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Thermodynamic Properties of ^{4}He: I. The hcp Phase at Low Densities*

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ABSTRACT

Improved apparatus has been developed for measurement of the constant-volume heat capacity, C_V, of condensed phases at low temperatures. The high pressure calorimeter is closed by a remotely operated valve at the calorimeter and several problems associated with the usual blocked-capillary technique are thus eliminated. The heat capacity of hcp ^{4}He has been measured from approximately 0.35 K to the temperature of the transition to a mixed phase and for molar volumes, V, between 20.5 and 21.0 cm^3/mole. The data permit reliable extrapolations to 0 K to determine Θ_o, the Debye characteristic temperature at 0 K, and the entropy. The interpolated value of Θ_o at 20.97 cm^3/mole is in excellent agreement with the elastic constants, which have been measured only at that molar volume. C_V can be represented by the same function of T/Θ_o for all molar volumes in the range studied. The data are in good agreement with Ahlers' recent measurements in the limited region of overlap, but the temperature dependence of C_V at low temperatures and densities is different from that deduced by Ahlers by extrapolation from higher temperatures and densities. The values of Θ_o obtained in this work and by Ahlers at higher densities can be represented by $\Theta_o = 2340^{-0.8114}e^{-0.09690\ V}$.

I. INTRODUCTION

The constant-volume heat capacity measurements reported in this paper and in two additional papers to be published later were originally undertaken to determine the thermodynamic properties of the bcc phase of ^{4}He. However, as the work progressed it became apparent that it would be interesting to extend the measurements through the adjacent two-phase mixtures and into the hcp and liquid phases. Accordingly, measurements were made at 35 molar volumes between the saturated vapor line and 20.5 cm^3/mole. Most of the measurements start at a temperature between 0.3 and 0.4 K (two thirds of them extend below 0.35 K). These temperatures are low enough to establish the coefficients of the T^3 terms in C_V and reliable extrapolations to 0 K and entropy determinations were therefore possible. At the higher densities many of the runs were terminated just above the melting temperature of the hcp or bcc phase, but 16 runs were extended to 4 K to obtain the thermodynamic properties of the liquid to that temperature. The measurements have been described in two theses,[1,2] and some of the results have been reported in brief communications.[3-6] This paper gives a description of the apparatus and general techniques, and the results of the measurements on the hcp phase. In a second paper,[7] hereafter referred to as II, the measurements on the bcc phase and measurements on the two-phase mixtures (which give information on the pressure-temperature phase diagram) will be described. The measurements on the liquid phases will be reported in a third paper,[8] III.

Dugdale[9] has summarized the results of heat capacity measurements on hcp ^{4}He that were reported prior to 1965. In most cases the measurements did not extend below 1 K and neither θ_0, the Debye characteristic temperature at 0 K, nor the low-temperature temperature dependence of the effective Debye temperature, $\theta(T)$, were well defined. In some measurements,[10-12] however, there were indications of anomalous behavior that was described either as a maximum in $\theta(T)$ or as a linear term in C_V. More recently, the heat capacity of hcp ^{4}He has been measured between 16.9 and 20.9 cm^3/mole and to 0.3 K by Edwards and Pandorf;[13] at 12.2 cm^3/mole and to 0.2 K by Sample and Swenson;[14] and between 13.7 and 20.9 cm^3/mole and to 1.4 K by Ahlers.[15] Only in the measurement by Sample and Swenson was there an indication of a linear term in C_V; it was smaller than those reported earlier and was attributed to an apparatus effect. The results reported in this paper cover only a limited range of volume but the precision is high enough to give reasonable accuracy in the volume dependence of the thermodynamic properties. Furthermore, the measurements extend to sufficiently low temperatures to establish unambiguously the T^3 term in C_V and therefore the properties at 0 K and $\theta(T)$.

In previous measurements of the constant-volume heat capacity of solid He the samples were held in the calorimeter by a plug of solid He in the filling capillary. A number of experimental problems and possible sources of error are associated with the use of this technique. First, the range of molar volumes that can be studied is limited to that in which the plug can be maintained solid (at some temperature,

not necessarily that of the sample). This is an inconvenient complication in studying the bcc phase of ^{4}He at low densities because the pure bcc phase or bcc-hcp mixtures are stable only in a very narrow temperature range and the stable phases or mixtures at both higher and lower temperatures include a fluid phase. Constant-volume measurements on ^{4}He in the liquid or solid-liquid mixtures at molar volumes greater than 21 cm^3/mole (approximately the maximum molar volume of the solid phases) are, of course, not possible with the blocked-capillary technique. Since solid helium is relatively soft, there is also some question as to how well the solid plug maintains constant volume conditions. Particularly at low densities or at temperatures near a melting point, a gradual slipping of the plug would seem to be a distinct possibility. Finally, the thermal conductivity of the He in the capillary is relatively large, and can introduce substantial heat leaks that reduce the precision of the measurements. In some cases systematic errors may also be introduced because the thermal relaxation time of the empty capillary is longer than that of the filled capillary. If the heat capacity of the capillary is large, as could be the case if it were made of steel, the apparent contribution of the capillary to the heat capacity of the empty cell could be significantly less than the effective contribution to the heat capacity of the full cell. The result would be an overestimate of the heat capacity of the sample, particularly at low temperatures where the linear term in the heat capacity of the capillary is larger relative to the sample heat capacity. It seems possible that in some cases this effect may have contributed to the appearance of a linear term in C_V.

In the measurements reported here the problems associated with the blocked capillary technique were avoided by using a valve to close the cell. The valve stem, which could be manipulated from outside the cryostat, was located inside the cell and sealed the opening to which the filling capillary was connected. Before each series of measurements the cell was filled with liquid at the required density at 4.2 K, the valve was closed, and the filling capillary was evacuated.

II. APPARATUS AND EXPERIMENTAL PROCEDURES

A. Cryostat

A schematic diagram of the low-temperature part of the cryostat is shown in Fig. 1. The vacuum jacket shown in the figure was surrounded by a pumped ^{4}He bath that could be regulated at temperatures between 1.1 and 4.2 K. The sample cell was supported by thin mylar discs and stainless steel tubes from a copper platform that could be reduced in temperature to 0.25 K by evaporation of ^{3}He in the ^{3}He chamber. The upper mechanical heat switch, which provided thermal contact between the ^{4}He bath and the ^{3}He stage, was operated from outside the cryostat by relative motion of two concentric stainless steel tubes attached to the threaded connections above and below the bellows. The lower heat switch was similar in construction and operation but served two purposes. It provided thermal contact from the ^{3}He stage to the sample cell, and, when closed, the jaws gripped a square neck on the cell to support the cell against the torque necessary to close the cell valve. In this way the light mylar discs that supported the cell vertically were protected from damage when the valve was operated. The cell valve was operated by engaging a square end on the actuating screw (see following section) with a square hole in a bushing at the lower end of a stainless steel tube. The tube could be rotated from outside the cryostat.

B. Sample Cell

1. Cell Construction

The construction of the cell is illustrated in Fig. 2. The body consists of three pieces of hardened Berylco 25 beryllium-copper alloy[16] held together with threaded connections for mechanical strength and sealed with indium solder. The valve stem is sealed to the body with a heavy beryllium-copper bellows and lead-tin solder. The material and wall thickness of the bellows was chosen to provide constant volume conditions in the range of temperature and molar volumes of the heat capacity measurements and to make corrections for expansion unnecessary. At the same time, however, it provided a safety that would rupture before the cell body in the event that the valve became inoperable.

The tip of the valve stem was made of annealed beryllium copper to permit deformation to match the hardened valve seat. However, it was found necessary to harden the valve stem over most of its length to avoid problems with deformation of the stem at the pressures necessary to provide a seal. The valve stem was therefore made in two parts held together by soft solder. In early versions of the cell the seat was machined to a 60° angle and heavily nickel plated, and the stem was machined to 59° and gold plated. It was later discovered that an effective seal could be obtained at lower pressures and consequently less deformation of the stem tip by increasing the area of the mating surfaces and carefully polishing both seat and stem tip. The stem tip angle was also changed to 58°. With these changes the plating was found to be

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unnecessary. Because the valve stem does not turn, but moves only vertically, it deforms to the exact dimensions of the seat on closing, and thereafter can be opened and closed successfully many times. However, if the cell is dismantled, changing the relative orientation of stem and seat, it is necessary to remachine and repolish both. All valves used in heat capacity measurements were tight to superfluid He^4 at pressures to 30 atm.

The valve stem was separated from the actuating screw by a hardened steel bearing. The bearing was located by dimples cut into the ends of the stem and actuating screw by a ball end mill. The ends of the stem and activating screw contacting the ball were also tapered 5°. Without this taper interference with the screw threads tended to develop as the beryllium copper was deformed by the harder ball.

A total of four slightly different sample cells were used for heat capacity measurements. They all used the same body but in the course of various alterations and repairs the valve stems and bellows were replaced and slightly different amounts of solder were used in reassembling. These modifications produced small changes in volume and heat capacity, which were therefore redetermined each time the cell was changed. The different cells will be designated by numbers 1 through 4.

2. Heat Capacity of Empty Cell

The data necessary to correct the measured heat capacity for the heat capacity of the empty cell was obtained in separate experiments, which were repeated each time the cell was modified or repaired.

Unfortunately the beryllium copper used in the cell, and several other commercial beryllium-copper alloys,[17] have significant heat capacity contributions of magnetic origin. (Beryllco 25 alloy contains 0.2 to 0.3% by weight of cobalt, and dilute cobalt in copper alloys have been observed to have large heat capacities in excess of that of pure copper.[18]) The heat capacity of the cell is about twice as large at 0.3 K as it would have been if this contribution were not present. Furthermore, a more complicated expression is needed to fit the heat capacity of the empty cell. For temperatures below 2 K an expression of the form $C_{cell} = \alpha + \gamma T + \beta T^3$ was found to be adequate, as illustrated in Fig. 3. Typical values of the parameters were $\alpha = 0.635$ mJ/K, $\gamma = 2.11$ mJ/K^2 and $\beta = 0.223$ mJ/K^4. At 0.35 K the heat capacity of the empty cell is 40% of the measured heat capacity in the hcp phase, 50% in the liquid near the saturation pressure, and 75% in the liquid near the freezing line. The relative contribution of the heat capacity of the empty cell is much smaller at higher temperatures. For example, for the liquid at the freezing line it is only 45% of the total at 0.45 K and decreases extremely rapidly with further increases in temperature. Different expressions were used to fit the heat capacities of the cells at temperatures above 2 K, but in that region the heat capacity of the cell was so small relative to those of the samples that accurate fits were not important.

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C. Gas Handling System and Measurement of Sample Molar Content

The gas handling system used for sample purification, cell filling, and measuring the number of moles of gas in the samples is illustrated in Fig. 4. High purity ^{4}He gas was taken from the purifier (silica gel at liquid nitrogen temperature) used in conjunction with the Giauque Low Temperature Laboratory He liquefier, and stored at high pressure in the storage tank. Before use the gas was passed over activated charcoal at liquid nitrogen temperatures and, after run 18, through an additional trap at 4.2 K. At the time the 4.2 K trap was installed we were unaware of the effect of impurities on C_V later reported by Ahlers[15] but the similarity of results obtained before and after the installation of the trap suggests that impurities were not important in any of the measurements.

Samples were delivered to the traps by a high pressure regulator and then admitted directly to the cell. The cell filling pressure was measured to ±1.5 psi by a 0-1500 psi Heise gauge.[19] The cell valve was always closed at 4.220 K and at a filling pressure calculated to give the desired molar volume. The PVT data obtained by Hill and Lounasmaa[20] were used for this calculation.

After most experiments, n, the number of moles of ^{4}He in the sample was determined by measuring the gas volume. For this purpose the sample was collected in a pair of thermally insulated copper tanks as the cell was warmed to liquid nitrogen temperatures. The volume of the tanks was accurately known, and the temperature and pressure at which the gas was collected were measured. The correction for the

dead volumes (cell, connecting lines, and high pressure manifold) was determined by evacuating these volumes, expanding the gas remaining in the tanks into them, and remeasuring the pressure. In the earliest runs on which useful heat capacity data were obtained, 9 and 11 to 18, the accuracy of the n determination was limited by the temperature stability of the collecting tanks. Improvements in the collecting system were made after sample 18 was studied, and the estimated accuracy of the n determinations for samples 19 to 45 is 0.02%.

