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Equation-of-State Measurements in Compressed Argon*

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A weighting technique used in obtaining experimental $P-V-T$ data for argon at high pressures is described. The data for fluid argon at pressures from 0.2 to 6.3 kbar and temperatures from 95° to 210°K are presented, along with melting data for argon in this range. The entropy and energy of argon are derived from these data. Recent theoretical calculations are compared with the results, and a discrepancy between the calculated and experimental values for the energy is discussed.

INTRODUCTION

Probably the simplest fluids from the theoretical point of view are the noble gases, excluding helium, since these substances behave nearly classically in their fluid phases, and are thought to be describable in terms of relatively simple intermolecular forces. However, the theoretical treatment of the dense fluid phase and of the solid–fluid transition in these substances is still an extremely difficult task. The theoretical difficulties, coupled with the total lack of accurate experimental data over much of the temperature and pressure range of interest, have long discouraged any systematic study of the dense fluid phase or of the melting transition for these substances. Recently, the development of high-speed computers has made possible renewed theoretical efforts in these areas, but a thorough investigation over a wide range of temperatures and pressures has still been hindered by the lack of accurate experimental thermodynamic data for comparison with the theoretical calculations.

For this reason, an experimental method was developed to obtain such thermodynamic data for these substances over a wider pressure and temperature range than has previously been covered. This paper provides a description of this method and the results obtained for the fluid phase and the solid–fluid transition in argon at pressures from 0.2 to 6.3 kbar and temperatures from 95° to 210°K. Recent theoretical calculations agree reasonably well with these data although considerable room for improvement remains.

EXPERIMENTAL

In order to determine the molar volume of a fluid as a function of pressure and temperature, it is necessary to measure both the sample volume and the number of moles of the fluid present in the sample as functions of these variables. The measurement of the number of moles in the sample has caused difficulty in many of the previous $P-V-T$ equation-of-state determinations for fluids at high pressures, so a somewhat different method for determining this quantity was employed in the present experiment.

In the method used for these measurements a pressure vessel is coupled to an external pressure system by means of very flexible pressure tubing, which in effect allows the vessel to be mechanically decoupled from the rest of the pressure system while still maintaining pressure communication with it. With the vessel thus mechanically decoupled, the weight of the fluid in it at various temperatures and pressures is determined by measuring the weight of the vessel and its contents, the weight of the empty vessel having been previously recorded. The number of moles in the sample is then obtained by dividing the weight of the fluid sample by the molecular weight of the fluid being studied. At the same time, the temperature of the vessel, and hence of the fluid sample, is controlled electronically and measured by sensors on the vessel, and the pressure is measured by means of a suitable pressure gauge at the other end of the flexible tubing.

Figure 1 shows the suspension system for coupling the pressure vessel to the analytical balance used in determining its weight. Details of this suspension system can be found elsewhere,[1] so only a few important features will be mentioned here. The electrical leads and the pressure tubing, which is hard-drawn stainless steel with 0.82-mm o.d. and 0.25-mm i.d., are brought to the vessel along the path ABCD in the figure. The sections AB and BC are each about 1.5 m long, so that the effect of the stiffness of the tubing upon the weight read at the balance is negligible. The portion BCD of the suspension is made rigid so that the vessel can be positioned directly beneath the balance by adjusting the movable support shown in the figure. This alignment, which is *essential* if the weight of the vessel and its contents is to be determined accurately, is checked by means of a calibrated weight which normally rests atop the vessel but which can be lifted free when desired.

Figure 2 shows details of the pressure vessel and the cryogenic apparatus. The pressure vessel itself is made of a hardened tool steel and has an estimated bursting pressure of about 10 kbar. It is about 15 cm long and 2.5 cm in diameter, with approximately 9-cm^3

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[1] R. K. Crawford, doctoral thesis, Princeton University, 1968 (unpublished).

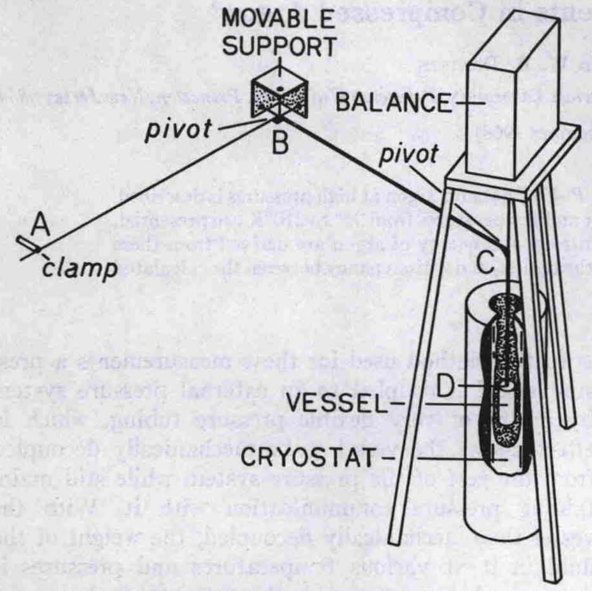

FIG. 1. Weighing apparatus.

internal volume. It is sealed by a standard Bridgman unsupported area seal using Teflon as the sealing gasket, with the pressure tubing silver-soldered into the "mushroom" part of the seal. A heater made of high-resistance wire is wound around the section of the pressure tubing which extends above the vessel and out of the cryostat. This heater serves to maintain the pressure tubing at a higher temperature than that of the vessel, thus preventing undesirable tubing blockage.

