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Compressibility of Liquid He^4 as a Function of Pressure*

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The compressibility, $\beta=-(1/V)(\partial V/\partial P)_T$, of liquid He^4 was measured from 1 atm to the melting pressure and between 1.6 and 2.5°K. ΔV and ΔP were determined from deflections of the cell walls. The normal decrease of β with increasing P was observed except in an area below the λ line. For an isotherm crossing the λ line, β showed a minimum at $P<P_\lambda$ and a peak at P_λ. The minimum also occurred between the lowest T_λ (1.76°K) and 1.70°K. The variation of β with P near P_λ, relative to β at 2.20°K, followed an equation of the form $\beta_T-\beta_{2.2}=a-b\log|P-P_\lambda|$, where a and b for $P<P_\lambda$ are greater than a and b for $P>P_\lambda$. Between the T limits of the λ line, $(\partial\beta/\partial T)_P$ was definitely negative for P just above P_λ, but it approached zero for $P\gg P_\lambda$.

I. INTRODUCTION

IN general, the isothermal compressibility coefficient, $\beta\equiv-(1/V)(\partial V/\partial P)_T$, of a liquid decreases with decreasing temperature and with increasing pressure. The anomalous increase of β with increasing pressure in liquid He^4 near the λ transition was first indicated by the density measurements of Keesom and Keesom.[1] Their Fig. 3 seems to show $(\partial\rho/\partial P)_T$ at 30 atm rising above the values at 25 and 20 atm in a narrow temperature interval 1.80–1.85°K. However, the authors left the point without comment while they noted "as a remarkable fact that the He II parts of the curves seem to approach at decreasing temperatures to a production of the He I parts. It looks as if there is an intermediary region of increased compressibility, which abruptly ends at the λ curve." On the other hand, no pressure anomaly was shown by the adiabatic compressibility derived from sound-velocity data of Atkins and Stasior.[2] Direct measurements of β, i.e., through small ΔP and ΔV at constant temperature, were made by Grilly and Mills[3] over a short range of pressure and at several temperatures. The values of β peaked at P_λ, but the continuity of β was indefinite. However, it was clear that β had an anomalous variation with temperature near the λ transition for $P>P_\lambda$. Then, Lounasmaa[4] measured β with very high resolution in the immediate vicinity (within 10^{-3} to 10^{-2} atm) of one λ point (2.023°K and 13.04 atm). He obtained a linear variation of β with pressure on each side of P_λ and a discontinuity of 10% in β at P_λ.

All these measurements left unanswered some questions. What is the nature of the expected minimum in the β versus P curve? Does the abnormal variation of β with temperature near the λ transition revert to normalcy at (P,T) far above (P_λ,T_λ)? To answer them, β was measured directly as a function of pressure at several constant temperatures.

II. EXPERIMENTAL

A. Method

The present measurements of compressibility in liquid He^4 were done in a cell designed for general P-V-T work in liquid and solid He^4 and He^3. Essentially, each ΔP and ΔV was measured by the deflection of diaphragms. The cell, shown in Fig. 1, consisted of three diaphragms joined circumferentially and left separated by two gaps, each of which was connected to a capillary tube leading to room temperature. The upper gap acted as the sample chamber, whose volume V_U could be changed at will by the pressure of the liquid in the lower gap. The sample under study was confined to V_U by a valve near the cell. The upper chamber pressure P_U was determined from the deflection of the top diaphragm, while the lower chamber pressure P_L was measured at room temperature through the capillary. At any time, V_U could be determined from P_U and P_L through the formula

$$V_U=V_{U_0}+(S_U+S_L)P_U-S_LP_L\,,$$

where V_{U_0} is the volume of the upper chamber for no deflection of the diaphragms, S_U is the sensitivity of the upper diaphragm in terms of volume change per unit pressure difference, and S_L is the sensitivity of the middle diaphragm. Therefore, the compressibility of

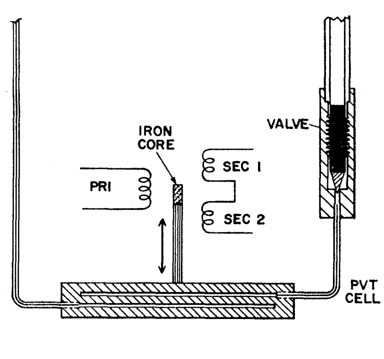

FIG. 1. The P-V-T cell.