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D. Determination of Cell Volume and Sample Molar Volumes

In addition to the number of moles of sample, the volume of the cell, V_c, must be known to derive the dependence of thermodynamic properties on the molar volume, V. The bcc phase is thermodynamically stable only between V = 20.84 and 21.10 cm^3/mole. Furthermore, no two samples with molar volumes differing by more than 0.04 cm^3/mole are thermodynamically stable at a common temperature. Particularly for this phase, therefore, very precise determinations of V are necessary. Accurate determinations of n and V_c together with measurement of the various transition temperatures would also establish the V-T phase diagram. Conversely, and this was the original intention, the phase diagram established in earlier work could be used to determine V from the observed transition temperatures and n would then have to be determined only to the accuracy necessary for calculation of the molar heat capacities (a much less stringent requirement). As the work progressed, however, it began to appear that there might be systematic errors in the V-T phase boundary reported by Grilly and Mills[21] for the bcc phase. The improvement in the accuracy of the n measurements after run 18 (see preceding section) was made to permit an independent determination of the relative values of V. The volume of cell number 4, which was installed at the time the improvements in the measurement of n were made, was calculated from the data of Grilly and Mills on the molar volume of bcc ^{4}He at the melting line and the measured n and melting temperature. A smooth curve was drawn through the Grilly and Mills

data, and the point V = 21.020 cm^3/mole, T = 1.6270 K, corresponding to the observed melting temperature was used with the measured n to obtain V_c = 11.4525 cm^3. The molar volumes of samples 24-45, which were studied in this cell, were assigned from the measured n's and V_c. The molar volumes of the other samples for which useful heat capacity data were obtained, 9 and 11-22, were assigned by a less direct comparison with the same point on the Grilly and Mills melting curve. In most cases this comparison involved the phase diagram established with cell 4, and the assignment of these molar volumes will be described in more detail in II. Samples 12-18 were all studied in cell 3 and in each case n was measured, although less precisely than in later runs. Values of V_c for cell 3 were calculated from the measured n's and assigned V's and were found to be consistent, i.e. to show no systematic dependence on V. The assigned values of V_c (or of V) can also be compared with the PVT data for liquid ^{4}He reported by Hill and Lounasmaa[20] because the cell was always filled with liquid at 4.220 K and at a measured pressure. The Hill and Lounasmaa data give values of the volumes that are an average of 0.2% higher than those assigned with no systematic dependence of the discrepancy on V. For molar volumes in the pure liquid region the assigned molar volumes can also be compared with Kierstead's recent work[22] on the V-T λ-line and the observed λ temperatures. The agreement is within 0.05% for molar volumes below 24.5 cm^3/mole, but systematic differences develop at higher molar volumes.

It appears probable that the relative values of V are in general accurate to about 0.02%, the estimated accuracy of the n measurements.

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The absolute values of V, however, depend on the accuracy of the determination by Grilly and Mills[21] of the V-T phase boundary of the bcc phase in the vicinity of the point chosen to determine V_c. Comparison with other data[20] suggests possible errors of up to 0.2%.

The triple point temperatures of the bcc phase determined by Grilly and Mills[21] are in conspicuous disagreement with an average of other values -- 27 mK low at the low temperature triple point and 12 mK low at the high temperature triple point -- and the shape of their bcc phase diagram differs significantly from that determined in this work. In view of these discrepancies some further discussion of their data and its use in assigning molar volumes is perhaps appropriate. Grilly and Mills determined the P-V isotherms by introducing He from a room temperature manometer and monitoring P as a function of the amount of He that had entered their experimental cell. Idealized isotherms, constructed from their reported volume changes and approximate values of compressibilities are shown in Fig. 5 for a temperature near the middle of the bcc phase and for a lower temperature at which the liquid is in equilibrium with the hcp phase. The molar volume of He in the cell should be accurately determined at any time that equilibrium is established. The molar volume of the solid at melting was determined by slightly overpressurizing to promote solidification and waiting for equilibrium. Equilibrium was more difficult to obtain at the solid-solid transition however and the width of the bcc phase in volume was not reported by Grilly and Mills. They obtained the triple point temperatures by extrapolating the observed width of the phase in pressure

to the temperatures at which the width vanished. This width varies only slowly with temperature near the middle of the phase, but more rapidly near the ends. Furthermore, both the pure bcc phase and the hcp-liquid I mixtures have a strong tendency to supercool before the hcp and bcc phases, respectively, appear. Thus, near the high temperature end of the stable region of the bcc phase the phase could be missed entirely, and at all temperatures at which it is observed it could appear to extend to higher pressures than the equilibrium pressure. Consequently, there are good reasons to expect relatively large errors in the triple point temperatures reported by Grilly and Mills, and particularly errors that tend to make both triple point temperatures low. There is no reason, however, to expect these errors to affect the reported melting volume at temperatures where there is no difficulty in obtaining the phase, i.e., near the middle of the phase. The general correctness of Grilly and Mills' temperature measurements is attested by the good agreement of their upper λ-temperature, the only "triple point" temperature for which they claim high accuracy, with other values. A different interpretation of Grilly and Mills' data was made by Ahlers,[23] who assigned a correction to Grilly and Mills' temperature scale that was linear in temperature and gave the calorimetrically observed triple points. The modified V-T curve so obtained was used by Ahlers and also by Edwards and Pandorf[24] in assigning molar volumes to bcc samples.

E. Energy and Temperature Measurement

1. Energy Measurement

A heater consisting of 60 ft. of 0.0009 in. diameter 91% platinum-9% tungsten wire was varnished to the surface of the sample cell. Several turns of copper wire which were also thermally anchored to the cell were connected between the heater and the leads. These copper terminals were intended to ensure that superheating of the heater wire during energy input did not produce a loss of heat to the surroundings that was not properly accounted for by the conventional extrapolation of fore- and after-drifts. The copper heater terminals were connected to the measuring instruments by separate current and potential leads of which the section between the cell and the ^{3}He temperature stage consisted of 1/4 in. lengths of the same wire used in the heater. It was assumed that half of the energy dissipated in the current leads by the heater current went to the sample and the very small correction for this effect was calculated from a rough measurement of the lead resistance at room temperature.

The heater current was drawn from a stepwise adjustable 0-500 V constant voltage power supply and adjusted by a decade resistance dividing network as well as by the voltage adjustment. The heater current was controlled by a mercury-wetter-contact relay. A second relay of identical type that was arranged with its control coil in series with that of the first controlled a constant voltage signal that actuated an electronic timer. The heating periods were measured to 0.1 msec and the

simultaneity of the two relays and the rise time of the heater pulse were established to be within that limit. The heating periods were normally 10 sec or longer. Various standard resistors could be switched into the circuit in series with the heater and were used to measure the heater current and heater resistance. A Leeds and Northrop type K-2 potentiometer and electronic null detector were used for voltage measurements. The potentiometer was guarded against leakage from the high voltage supply and the working batteries. The heater current stability and reproducibility were good enough that no measurement of the heater current was necessary during the heat capacity points. The total error in the energy measurements should be approximately 0.05%.

2. Resistance Thermometers

The same two four-terminal germanium resistance thermometers were mounted on the sample cell and used for the heat capacity measurements on all samples. The main thermometer had resistances of 500, 88, and 28 Ω at 0.30, 1.0 and 4.2 K, respectively, and was calibrated between 0.3 and 25 K as described in the following section. With appropriate working currents, e.g., 1 μA at 0.3 K, 5 μA at 1 K, and 20 μA at 4.2 K, this thermometer could be operated with adequate sensitivity for most purposes at all temperatures within the range of the measurements. These working currents were low enough that no significant deviations from the "zero-current" resistance temperature relation were produced. A second higher resistance (23,000 Ω at 1.1 K and 1800 Ω at 4.2 K) germanium thermometer was used to obtain a higher sensitivity for measurements on

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the bcc phase. This thermometer was calibrated against the first at sixteen temperatures between 1.09 and 2.16 K and the data were fitted by a two-parameter equation to 0.5% in temperature. This equation and a smooth curve through the deviations of the calibration points from the equation were used for calculating heat capacities. A current of 4.7 μA was used in the second thermometer. At this current there were substantial temperature differences between the thermometer element and the sample cell but they were accurately reproducible from run to run and the sensitivity achieved was substantially higher than would have been possible otherwise. The second thermometer made possible heat capacity measurements in the bcc phase over temperature intervals of 1 or 2 mK to ±1% -- a useful capability in view of the narrow range of existence of that phase.

The thermometer resistances were measured by a DC potentiometric method. The potentiometer was a six dial Rubicon instrument. Unbalance voltages were amplified by a Kiethley breaker amplifier with constant gain and displayed on a recording potentiometer. Approximate constancy of thermometer current, without the use of AC-line operated devices, was achieved by drawing the current from a 90 V battery of low-temperature-coefficient mercury cells and a stable stepwise-adjustable series resistance. The potentiometer was guarded from leakage from the high voltage parts of the current source.

3. Thermometer Calibration and Temperature Scale

Three independent calibrations of the main thermometer were carried out. In the first calibration (in 1964, before the first heat capacity

measurements) the therometer was calibrated against ^{4}He vapor pressures[25] (T_{58}) between 1.1 and 4.2 K and the calibration was extended below 1.1 K on the assumption of a curie law for the magnetic susceptibility of a spherical single crystal of CMN [$Ce_2Mg_3(NO_3)_{12}\cdot 24H_2O$]. For the vapor pressure measurements, a copper vapor pressure bulb that was connected to the manometers by a vacuum jacketed tube was arranged with its lower half projecting into an evacuated chamber. The thermometer was placed in thermal contact with the lower end of the bulb and the whole assembly immersed in a temperature regulated ^{4}He bath. Above the λ temperature the vapor pressure of liquid in the bulb was measured; below the λ temperature the bulb was evacuated and the pressure above the surface of the bath was measured. For the calibration at lower temperatures the thermometer was placed in thermal contact with the CMN and both were cooled by contact to a ^{3}He chamber. The susceptibility of the CMN was measured by a 23 Hz mutual inductance bridge.

At an early stage of the heat capacity measurements (in 1965) the thermometer was removed from the sample cell and recalibrated. In this second calibration the primary thermometer and several other germanium thermometers, some of which had also been calibrated at various earlier times, were compared with CMN susceptibility and ^{4}He vapor pressure measurements and the calibration was extended above 4.2 K by gas thermometry. Although the vapor pressure measurements were made by techniques similar to those used in the earlier measurements, inconsistencies of several mK in the various ^{4}He vapor pressure measurements were apparent at this point. In particular, the new vapor pressure measurements gave

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temperatures an average of 2 mK higher in the region between 1.5 and 2.5 K than the earlier calibration. The reasons for the inconsistencies were not clear, but the heat capacities were calculated on a temperature scale that gave more weight to the new data. (The possibility that the thermometer resistance changed with time was ruled out by the consistency of determinations of transition temperatures, particularly the low-temperature triple point temperature of the bcc phase, that had been made at various times between the two calibrations.)

Several years after the heat capacity measurements were completed (1971) the primary thermometer and one other thermometer that had been included in the second calibration were again calibrated. On this occasion both He^3 vapor pressures[26] (T_{62}) and He^4 vapor pressures were measured, and both gave results that were in good agreement with the first calibration. (Within the precision of the measurements, both germanium thermometers indicated the same discrepancies between the second and third sets of vapor pressure measurements, providing additional evidence for the stability of the main thermometer.) It therefore seems probable that the temperature scale on which the heat capacity data were calculated is in error (too high) by several mK in the 1.5 to 2.5 K region. Since the associated maximum error in the heat capacity is only 0.3%, and tends to be smoothed out by the procedures used in deriving thermodynamic properties from the heat capacities, the heat capacity data have not been corrected. However, the values reported for the temperature coordinate of V-T and P-T phase boundaries have been corrected.

III. RESULTS AND DISCUSSION

A. Temperature and Volume Dependence of C_V

The heat capacity of hcp ^{4}He was measured at nine molar volumes between 20.456 and 20.960 cm^3/mole. At each volume the measurements extend from between 0.3 and 0.4K to the upper limit of the hcp phase. The data for representative samples are shown plotted various ways in Figs. 6-8. As demonstrated in these figures, there is no indication of a linear term in the heat capacity. The data were fitted, by several different methods, to

$$C_V = A_3 T^3 + A_5 T^5 + A_7 T^7 + \ldots \qquad (1).$$

The rms deviations obtained by a least-squares fitting procedure were not significantly smaller when the T^5 term was included than when it was omitted. For temperatures up to 1.2K, the data are adequately represented by the T^3 and T^7 terms, as illustrated in Fig. 7. The coefficients of these terms, obtained graphically from plots of the type shown in Fig. 7, are given in Table I. At temperatures above 1.2K a small negative T^9 term is required, in addition to the T^5 and T^7 terms, to obtain a good fit. Values of Θ_o and Θ were calculated from A_3 and C_V according to the definitions

$$A_3 = \frac{12}{5} \pi^4 R \frac{1}{\Theta_o^3}, \qquad (2)$$

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and

$$C_V = \frac{12}{5}\pi^4 R\left(\frac{T}{\Theta}\right)^3 \quad . \tag{3}$$

The values of Θ_o are given in Table I, and Θ/Θ_o is plotted vs. T/Θ_o in Fig. 8. This figure includes only data for four molar volumes for which the precision is relatively high, and for which a high density of points was taken close to the temperatures of the transition to a two-phase mixture.

