

COMPRESSIBILITY OF LIQUID He⁴

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ABSTRACT

The refractive index n , density ρ , and isothermal compressibility $k_T = (1/\rho) \times (\partial\rho/\partial P)_T$ of liquid He⁴ have been measured along isotherms between the saturated vapor pressure and 4.5 atmospheres at 3.0°, 3.5°, 4.0°, 4.5°, and 5.0° K. The liquid was compressed in an optical cell 9.58 cm long in a Jamin interferometer. Changes in density were inferred through the Lorenz-Lorentz equation from refractive index changes measured with a photomultiplier fringe recorder. One fringe corresponds to a change in refractive index of $(5.699 \pm 0.003) \times 10^{-6}$ in this apparatus. Densities range between 0.0995 g cm⁻³ at 5.0° K at the saturated vapor pressure and 0.1501 g cm⁻³ at 3.0° K and 4.5 atmospheres pressure. Compressibilities range between 65×10^{-8} cm² dyne⁻¹ at 5.0° K at the saturated vapor pressure and 1.16×10^{-8} cm² dyne⁻¹ at 3.0° K and 4.5 atmospheres pressure. The limiting liquid structure factors for zero-angle X-ray scattering and for coherent scattering of slow neutrons have been calculated from these density and compressibility measurements. In addition, the ratio of heat capacities has been calculated at 3.0°, 3.5°, and 4.0° K where other measurements of the velocity of first sound are available.

INTRODUCTION

A study of the refractive index of He⁴ (Edwards 1956, 1957, 1958) has been extended to give further information on the liquid density. The refractive index n , the density ρ , and the isothermal compressibility $k_T = (1/\rho)(\partial\rho/\partial P)_T$ of liquid He⁴ have now been measured along isotherms between the saturated vapor pressure (SVP) and 4.5 atmospheres at 3.0°, 3.5°, 4.0°, 4.5°, and 5.0° K. The complete absence of "dead space" corrections makes this optical method particularly attractive at temperatures and pressures where the gas in the connecting tubing is a large correction for direct pycnometric methods. The liquid density has not previously been measured above 4.2° K at any pressure above the SVP, nor has the liquid compressibility been determined directly at any temperature or pressure.

A knowledge of the isothermal compressibility of the liquid is needed for the interpretation of the scattering of X rays through small angles, and the coherent scattering of slow neutrons, since such scattering is attributable to liquid density fluctuations. Furthermore, the liquid compressibility is a more important factor in the electrostriction calculations involved in the analysis of the movement of ions in liquid helium (Atkins 1959; de Boer and 't Hooft 1961).

2. INSTRUMENTATION

The liquid was contained and compressed in an optical cell 9.58 cm long in a special optical cryostat mounted on a Jamin interferometer (Edwards 1956, 1957, 1958). A shift of one fringe in this apparatus implies a refractive index

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change of $(5.699 \pm 0.003) \times 10^{-6}$. Pressures in the optical cell and in the helium bath were determined with Wallace and Tiernan absolute and differential mercury manometers and Wallace and Tiernan precision dial manometers.

The interferometer was modified so that the interference fringes could be watched visually and recorded photoelectrically at the same time. The normal viewing telescope of the Jamin interferometer was altered as follows. A cylindrical lens was used for the eyepiece lens of the Jamin telescope to give magnification perpendicular to the fringe pattern only. Then a Bausch and Lomb eyepiece camera viewing head was attached to the telescope, and a 1P21 photomultiplier tube mounted in a lighttight box behind a slit in the focal plane of the camera. The camera viewing head contains a beam splitter which sends about 10% of the light to the viewing eyepiece while 90% falls on the photomultiplier slit. This slit allows light from about a quarter of one fringe to fall on the photomultiplier tube. The photomultiplier output was recorded on a 10-mv Varian G10 recorder with a 1-second full-scale balancing time. The noise level and drift of the over-all system rarely exceeded about 0.1 of a fringe, corresponding to 5.7×10^{-7} in refractive index.

