
1.35	−1.39	−1.70	−2.47	−3.26	−4.10	−4.68	−5.49	−6.07	−7.15	−7.94	−8.71	−9.83	in solid	in solid
1.40	−1.89	−2.06	−2.82	−4.06	−5.04	−5.94	−6.63	−7.29	−8.65	−9.48	−10.68	−11.86	in solid	in solid
1.50	−2.73	−3.10	−4.32	−5.73	−7.12	−8.07	−9.71	−11.10	−12.37	−14.68	−15.69	−19.0	in solid	in solid
1.60	−3.79	−4.39	−6.14	−7.79	−10.21	−11.18	−13.62	−15.27	−17.8	−19.8	−22.1	−28.3	(−35.8)	in solid
1.70	−5.22	−6.15	−8.32	−10.85	−14.41	−15.5	−19.1	−21.7	−25.8	−29.6	−34.6	−43.0	−52.5	−65.5
1.80	−7.16	−7.98	−11.01	−14.54	−18.82	−21.7	−27.0	−30.0	−36.6	−45.1	−54.2	−75.1	−116.4	−34.8
1.90	−9.38	−10.7	−15.1	−19.8	−25.2	−29.8	−38.5	−45.6	−61.8	−77.5	−21.8	−1.5	+2.0	+2.7
2.00	−12.9	−14.4	−19.6	−26.6	−35.3	−46.3	−65.2	−27.9	−2.3	+1.6	+4.4	+6.4	+7.2	+8.5
2.10	−18.7	−22.0	−31.0	−48.0	−12.5	0.0	+3.6	+5.4	+7.8	+8.7	+9.2	+9.8	+9.4	+10.6
2.20	+12.3	+11.8	+12.5	+9.7	+10.7	+10.7	+10.3	+11.0	+10.8	+11.9	+11.5	+11.9	+11.5	+11.9
2.30	+27.0	+25.0	+20.6	+18.5	+16.3	+15.3	+14.1	+13.8	+13.4	+12.6	+13.3	+12.9	+12.9	+12.9
2.40	+33.1	+31.9	+27.0	+23.2	+19.9	+18.6	+16.5	+16.2	+15.5	+15.4	+14.7	+13.7	+13.9	+13.9
2.50	+38.9	+37.2	+32.1	+27.0	+23.2	+21.4	+18.5	+18.4	+17.2	+16.3	+15.6	+14.6	+15.0	+14.7
2.70	+50.8	+48.0	+39.3	+33.0	+27.7	+25.1	+22.4	+21.0	+19.6	+19.0	+17.4	+16.5	+16.3	+16.0
3.00	+64.1	+61.0	+51.6	+40.3	+33.8	+30.0	+27.2	+24.4	+22.2	+21.1	+20.5	+19.1	+18.6	+18.1
3.20	+78.7	+72.0	+57.7	+46.0	+38.1	+33.6	+29.7	+26.7	+24.4	+23.5	+21.7	+20.3	+19.8	+18.9
3.50	+101.3	+92.8	+70.4	+54.1	+43.2	+38.9	+33.4	+31.0	+27.8	+25.8	+24.7	+22.4	+21.5	+21.1
3.80	in gas	+119.5	+84.0	+64.5	+49.3	+44.5	+37.4	+34.5	+30.7	+28.2	+26.7	+25.0	+23.0	+23.3
4.00	in gas	+153.6	+101.0	+73.0	+53.6	+47.5	+39.3	+37.0	+32.8	+29.2	+28.6	+26.5	+24.0	+24.8

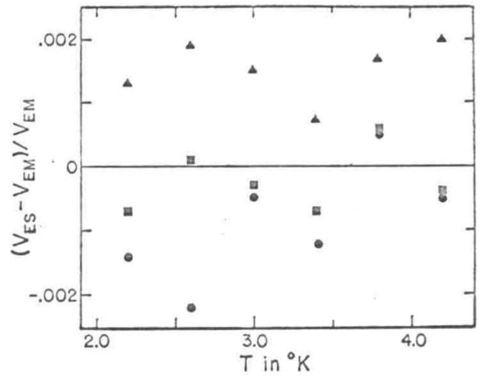

FIG. 3. Relative difference of the molar volumes measured by Edeskuty and Sherman[10] (V_{ES}) and by the present authors (V_{EM}). Black circles: 1 atm, black squares: 10 atm, black triangles: 25 atm.

second one gives the detailed results near the transition and a comparison with relevant work.

