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THE LATTICE HEAT CAPACITY OF SOLID HYDROGEN

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Submitted for publication in
J. Chem. Physics

UCRL-11045

UNIVERSITY OF CALIFORNIA
Lawrence Radiation Laboratory
Berkeley, California

AEC Contract No. W-7405-eng-48

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Guenter Ahlers

December 1963

THE LATTICE HEAT CAPACITY OF SOLID HYDROGEN*†

by

Guenter Ahlers**&
Inorganic Materials Research Division of
Lawrence Radiation Laboratory and Department of Chemistry
University of California, Berkeley, California

ABSTRACT

The lattice heat capacity of solid hydrogen was measured at constant pressure, and at three constant volumes. The measurements extend from 2°K to the triple point for the constant pressure data, from 2°K to the melting temperature at 22.56 cc/M, and from 4°K to 20°K at 19.83 and 18.73 cc/M. The Debye thetas at 0°K are 128°K, 169°K, and 189°K at 22.56, 19.83, and 18.73 cc/M respectively. The temperature dependences of the Debye thetas are similar to those for other simple solids.

Some information about other thermodynamic properties was obtained from the heat capacities. The isothermal compressibility at 16.35°K at the melting pressure is essentially the same as at 4.2°K at the same pressure. The thermal expansion

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*Based on part of a thesis submitted in partial fulfillment of the requirements for the PhD Degree, University of California, Berkeley, California.

†This research was supported by the United States Atomic Energy Commission.

**National Science Foundation Predoctoral Fellow, 1960-61, and General Electric Predoctoral Fellow, 1961-62.

&Present address: Bell Telephone Laboratories, Incorporated, Murray Hill, New Jersey.

coefficient at 82 atm appears to have a maximum at about 12°K. At zero pressure the thermal expansion coefficient is approximately proportional to the temperature. The thermodynamic expression for the Grüneisen relation is not obeyed in solid hydrogen.

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I. INTRODUCTION

The lattice heat capacities of the solidified gases are of considerable interest in relation to the theory of lattice dynamics. From this theoretical point of view the quantity of interest is the heat capacity at constant volume C_v. Aside from fairly extensive measurements on solid helium[1-6] and rather limited measurements on hydrogen,[7] all data available so far refer to the heat capacity at the saturation vapor pressure, or essentially constant and zero pressure C_p. Whereas the correction of constant pressure data to constant volume conditions is small at low temperatures for the heavier solidified gases, it can be expected to become very appreciable for the lighter elements He, H_2, D_2, and Ne. Even for argon above 40°K this correction is large enough to cause considerable

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uncertainty in C_v.[8] The difference between C_p and C_v is given by

$$C_p - C_v = \frac{\alpha^2 VT}{K} \tag{1}$$

where α is the thermal expansion coefficient and K is the isothermal compressibility. Thus, if α and K are known with sufficient accuracy, and if furthermore $C_p - C_v$ is small, then reasonable estimates of C_v can be made from the C_p data. These conditions seem to be reasonably met at low temperatures in the case of argon and krypton.[8] It must, however, be further realized that C_v obtained from C_p by means of Eq. (1) refers to the volume of the substance at the pressure and temperatures of the C_p measurements. This C_v will be designated as $C_v(V_T)$. The quantity which it is desirable to obtain from a theoretical point of view is $C_v(V_o)$, i.e., C_v at the molar volume at 0°K. Thus, a further correction to $C_v(V_T)$ is necessary, and is given by

$$\theta(V_o) = \theta(V_T)(V_T/V_o)^{\gamma} \tag{2}$$

in terms of the Debye θ. Here γ is the Grüneisen constant

$$\gamma = -\left(\frac{\partial \ln \theta}{\partial \ln V}\right)_T. \tag{3}$$

The Grüneisen constant appears to be of the same magnitude for all substances, and generally has a value between 2 and 4. However, its exact value is usually not known and there is no guarantee that γ is indeed a constant.