Temperatures inside the copper-walled optical cell were taken to be equal to the bath temperatures just outside the cell. These temperatures were determined from the pressure at the surface of the bath (on the 1958 scale of temperatures, T_{53}) (Brickwedde *et al.* 1960) plus a hydrostatic correction due to the depth of liquid over the cell. A separate experiment with a vapor pressure thermometer outside the cell showed that this procedure correctly accounts for the increase of bath temperature with bath depth to within about 10^{-4} ° K, in this metal cryostat. Temperatures outside the cell were monitored with a carbon resistance thermometer also. In fact, the temperatures inside the cell may have been higher than the temperatures outside the cell. Using the optical cell itself as a vapor pressure thermometer led to the conclusion that when the cell was only partially filled at the SVP, the surface of the liquid in the cell may have been hotter than the bath temperatures outside by up to 4 mdeg at 5.0°, 8 mdeg at 4.5°, 13 mdeg at 4.0°, 20 mdeg at 3.5°, 23 mdeg at 3.0°, 20 mdeg at 2.5°, 8 mdeg at 2.2°, and 1 mdeg below the λ -temperature. These apparent differences may be due to a thin layer of warmer liquid at the upper surface of the liquid helium I, when the cell is only partially filled. Such a layer would vanish below the λ -point and at higher pressures. As we could not increase these apparent differences reproducibly by increasing the radiant heat input to the cell, we did *not* apply a correction for this possible systematic error in temperature. When isotherms were performed, the temperatures were stabilized by controlling the pumping speed to the bath with a Greiner Manostat No. 8, and (or) by manual settings of two Edwards type LB1A needle valves, as well as by varying the power input supplied to the bottom of the bath by an electric heater. This procedure prevented the temperature of the cell from drifting more than ± 0.5 mdeg during any run.

3. ANALYSIS

The refractive index, n , of liquid helium or helium vapor is related to the density, ρ , by the Lorenz-Lorentz law,

$$(3.1) \quad \frac{n^2-1}{n^2+2} = \frac{4\pi}{3M} (N_0\alpha)$$

through the molar polarizability ($N_0\alpha$). The single important assumption in the following analysis is that this molar polarizability is independent of density or temperature. The evidence on which we base this assumption is as follows. Edwards (1957) showed that, for saturated helium vapor, ($N_0\alpha$) is constant from 1.5° K to 4.2° K and equal to (0.1245 ± 0.0005) cm³ mole⁻¹ for $\lambda = 5462.27$ Å. He also calculated that, for helium gas at N.T.P., ($N_0\alpha$) is (0.1246 ± 0.0002) cm³ mole⁻¹ for $\lambda = 5462.27$ Å, from the data of Cuthbertson and Cuthbertson (1910, 1932). Edwards (1958) measured ($N_0\alpha$) = (0.12454 ± 0.00021) cm³ mole⁻¹ for liquid He⁴ for $\lambda = 5462.27$ Å at 3.7° K and showed ($N_0\alpha$) was independent of temperature from 1.6° K to 4.2° K for liquid He⁴ along the SVP curve. In what follows, we assume that this last value of ($N_0\alpha$) is correct at higher temperatures and pressures as well. Consequently, refractive index measurements may be considered as measurements of the vapor or liquid density ρ , through

$$(3.2) \quad \rho = (7.67523 \pm 0.0077) (n^2-1) (n^2+2)^{-1},$$

and the isothermal compressibility, k_T , of the liquid, through

$$(3.3) \quad k_T = 6n(n^2-1)^{-1}(n^2+2)^{-1}(\partial n/\partial P)_T.$$

The numerical factor for equation (3.2), and its uncertainty, come from a combination of Kerr's (1957) absolute value of the density of liquid He⁴ at 3.7° K and Edwards' (1958) absolute value of the refractive index of liquid He⁴ at 3.7° K. Equation (3.3) follows by differentiation of equation (3.1), assuming that ($N_0\alpha$) is independent of temperature and pressure.