* Work performed under the auspices of the U. S. Atomic Energy Commission.
[1] W. H. Keesom and A. P. Keesom, Physica 1, 128 (1934); Leiden Comm. Suppl. No. 7b (1933).
[2] K. R. Atkins and R. A. Stasior, Can. J. Phys. 31, 1156 (1953).
[3] E. R. Grilly and R. L. Mills, Ann. Phys. (N. Y.) 18, 250 (1962).
[4] O. V. Lounasmaa, Phys. Rev. 130, 847 (1963).

the sample in V_U is

$$\beta=-\frac{1}{V_U}\frac{dV_U}{dP_U}=\frac{S_L}{V_U}\left(\frac{dP_L}{dP_U}-\frac{S_U+S_L}{S_L}\right). \quad (1)$$

Generally, the values of ΔP are small enough to represent the differentials directly. With the cell characteristics $V_{U_0}=0.3380$ cm^3, $S_U=1.31\times10^{-3}$ cm^3 atm^{-1}, and $S_L=1.09\times10^{-3}$ cm^3 atm^{-1},

$$\beta\approx2.5\times10^{-3}(\Delta P_L/\Delta P_U-2.2)\ \mathrm{atm}^{-1}. \quad (2)$$

B. Apparatus

The P-V-T cell was made from Be-Cu (Berylco-25) disks, welded together by an electron beam, then heat-treated for favorable strength and elasticity. The cell was designed to measure a range of $\Delta V/V$ values from 5×10^{-5} for thermal expansion to 10^{-1} for melting, a much greater range than needed here for the liquid compressibility. At 4°K, the diaphragm displacement at the center was 3×10^{-4} cm atm^{-1} up to the maximum working pressure of 68 atm. The upper diaphragm deflection was measured with a Sanborn 959 DT 005 differential transformer, whose output was put through a Sanborn 311 amplifier and read on a Weston dc voltmeter. The resolution of 0.01 V corresponded to 10^{-3} atm. The sensitivity was frequently checked between compressibility measurements against a room-temperature gauge. The diaphragm behavior seemed to stay constant, but the over-all sensitivity varied slightly with bath height (an effect of lead resistance) and with axial position of the transformer core.

The volume of the upper (sample) chamber was calibrated against various pressures in the upper and lower chambers by metering withdrawn helium, gas at 296 and 76°K, liquid at 4°K. The molar volumes at 4°K were taken from Edeskuty and Sherman[5] after a -0.30% correction. The observed values of the volume sensitivity increased with temperature, 5% for 4 to 76°K and 14% for 4 to 296°K but were constant with pressure to 68 atm.

A rigid requirement in the ΔV measurements was the tightness of the valve sealing the sample in the cell. The valve tip was a 55° cone of Teflon; its seat was a 0.5-mm hole in the brass body. A leak test after each closing showed the valve to be tight in all cases.

The pressure standards were: (a) a Consolidated Electrodynamics Corp. 6-201 gas piston gauge to 34 atm; and (b) an Ashcroft 1313A oil piston gauge to 68 atm. The first was calibrated against other standard gauges and the CO_2 sublimation pressure at the ice point; accuracy was better than 0.01%. Both piston gauges had calibrated weights so that pressure changes of 0.3 atm were known to 0.01%; this was useful in checking the consistency of the P-V-T cell diaphragm sensitivity. Routine pressure measurements were made with Heise and Seegers Bourdon-type and Consolidated diaphragm-type gauges.