In view of the need for C_v data on simple crystals, and the difficulties involved in deducing these data from C_p, it is most desirable to obtain direct measurements at constant volume. From the lattice dynamical point of view, the most urgent need is for data on the heavier rare gases. Accurate theoretical treatment of lattice dynamics is at the present limited to substances with negligible zero point energy and anharmonicity.[9] Even for argon the zero point energy amounts to 8% of the cohesion energy at 0°K.[8] For hydrogen this figure is approximately 47%,[10] and any harmonic theory which neglects the effect of zero point energy cannot be expected to yield reasonable results. On the other hand, comparison of data on the lighter elements with theory may be expected to yield some information on the manner in which zero point energy manifests itself. From the experimental point of view, the heavier rare gases present more severe difficulties because the relative magnitudes of the thermal expansion of the solid, the compressibility of the fluid, and the melting temperature are such that rather high pressures would be required to reach molar volumes in the fluid smaller than V_o for the solid. Hydrogen, however, does not present any unreasonable problems.

Aside from the lattice dynamical interest in the heat capacity of the solidified gases, the thermodynamic properties of those solids which may be expected to show considerable quantum effects are of interest for their own sake. There is some evidence that solid helium exhibits rather unusual

properties near the solid-liquid equilibrium pressure.[11] In particular its thermal expansion coefficient is believed to be negative over certain temperature ranges. It is of interest to see if similar unusual behavior can be observed in other solids, or if these properties are peculiar to solid helium.

The lattice heat capacity of hydrogen was thus measured at three molar volumes, and at constant pressure. The temperature range of the measurements extends from liquid helium temperatures either to the melting point, or to 20°K.

II. APPARATUS AND PROCEDURES

A. General Description

The apparatus used for these measurements was described elsewhere.[12]

The hydrogen was prepared electrolytically, passed over silica gel at 78°K, and stored in steel cylinders at about 100 atm pressure. One day prior to an experiment the sample to be used was passed over copper at 600°C, through a liquid nitrogen cold trap, and through an ortho-paraconverter at 20°K. It was then stored in large glass bulbs at approximately one atm pressure. The ortho-paraconversion in these bulbs was determined by the thermal conductivity method, and found to be less than 1% per month.

Just prior to the thermal measurements, the sample was forced into a cell of 8 cc volume at a temperature above the melting temperature at the desired density by means of a pressure

generating system consisting of a series of U-tubes. When too much of the sample was exposed to the pressure system at high density, some para-orthoconversion occurred. The concentration of orthohydrogen was determined after the experiment. When the sample was in the cell at the desired density, it was frozen and cooled to the minimum temperature at which measurements were to be made. The amount of the sample was determined after the thermal measurements by expanding the gas into thermostated calibrated bulbs at room temperature, and by measuring the pressure after expansion. The density was determined from the volume of the cell with an accuracy of 0.5%.

Basically the thermal measurements were conventional and will not be discussed here. However, the thermometer calibration is of some special interest, and will be described.

B. Thermometry

A germanium thermometer was calibrated against the vapor pressure of liquid helium and of solid and liquid parahydrogen. The 1958 He^4 scale of temperatures[12] and the data of Wooly et al on the hydrogen vapor pressure[13] were used. These calibration data were fitted to the analytical expression

$$T_c = \frac{\log R}{[A + B \log R + C \log (1 + DR^E)]^2} \qquad (4)$$

where R is the thermometer resistance, and A, B, C, D, and E are adjustable parameters. This equation fitted the data to better than 0.5% in T everywhere where calibration data were

available from 1.3°K to 20°K. The quantity T/T_c was plotted on large scale graph paper, and all temperatures T_c calculated from resistances were corrected to the true temperatures by means of this difference plot.

One of the main problems in thermometry in the temperature range of interest here is the thermometer calibration between 4.2 and 10°K. There is no vapor pressure scale available, and only gas thermometry can be used for direct calibration. An alternative indirect calibration can be obtained by the extrapolation of the difference plot from both the hydrogen and the helium regions into this range so as to give a smooth relation. This procedure in conjunction with suitable empirical equations has frequently been used for the calibration of carbon thermometers.[15] Equation (4) represents the behavior of the germanium thermometer as well as any known relations represent the behavior of carbon thermometers in the regions where calibration data are available. The extrapolation of the difference plot is thus equally justified. A comparison of the direct extrapolation of the difference plot with that obtained by calibrating the germanium thermometer against a carbon thermometer for which the difference plot had been extrapolated was also made. No benefit could be derived from this procedure. Any extrapolation will of course introduce considerable errors in the temperature scale for any thermometer; but the effect on the heat capacity should only be a few percent. This extrapolation procedure was used in the present work.