Once the density and isothermal compressibility are known, γ , the ratio of heat capacities, may be calculated for the liquid using

$$(3.4) \quad \gamma = \rho u_1^2 k_T$$

where u_1 is the velocity of first, or ordinary, sound.

Conventional theories of X-ray scattering by liquids (Zernicke and Prins 1927; and Brillouin 1922) predict that in the limit of zero-angle scattering, and not too near the critical temperature, the liquid structure factor is given by

$$(3.5) \quad \mathcal{L}_0 = N_0 k M^{-1} \rho k_T T$$

where N_0 is Avogadro's number, k is Boltzmann's constant, M is the molecular weight, ρ is the density, k_T is the isothermal compressibility, and T is the absolute temperature. Goldstein (1951a, b) has obtained the same result and has shown that equation (3.5) holds also for the coherent scattering of slow neutrons with vanishing momentum change, for atoms with zero spin nuclei. Furthermore, Goldstein and Sommers (1956) and Egelstaff and London (1957) have given expressions for various slow neutron scattering cross sections which involve the quantity \mathcal{L}_0 also.

4. EXPERIMENTAL RESULTS AND DISCUSSION

At five temperatures, 3.000°, 3.500°, 4.000°, 4.500°, and 5.000° K, n - P isotherms were measured. At each steady temperature, the cell was filled to a pressure slightly over 4.5 atmospheres. Then the cell pressure was slowly decreased to the SVP at that temperature, while fringes were recorded. The pressure in the cell was marked on the fringe record as the pressure fell. Figure 1 is a photograph of a portion of the chart record of the 3.000° K isotherm. Due to a slight viscous pressure drop in the capillary tube leading to the optical cell, these recorded pressures were occasionally as much as 0.01 atmosphere lower than the actual pressures. Furthermore, as the density of the liquid helium in the cell was a pronounced function of temperature, the unavoidable slow temperature drifts of ± 0.5 mdeg during an isotherm required small corrections to be applied to the fringe numbers obtained to make them appropriate to the nominal temperature of the isotherm being taken. Thus the extreme precision to which a fringe number could be read, viz. about 0.05 of a fringe, corresponding to about 2.35×10^{-7} in refractive index, was much better than the actual accuracy of the measurements. However, small changes in n with pressure P could be measured fairly accurately and give values of the isothermal compressibility k_T . We estimate the increase of the length of the optical cell itself due to an internal pressure of 4.5 atmospheres to be only about $3.5 \times 10^{-4}\%$. The resulting correction to n , ρ , and k_T has been omitted as entirely negligible. The *absolute* values of refractive index obtained all depend on the accuracy of the one absolute value at 3.700° K, $n = (1.026,124 \pm 0.000,035)$ (Edwards 1958) and upon the accuracy of the comparison of changes from this one value. Values of n at the SVP have been determined in separate experiments (Edwards 1958; Edwards and Woodbury, to be published) for temperatures from 1.6° to 5.2° K. From these known values at the SVP the absolute value anywhere along an isotherm ending at the SVP could be determined.

The results of these measurements are given in Table I at the SVP and at intervals of 0.5 atmosphere to 4.5 atmospheres pressure. Because of limitations of space, the original data of fringe numbers versus pressure are not shown, since at 5.000° K, for example, about 950 fringes were obtained. The absolute values of the refractive index are believed to be within $\pm 4 \times 10^{-5}$, while relative values along any isotherm are probably within $\pm 5 \times 10^{-6}$. The absolute uncertainty in the liquid densities, obtained through equation (3.2), is about $\pm 0.15\%$ or roughly $\pm 2 \times 10^{-4}$ g cm⁻³, while relative values along any isotherm are probably within $\pm 5 \times 10^{-3}$ g cm⁻³. Figure 2 shows these isobaric densities of liquid He⁴ as a function of temperature for pressures up to 4.5 atmospheres. Keesom and Keesom's smoothed 1933 values (Keesom 1942, p. 242) of the liquid density at 1.0 and 2.5 atmospheres, at 3.0°, 3.5°, and 4.0° K (after correction to the 1958 temperature scale), vary between 0.1 and 0.7% lower than the present results. Edeskuty and Sherman's (1957) values of the liquid density at 3.0° K at 1.0 and 2.0 atm are 0.06% and 0.08% lower than the present results.

