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SOUND VELOCITY AND EQUATION-OF-STATE MEASUREMENTS
IN HIGH PRESSURE FLUID AND SOLID HELIUM*

by

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I. INTRODUCTION

Helium, the second most abundant element, has thermodynamic properties of importance to industry and high-technology development and to fundamental models of interatomic interaction. Static measurements of basic thermodynamic properties, P , V , and T have been made in the fluid at pressures generally less than 1 kbar.¹ Recently, compressibility measurements to 7 kbar² and sound velocity measurements along a single isotherm to 10 kbar³ have been reported. We have used our previously developed piston-cylinder apparatus to obtain P , V , T , and simultaneous values of longitudinal sound velocity in helium fluid throughout the ranges 75-300 K and 3-20 kbar. Some 670 data sets were obtained for the fluid and used in a double-process least-squares fit to an equation of state of the Benedict type.⁴ Additional measurements extended across the melting line into the solid phase at pressures up to 18 kbar. Measurements of the compressibility are compared with those obtained by Stewart along the 4 K isotherm up to 20 kbar.⁵ We discuss the use of helium as a pressure medium in high-pressure diamond anvil cells.

II. EQUIPMENT

The piston-cylinder equipment has been previously described.^{6,7,8} A major limitation for high-pressure studies of helium fluid has been the

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development of tight seals. Our apparatus incorporates two unsupported area Bridgman seals, one on the movable piston and a fixed seal on the end plug of the cylinder. Leakage has been reduced to the point where, within our experimental error, no systematic shifts of the P, V, T data are observed with a single charge kept under pressure for several weeks.

Sound velocity measurements were made with a single crystal transducer bonded to the unsupported area of the fixed Bridgman seal. Pulse timing of 0.5 μ s duration pulses from an Arenberg PG-650C generator was accomplished with a Tektronix 7704A scope. A reading accuracy of ± 10 ns was used for most measurements although some measurements were timed to a reading accuracy of ± 1 ns. Phase information of each pulse was preserved. An average error measurement is $\pm 0.5\%$.

Temperatures were established with a direct immersion of the apparatus in liquid nitrogen at the lowest temperatures and by cooling with cooled nitrogen gas at higher temperatures up to room temperature. A precision of ± 0.3 K was characteristic of the measurement error and the observed variations during the course of a several hour run. Pressures were determined with a dead weight tester and, with corrections for hysteresis, had a precision of $\pm 0.5\%$. Volume measurements in the tungsten-carbide supported cylinder required small corrections and have a precision of $\pm 0.4\%$.

III. RESULTS

Over the ranges 75-300 K and 3-20 kbar we determined some 670 data sets of P, V, T, and v_s . Computer analysis of these data sets enabled us to form graphic plots of data along isotherms and test the internal consistency of the data.

Previously, we have fit a variety of diatomic molecular fluid data to an equation of state of the general form

$$V = \sum_{m=1}^3 \sum_{n=-2}^2 A_{nm} T^{n/2} P^{-m/3} , \quad (1)$$

which is simplified to eliminate highly correlated terms and becomes:

$$V = (A+BT+CT^{-1/2})P^{-1/3} + (D+ET)P^{-2/3} + (F+GT+HT^{-1/2}+JT^{-1})P^{-1} . \quad (2)$$

This is a form used by Benedict⁴ for nitrogen. In addition to extending the fit to nitrogen over a larger temperature range, this equation was fit to hydrogen,⁹ deuterium¹⁰ and tritium.¹¹ We show that the present data for atomic helium can also be fit with this form of the equation in the range studied. The overall average errors for the double-process least-squares fit⁹ are $\pm 0.3\%$ for volume and $\pm 0.51\%$ for sound velocity, and both are within the standard deviation for the data sets.

Measurements extended into the high-pressure solid up to 18 kbar. Together with existing data points of the melting temperature and pressure up to 3.5 kbar by Mills and Grilly¹², a new melting curve of the Simon type has been determined. We find

$$P_m = -0.0160 + 0.01697 T_m^{1.555} , \quad (3)$$

where P_m is in kbar and T_m in K. The change in volume on melting was measured and fit to an equation of the form previously used with hydrogen and deuterium.⁷ That is,

$$V_m = 0.6359 (P_m + 0.088)^{-0.323} . \quad (4)$$

IV. DISCUSSION

We briefly discuss comparisons with the limited existing data above 3 kbar. Molar volumes as measured by Tsiklis et al² at 20 C give an average error of 0.7% with our EOS which is within the combined errors; $\pm 0.4\%$ reported for each investigation. The error is largest at the higher pressure becoming 2.2% at 7 kbar. The EOS used by Tsiklis et al is for isothermal data and no attempt was made to compare derived thermodynamic properties such as sound velocity.

Comparison at 25 C between our sound velocity EOS values and those measured by Nishitake and Hanayama³, gives differences of 1.1% at 2.94 kbar and 1.3% at 9.31 kbar. A measurement error of 3% is stated by Nishitake and Hanayama so this agreement is satisfactory. We can compare our findings with the sound velocity measurements of Pitaevskaya and Bilevich¹² along their 25 C isotherm up to 4 kbar, their highest pressure. Their values are lower by 2.1% at 3 kbar and by 0.95% at 4 kbar. These values are somewhat outside the

combined $\pm 0.3\%$ error of Pitaevskaya and our own errors of $\pm 0.5\%$. Differences in the frequency used for measurement of 10 and 30 MHz for the present experiments and 3.2 MHz by Pitaevskaya and Rilevich will not account for the variations in velocity. We have no evidence of dispersion at the higher frequencies. And we note that at all temperatures over this extended range toward the critical temperature the value $\partial V_g / \partial T > 0$, indicating a gas-like behavior for helium throughout the measurement range.

The melting curve was discussed recently by Spain and Segall¹³ on the basis of earlier data. The present melting curve predicts $P_m = 14.63$ kbar at 77.3 K, while Langer¹⁴ attained 14.18 ± 0.2 kbar as a single measurement.

A smooth interpolation is possible between the compressibilities determined in solid helium from the present experiments and those of Stewart.⁵ The higher compressibility in helium will minimize departures from hydrostatic equilibrium when helium is used to surround samples at very high pressures as in diamond anvil cells.

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