The reliability of the thermal measurements in general and of the temperature scale between 4.2 and 9°K in particular was estimated by measuring the heat capacity of 99.999% pure copper. The heat capacity of a metal at sufficiently low temperatures can be expressed as

$$C = \gamma T + \alpha T^3 \qquad (5)$$

The values of γ and α found here are compared with those observed by others in Table I. The agreement is very satisfactory. The heat capacity of copper at higher temperatures was recently measured by Franck et al[19] and Debye thetas calculated from the heat capacity after subtracting the linear term with $\gamma = 0.704$ in J/M°K are compared with Franck's results in Fig. 1. The effect of systematic errors in the temperature scale between 5 and 10°K can clearly be seen. Aside from this, the agreement with Franck et al is satisfactory.

Heat capacity errors due to temperature scale effects are to a first approximation proportional to the heat capacity.[22] Therefore, all measurements on hydrogen were corrected by multiplying the measured heat capacities by the ratio of the copper heat capacity calculated from the solid line in Fig. 1 to the measured heat capacity of copper. The largest value of this ratio occurred at 7.0°K, and was 1.038.

C. Errors

It is believed that after the corrections described in the previous section temperature scale errors in the heat

TABLE I

Recent heat capacity results on copper.

Investigator	$\gamma(\frac{mJ}{M^\circ K^2})$	$\alpha(\frac{mJ}{M^\circ K^4})$
N. E. Phillips[16]	0.694	0.0482
W. S. Corak et al[17]	0.688	0.0478
F. J. du Chatenier and J. de Nobel[18]	0.721	0.0500
J. P. Franck et al[19]	0.690	0.0478
H. R. O'Neal[20]	0.702	--
F. D. Manchester[21]	0.696	0.0478
M. Giffel et al[22]	0.691	0.0486
This work	0.704	0.0478

capacity are considerably less than 1%. The estimated overall accuracy of the measurements of the total heat capacity varies somewhat with the sample density, but in general is believed to be approximately 1%. The primary source of error aside from the temperature scale was the thermal relaxation in the high pressure capillary leading to the cell. This effect is discussed in detail elsewhere.[23] The sample heat capacity is, of course, somewhat less accurate particularly at the smaller molar volumes because the heat capacity of the empty cell had to be subtracted. The contribution of the lattice heat capacity to the total heat capacity varied with temperature because of the electronic heat capacity of the empty cell, and with molar volume because of the large change in the Debye theta of the sample. At constant pressure it was 25% at 2.5°K and 70% at 9°K. At 19.83 cc/M it was 20% at 4°K and 40% at 9°K.

For two of the samples there was an anomalous contribution to the heat capacity at low temperatures because the samples contained some orthohydrogen. This contribution was subtracted, and caused a small additional uncertainty where it was appreciable.

III. RESULTS

A. The Heat Capacity at Constant Pressure

The sample consisted of 0.303 moles, and contained 0.2% orthohydrogen. The results are shown in Fig. 2. No

anomalous contribution to the heat capacity from orthohydrogen was observed. It was not found necessary to make corrections for the vaporization of the solid because the volume available to the vapor was very small, and essentially only equal to the volume change due to solidification.

Also shown in Fig. 2 are the results of Hill and Lounasmaa.[24] They are in general somewhat higher than those reported here. The difference is as large as 14% at 3°K, and at low temperatures decreases with increasing temperature. At 7°K the difference has vanished. At 9°K Hill and Lounasmaa's data are again slightly higher. The scatter in Hill and Lounasmaa's data is approximately ± 6%. Above 4°K the scatter of the two measurements overlaps. Below 4°K, however, there seems to be a real discrepancy which cannot be easily explained.

Comparison with other measurements on solid para-hydrogen was made by Hill and Lounasmaa, and will not be repeated here because of the relatively large scatter exhibited by all other data.

The heat of melting at the triple point was also determined on this sample and found to be (118 ± 1) J/M. The uncertainty in this value is rather large due to the fact that upon heating above the triple point also, some of the solid in the capillary melted. The value obtained here compares well with that found by others (117.3 J/M).[25]

B. The Heat Capacity at Constant Volume

The heat capacity was measured at three constant volumes. Information on the nature of the samples is given in Table II. The results at 22.56 cc/M are shown in Fig. 2, and those at 19.83 and 18.73 cc/M are presented in Fig. 3.