Within the precision of the data, and for the very limited range of molar volumes studied, Θ/Θ_o is given by a universal function of T/Θ_o except very close to the transition temperature. The data for the four samples represented in Fig. 8 define an envelope for Θ/Θ_o that the data for each sample follow to about 0.08K below the transition temperature. In the 0.08K interval below the transition temperature the data drop below the envelope. The drop in Θ/Θ_o corresponds to an increase in C_V that is associated with terms beyond the T^7term in Eq. (1): within the experimental precision, the volume dependence of A_7 is given by $A_7 \propto \Theta_o^{-7}$ The deviation of Θ/Θ_o from the envelope is independent of the type of transition that it precedes: sample 26 melts to liquid II, samples 29 and 42 transform to bcc solid, and sample 31 melts to liquid I. It is not surprising that Θ/Θ_o deviates from a universal function of T/Θ_o, but it is surprising that the deviations are strongly correlated with the transition temperature rather than with Θ_o. One might think that the observed deviations are spurious and originate in a local superheating that produces mixed-phase regions at temperatures below the equilibrium

transition temperature. If the time required for thermal equilibrium to be attained from the unstable two-phase mixture were much greater than in the single phase sample, an erroneously high value of C_V could be recorded. However, the equilibrium time would be expected to depend on the type of two-phase mixture formed, and in particular to be short for the hcp-II mixture. As noted above, the "pre-transition anomaly" is not correlated with the type of two-phase mixture formed. Furthermore, no difference in thermal relaxation behavior was observed between points taken in the pre-transition region and points taken at lower temperatures, but there was a sharp change in behavior, which did depend on the type of two-phase mixture formed, at the point that spanned the equilibrium transition temperature. There is theoretical evidence for the occurrence of vibrational instabilities in solids as the melting temperature is approached[27], but, thermodynamically, the observed effect in C_V is in the direction of stabilising the solid. A similar but more pronounced effect was observed in the bcc phase. That effect was studied in more detail, and will be discussed in II .

The Guineisen parameter γ , which can be defined by

$$\left(\frac{\partial S}{\partial V}\right)_T \equiv \frac{\gamma C_V}{V} \quad , \tag{4}$$

provides a convenient basis for discussion of the volume dependence of thermodynamic properties. If $C_V = C_V(T/\Theta)$ and the volume dependence of of C_V arises only through the volume dependence of Θ, $\gamma = -\, d\ln\Theta/d\ln V$ and is independent of temperature. In the low-temperature limit, by Eqs. (1), (2) and (4),

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$$\gamma_o = -\frac{d\ln\Theta_o}{d\ln V} \qquad (5)$$

At higher temperatures deviations of C_V from $C_V = C_V(T/\Theta)$, or of Θ/Θ_o from a universal function of T/Θ_o, correspond to a temperature dependence of γ. A graphical determination of γ_o from the data reported here is shown in Fig. 9. Within an estimated uncertainty of ±0.05, $\gamma_o = 2.80$. Apart from the "pre-transition anomaly" discussed above, $C_V = C_V(T/\Theta_o)$ to the accuracy set by the sample-to-sample precision of the measurements and the limited range of volumes studied. With these qualifications, $\gamma = \gamma_o = 2.80$. The "pre-transition anomaly" corresponds to a sharp increase in γ in the 0.08K interval below the transition temperature. The accuracy with which the effect is determined does not justify a detailed analysis but, very approximately, it corresponds to an increase of γ to 3.7.

Except for the pretransition region, which is only about 0.08 K wide, Θ/Θ_o is a universal function of T/Θ_o for the limited range of molar volumes studied. Under these conditions C_V, S, $E-E_o$ and $\kappa_o^{-1} - \kappa^{-1}$ [E is the energy and $\kappa = -V^{-1}(\partial V/\partial P)_T$] depend only on the reduced temperature T/Θ_o. Table II gives smoothed values of these properties as functions of T/Θ_o. The volume dependence of these properties is determined by the volume dependence of Θ_o for which a relation is presented in the following section.

B. Comparison with Other Calorimetric Data

Edwards and Pandorf[13] have measured C_V for hcp ^{4}He at six molar volumes between 16.90 and 20.93 cm^3/ mole. They reported smoothed values of Θ which are compared with this work as plots of Θ/Θ_o vs. T/Θ_o in Fig. 10. To obtain values of Θ_o for their samples, $\Theta_{0.03}$ the value of Θ at T/Θ = 0.03, was read from curves drawn through their smoothed values and was divided by 0.9893, the value of $\Theta_{0.03}/\Theta_o$ obtained in this work. This procedure gave Θ_o values approximately 0.5% higher than the ones reported by Edwards and Pandorf for four samples, but produced no significant change in Θ_o for the 16.90 or 20.93 cm^3/mole samples. In comparison with their plot of $\Theta/\Theta_{0.05}$ vs. T/Θ (Fig. 3 of Ref. 13) this procedure reduced the sample-to-sample differences in their data at low temperatures, but increased it at high temperatures. Edwards and Pandorf's data for individual samples show systematic deviations from the Θ/Θ_o vs. T/Θ_o curve obtained in this work, but the deviations do not show a simple dependence on volume. The only volume studied by Edwards and Pandorf that falls in the range covered by this work is 20.93 cm^3/ mole. For that sample their values of C_V are in good agreement with ours below 1 K, but are approximately 5% higher near the melting point. The value of γ_o obtained by Edwards and Pandorf, 2.60, is in reasonable agreement with that obtained in this work.

Ahlers[23] has measured C_V for hcp ^{4}He at several molar volumes near 20.9 cm^3/mole, and, more recently[15], at nineteen molar volumes between 13.7 and 20.7 cm^3 mole. None of these measurements extends below 1 K and most of the more extensive second set of data are for temperatures

above approximately 1.4 K. The overlap with this work is therefore very limited. However, where a direct comparison can be made the agreement is very good, as shown in Fig. 10. In Fig. 10 Ahlers' data have been plotted using Θ_o values obtained by interpolation from values found in this work, so the comparison of his points with the curve is equivalent to a direct comparison of the two sets of C_V data.

Ahlers' measurements and ours are complementary in that our data, which extend to lower temperatures, permit an extrapolation to 0 K in the high molar volume region where his data do not. It is of interest to compare the temperature and volume dependence of the two sets of measurements in more detail because taken together they cover the entire temperature range of the hcp phase for a wide range of density. This could be done either in terms of the temperature and volume dependence of γ, or in terms of a Θ/Θ_o vs. T/Θ_o plot. In either case an extrapolation of Ahlers' data to 0 K is necessary (to obtain S for the calculation of $(\partial S/\partial V)_T$ in the first case, and to obtain Θ_o in the second). This extrapolation is hindered not only by the lack of data below 1.4 K but also by the effect of an impurity in the gas sample from which all but three of Ahlers' samples were prepared (see Figs. 8 and 9 of Ref. 15). For molar volumes near 14 cm^3/mole it was established that use of higher purity He reduced C_V in the region 1.5 to 3 K. The effect did not exceed 1% at any temperature, but it was well outside the precision of the measurements.

To obtain the properties at 0 K, Ahlers[28] introduced a parameter γ',

$$\gamma' \equiv \frac{(\partial \ln C_V/\partial \ln V)_T}{(\partial \ln C_V/\partial \ln T)_V}, \qquad (6)$$

which is probably more strongly temperature dependent than γ,[29] but which can be derived directly from C_V. γ' and γ are thermodynamically related but the calculation of γ from γ' requires an extrapolation of C_V to 0 K:

$$\gamma = \frac{1}{C_V}\int_0^T \gamma' \left(\frac{\partial C_V}{\partial T}\right)_V dT \quad . \qquad (7)$$

Ahlers calculated the volume and temperature dependence of γ in five steps: i. Eq. (6) was used to derive γ' from C_V. All C_V data were included. ii. γ' was extrapolated to 0 K to obtain $\gamma_o = 1.02 + 0.083\ V$ (at 0 K $\gamma' = \gamma$). For molar volumes below 15.91 cm^3/mole, γ' was essentially constant up to 2.5 K and γ_o was well defined, but for higher molar volumes the values of γ_o obtained become increasingly arbitrary. iii. Θ_o was obtained at V = 14.208 cm^3/mole by fitting C_V data for a pure sample to Eq. (1) and using Eq. (2). Θ_o and A_3 were then assigned for all volumes from the values at 14.208 cm^3/mole, the expression for γ_o, and Eqs. (2) and (5). iv. The C_V data were refitted by Eq. (1) with A_3 constrained to have the values determined in step iii. Data for $T/\Theta_o <$ 0.03 were omitted to reduce the effect of the impurity. v. Entropies were calculated from the new expressions for C_V and were differentiated to obtain γ from Eq. (4).

Ahlers' expression[28] for γ_o gives $\gamma_o = 2.74$ for the average value over the range of molar volumes studied in this work. This is in excellent

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agreement with our value, 2.80, even though Ahlers' relation for γ_o is to a large extent an extrapolation for $V \geq 16$ cm^3/mole.

Reduced Θ vs. T plots for several of Ahlers' samples are compared with this work in Fig. 11. The striking feature of Fig. 11 is that the curves for Ahlers' data at low molar volumes are closely similar to that for this work, but the curve for his 20.725 cm^3/mole sample, which is in the middle of our volume range, is not. It must be remembered, however, that Ahlers' data at 20.725 cm^3/mole are based on extrapolation, both in V and T, below $T/\Theta_o = 0.05$. In view of the very good agreement between our C_V data and Ahlers where direct comparisons are possible and between our value of γ_o and Ahlers' expression for γ_o, it seems reasonable to assume that Ahlers' interpolated curves for high volumes and low T/Θ_o are in error (but only by 1% in Θ) and that the temperature and volume dependence of C_V is represented by the curve found in this work for molar volumes near 20 cm^3/mole and by Ahlers' curves near 14 cm^3/mole. The difference between these curves corresponds to less than 0.2% in Θ for $T/\Theta_o < 0.038$. This is outside the scatter in either set of data, but not necessarily outside the combined systematic errors. The difference in shape between Ahlers' curve for 14.815 cm^3/mole and the curve obtained in this work is related to the different ratios A_5/A_3: Ahlers found small positive values for this ratio for the three samples between 13.718 and 14.815 cm^3/mole for which the temperature dependence of C_V was not influenced by the impurity effect; in this work A_5 was found to be zero, within the experimental error. It is possible that this difference is real and reflects a volume dependent property of hcp ^{4}He. Ahlers measurements of A_5 and A_3 are confined to a narrow volume range

and do not show a smooth volume dependence so it is not possible to extrapolate his values to the molar volumes studied in this work. Nevertheless, there is a clear indication of a decrease in his values of A_5/A_3 and an increase in A_7/A_3 with increasing molar volume, which is consistent with this work. It is perhaps worth mentioning that we do not believe that our measurements were influenced by the impurity effect discovered by Ahlers, for two reasons. First, the introduction of a much more effective trap in the cell filling line at liquid helium temperatures did not change the temperature dependence of C_V. Second, we found that C_V was fitted by a simple expression of the expected form--three terms of Eq. (1) over a wide range of temperature. Ahlers found that this was not the case for the impure samples. It should also be emphasized that the deviations from a common curve for Θ/Θ_o vs. T/Θ_o found in this work (see Fig. 8) do not correspond to those found by Ahlers (see Fig. 11 or Fig. 11 of Ref. 15). The range of molar volumes covered in this work was too small to observe the gradual deviations found by Ahlers. The deviations that we did observe occurred in a much narrower temperature interval and would not have been apparent in Ahlers' data which are less closely spaced in temperature and molar volume.

Although Ahlers' relation for γ_o gives good agreement with the value of γ_o observed in this work, the agreement with Θ_o values, which are determined more accurately, is less satisfactory. Ahlers' relation for γ_o and his value of Θ_o at 14.208 cm^3/mole predict Θ_o values that are about 1% higher than those measured. This corresponds to a discrepancy of 3% in C_V, which is appreciably greater than our expected experimental error. The Θ_o values determined by Edwards and Pandorf[13] are also, on

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the average, lower than those calculated from Ahlers' relation. The discrepancies in Θ_o at high molar volumes could be eliminated without changing Ahlers' values of γ_o at lower molar volumes by introducing a quadratic term in the relation for $\gamma_o(V)$. The accuracy with which γ_o can be determined, however, does not seem to justify this complication. We have therefore derived a modified relation for γ_o. It has the form suggested by Ahlers and gives the same value of γ_o at 15.000 cm^3/mole, which is near the middle of the range of molar volumes in which his γ_o values appear to be most accurate, but it extrapolates to the Θ_o values measured in this work. The relation is

$$\gamma = 0.8114 + 0.09690V \ , \tag{8}$$

and the derived relation for Θ_o is

$$\Theta_o = 2340\ V^{-0.8114} e^{-0.09690V} \tag{9}$$

Eq. (9) accurately reproduces the Θ_o values determined in this work and those determined by Ahlers for his higher purity samples near 14 cm^3/mole. It also gives better agreement than the corresponding equation derived by Ahlers with Edwards and Pandorf's Θ_o values. Fig. 12 summarizes the comparison of Eq. (9) with these and with other experimental data, and shows that the agreement is in general within the scatter of the data. At 20.7 cm^3/mole, the middle of the volume range covered in this work, Eq. (8) gives $\gamma_o = 2.82$. This is in slightly better agreement than the value derived from Ahlers relation with our experimental value, but the difference is not significant relative to the experimental accuracy. Eq. (8) also reproduces Ahlers' values of γ_o for molar volumes less than 17 cm^3/mole to within approximately 1%. At higher molar volumes the discrepancies with Ahlers' data

are greater, but there the probable error in his values is also greater.