Temperatures of the liquid He[4] bath were determined from vapor pressures on the "1958 Scale".[6] The bath pressure was regulated to less than 0.5 mdeg equivalent.

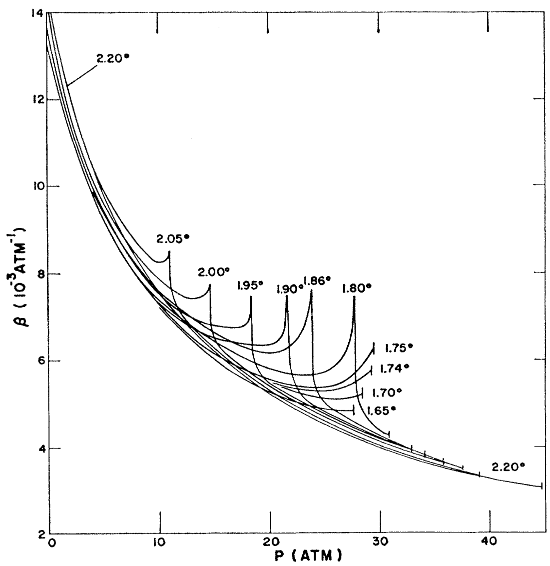

FIG. 2. Isothermal compressibility coefficient versus pressure for liquid He[4] at several temperatures. The measurements show no deviation from the curves on this scale.

III. RESULTS

The isothermal compressibility coefficient β was measured directly over a wide pressure range, usually from about 1 atm to the melting pressure, for temperatures between 1.60 and 2.50°K. Typical results are shown in Fig. 2. The 2.20°K curve illustrates the monotonic decrease of β with increasing pressure for

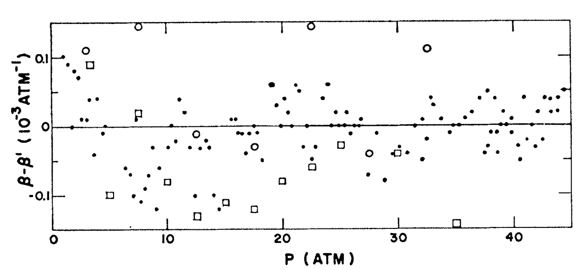

FIG. 3. Deviations of liquid He[4] compressibility at 2.200°K from $0.30\times10^{-3}+(72.0\times6.66P)^{-1}$. ● present measurements; ○ derived from density data of Keesom and Keesom (Ref. 1); □ derived from density of Edeskuty and Sherman (Ref. 5).

[5] F. J. Edeskuty and R. H. Sherman, in *Low Temperature Physics and Chemistry*, edited by J. R. Dillinger (University of Wisconsin Press, Madison, Wisconsin, 1958), p. 102.

[6] F. G. Brickwedde, H. van Dijk, M. Durieux, J. R. Clement, and J. K. Logan, J. Res. Natl. Bur. Std. (U. S.) **64A**, No. 1 (1960).

$T > 2.17$°K. It was fitted with an empirical formula,

$$\beta'(2.200°\mathrm{K}) = 0.30\times10^{-3} + (72.0+6.66P)^{-1}\ \mathrm{atm}^{-1}, \quad (3)$$

to about 1.5%; deviations of the measurements are given in Fig. 3. Also given there is a comparison with β derived from density data of Keesom and Keesom[1] and of Edeskuty and Sherman.[5] Agreement between the three sets of results seems reasonable and the comparison is valid since no λ anomalies exist at this temperature.