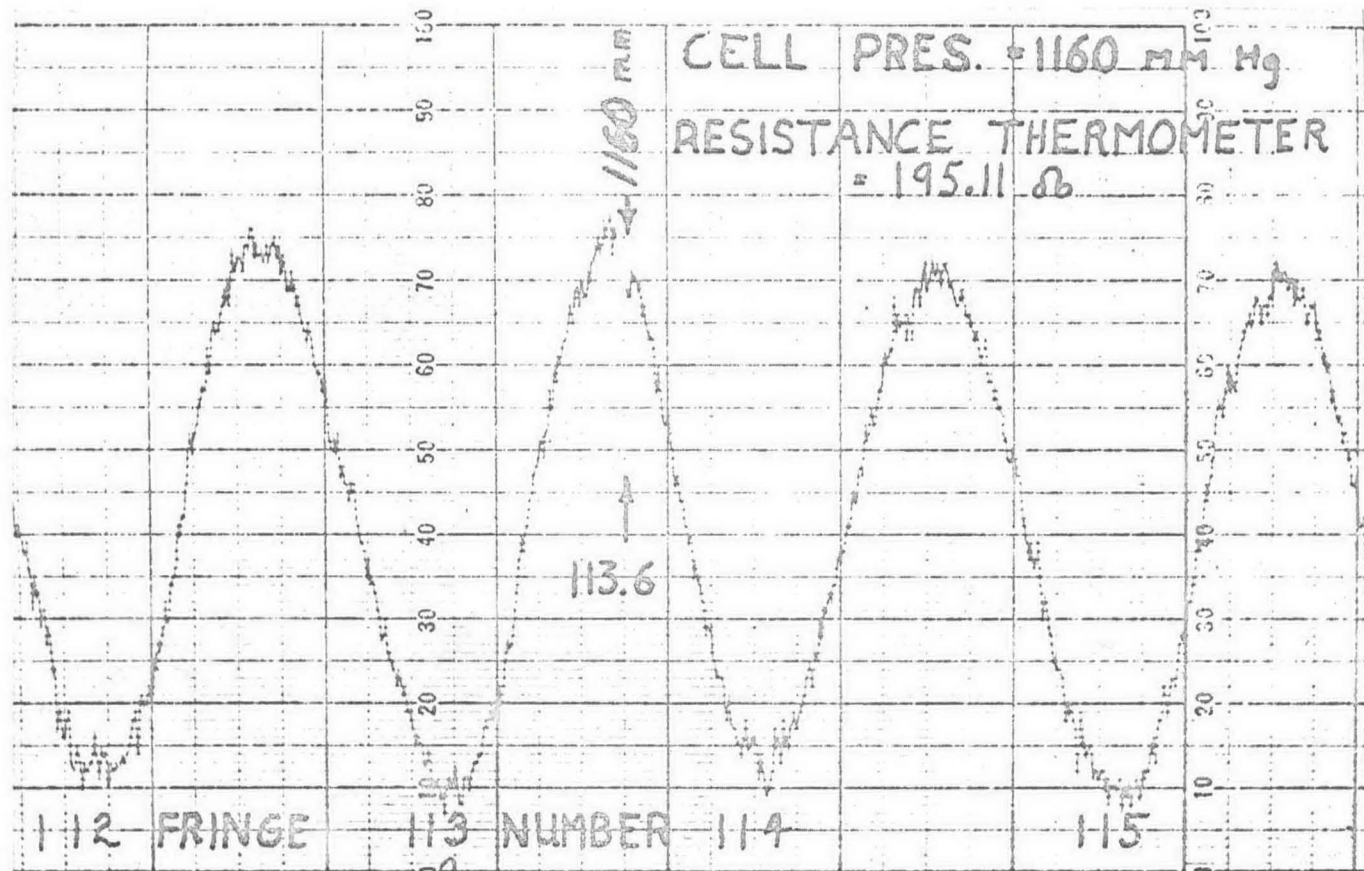


FIG. 1. A portion of the chart record of fringes obtained during the 3,000° K μ - P compressibility isotherm

TABLE I
Compressibility isotherms

(Refractive index n , at $\lambda = 5462.27 \text{ \AA}$, density ρ , isothermal compressibility k_T , ratio of heat capacities γ , and liquid structure factor \mathcal{L}_0 , of liquid He⁴ at even pressures for five temperatures)

P (atm)	$10^6(n-1)$	$10^3\rho$ (g cm ⁻³)	10^3k_T (cm ² dyne ⁻¹)	γ	\mathcal{L}_0
$T_{ss}, 3.000^\circ \text{ K}$					
SVP	27654	140.83	19.7	1.32	0.173
0.5	27792	141.52	18.7	1.27	0.165
1.0	28043	142.80	17.0	1.25	0.152
1.5	28280	144.00	15.8	1.23	0.142
2.0	28503	145.13	15.0	1.22	0.135
2.5	28716	146.20	14.2	1.21	0.129
3.0	28920	147.24	13.5	1.20	0.124
3.5	29115	148.23	12.8	1.19	0.118
4.0	29301	149.17	12.2	1.18	0.113
4.5	29480	150.07	11.6	1.17	0.108
$T_{ss}, 3.500^\circ \text{ K}$					
SVP	26632	135.65	25.7	1.48	0.253
0.5	26645	135.71	25.6	1.47	0.252
1.0	26980	137.41	23.2	1.44	0.231
1.5	27284	138.95	21.0	1.40	0.213
2.0	27561	140.35	19.3	1.36	0.197
2.5	27821	141.67	17.8	1.33	0.183
3.0	28067	142.92	16.6	1.31	0.172
3.5	28301	144.10	15.6	1.32	0.164
4.0	28525	145.24	15.0	1.32	0.158