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C. Comparison with Elastic Constants

Crepeau et al.[31] have recently measured the velocities of longitudinal and transverse sound waves in oriented single crystals of hcp ^{4}He at 1.32 K and 20.97 cm^3/mole. Their data make available values for each of the five elastic constants, and these have been used by Strauss[32] and by Wanner and Franck[33] to derive values of Θ_o of 26.0 and 25.87 K, respectively. These values are in excellent agreement with the value 25.96 given by Eq. (9) and, therefore, with this work.

D. Comparison with Measurements of $(\partial P/\partial T)_V$

Techniques based on the use of sensitive strain gauges have recently been used to measure $(\partial P/\partial T)_V$ for hcp ^4He[34,35]. Since $(\partial P/\delta T)_V = (\partial S/\delta V)_T$, these data can be used with experimental C_V data and Eq. (4) to obtain values of γ without the necessity of differentiating the experimentally measured quantities with respect to volume. The values of γ so obtained can then be compared with those derived from the volume dependence of C_V as a test of the consistency of the measurements.

Henriksen et al.[35] give plots of $\Theta/\gamma^{1/3}$ [which can be derived from $(\partial P/\partial T)_V$] vs T for three molar volumes between 18.75 and 20.16 cm^3/mole. Extrapolation of their data to 0 K and the use of Θ_o values from Eq. (9) gives values of γ that vary between 5% greater and 15% smaller than those calculated from Eq. (8). However, the spread in their values of $\Theta_o/\gamma^{1/3}$ is of the order of 4%, so the discrepancies are comparable to the precision of the data.

Jarvis, Ramm and Meyer have given tables of smoothed values of $(\partial P/\partial T)_V$ as a function of temperature for eight molar volumes between 17.77 and 20.72 cm^3/mole.[34] Since γ is expected to be only weakly temperature dependent, it is reasonable to try to fit the temperature dependence of $(\partial P/\partial T)_V$ at low temperatures with an expression of the form of Eq. (1). Plots of $T^{-3}(\partial P/\partial T)_V$ vs T^2 and T^4 suggest that, like C_V, $(\partial P/\partial T)_V$ is represented by a sum of T^3 and T^7 terms in the low temperature limit. Fig. 13 shows plots of this type for the two highest molar volumes and includes the straight lines calculated from interpolated values of A_3

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and A_7 and values of γ_o derived from Eq. (8). A more general comparison of $(\partial P/\partial T)_V$ and C_V, for the same two molar volumes, is presented in Fig. 14. In Fig. 14 the values of $T^{-3}(\partial P/\partial T)_V$ given by Jarvis, Ramm and Meyer are compared with those calculated from C_V and the values of γ_o given by Eq. (8). The values of C_V were obtained by smoothing and interpolating the experimental data in both volume and temperature. For each molar volume the upper and lower curves represent, respectively, values of γ_o 2% greater and 2% less than those given by Eq. (8). Most of the $(\partial P/\partial T)_V$ points fall between the two curves calculated from C_V, indicating agreement between γ and the γ_o from Eq. (8) to within 2%. There is, however, an indication, previously noted by Jarvis, Ramm and Meyer, of a minimum in γ near 1 K. This effect appears to be outside the combined experimental errors, but it should be noted that it is very sensitive to temperature scale errors. Both sets of data [C_V and $(\partial P/\partial T)_V$] involve temperature derivatives, and a comparison of the type presented in Fig. 14 can be strongly influenced by small errors in the temperature scales if those errors have different temperature dependences.

IV. Summary

Apparatus that is free of the major problems associated with the filling capillary has been developed for low-temperature C_V measurements on condensed phases under pressure. The heat capacity of hcp ^{4}He has been measured for molar volumes near the maximum volume for thermodynamic stability of the phase. The measurements extend to low enough temperatures to permit reliable extrapolations to 0 K and the determination of Θ_o as a function of volume and of the entropy as a function of temperature and volume. Over the limited range of molar volumes studied, and excluding a 0.08 K interval preceding the transition to a mixed phase, Θ/Θ_o is a universal function of T/Θ_o. This function is very similar to that determined by Ahlers[15] for $T/\Theta_o < 0.04$ and smaller molar volumes, but is significantly different from that deduced by Ahlers for the temperature and volume region covered in this work by extrapolation of his data from higher temperatures. Ahlers' data[15], however, are entirely consistent with ours as shown by the good agreement between γ_o values and between C_V values where they can be compared directly. Together, the two sets of measurements give the volume and temperature dependence of C_V for molar volumes greater than 13.7 cm^3/mole and temperatures between 0 K and the transition temperature. Over this volume range γ_o and Θ_o are given by Eqs. (8) and (9), and for $T/\Theta_o < 0.04$ a number of thermodynamic properties are functions only of T/Θ_o, as given in Table II. These relations are probably valid at lower molar volumes, to within the probable accuracy of other work.

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Table I. Low temperature heat capacity coefficients [see Eq. (1)] and Θ_o for hcp ^{4}He.

Sample	V(cm^3/mole)	A(mJ/mole-K^4)	C(mJ/mole-K^8)	Θ_o(K)
26	20.960_2	109.65	11.38	26.074
18	20.921_5	109.05	10.95	26.122
29	20.903_1	107.15	10.45	26.280
15	20.900	108.15	10.42	26.194
14	20.846	105.85	9.60	26.383
13	20.742	101.55	8.57	26.750
42	20.705	98.85	8.56	26.990
9	20.521	92.60	8.0	27.586
31	20.456	89.30	6.66	27.921

$$T < 1.25; \quad C_V = AT^3 + CT^7$$

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Table II. Reduced thermodynamic properties of hcp ^{4}He at low densities.

T/Θ_o	Θ/Θ_o	$10^3 C_v/R$	$10^3 S/R$	$10^3(E-E_o)/RT$	$(\frac{1}{\kappa_o} - \frac{1}{\kappa})\frac{V}{RT}$
0.	1.0000	0.	0.	0.	0.
.002	1.0000	.0019	.0006	.0005	.0000
.004	.9999	.0150	.0050	.0037	.0001
.006	.9998	.0505	.0168	.0126	.0003
.008	.9997	.1198	.0399	.0299	.0006
.010	.9996	.2340	.0780	.0585	.0012
.012	.9995	.4046	.1348	.1011	.0021
.014	.9991	.6432	.2141	.1606	.0033
.016	.9988	.9610	.3198	.2399	.0050
.018	.9980	1.3716	.4557	.3419	.0071
.020	.9972	1.8860	.6258	.4696	.0098
.022	.9962	2.5179	.8342	.6261	.0131
.024	.9950	3.2808	1.0849	.8146	.0171
.026	.9932	4.1939	1.3825	1.0384	.0218
.028	.9911	5.2715	1.7316	1.3011	.0275
.030	.9883	6.5389	2.1373	1.6069	.0342
.032	.9850	8.0159	2.6051	1.9600	.0420
.034	.9809	9.7358	3.1413	2.3655	.0512
.036	.9760	11.7319	3.7530	2.8291	.0619
.038	.9701	14.0511	4.4478	3.3572	.0744
.040	.9637	16.7172	5.2347	3.9569	.0890
.042	.9569	19.7678	6.1228	4.6358	.1057
.044	.9493	23.2786	7.1217	5.4018	.1250
.046	.9416	27.2573	8.2421	6.2634	.1471
.048	.9334	31.7929	9.4961	7.2308	.1723
.050	.9251	36.9108	10.8958	8.3138	.2009
.052	.9162	42.7414	12.4543	9.5231	.2338
.054	.9076	49.2388	14.1865	10.8711	.2704
.056	.8989	56.5248	16.1075	12.3701	.3115
.058	.8900	64.7028	18.2313	14.0313	.3580
.060	.8818	73.6466	20.5724	15.8663	.4086
.062	.8735	83.5979	23.1464	17.8876	.4651
.064	.8650	94.6893	25.9743	20.1130	.5284
.066	.8562	107.0817	29.0752	22.5582	.5995
.068	.8480	120.5448	32.4694	25.2397	.6765
.070	.8400	135.2899	36.1729	28.1700	.7609

FIGURE CAPTIONS

Figure 1 The sample cell and inner part of the cryostat.

Figure 2 Details of the sample cell design.

Figure 3 Heat capacity of empty cell number 1, shown as fractional deviations from a three parameter equation. The different symbols represent measurements made at different times. In later measurements, on the other cells, the precision was improved by approximately a factor of three.

Figure 4 The gas handling system. A 4.2 K trap was inserted in the line to the cell in the later measurements.

Figure 5 Isotherms for ^{4}He constructed from quantities reported in Ref. 21. ΔV_m and ΔV_{tr} represent the volume change at melting of the hcp phase and the volume change at the transition from the hcp to the bcc phase.

Figure 6 The heat capacity of hcp ^{4}He plotted as C_V/T^3 vs. T.

Figure 7 The heat capacity of hcp ^{4}He plotted as C_V/T^3 vs T^4 for T< 1.2 K.

Figure 8 Reduced Debye temperature as a function of reduced temperature for hcp He^4. Only the later runs, for which the precision is highest, are shown.

Figure 9 $Log_{10}\Theta_o$ vs $log_{10}V$ for hcp ^{4}He.

Figure 10 Comparison of C_V, represented by Θ, as measured in this work, by Edwards and Pandorf (Ref. 13) and by Ahlers (Refs. 15 and 23). See text for description of Θ_o values used.

Figure 11 Temperature dependence of Θ as determined in this work and at several molar volumes by Ahlers (Ref. 15).

Figure 12 Percentage deviations of Θ_o values from Eq. (9). (Note the non-linear scale for the deviations.) In the measurements by Heltemes and Swenson (Ref. 11) and by Franck (Ref. 12) anomalous behavior was found at low temperatures and the two sets of points coyrespond to different analyses of the data. Four of the Θ_o values reported by Edwards and Pandorf (Ref. 13) have been revised upwards by approximately 0.5%, as discussed in the text. Dugdale and Franck (Ref. 30) reported values of Θ at $\Theta/T = 18$, and approximate values of Θ_o were estimated with the aid of Fig. 11. The dashed curve represents the expression (Eq. 13 of Ref. 15) deduced by Ahlers for Θ_o. The Θ_o value calculated from elastic constants is from Refs. 31-33.

Figure 13 Temperature dependence of $(\partial P/\partial T)_V$ in the low-temperature limit. The straight lines representing this work and the circles representing the smoothed data reported by Jarvis, Ramm, and Meyer (Ref. 34) are to be read against the T^4 scale at the bottom of the figure. The squares represent the same data points as the circles but are plotted against the T^2 scale at the top of the figure.

Figure 14 Comparison of $(\partial P/\partial T)_V$ as calculated from this work with that measured by Jarvis, Ramm, and Meyer (Ref. 34). The circles and squares represent the smoothed data reported by Jarvis, Ramm and Meyer. For each volume the two curves represent $(\partial P/\partial T)_V$ calculated from smoothed C_V data with γ values 2% higher and 2% lower than that given by Eq. 8.