At 22.56 cc/M an independent check on the volume determination was possible. The direct determination yielded 22.60 cc/M. The heat capacity measurements extended into the two-phase region, and melting was found to start at 16.35°K. Bartholomé[26] determined the volume change on melting for normal hydrogen, and recently Goodwin and Roder[27] determined the molar volume of fluid parahydrogen in equilibrium with solid. Assuming that Bartholomé's data can be applied to parahydrogen, the molar volume corresponding to 16.35°K along the melting line should be 22.52 cc/M. The largest uncertainty in this value is the one due to the uncertainty in the volume change on melting, and this was estimated by Bartholomé to be 4% or 0.1 cc/M. The molar volume of the sample, therefore, was 22.56 ± 0.06 cc/M. At the other volumes melting started at too high a temperature to permit a similar check. In these cases the uncertainty in the volumes was estimated to be ± 0.1 cc/M.

The samples at 22.56 cc/M and 18.73 cc/M showed an anomalous contribution to the heat capacity from the ortho hydrogen which they contained. This anomalous contribution was subtracted from the total heat capacity. At temperatures

TABLE II

Properties of the Samples for the Heat Capacity at Constant Volume Measurements

V(cc/M)	% σ - H_2	No. of Moles
22.56 ± 0.06	2 ± 1	0.364
19.83 ± 0.1	0.2	0.417
18.73 ± 0.1	6.5 ± 0.5	0.441

which are much larger than the difference between the energy levels responsible for the anomaly, one can expand the heat capacity contribution in the form

$$C_A = aT^{-2} + bT^{-3} + \ldots \quad (6)$$

At the temperature at which the anomalous contribution is appreciable, the lattice heat capacity could be written in the form

$$C_L = AT^3 + BT^5 \quad (7)$$

B could be estimated at temperatures at which the anomalous contribution was negligible. Several values of A were used with the same value of B to calculate trial values of C_A from

$$C_A = C - AT^3 - BT^5 \quad (8)$$

C_A was then plotted as $C_A T^2$ vs T^{-1}. This is illustrated in Fig. 4a for the data at 18.73 cc/M. It is seen that this plot is very sensitive to the choice of A, and A could be estimated with an accuracy of ± 1%. The heat capacity of this sample was measured a second time after it had been heated to 20°K. This heating affected the anomalous contribution because it changed the configurations of the ortho molecules. This change was accompanied by heat evolution at about 14°K. The anomalous contribution from the second set of measurements is shown in Fig. 4b. These data were calculated with those values for A and B which gave the best linear relation in Fig. 4a. The

linearity of the plot in Fig. 4b tends to justify the separation of the total heat capacity into lattice and anomalous contributions, and the use of Eqs. (6) and (7). For the data at 22.56 cc/M the anomalous contribution was much smaller, and the T^{-3} term was negligible. The lattice heat capacities were calculated by subtracting

$$C_A = 160T^{-2} \text{ mJ/M°K} \tag{9}$$

at 22.56 cc/M, and

$$C_A^{(1)} = 4400T^{-2} - 10250T^{-3} \text{ mJ/M°K} \tag{10}$$

$$C_A^{(2)} = 3200T^{-2} - 6400T^{-3} \text{ mJ/M°K}$$

for the first and second set of measurements at 18.73 cc/M respectively. The data in Figs. 2 and 3 are the resulting lattice heat capacity. No anomalous contribution was observed at 19.83 cc/M. The only previous measurements of C_v of para hydrogen with which the present measurements can be compared are those by Bartholomé and Eucken.[7] There seems to be considerable confusion in the literature about the molar volume at which Bartholomé's measurements were made. Megaw[28] believed that it was the molar volume at zero pressure and 11°K, which would be 23.0 cc/M. Megaw assumed that Bartholomé and Eucken had filled their calorimeter at this temperature. This idea was taken over by Hill and Lounasmaa.[24] Actually, Bartholomé and Eucken's calorimeter was filled with solid at

a temperature somewhere in the liquid hydrogen region, and the exact temperature was not specified. Their molar volume thus is not known at all. However, their heat capacity measurements extended at least up to 17.9°K, giving an upper limit of 22.1 cc/M to the molar volume on the basis of the molar volume of solid in equilibrium with liquid. Their molar volume thus was at least 2% less than 22.56 cc/M. Nonetheless, their heat capacity is 7% larger than the one found here. There is, therefore either a considerable discrepancy between the old data and the ones reported on here, or a very unusual behavior of the lattice heat capacity in the vicinity of 22 cc/M. Bartholomé and Eucken's data are also shown in Fig. 2.