A. The Broad Range: 1.25 to 4.2°K

Our molar-volume results are presented at standard temperatures in Table I for all the isobars that we have studied. These values were obtained from curves drawn through the data by hand and the scatter was no more than 0.001 cm³/mole even though the data were always taken in two long passes, first cooling and then warming, and frequently were taken on more than one day. It is because of this high relative accuracy along a given isobar that we have chosen to present the data without smoothing them, which would otherwise have removed a significant figure. This significant figure, however, is in relative accuracy; absolute values are known only to ±0.1%. It is particularly interesting that along successively higher isobars the decrease of V with increasing T below T_λ becomes considerably greater, and the displacement of the volume minimum from T_λ becomes larger, while the subsequent increase of V with T becomes smaller. We have compared our results at 0.996, 10.01, and 24.93 atm with those of Edeskuty and Sherman[10] (corrected by −0.3%) at 1, 10 and 25 atm, respectively. The relative difference, $(V_{ES}-V_{EM})/V_{EM}$, is plotted in Fig. 3. Corrections for the slight pressure differences do not effect the points noticeably. There is a slight systematic difference between the two sets of data but it does not exceed the combined uncertainties so that the results are basically in agreement. Also there is agreement between our results at 1.3°K and those of Boghosian and Meyer[14] to within the combined uncertainties.

The α_P results are given in Table II at regular temperatures for the various isobars. The estimated error is 3% or 0.3×10^{-3}°K^{-1}, whichever is greater. Figure 4 shows a comparison of the various results at low temperatures. There is also reasonable agreement with the

[14] C. Boghosian and H. Meyer, Phys. Rev. **152**, 200 (1966); 164, 205(E) (1967).

TABLE III. Entropy of compression of liquid He^4 ($mJ/g°K$). For explanation for those isotherms that pass through T_λ, see text.

T(°K) \ P(atm)	1	2	5	10	15	20	24	25	28
1.30	0.60	1.51	5.67	16.1	30.0	47.4	64.7	69.7	...
1.40	1.27	2.88	9.56	25.4	46.0	71.3	96.0	102.9	...
1.50	1.92	4.33	13.9	36.3	65.8	103.4	140.8	151.5	...
1.60	2.71	6.15	19.7	51.1	92.3	144.5	197.2	212.0	...
1.70	3.62	8.25	27.8	70.0	127.6	204.0	284.0	308.0	396.0
1.80	4.81	10.9	35.4	93.8	174.1	284.0	409.0	449.0	0
1.90	6.33	14.5	47.6	126.0	241.1	418.0	0	1.39	−1.59
2.00	8.65	19.6	63.5	174.5	0	17.2	7.7	4.05	−8.75
2.10	12.4	29.3	102.4	0	−10.65	−32.4	−53.5	−59.02	−76.3
2.20	−7.77	−15.9	−39.0	−74.0	−107.25	−140.3	−166.9	−173.53	−193
2.30	−17.3	−33.4	−73.6	−126.7	−171	−210	−240	−248	−270
2.40	−20.9	−41.6	−94.0	−160.1	−212	−258	−293	−301	−325
2.50	−24.2	−48.8	−110.4	−187	−247	−298	−335	−334	−370
2.70	−30.1	−61.2	−136.6	−229	−300	−359	−400	−410	−438
3.00	−34.4	−74.5	−170.1	−284	−370	−438	−486	−497	−530
3.20	−37.4	−85.2	−196	−325	−420	−495	−547	−559	−594
3.50	−38.3	−100.5	−236	−388	−497	−583	−641	−655	−693
3.80	−32.4	−112.3	−278	−456	−581	−678	−742	−757	−799
4.00	−22.8	−126.8	−325	−522	−656	−758	−827	−842	−887

results of Grilly and Mills[5] although for the 1.3 and 1.4°K points they give values somewhat below our curves. On the other hand, while there is better than order-of-magnitude agreement with Mills and Sydoriak[15] there is a basic difference in that the slope of their isotherm would seem to decrease monotonically with pressure while our isotherms show an initial decrease followed by an increase at high pressures. The only comment that we would make on this is that our form is consistent with results along isotherms that pass through the λ line and hence must have a negative singularity. Finally, while we do not give their points, our results extrapolate quite well to the vapor-pressure results of Kerr and Taylor[4] and of Atkins and Edwards.[1]

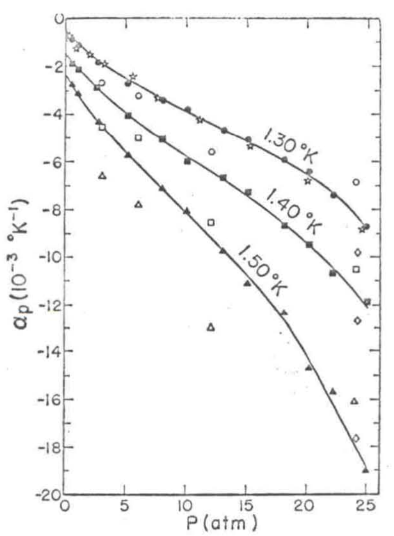

FIG. 4. Thermal expansion coefficient of He^4 along the 1.30, 1.40, and 1.50°K isotherms. The closed symbols are the present results, the corresponding open symbols are the results of Mills and Sydoriak (Ref. 15). The diamonds are the results of Grilly and Mills (Ref. 5), given at 24 atm at these same temperatures. The stars are the results of Boghosian and Meyer (Ref. 14) at 1.30°K.