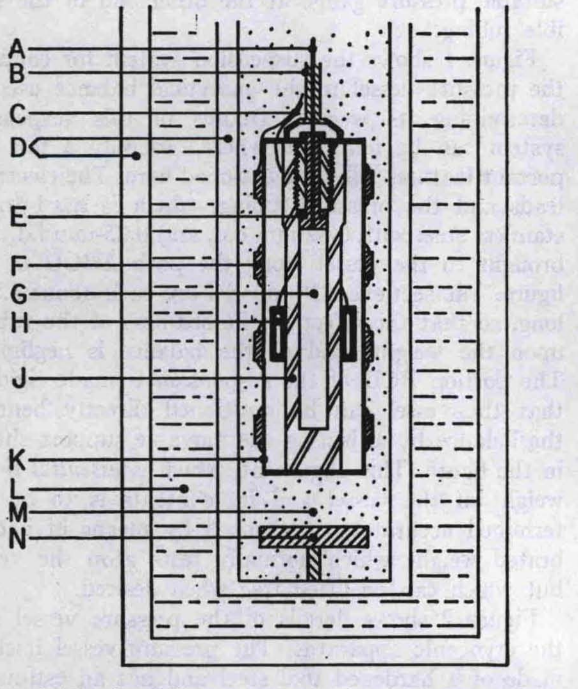

FIG. 2. Details of the pressure vessel and the cryogenic apparatus. A—pressure tubing; B—vertical portion of suspension (CD in Fig. 1); C—electrical leads; D—vacuum; E—Teflon high-pressure seal; F—heaters; G—sample volume; H—temperature sensor; J—pressure vessel; K—aluminum thermal enclosure for vessel; L—liquid nitrogen; M—dry nitrogen gas; N—heater for temperature gradient control.

The temperature of the vessel is measured with small calibrated platinum resistance elements mounted in an aluminum collar which fits around the center of the vessel. The vessel temperature is controlled by adjusting the current through heaters mounted on the aluminum can which surrounds the vessel and is attached to it. The temperature gradient along the vessel is detected by means of a copper–constantan differential thermocouple between the ends of the vessel, and is controlled by adjusting the current through a heater mounted below the vessel.

The pressure vessel and attached devices are suspended in an atmosphere of dry nitrogen gas which is separated from the resevoir of liquid nitrogen by a partial vacuum. The dry nitrogen gas flows slowly into the bottom of the inner chamber of the cryostat and out the top. This flow prevents any moisture which may be in the air in the room from entering the cryostat and condensing on the pressure vessel and the suspension. The flow is interrupted briefly whenever the weight of the vessel is to be determined, as otherwise the viscous drag of the gas flowing past the vessel would introduce a small error in the measured weight.

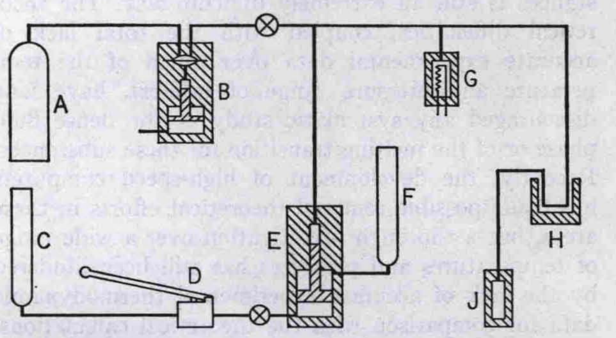

FIG. 3. Pressure system. A—argon supply; B—diaphragm gas pump; C—oil supply; D—oil pump; E—15:1 intensifier; F—oil reservoir used to indicate piston position; G—pressure gauge; H—cold trap; J—pressure vessel.

The pressure generating and measuring system is indicated schematically in Fig. 3. This system is leak free and reliable for gases at pressures of at least 7 kbar. A manganin resistance pressure gauge with a precision better than ±0.5 bar was used to measure pressure in all the data runs in the fluid phase of argon. This gauge was calibrated at the freezing pressure of mercury at 273.15°K (7.5662 kbar[2]) and at the freezing pressure of argon at 113.648°K (1.32384 kbar[3]), with an accuracy estimated to be better than

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[2] D. H. Newhall, L. H. Abbot, and R. A. Dunn, in *High Pressure Measurement*, A. A. Giardini and E. C. Lloyd, Eds. (Butterworths, Inc., Washington, D.C., 1963).

[3] A. Michels and C. Prins, Physica **28**, 101 (1962).