A view of Fig. 2 again shows that a compressibility curve between 1.80 and 2.05°K parallels the 2.20°K curve at low pressures, but with increasing pressure it rises above the 2.20°K curve, reaching a peak at P_λ. At $P > P_\lambda$, the values of β drop continuously and approach the 2.20°K value. The minima in the β-versus-P curves increase in depth and breadth as P_λ increases, but they seem flattest in the middle of the P_λ range. Although the peaks become more distinct with increased P_λ, the sharpness of all the peak tips required a

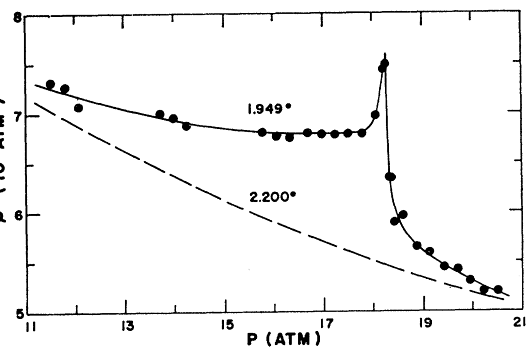

FIG. 4. Compressibility of liquid He⁴ at 1.95 and 2.200°K.

higher than normal resolution; therefore the pressure increment of a measurement was reduced from the usual 0.27 to 0.05 atm in the vicinity of the peak. Portions of the 1.95 and 1.80°K curves are shown in Figs. 4 and 5, respectively, along with the 2.20°K values for comparison. The peak at P_λ fades away with increasing temperature until it almost disappears at 2.05°K, although the compressibility excess over the 2.20°K value is still obvious.

In the region between 1.60 and 1.75°K, no λ transition occurs. However, the results in Fig. 6 show that a minimum in the β-versus-P curve persists down to 1.70°K; at 1.75°K, the rate of rise beyond the minimum is similar to that at 1.80°K. Below 1.70°K, (the 1.65°K curve is omitted for clarity) the minimum disappears, but a compressibility excess over the 2.20°K curve remains, amounting to 15% at 1.60°K near the melting pressure.

The temperature variation of β at constant pressure changed according to the proximity of (T,P) to (T_λ,P_λ). For all temperatures, β at $P \ll P_\lambda$ increased with in-

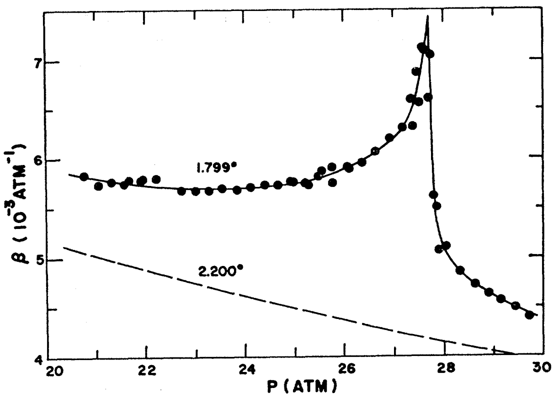

FIG. 5. Compressibility of liquid He⁴ at 1.80 and 2.200°K.

creasing temperature. Near the λ transition, the variation of β with temperature became inverted. The reversion of $(\partial\beta/\partial T)_P$ to the normal plus sign at $P \gg P_\lambda$ was not indicated—the compressibilities for different temperatures merged to a common value within ~2%, the experimental error, at the highest pressures.

The accuracy of the measurements is summarized here. From a straight sum of possible individual errors in cell calibration plus those from readings of ΔV and ΔP, the maximum error in an individual β should be 2.5 to 5.0% for high to low values of β, respectively; from the root mean square of individual errors, a probable error in β is 1.5 to 3.0% for high to low values. Consideration of $\Delta P_L/\Delta P_U$ alone in Eq. (2) leads to a precision error of 1.0 to 1.7% for high to low values of β. Near the λ transition, the decrease in ΔP for greater resolution probably lowered the accuracy, but here we are mainly interested in the reproducibility of results over a short range of pressure and time. Error in these results is estimated at 2%.