We have calculated the entropy of compression from our data by graphically determining areas for

$$S(T,P)-S(T,P_0)=-\int_{P_0}^{P}\left(\frac{\partial V}{\partial T}\right)_P dP. \qquad (3)$$

These values are given in Table III, where it should be noted that P_0 is the saturated vapor pressure except for those regions that can not be reached along isotherms without crossing the λ line. In this last case P_0 is the lowest pressure above the transition for which data are given. The uncertainties in the integration probably

TABLE IV. The change of compressibility with temperature at standard pressures (10^{-4} atm^{-1}). The values given are $k_T-k_{1.3°K}$ for $T<T_\lambda$ (ordinary numerals), and $k_T-k_{2.2°K}$ for $T>T_\lambda$ (italic numerals). Values in parentheses are considered uncertain.

T(°K) \ P(atm)	1	5	10	13	15	20	25
1.30	0	0	0	0	0	0	0
1.40	0.49	0.36	0.28	0.28	0.31	0.39	0.68
1.50	1.12	0.85	0.68	0.69	0.79	0.97	1.70
1.60	1.98	1.53	1.25	1.31	1.47	1.88	3.43
1.70	3.14	2.46	2.05	2.21	2.48	3.46	6.47
1.80	4.70	3.70	3.26	3.55	4.03	6.34	12.84
1.90	6.87	5.33	5.25	5.96	6.90	(12.5)	*1.82*
2.00	10.05	7.65	(9.1)	11.22	*large*	*0.99*	*0.45*
2.10	(14.8)	(12.7)	*(0.95)*	*0.45*	*0.34*	*0.22*	*0.07*
2.20	*0*	*0*	*0*	*0*	*0*	*0*	*0*
2.30	*1.48*	*0.52*	*0.17*	*0.06*	*0.02*	*0.00*	*−0.03*
2.40	*4.11*	*1.62*	*0.70*	*0.40*	*0.26*	*0.14*	*0.01*
2.50	*7.52*	*3.18*	*1.45*	*0.92*	*0.65*	*0.40*	*0.08*
2.70	*16.02*	*7.32*	*3.46*	*2.34*	*1.77*	*1.14*	*0.48*
3.00	*33.95*	*15.74*	*7.50*	*5.25*	*4.04*	*2.58*	*1.41*
3.20	*50.28*	*22.75*	*10.80*	*7.61*	*5.91*	*3.76*	*2.22*
3.50	...	*35.70*	*16.69*	*11.75*	*9.23*	*5.90*	*3.72*
3.80	...	*52.75*	*23.70*	*16.55*	*13.17*	*8.49*	*5.47*
4.00	...	*67.54*	*29.25*	*20.24*	*16.21*	*10.45*	*6.75*

[15] R. L. Mills and S. G. Sydoriak, Ann. Phys. (N. Y.) 34, 276 (1965).

lead to an error of about 3%. In Fig. 5 we show the relative difference between our calculated results and those determined by Van den Meijdenberg *et al.*[16] from fountain-effect work. The agreement is within the combined uncertainties except at 2.0°K, where their results are considerably larger than ours. This may be due to experimental difficulties they encountered near the λ transition. Our results agree well with those of Boghosian and Meyer[14] at 1.3°K, their values being between 1 and 3% above ours. Finally, we find that the entropy results of Wiebes and Kramers[17] give values for the entropy of compression that are 10 to 25% above our results, giving a disagreement that is greater than the combined uncertainties.

We have also calculated changes in the isothermal compressibility along various isobars from

$$\Delta k_T = -\int_{T_0}^{T}\left(\frac{\partial \alpha_P}{\partial P}\right)_T dT, \tag{4}$$

using graphical integration. Our results are given in Table IV, where $T_0 = 1.3°\mathrm{K}$ for $T < T_\lambda$ and $T_0 = 2.2°\mathrm{K}$ for $T > T_\lambda$. The chief value of such data is that the method used in obtaining them is sensitive to small changes along the isobars that otherwise would be calculated as the difference between large numbers. The only systematic direct calculations of k_T throughout this region are those of Grilly.[18] We have obtained k_T at 2.2°K directly from our data and the agreement is within 3% except at 1 atm, where our values are about 5% smaller. This is reasonable agreement, since the spacing of the isobars along which we have taken data is not particularly suited for making such calculations. Grilly's results show some internal inconsistency along the isobars. Our data show the systematic variation of k_T along these isobars.

Finally it should be mentioned that the velocity of sound calculated from the compressibility data at 1.3°K (tabulated in Table V) under the assumption that the isothermal compressibility can be substituted for the isentropic compressibility, is in excellent agreement with the values observed by Atkins and Stasior.[19]

TABLE V. The compressibility k_T at standard pressures (10^{-3} atm^{-1}).