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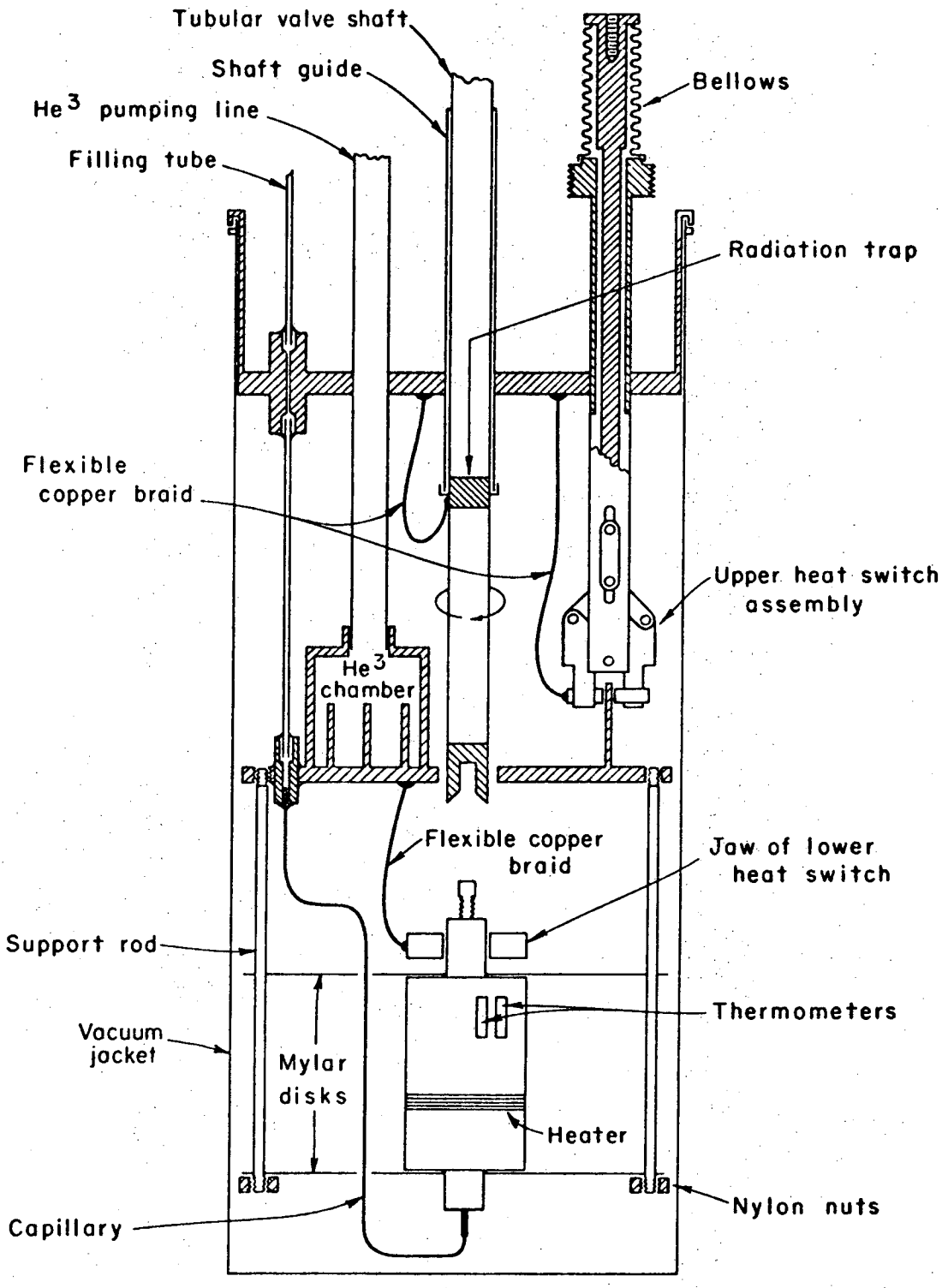

Figure 1

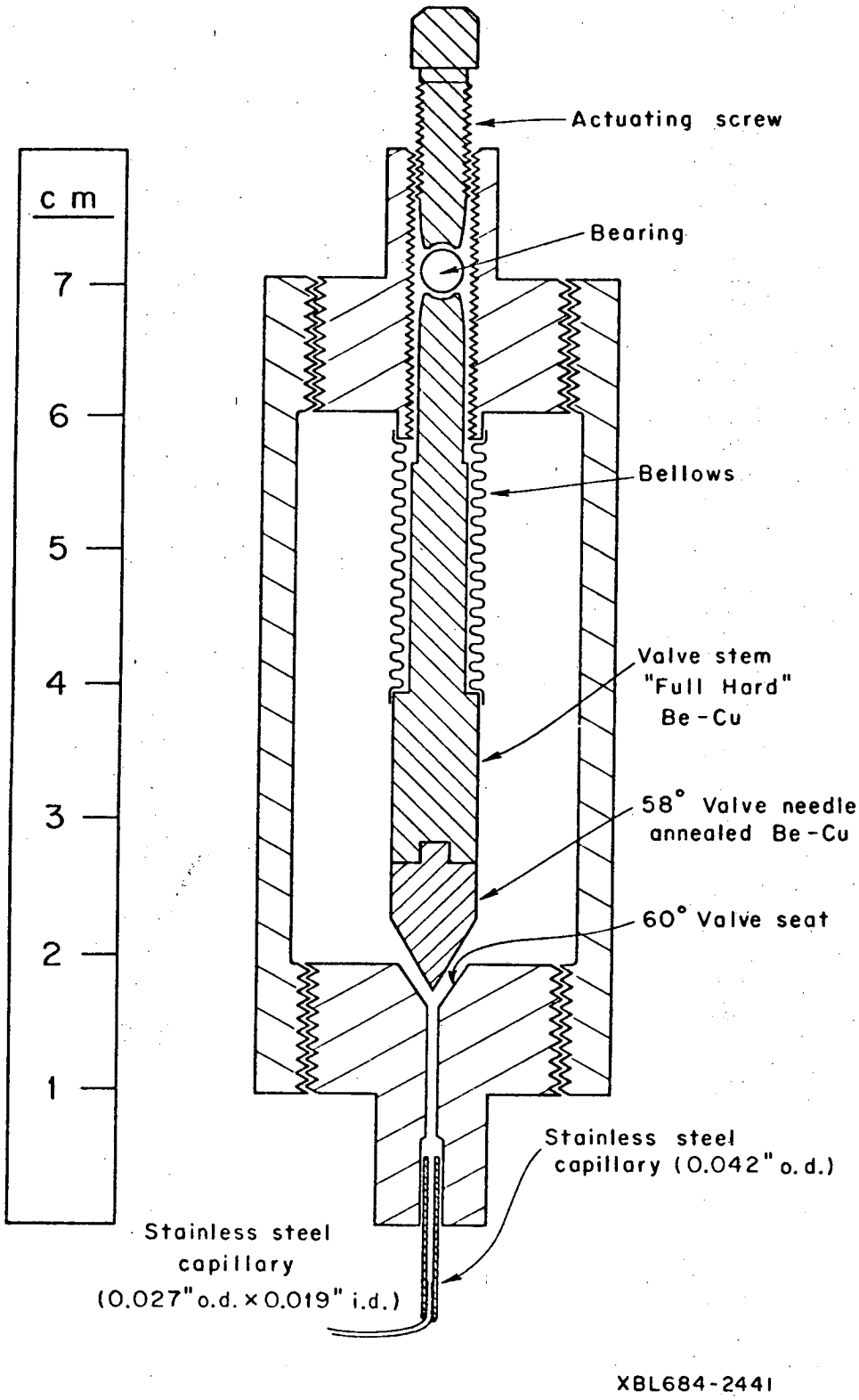
cm
7
6
5
4
3
2
1
Actuating screw
Bearing
Bellows
Valve stem
"Full Hard"
Be-Cu
58° Valve needle
annealed Be-Cu
60° Valve seat
Stainless steel
capillary (0.042" o.d.)
Stainless steel
capillary
(0.027" o.d. × 0.019" i.d.)
XBL684-2441

Figure 2

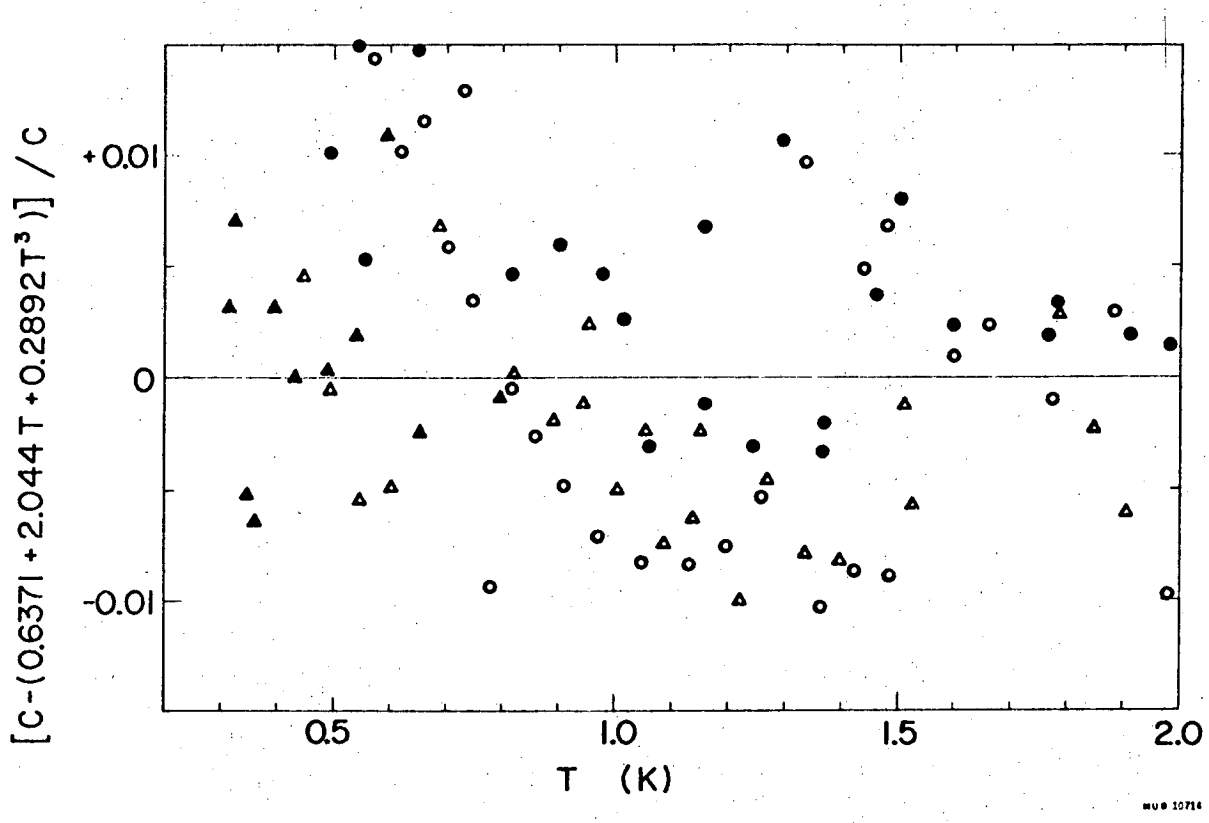

Figure 3

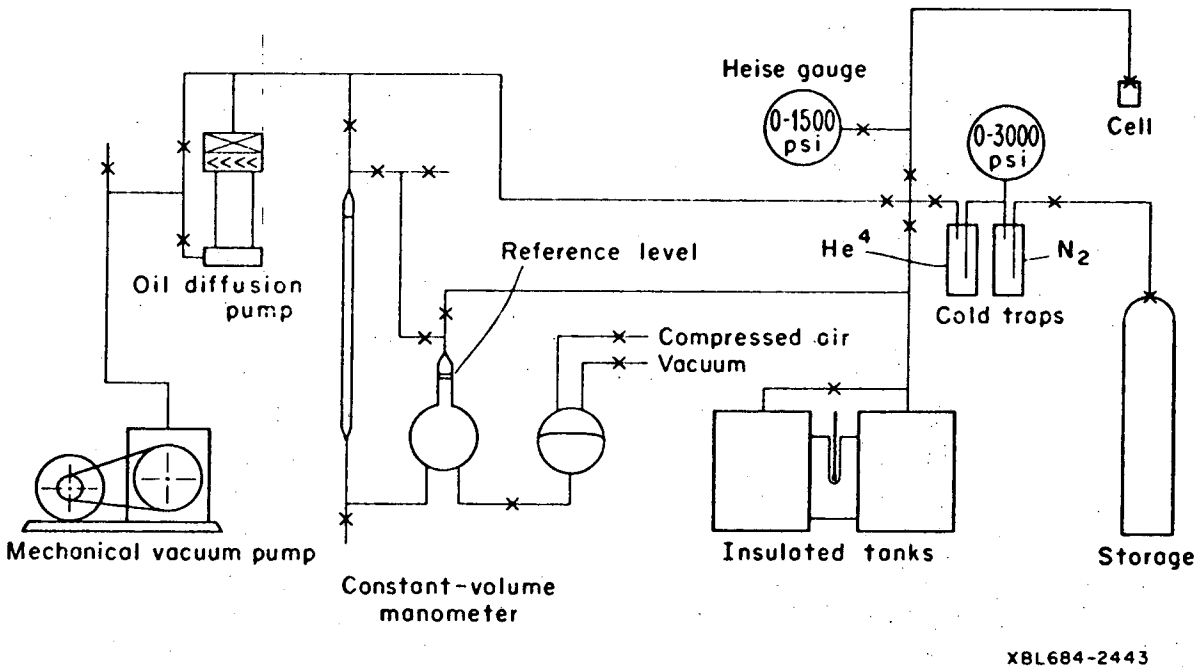
Heise gauge
0-1500 psi
0-3000 psi
Cell
Oil diffusion pump
Reference level
He 4
N2
Cold traps
Compressed air
Vacuum
Mechanical vacuum pump
Constant-volume manometer
Insulated tanks
Storage
XBL684-2443