$T_{ss}, 4.000^\circ \text{ K}$					
SVP	25223	128.50	41.4	1.92	0.442
1.0	25416	129.48	38.3	1.85	0.412
1.5	25873	131.80	32.0	1.71	0.350
2.0	26270	133.81	28.0	1.63	0.311
2.5	26626	135.61	24.8	1.57	0.280
3.0	26948	137.25	22.6	1.53	0.257
3.5	27243	138.74	20.6	1.50	0.237
4.0	27517	140.13	19.0	1.48	0.221
4.5	27774	141.43	18.0	1.47	0.212
$T_{ss}, 4.500^\circ \text{ K}$					
SVP	23180	118.14	81.7		0.902
1.5	23548	120.00	71.3		0.800
2.0	24289	123.76	52.7		0.610
2.5	24883	126.78	42.0		0.498
3.0	25370	129.25	35.2		0.425
3.5	25796	131.41	30.4		0.373
4.0	26168	133.29	27.0		0.336
4.5	26509	135.02	24.4		0.308
$T_{ss}, 5.000^\circ \text{ K}$					
SVP	19519	99.54	(650 ± 100)		(6.72)
2.0	19951	101.74	380		4.01
2.5	21990	112.09	117		1.36
3.0	23041	117.43	73.6		0.898
3.5	23788	121.22	53.4		0.673
4.0	24391	124.28	43.9		0.567
4.5	24904	126.88	36.8		0.485

The isothermal compressibilities k_T were obtained through equation (3.3) taking values of $(\partial n / \partial P)_T$ read from large graphs of n versus P near the pressures required. For some of the k_T values second differences have been smoothed graphically. This smoothing process rarely altered any $(\partial n / \partial P)$