T (°K) \ P (atm)	1	3	5	10	15	20	25
1.30	11.1	10.2	9.0	7.24	5.93	5.18	4.58
2.20	12.3	10.0	7.37	6.63	6.19	5.27	4.38

[16] C. J. Van den Meijdenberg, K. W. Taconis, and R. De Bruyn Ouboter, Physica 27, 197 (1961).

[17] J. Wiebes and H. C. Kramers, Phys. Letters 4, 298 (1963); in *Proceedings of the Ninth International Conference on Low-Temperature Physics, Columbus, Ohio, 1964*, edited by J. G. Daunt, D. O. Edwards, F. J. Milford, and M. Yaqub (Plenum Press, Inc., New York, 1965), p. 258; (private communication, 1966).

[18] E. R. Grilly, Phys. Rev. 149, 97 (1966).

[19] K. R. Atkins and R. A. Stasior, Can. J. Phys. 31, 1156 (1953).

TABLE VI. P_λ, T_λ, and V_λ for liquid He^4.

P (atm)	T (°K)	V cm³/mole
		Run I
0.493±0.005	2.1685	27.20
2.70±0.05	2.1455	26.48
13.00±0.05	2.0215	24.24
		Run II
0.0497	2.17312	27.3730 (lower triple point)
0.0524	2.17309	27.3725
0.0548	2.17308	27.3710
0.0792	2.17288	27.3618
0.0924	2.17277	27.3557
0.1050	2.17263	27.3516
0.1398	2.17233	27.3373
0.1588	2.17214	27.3294
8.00±0.05	2.0865	25.12
20.10±0.05	1.9225	23.22
27.10±0.05	1.8085	22.45
		Run III
0.494	2.1675	27.22
0.996	2.1635	27.03
5.06±0.01	2.1205	25.81
10.01±0.01	2.0615	24.74
15.01±0.01	1.9955	23.90
17.97±0.01	1.9535	23.47
22.08±0.01	1.8905	22.96
24.93±0.01	1.8455	22.65
28.00±0.01	1.7935	22.32

B. The Temperature Range Close to the Transition

As we have noted, the λ transition is characterized by a discontinuity in the slope of the molar volume-versus-temperature curve (Fig. 2). We have thus determined values of T_λ and V_λ as a function of pressure P_λ and we give these values in Table VI. The carbon thermometers were recalibrated for each of the three runs which were separated by intervals of several months. Since the calibration accuracy was about ±1 mdeg, the different runs are consistent with one another only to this amount. The low-pressure region was investigated with particular care. A number of passes below 0.16 atm were made within a period of 20 h in order to avoid the effects of thermometer drift. The best straight-line fit to these data yields a limiting slope $(dP/dT)_\lambda = -114 \pm 1$ atm/°K and the slight curvature of the points indicates that the true limit may have a somewhat greater value.

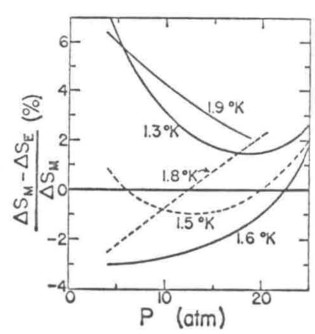

FIG. 5. The relative difference between the entropy of compression results of Van den Mejdenberg *et al.* (Ref. 16) (ΔS_M) and those of this paper (ΔS_E).

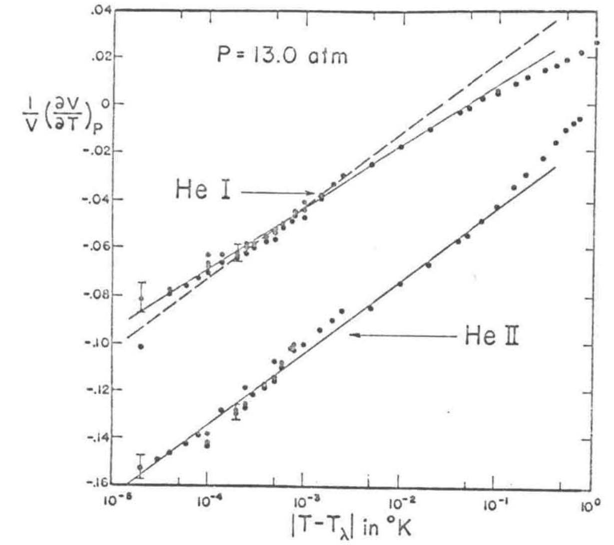

FIG. 6. Logarithmic plot of α_P (in deg^{-1}) at 13 atm close to the transition. The numerical data for the points at all pressures are available in tabulated form in the Ph.D. thesis of Elwell (Ref. 11). The dashed line is drawn parallel to the lower solid line.