Figure 4

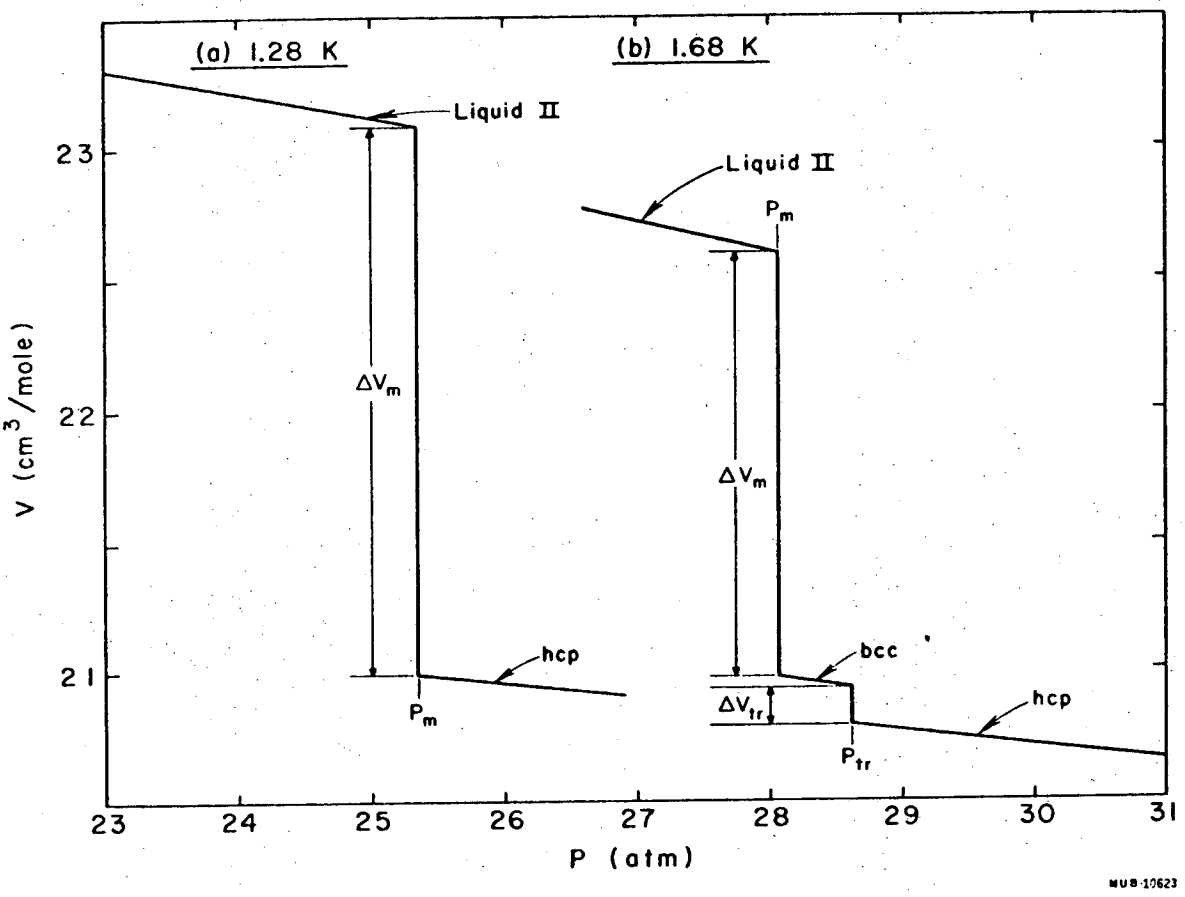
(a) 1.28 K
(b) 1.68 K
Liquid II
Liquid II
P_m
ΔV_m
ΔV_m
hcp
bcc
hcp
ΔV_{tr}
P_m
P_{tr}
V (cm^3/mole)
P (atm)
23
22
21
23
24
25
26
27
28
29
30
31
MUB-10623

Figure 5

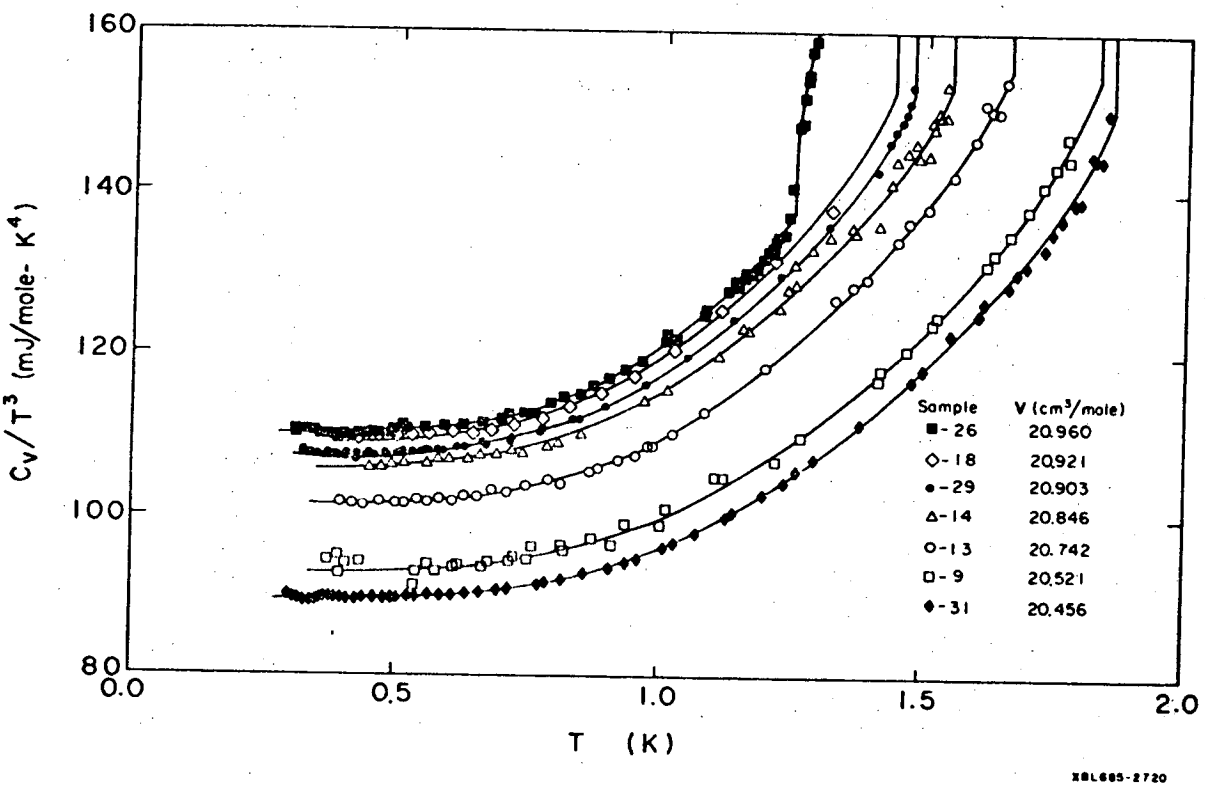
160
140
120
100
80
0.0
0.5
1.0
1.5
2.0
C_v/T^3 (mJ/mole- K^4)
T (K)
Sample
V (cm^3/mole)
■-26 20.960
◇-18 20.921
●-29 20.903
△-14 20.846
○-13 20.742
□-9 20.521
◆-31 20.456
XBL685-2720

Figure 6

0 0 0 0 3 8 0 3 7 2

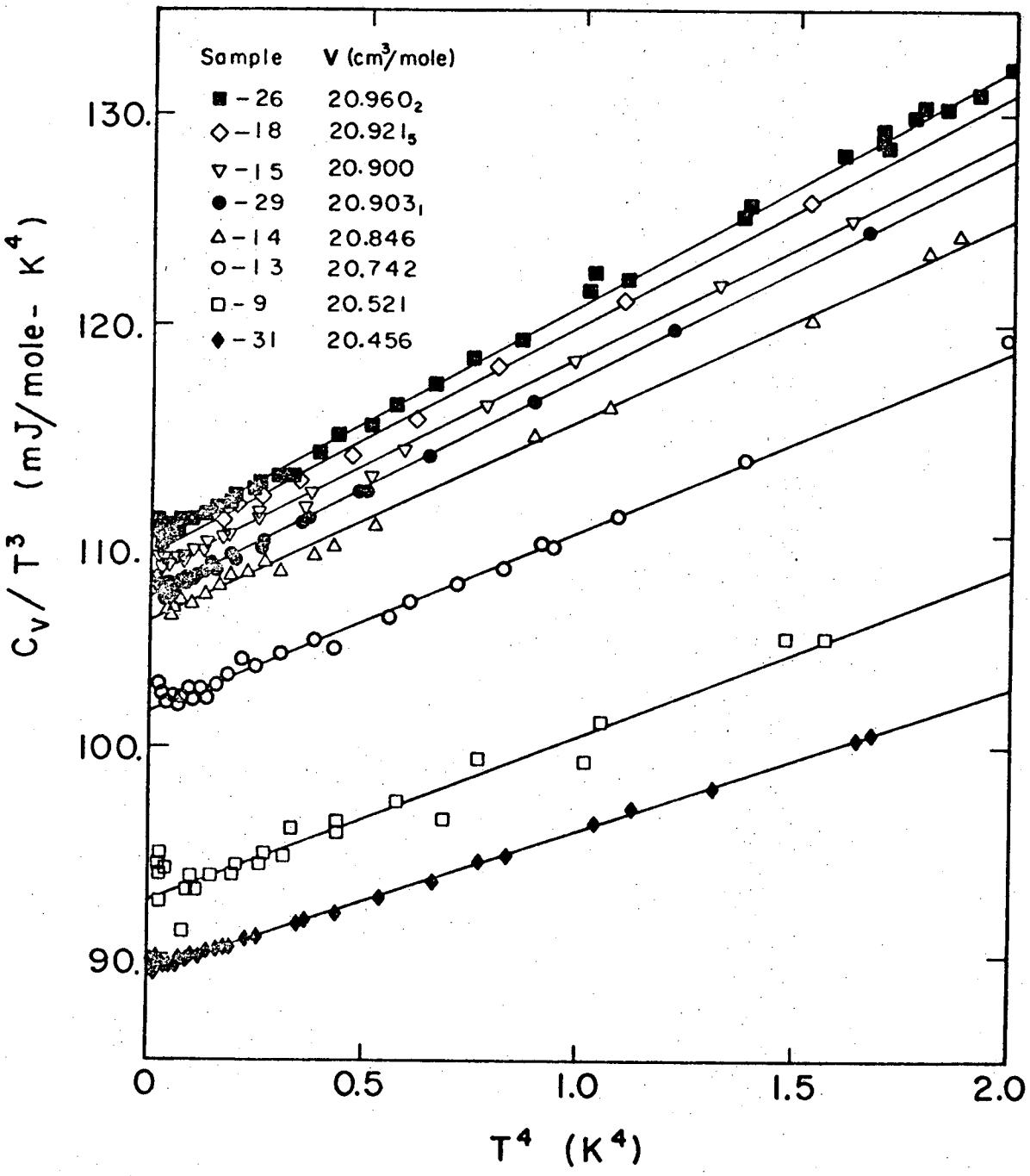

Figure 7

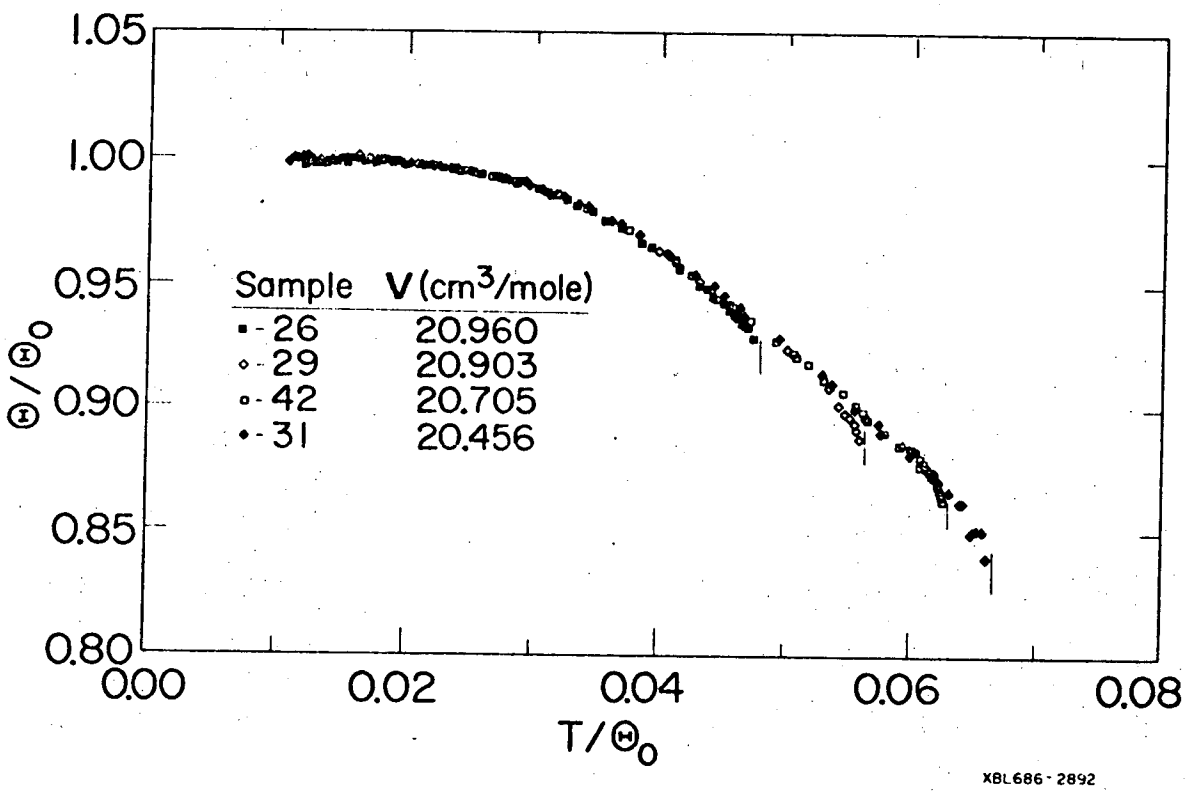
1.05
1.00
0.95
0.90
0.85
0.80
Θ/Θ0
0.00
0.02
0.04
0.06
0.08
T/Θ0
Sample V(cm3/mole)
▪-26 20.960
◇-29 20.903
▫-42 20.705
◆-31 20.456
XBL686-2892