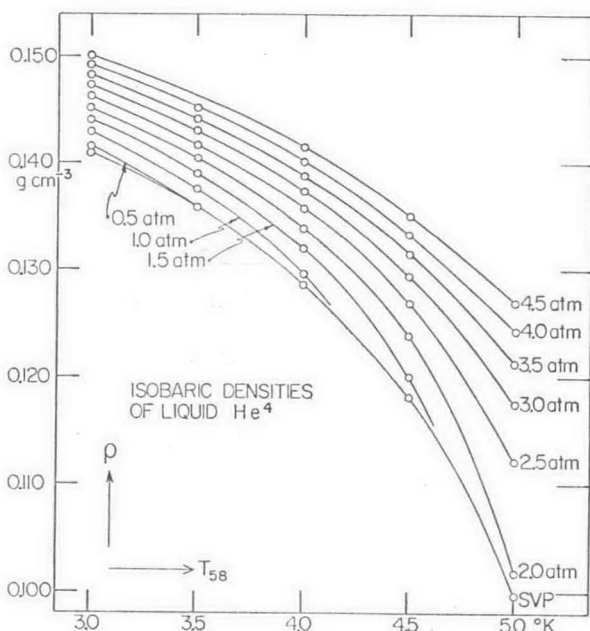


FIG. 2. Isobaric densities of liquid He^4 as a function of temperature for pressures up to 4.5 atmospheres.

value by more than 2%. We believe that the resulting uncertainty in k_T is about $\pm 3\%$, except for one point at the SVP at 5.000°K where the uncertainty is about 15%. Figure 3 shows these isothermal compressibility results as a function of pressure along the five isotherms. Keesom and Keesom (Keesom 1942, p. 243) obtained a smoothed graph of $(\partial\rho/\partial P)_T$ against T from which the isothermal compressibility of liquid helium may be obtained at 2.5 atmospheres and 3.0, 3.5, and 4.0°K to compare with the present measurements. After correction to the 1958 scale of temperatures, Keesom and Keesom's values are between 2 and 5% higher than our present results.

Table I also shows values of the ratio of heat capacities γ calculated from equation (3.4). Atkins and Stasior's (1953) smoothed values of u_1 were used, interpolating graphically where necessary. If these u_1 values are uncertain by $\pm 2\%$, then our γ values are uncertain by $\pm 5\%$. As no measurements have been made of u_1 at 4.500°K or 5.000°K , no calculation of γ was possible for those two isotherms.

Finally, Table I shows values of the liquid structure factor \mathcal{L}_0 calculated entirely from the results of the present measurements, using equation (3.5). The estimated uncertainty in \mathcal{L}_0 is the same as that for k_T , namely $\pm 3\%$, except for the one point at the SVP at 5.000°K where the uncertainty is about 15%. Gordon, Shaw, and Daunt (1954) have measured scattering of X rays down to angles of 1.5° at 4.2°K at the SVP. Their data extrapolated to zero angle gives $\mathcal{L}_0 = 0.575 \pm 0.040$.^{*} Our results listed in Table I may be

^{*}Due to a misprint, their paper states 0.475, but their Fig. 2 shows that 0.575 is meant for this quantity.