We have found that the relation

$$P_\lambda(\mathrm{atm}) = 0.0497 - 64.6X^{1.342} + 120X, \qquad (5)$$

where $X = T_\lambda(\mathrm{SVP}) - T_\lambda(P)$ and $T_\lambda(\mathrm{SVP}) = 2.173\ 12$°K, is an excellent fit to all our data. This equation indicates that the limiting slope is -120 atm/°K. Since the slope according to Eq. (5) varies strongly very close to the lower triple point, this limiting slope is probably too high. More data within 0.5 m°K of the triple point will clarify this question. The temperature of the lower λ point is about 1 mdeg K higher than that listed in the He^4 *1958* vapor-pressure tables, but this difference is still within the limits of the calibration uncertainty and does not affect noticeably the slopes of the thermodynamic quantities along the λ line (Table VII). Kierstead[20] has recently completed an article on the λ line in which he presents new determinations of his own of the shape of the transition line and in which he reviews the work of other authors including our data presented elsewhere[8] and here. Therefore we confine our discussion to a few comments on the current state of knowledge. In general there is good agreement (to within 1 mdeg) on the location of the transition at all pressures, so that except in the low-pressure limit where $(dP/dT)_\lambda$ is changing rapidly there is basic agreement on the pressure derivative of the transition. Kierstead has taken the most extensive data of any of the investigators below 3 atm down to the upper limit of our high-resolution data, and we feel that in this range his data are most to be relied on. However, our high-resolution data at very low pressures indicate that the limiting slope is somewhat greater in magnitude than the value he obtains. Because of this, we prefer our simpler form, Eq. (5) excluding perhaps the portion within 0.5 m°K of the lower triple point. We have found no such simple relation that gives a satisfactory fit to the molar volume curve, but we have found that the straight-line value for the slope at low pressures is 45.5 ± 0.5 cm^3/mole °K, and this is in excellent agreement with the value of 47.6 cm^3/mole calculated by Barmatz.[21]

TABLE VII. Temperature derivatives of the λ line.

T (°K)	$(dP/dT)_\lambda$ atm/°K	$(dV/dT)_\lambda$ cm^3/mole deg
1.800	−58.5	6.10
1.850	−61.5	6.58
1.900	−65.2	7.54
1.950	−67.4	9.1
2.000	−72.5	11.1
2.050	−77.0	13.8
2.100	−85.0	18.9
2.150	−94.6	29.7
2.160	−100[a]	35.6
2.170	−108[a]	42.5
2.172	−111[a]	44.0
2.173	−114[b]	45.5[b]
	−120[a]	

[a] From the fit to Eq. (5).
[b] From linear fit to the points of Run II in Table VI.

A representative plot of the thermal expansion coefficient data is shown in Fig. 6. Here the 13-atm data are plotted as a function of $|T - T_\lambda|$ on a semilogarithmic

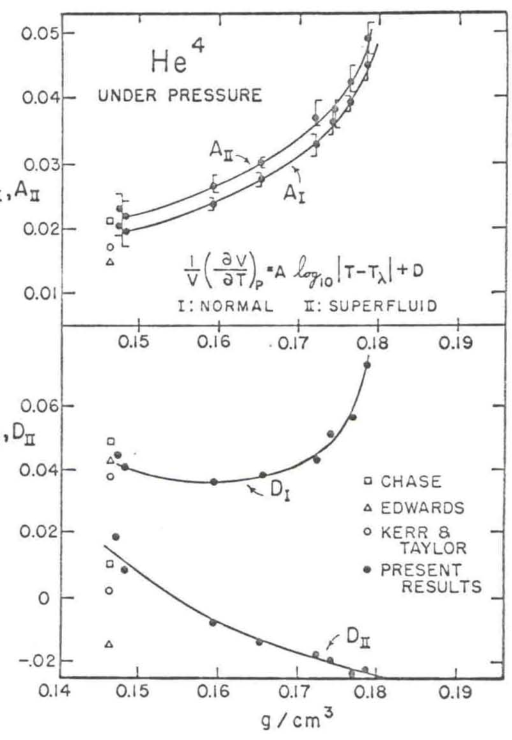

FIG. 7. The parameters A and D (in deg^{-1}) of the logarithmic plot for α_P as a function of density along the transition and comparison with results of other authors at saturated vapor pressure.

[20] H. A. Kierstead, Phys. Rev. (to be published).

[21] M. Barmatz, thesis, University of California, 1966 (unpublished).

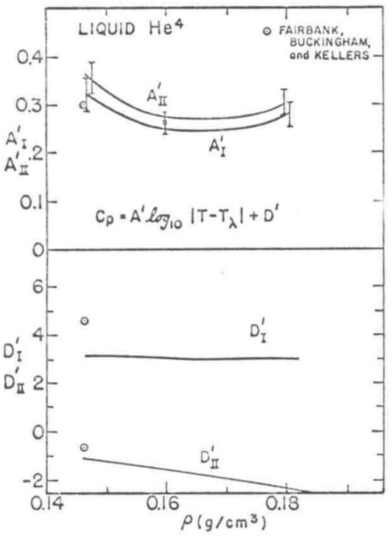

FIG. 8. The A' and D' parameters (in deg^{-1}) for the logarithmic expression of the specific heat.