Figure 8

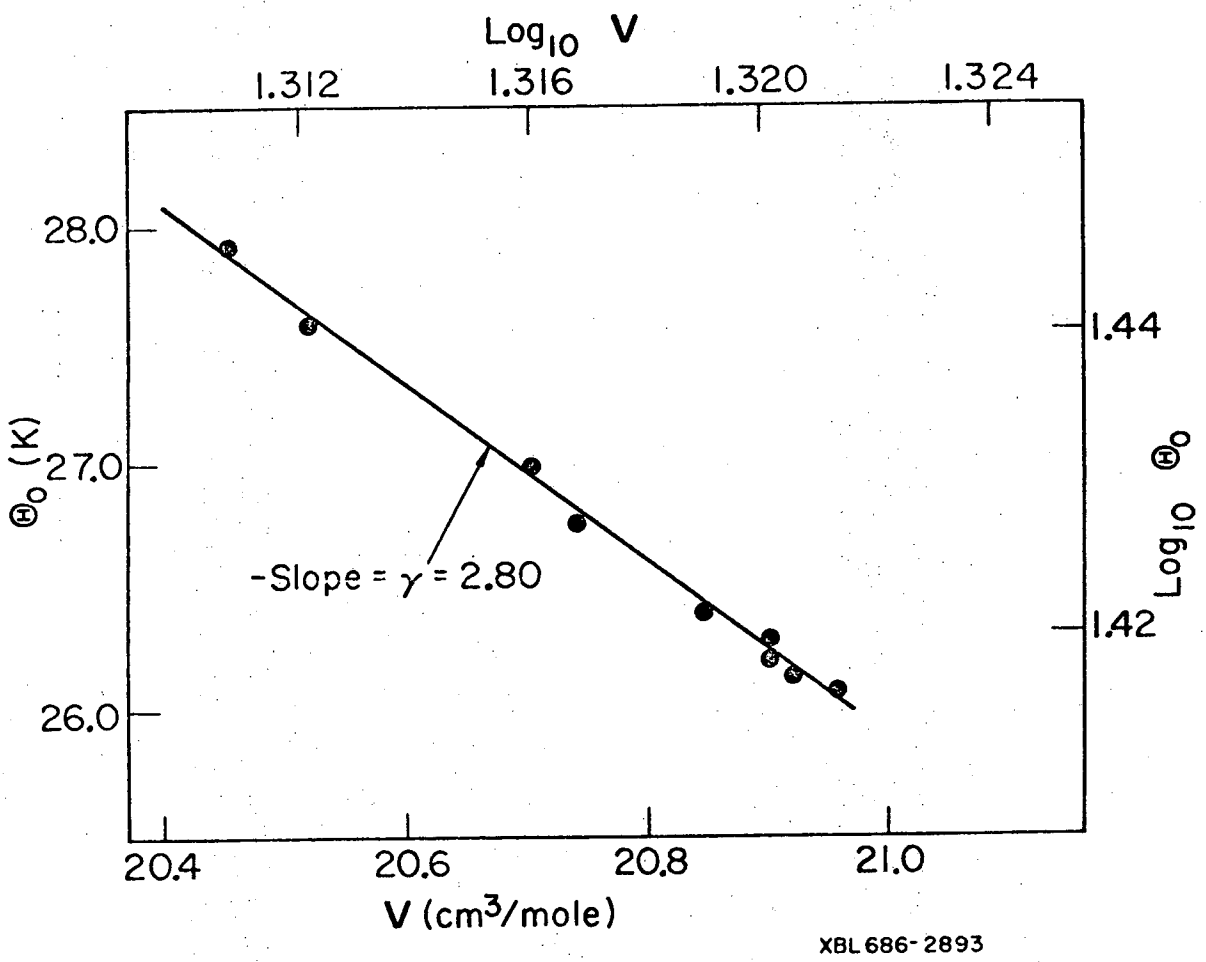
Log10 V
1.312
1.316
1.320
1.324
28.0
27.0
26.0
Θo (K)
1.44
1.42
Log10 Θo
-Slope = γ = 2.80
20.4
20.6
20.8
21.0
V (cm3/mole)
XBL 686-2893

Figure 9

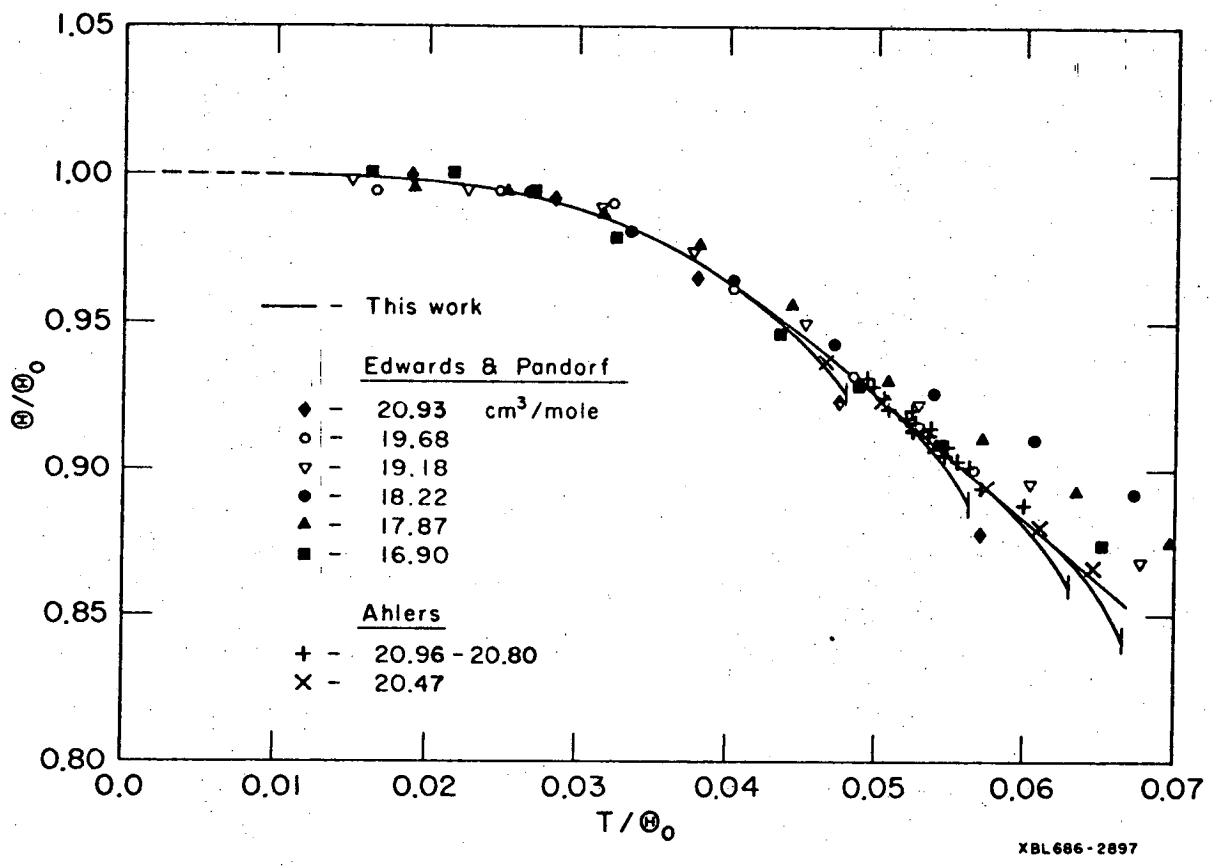
1.05
1.00
0.95
0.90
0.85
0.80
0.0
0.01
0.02
0.03
0.04
0.05
0.06
0.07
Θ/Θ₀
T/Θ₀
— This work
Edwards & Pandorf
◆ - 20.93 cm³/mole
○ - 19.68
▽ - 19.18
● - 18.22
▲ - 17.87
■ - 16.90
Ahlers
+ - 20.96 - 20.80
× - 20.47
XBL686-2897

Figure 10

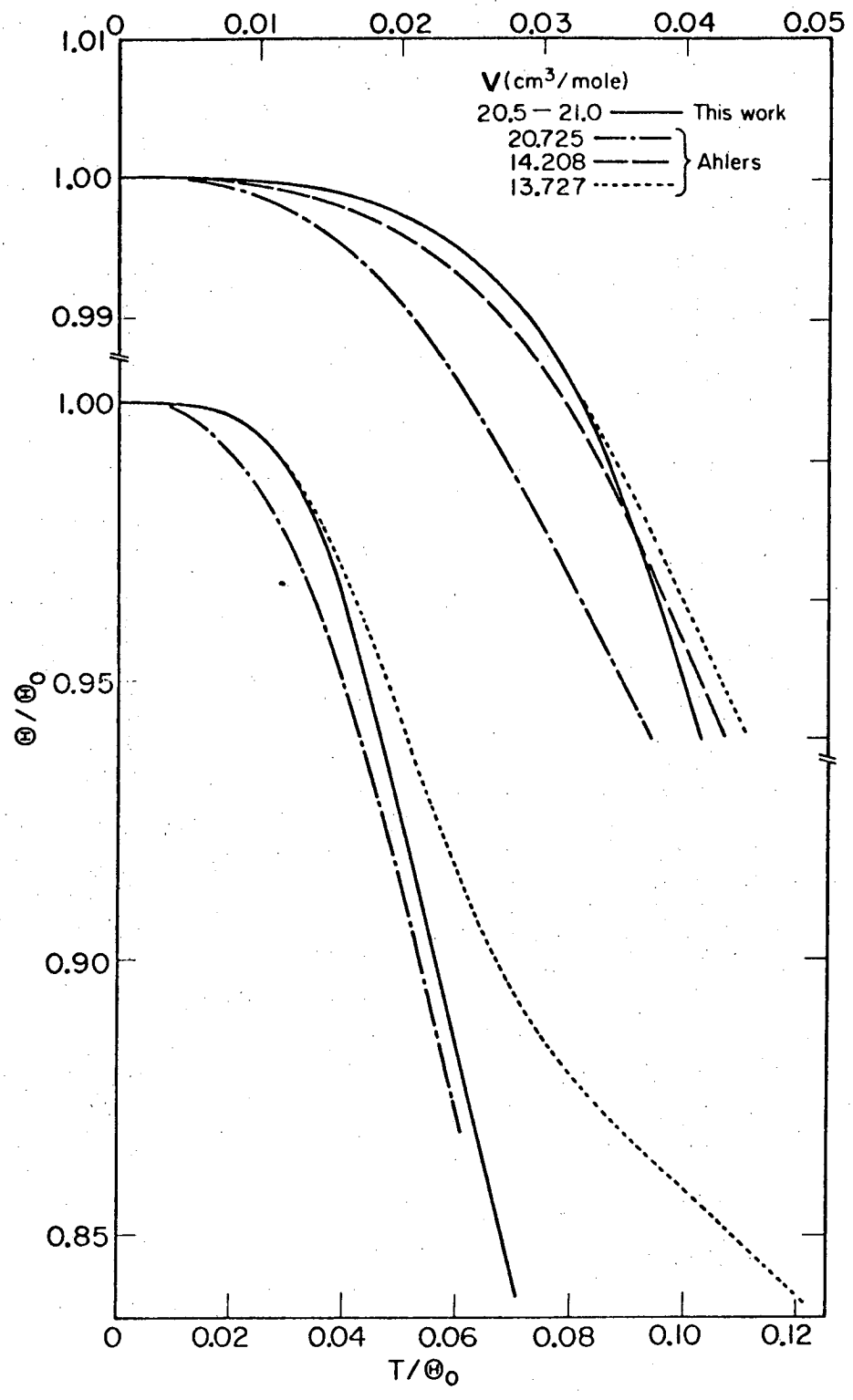
V(cm³/mole)
20.5 — 21.0 This work
20.725
14.208 Ahlers
13.727
1.01
1.00
0.99
1.00
0.95
0.90
0.85
Θ/Θ₀
0
0.01
0.02
0.03
0.04
0.05
0
0.02
0.04
0.06
0.08
0.10
0.12
T/Θ₀
XBL727-3611