IV. DISCUSSION

The present compressibility measurements provide a view of normal and abnormal behavior in liquid He⁴

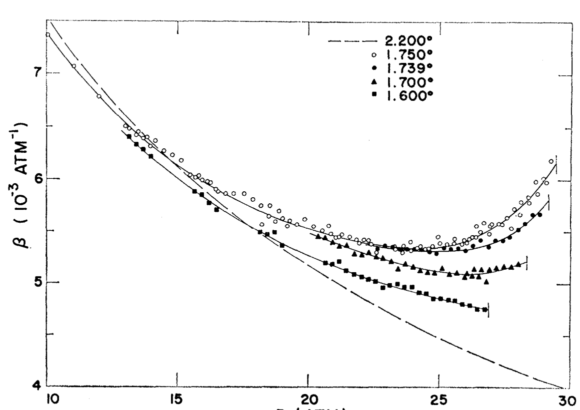

FIG. 6. Compressibility of liquid He⁴ at several temperatures below 1.76 and at 2.200°K.

TABLE I. Compressibility minima in liquid He[4].

T (°K)	$\beta_{\min}$ (10^{-3} atm^{-1})	$P(\beta_{\min})$ (atm)
2.050	8.20	10.3±0.3
2.000	7.42	13.7±0.5
1.949	6.75	17.0±0.7
1.899	6.35	19.0±1.0
1.880	6.27	20.0±1.0
1.865	6.15	20.5±0.5
1.799	5.65	23.0±0.5
1.750	5.35	24.5±0.5
1.739	5.27	25.0±0.5
1.700	5.07	26.0±0.5

through pressure variations. Generally, $(\partial\beta/\partial P)_T$ is negative because of the increase in intermolecular repulsive force. In this sense, the present results show liquid He[4] is normal for all pressures at $T>2.17$°K. In particular, the liquid at 2.200°K seems to have a high degree of normalcy, as here β versus P closely follows Tait's relation

$$V\beta=J(L+P)^{-1}, \tag{4}$$

where V is the corrected molar volume of Edeskuty and Sherman[5] and $J=3.390$ and $L=8.47$ are empirical constants. This relation fits a wide variety of liquids and was given a fundamental basis for liquids in general by Ginell.[7]

At $T<2.17$°K, the sign of $(\partial\beta/\partial P)_T$ changes as $P\rightarrow P_\lambda$ from below. The minimum shown in β versus P is lacking in the curves of specific heat and thermal expansion versus temperature, which simply continue the trends set by the low-temperature portions of their curves, albeit at accelerated rates. The minima in the β-versus-P curves follow a regular pattern for both

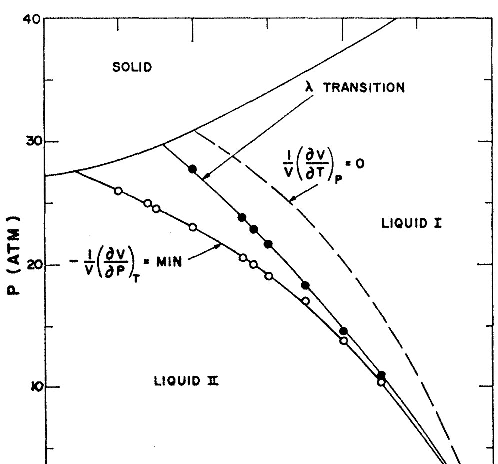

FIG. 7. Phase diagram of He[4] showing the melting curve, the λ line, the locus of zero expansion coefficient, and the locus of minimum in compressibility.

[7] R. Ginell, J. Chem. Phys. 34, 1249 (1961).

$\beta_{\min}$ and $P(\beta_{\min})$. The values given in Table I show that $\beta_{\min}$ decreases linearly with increasing $P(\beta_{\min})$. In the phase diagram of Fig. 7 are shown the locus of $\beta_{\min}$ and the locus of zero thermal expansion, determined by Grilly and Mills.[3] These two loci indicate a sizable area of anomalous behavior in the P-V-T relations. Goldstein[8] gave a possible explanation for the value of $(\partial\beta/\partial P)_T>0$ as P increases toward P_λ: The exchange-energy density, decreasing rapidly as the number of normal atoms increases with pressure, provides a net decrease in energy density, which is measured by $1/\beta$. The same mechanism could account for the minima shown at $T<1.76$°K, where a λ transition is cut short by the formation of solid.