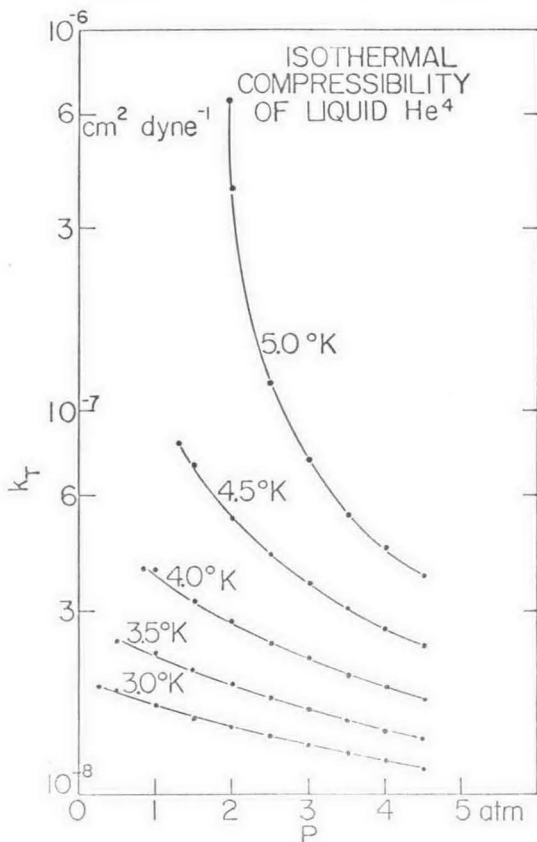


FIG. 3. Isothermal compressibility of liquid He⁴ as a function of pressure along five isotherms. Along each isotherm the lowest pressure point corresponds to the saturated vapor pressure.

interpolated graphically to give a calculated $\mathcal{L}_0 = 0.58 \pm 0.02$ at 4.2° K. There is clearly excellent agreement with experiment here. Unfortunately, there is not good agreement with the calculations of \mathcal{L}_0 made earlier by Goldstein and Reekie (1955) and used extensively by them in their analysis of the structure of liquid He⁴. At 4.2° K and the SVP, they calculated $\mathcal{L}_0 = 0.458$, which is well outside our limits of error. Tweet (1954) also calculated \mathcal{L}_0 at 4.16° K and the SVP and obtained approximately $0.61 \pm 0.03^*$ which agrees with our value. The earlier calculations were limited by the lack of direct measurements of the isothermal compressibilities of the liquid.

Egelstaff and London (1957) have calculated the expected zero-angle differential scattering cross section σ_s for slow neutrons scattered by liquid helium at the SVP, using, in effect,

$$(4.1) \quad \sigma_s = \left(\frac{5}{4}\right)^2 \frac{\sigma_t}{4\pi} \mathcal{L}_0 = 0.093 \mathcal{L}_0.$$

They took, σ_t , the free atom scattering cross section of helium, to be 0.75 barn (Sommers, Dash, and Goldstein 1955). At the highest temperatures

*Another unfortunate misprint in a "note added in proof" records this as 0.16.

liquid compressibilities were inferred by a considerable extrapolation of Keesom and Keesom's 1933 data. Our calculated σ_s values (obtained by multiplying our \mathcal{L}_0 values by 0.093) are higher than Egelstaff and London's by 6.8% at 3.0° K, 6.8% at 3.5° K, 15% at 4.0° K, 26% at 4.5° K, and 68% at 5.0° K. Egelstaff and London also measured σ_s for cold neutrons (45°) for angles of scatter of 4.6° to 12.3° at liquid helium temperatures of 1.5 to 5.2° K. Their experimental data have been extrapolated to zero angle in plots of σ_s against $\sin^2(\theta/2)$, and are shown as lying close to their calculated σ_s values. At 3.19° K and below, these plots are nearly horizontal straight lines, and their extrapolated intercepts unambiguous. At higher temperatures however, we believe the extrapolation, allowing for possible curvature at low angles, could equally well pass through our calculated σ_s values.

5. CONCLUSIONS

The experiments reported here have given accurate information about the phase diagram of state of liquid helium in a region not covered previously. They provide the first direct measurements of the liquid compressibility. These results have been used to calculate the ratio of heat capacities γ , of liquid He⁴ at 3.0, 3.5, and 4.0° K where first sound velocities u_1 are known. At 4.0 and 5.0° K, γ may also be obtained from these results when u_1 results become available. These results also permitted calculations of the limiting liquid structure factor to be made over the region covered, for zero-angle scattering of X rays and of slow neutrons.

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