scale. It should be noted that these results extend an order of magnitude closer to the transition than previous data at saturated vapor pressure. This is due in part to the improved density resolution of the apparatus. However, as has been noted, pressure equilibrium times are more favorable at pressures above 1 atm so that our low-pressure data are not of as high quality as that shown in Fig. 6 and are of comparable resolution to the vapor-pressure work.[2–4]

We have analyzed our data in terms of a logarithmic singularity in temperature displacement from T_λ:

$$\left.\begin{aligned}\alpha_P &= A_{\mathrm{I}} \log_{10}|T-T_\lambda| + D_{\mathrm{I}} \quad T>T_\lambda\\ \alpha_P &= A_{\mathrm{II}} \log_{10}|T-T_\lambda| + D_{\mathrm{II}} \quad T<T_\lambda\end{aligned}\right\}$$
$$\text{for } 10^{-2} > |T-T_\lambda| > 2\cdot 10^{-5}\,°\mathrm{K}. \quad (6)$$

It is apparent from Fig. 6 that $A_{\mathrm{I}} \neq A_{\mathrm{II}}$. The various coefficients for these equations for the data at each pressure are plotted in Fig. 7 as a function of the density along the λ line. In all cases the fit to the data is good until $|T-T_\lambda| = 10^{-2}\,°$K. As can be seen, the slope parameters increase sharply at higher densities. On a plot of A versus pressure this increase is more linear. The low-pressure results are in reasonable agreement with the vapor-pressure results of Chase *et al.*[3] and Kerr and Taylor[4] with our uncertainty corresponding roughly to the difference between their values.

The specific heat C_P may be calculated from our data in a region close to the transition by means of the relation

$$\frac{C_P}{T} = \left(\frac{\partial S}{\partial T}\right)_t + \left(\frac{dP}{dT}\right)_\lambda \left(\frac{\partial V}{\partial T}\right)_P, \quad (7)$$

where $t = T - T_\lambda$ at constant pressure. We assume that over the range $10^{-2} > |T-T_\lambda|$ the slope $(\partial S/\partial T)_t = (dS/dT)_\lambda$, and by using the entropy data of Lounasmaa and Kojo[22] along the λ line and the present results for $(dP/dT)_\lambda$, V_λ, and α_P, we have obtained the results shown in Fig. 8. The validity of this estimate of C_P extends of course only over the range of the α_P data. We note that the change in slope is relatively much less than that for the α_P coefficients. This is because the increase of the α_P coefficients with pressure is compensated for by the corresponding decrease of $(dP/dT)_\lambda$ and we note that the increase in the C_P parameters at low pressures is due to the strong increase of the slope of the λ line. Our calculations give results that extrapolate reasonably well to the experimental results of Kellers[6] (Fig. 8).

It is now of interest to check the consistency of our data with other recent results at elevated pressures. Our values of $V_\lambda(T)$ and of the coefficients of α_P given by the lines in Fig. 7 in effect completely define the volume surface near the λ line. Thus we may calculate (by numerical interpolation on a computer) V at any point between 10^{-2} and $10^{-5}\,°$K separation the λ line and in particular may determine the shapes of the isochores and isotherms in this interval. Thus, while there are

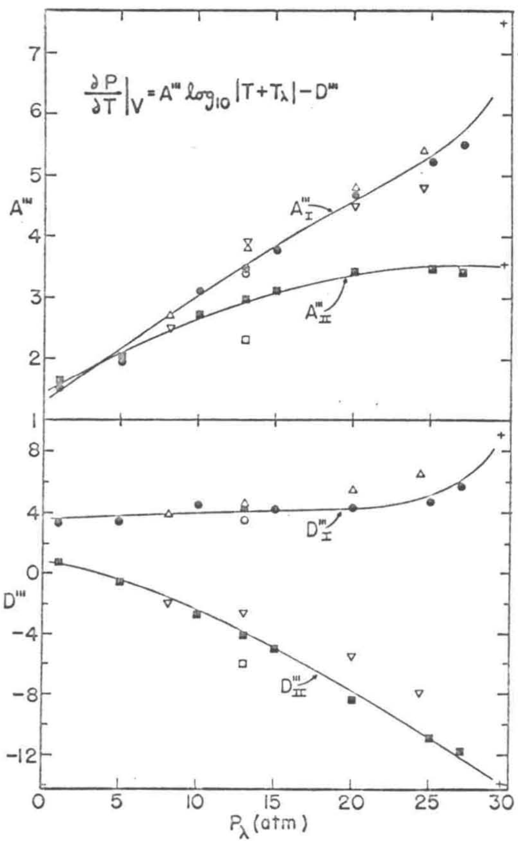

FIG. 9. Parameters A''' and D''' (in atm deg^{-1}) for a logarithmic fit to the slope $(\partial P/\partial T)_V$. Black circles and squares: present results. Open triangles: Lounasmaa and Kaunisto (Ref. 23); open circles and squares: Lounasmaa (Ref. 25), + Kierstead (Ref. 24).