Near P_λ, the variation of β with P is best expressed by a logarithmic fit

$$\begin{aligned}10^3(\beta_T-\beta_{2.2})&=a_{-}-b_{-}\log_{10}|P-P_\lambda| \quad \text{for} \quad P<P_\lambda\\ &=a_{+}-b_{+}\log_{10}|P-P_\lambda| \quad \text{for} \quad P>P_\lambda.\end{aligned} \tag{5}$$

Here, β_T and $\beta_{2.2}$ are the measured compressibilities

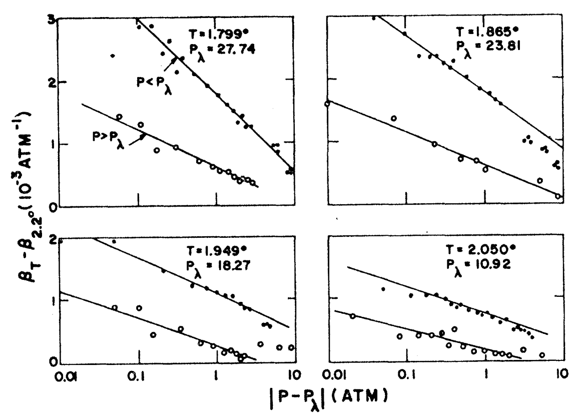

FIG. 8. $\beta_T-\beta_{2.2}$ versus $\log|P-P_\lambda|$ for liquid He[4] at several temperatures. The upper curve is for $P<P_\lambda$ and the lower curve is for $P>P_\lambda$ at each T.

at (T,P) and at (2.200°K, P), respectively, and P is in atmospheres. The constants a, b, and P_λ were determined from plots of $\beta_T-\beta_{2.2}$ versus $\log|P-P_\lambda|$. Some graphical examples are given in Fig. 8, while the constants are given in Table II. We see that the linear plots become more definite as the temperature is decreased, or as the λ transition of β is accented. At the lowest observed T_λ values, 1.86 and 1.80°K, Eq. (5) appears to hold for $5\times10^{-2}<|P-P_\lambda|<10$ atm. This resembles the linear functions of $\log|T-T_\lambda|$ fitted to the thermal expansion, $\alpha_P=(1/V)(\partial V/\partial T)_P$,[9–12] and

[8] L. Goldstein, Phys. Rev. 140, A1547 (1965).
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[11] C. E. Chase, E. Maxwell, and W. E. Millett, Physica 27, 1129 (1961).
[12] E. C. Kerr and R. D. Taylor, Ann. Phys. (N.Y.) 26, 292 (1964).

the constant-pressure specific heat, C_p,[13] derived from measurements on the saturated liquid. If the relations hold at higher pressures, then for the limits $5\times10^{-2} < |P-P_\lambda| < 10$ atm or $5\times10^{-4} < |T-T_\lambda| < 10^{-1}$ °K, β tends to vary linearly with α_P and C_p, which is consistent with the Buckingham-Fairbank[14] derivations. Unfortunately, the experimental ranges of pressure do not overlap. Therefore direct comparisons between the data cannot be made. However, at the λ point of 2.023°K and 13.04 atm Lounasmaa[4] found that β, measured with 10^{-3} atm resolution, varied linearly with $|P-P_\lambda|$ for $10^{-3} < |P-P_\lambda| < 10^{-2}$ atm. At $|P-P_\lambda| = 10^{-3}$ atm, his results coincide with the values from Eqs. (3) and (5), namely, $\beta_- = 8.8$ and $\beta_+ = 7.9$ in 10^{-3} atm^{-1} units. At $|P-P_\lambda| = 10^{-2}$ atm, the agreement is poorer but still acceptable. It is notable that the highest values of β observed near a λ point are only $\sim10^{-2}$ atm^{-1}.