Figure 11

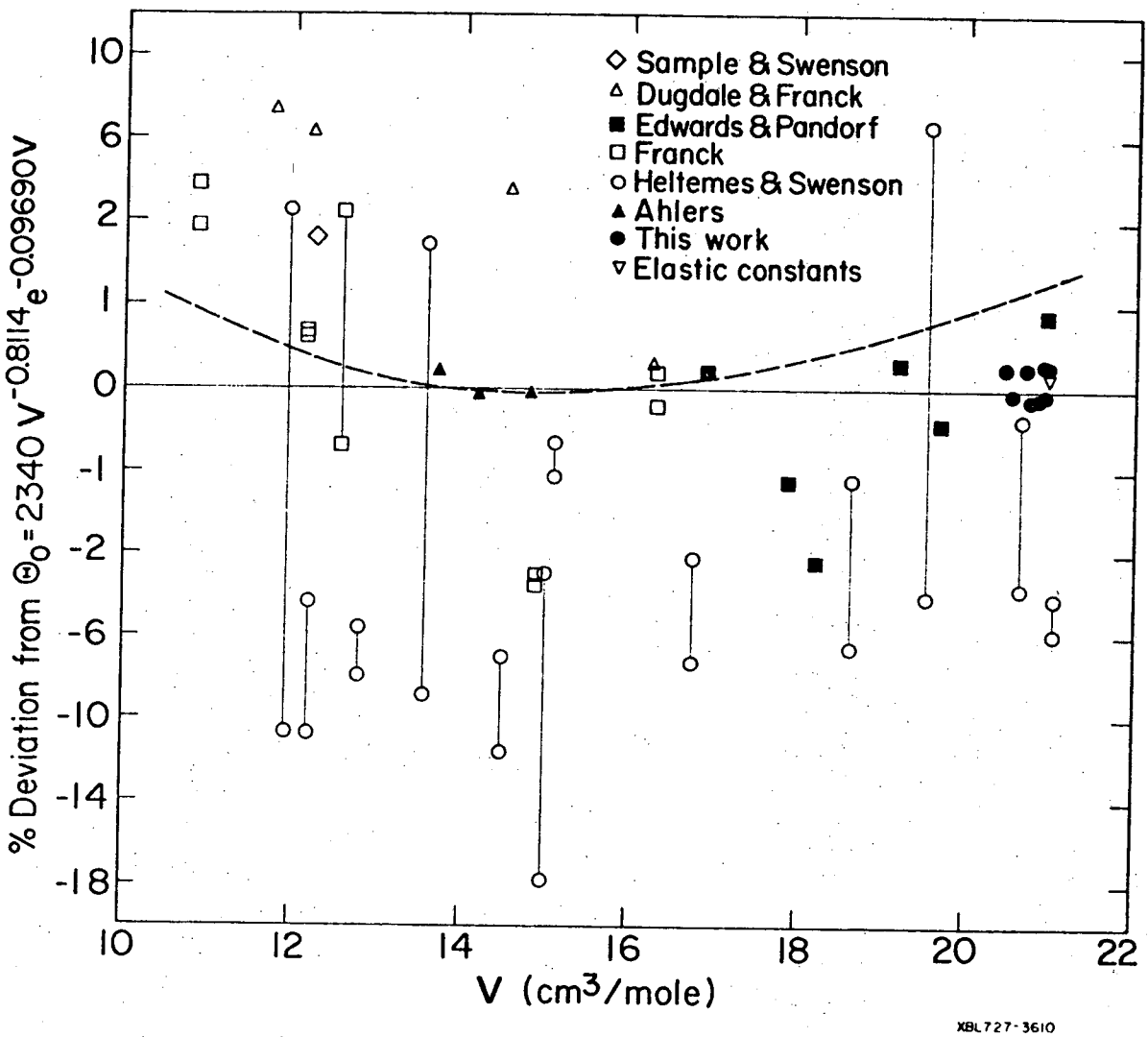
Sample & Swenson
Dugdale & Franck
Edwards & Pandorf
Franck
Heltemes & Swenson
Ahlers
This work
Elastic constants
% Deviation from $\Theta_0 = 2340\, V^{-0.8114} e^{-0.09690V}$
V (cm³/mole)
10
6
2
1
0
-1
-2
-6
-10
-14
-18
10
12
14
16
18
20
22
XBL727-3610

Figure 12

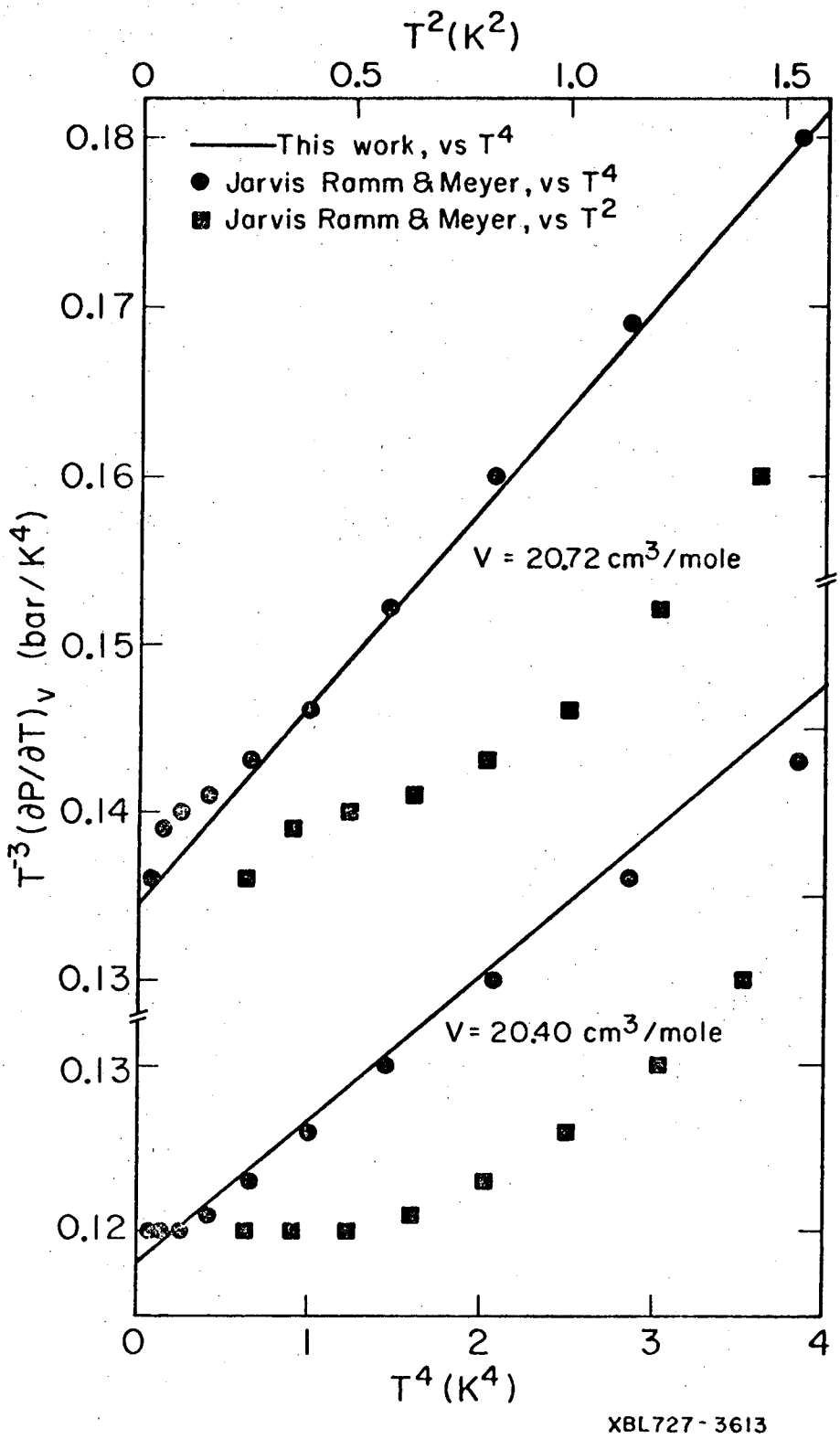
$T^2(K^2)$
0
0.5
1.0
1.5
0.18
0.17
0.16
0.15
0.14
0.13
0.13
0.12
This work, vs T^4
Jarvis Ramm & Meyer, vs T^4
Jarvis Ramm & Meyer, vs T^2
V = 20.72 cm^3/mole
V = 20.40 cm^3/mole
$T^{-3}(\partial P/\partial T)_V$ (bar/K^4)
0
1
2
3
4
$T^4(K^4)$
XBL727-3613

Figure 13

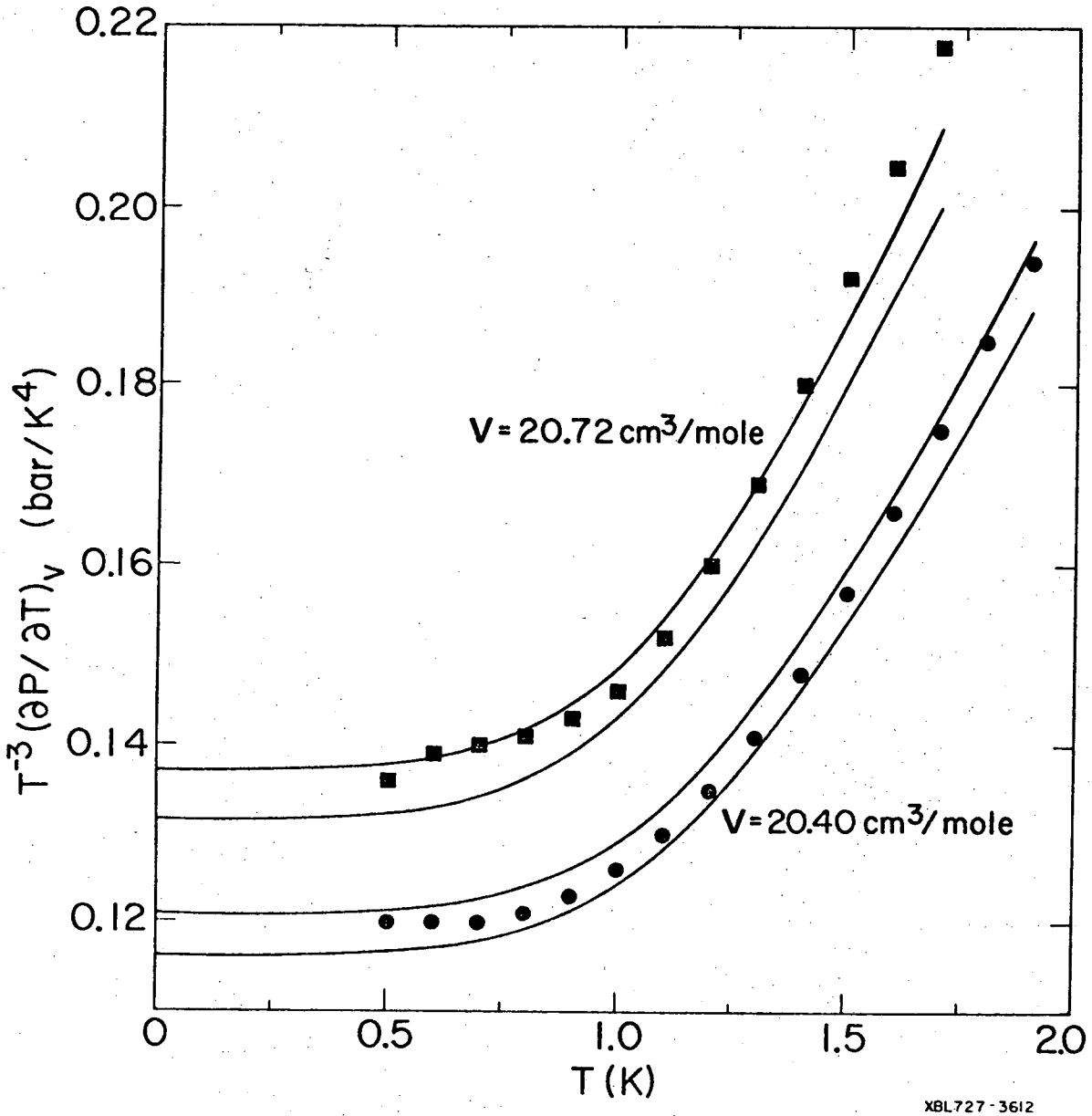
0.22
0.20
0.18
0.16
0.14
0.12
$T^{-3}(\partial P/\partial T)_V$ (bar/K^4)
V = 20.72 cm^3/mole
V = 20.40 cm^3/mole
0
0.5
1.0
1.5
2.0
T (K)
XBL727-3612

Figure 14

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