[22] O. V. Lounasmaa and E. Kojo, Ann. Acad. Sci. Fennicae Ser. AVI, No. 36 (1959).

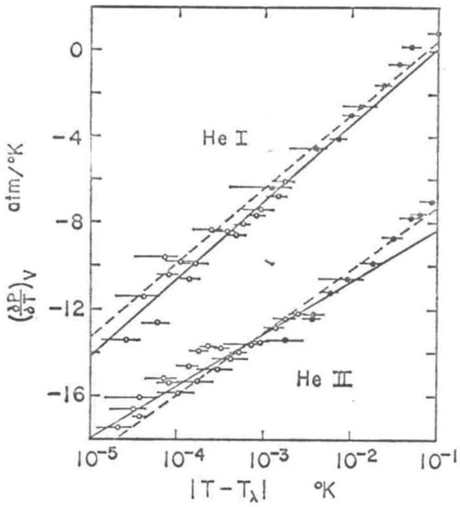

FIG. 10. Comparison of the calculated $(\partial P/\partial T)_V$ at 13 atm with that measured by Lounasmaa. Solid lines: Logarithmic fit by Lounasmaa. Open circles: experimental points of Lounasmaa (Ref. 25). Closed circles: experimental points of Lounasmaa and Kaunisto (Ref. 23). Dashed lines: $(\partial P/\partial T)_V$ as calculated from our data by interpolation.

no other results on the expansion coefficient, we are able to compare our work with data on the pressure coefficient and the isothermal compressibility. It should be noted that such calculations are limited only by the accuracy of our results and the uncertainty of interpolation, and do not depend in any way on thermodynamic approximations. Turning first to the isochores, we note that although the pressure coefficient $(\partial P/\partial T)_V$ must remain finite, our calculations of the isochores yield results that can be represented by a logarithmic expression over the interval of $|T-T_\lambda|$ from 10^{-2} to 10^{-5}°K. Thus it is convenient to express the results of our calculations in terms of the same parameters as have been used for α_P and C_P. These are shown in Fig. 9, along with the previous experimental results of various authors. The early results of Lounasmaa and Kaunisto[23] had a limiting resolution of only 10^{-3}°K; thus, as has been pointed out by Lounasmaa, they did not succeed in obtaining the limiting form of the singularity, and therefore the disagreement with our values, which is pronounced in the He II region, is not significant. We consider that the agreement with Kierstead[24] is generally gratifying but that his results indicate that A_I''' is increasing more rapidly at high pressures than our calculations indicate. His data are apparently very good and extend down to a resolution of 2×10^{-6}°K. The agreement with Lounasmaa's parameters[25] at 13.0 atm is not so good, and in order to assess the difference we have plotted our calculated values directly on Lounasmaa's data in Fig. 10. While our results are not the best fit to his data, they do fall within most of the error bars that he gives, and therefore we conclude that the agreement is reasonable. There are no experimental results below 8 atm so that our calculated results must stand in this area.

Similar calculations along various isotherms yield values for the compressibility, and these values are given in Fig. 11 in terms of the parameters of a logarithmic singularity. The range over which our calculations are valid is from roughly 10^{-3} to 1 atm on each side of the transition. It will be noted that there is considerable scatter in the calculated points. This is presumably due to difficulties in the calculation which arise because the singularity appears as a small change in a large quantity. The same difficulties arise in the experimental work. Kierstead[24] has obtained very good resolution of the transition in his work near the melting curve. We have plotted the equations he presents for k_T and find that the results thus obtained are increasing more rapidly than a logarithmic singularity. Grilly[18] has obtained results of moderate resolution at a number of temperatures and while he does not present these directly in the form we are using, we have been able to estimate the values of the parameters that fit his data. These values are also shown in Fig. 11, and considering both the scatter of the points and the fact that the