TABLE II. Constants in Eq. (5).

T (°K)	P_λ (atm)	a_- (atm^{-1})	b_- (atm^{-1})	a_+ (atm^{-1})	b_+ (atm^{-1})
2.050	10.92	0.75	0.42	0.16	0.34
2.000	14.62	0.93	0.48	0.20	0.41
1.949	18.27	1.08	0.58	0.25	0.46
1.899	21.65	1.38	0.74	0.55	0.53
1.880	22.86	1.52	0.77	0.55	0.44
1.865	23.81	1.78	0.92	0.58	0.53
1.799	27.74	1.79	1.23	0.62	0.60

Therefore, the validity of an expression like Eq. (5) cannot continue indefinitely as the λ point is approached. Goldstein[15] pointed out that the root-mean-square temperature fluctuations of the system, the upper limit of meaningful $|T-T_\lambda|$ values, is $\sim10^{-12}$°K.

The sound velocities of Atkins and Stasior[2] were combined with the densities of Keesom and Keesom[1] to derive the adiabatic compressibilities, $\beta_S = (\rho u^2)^{-1}$. Although the velocities should have high resolution, no anomalous variation of β_S with pressure was seen near

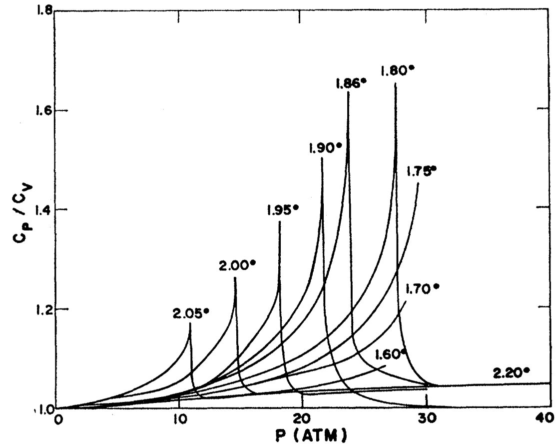

FIG. 9. The ratio of specific heats C_P/C_V versus pressure for liquid He^4 at several temperatures.

the λ transition. The β_S values were combined with the present isothermal compressibilities to derive $C_P/C_V = \beta/\beta_S$, the ratio of specific heats. Figure 9 shows C_P/C_V rising with pressure, reaching peaks of ~1.6 at the λ transition, before dropping to the values at 2.20°K, which are at most 1.05. The peak heights of the C_P/C_V ratio are indefinite, as are those of β, whereas the derivations of Buckingham and Fairbank[14] indicate that if $C_P\rightarrow\infty$, $\beta\rightarrow\infty$ while C_V and β_S remain finite. However, this behavior of C_V and β_S can be questioned if the λ transition is connected with the liquid-gas critical point [see Tisza[16] and Green[17]]. As the critical point is approached, singular functions are indicated for β_S and C_V by Chase, Williamson, and Tisza[18] and by Moldover and Little,[19] respectively. Therefore, the functions for β_S and C_V might be similar enough to those for β and C_P that $C_P/C_V = \beta/\beta_S$ remains finite at the λ transition.

ACKNOWLEDGMENT

It is a pleasure to thank Dr. Louis Goldstein for his interest, suggestions, and encouragement in this investigation.

[13] W. M. Fairbank, M. J. Buckingham, and C. F. Kellers, in *Low Temperature Physics and Chemistry*, edited by J. K. Dillinger (University of Wisconsin Press, Madison, Wisconsin, 1958), p. 50.

[14] M. J. Buckingham and W. M. Fairbank, in *Progress in Low Temperature Physics*, edited by C. J. Gorter (North-Holland Publishing Company, Amsterdam, 1961), Vol. 3, Chap. III.

[15] L. Goldstein, Phys. Rev. **135**, A1471 (1964); **137**, AB4(E) (1965).

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