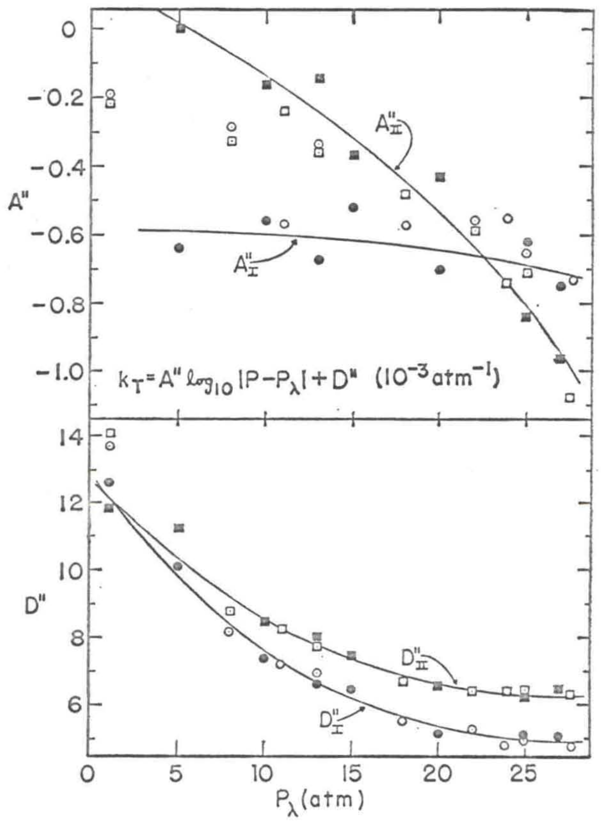

FIG. 11. The parameters A'' and D'' (in atm^{-1}) for the logarithmic fit to k_T. Circles are for $T>T_\lambda$; squares are for $T<T_\lambda$. Black circles and squares: present direct calculations from experiment; circles and squares with dot: cylindrical approximation calculations; open circles and squares: Grilly (Ref. 18).

[23] O. V. Lounasmaa and L. Kaunisto, Ann. Acad. Sci. Fennicae Ser. AVI, No. 59 (1960).

[24] H. A. Kierstead, Phys. Rev. 153, 258 (1967).

[25] O. V. Lounasmaa, Phys. Rev. 130, 847 (1963).

comparison had to be rather indirect, we find that the agreement is excellent.

It is also possible to calculate the isothermal compressibility from our expansion-coefficient data by using the thermodynamic relation

$$\left(\frac{\partial V}{\partial T}\right)_P=\left(\frac{\partial V}{\partial T}\right)_t-\left(\frac{\partial P}{\partial T}\right)_t Vk_T. \qquad (8)$$

We have calculated k_T from this expression for the region $10^{-3}<|P-P_\lambda|<1$ atm by using the cylindrical approximation[26] and these points are also shown in Fig. 11. It is apparent that while the new intercept parameters are in good agreement with the other values, the slope parameters are not. In particular the cylindrical approximation indicates that the two logarithmic branches are close to being parallel. This is the consequence of the two branches of α_P being nearly parallel and the form of the approximation used. Since there is this disagreement we conclude that the conditions required for the cylindrical approximation to be valid have not been fulfilled. It should be noted that according to our first calculations, A_{II}'' is greater than zero at low pressures. This means only that the minimum in k_T along the isobars is closer to the transition than 10^{-3} atm. Thus the limiting form of the compressibility has not been reached and the cylindrical approximation can not be valid under these conditions.

Some of the anomalies of certain properties are shown in Fig. 12. The k_T minima along the isotherms and along the isobars and the minima of the isobaric molar volume are presented in a P-T diagram. The locus of $\alpha_P=0$ is also the locus of entropy maxima, in virtue of a Maxwell relation. It is interesting to note the gradual widening of the separation of the curves from the λ line as the pressure increases. The $\alpha_P=0$ curve becomes roughly parallel to the λ line above about 20 atm.

IV. CONCLUSION

We have presented and examined molar volume data for liquid He⁴ and have used them to calculate various other thermodynamic properties of the fluid. In particular we have made a detailed study of the isobaric coefficient of thermal expansion to within about 2.10^{-5}°K of the λ line. This coefficient can be represented for all pressures in terms of a logarithmic singularity which becomes steeper as the pressure is increased. This conclusion is reached at least for the interval $10^{-2}\geqslant|T-T_\lambda|\geqslant 2\times10^{-5}$. The derivative $(\partial P/\partial T)_V$ can also be expressed in terms of a logarithmic singularity over this range of $|T-T_\lambda|$, although it is clear that this relationship cannot hold at the λ line. The derivatives $(\partial P/\partial T)_V$ as well as k_T are in agreement with all available direct measurements. On the other hand, we have attempted to use the cylindrical approximation for calculating k_T and have found that it does not give satisfactory results over the range of temperature displacement down to 10^{-5}°K.

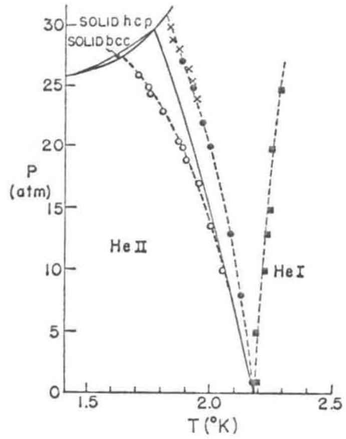

FIG. 12. The P-T phase diagram of He⁴ close to the λ line. Black circles: locus of $\alpha_P=0$ (present results); X: locus of $\alpha_P=0$ [Grilly and Mills (Ref. 5)]. Open circles: k_T minima along the isotherms [Grilly (Ref. 18)]. Black squares: k_T minima along the isobars (present results). Solid line: λ line

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[26] A. B. Pippard, *The Elements of Classical Thermodynamics* (Cambridge University Press, Cambridge, England, 1957), Chap. IX.