Hill and Lounasmaa attempted to estimate C_v from their C_p measurements. The basic relation, of course, is Eq. (1). In view of the fact that α and K are not known, they assumed the validity of the Grüneisen relation

$$\alpha = \frac{\gamma C_v K}{V} \tag{11}$$

which yields

$$C_p - C_v = ATC_v^2 \tag{12}$$

with

$$A = \frac{\gamma^2 K}{V}. \tag{13}$$

They determined A at high temperatures from their data for C_p and Bartholomé and Eucken's data for C_v. Once A is known, Eq. (12) can be solved for C_v if C_p is known. This method has several faults. Equation (1) involves $C_v(V_T)$, as pointed out previously. In the case of hydrogen, V varies considerably with T. Bartholomé's data were, however, determined at constant volume. Furthermore, Bartholomé's volume was considerably smaller than even the 0°K and zero pressure volume. And lastly, the Grüneisen relation leading to Eq. (12) is not likely to hold in the case of hydrogen as pointed out by Megaw.[28] Hill and Lounasmaa's values for C_v are thus likely to be in error by a considerable amount. They are also shown in Fig. 2 and indeed they do not agree with the measurements reported here for a volume of 22.56 cc/M.

C. Summary of Results

The experimental values of the lattice heat capacity were plotted on large scale graphs in the form of C/T^3 vs T^2. These graphs were extrapolated to $T^2 = 0$. Smoothed values were read off these graphs at integral values of T, and Debye thetas were calculated from these values. These smoothed results are given in Table III. The uncertainty in θ at zero degrees is estimated to be ± 2°K at 22.56 cc/M, ± 4°K at 19.83 cc/M, and ± 5°K at 18.73 cc/M. Approximately half of these errors are due to uncertainties in the extrapolation of the experimental data to 0°K.

TABLE III

Smoothed Values for the Lattice Heat Capacities and the Debye Thetas for Hydrogen

T[°K]	$C_p[\frac{mJ}{M°K}]$	$C_v[\frac{mJ}{M°K}]$ at			θ_D[°K] at		
		22.56 cc/M	19.83 cc/M	18.73 cc/M	22.56 cc/M	19.83 cc/M	18.73 cc/M
0	0.00	0.00	0.00	0.00	128.1	169.0	189.4
1	1.03	0.93	0.40	0.29	127.8	168.8	189.2
2	8.57	7.58	3.26	2.31	127.0	168.3	188.8
3	30.7	26.4	11.18	7.88	125.7	167.4	188.1
4	78.7	65.3	27.1	18.94	123.9	166.2	187.3
5	168.5	134.6	54.2	37.5	121.8	164.9	186.4
6	318.8	247	96.8	66.3	119.3	163.1	185.0
7	551	418	159.1	107.7	116.9	161.2	183.6
8	882	662	247	164.9	114.5	159.1	182.1
9	1333	990	367	242	112.5	156.9	180.0
10	1917	1413	523	343	110.7	154.9	178.3
11	2651	1919	723	471	109.4	152.8	176.4
12	3548	2499	968	632	108.5	151.2	174.4
13	4618	3142	1259	830	107.8	149.8	172.4
14	5910	3866	1597	1067	107.0	148.6	170.7
15	-	4678	1978	1340	105.8	147.6	169.2
16	-	-	2405	1655	-	146.7	167.7
17	-	-	2869	2009	-	146.0	166.4
18	-	-	3359	2409	-	145.5	165.1
19	-	-	3882	2860	-	144.9	163.4
20	-	-	4432	3360	-	144.4	161.6

IV. DISCUSSION

A. The Debye Theta and the Grüneisen Gamma

The temperature dependence of θ is conveniently displayed in the form of a graph of θ/θ_o, where θ_o is the Debye temperature at zero degrees. Values of θ/θ_o vs T/θ_o are presented graphically in Fig. 5. Also shown for comparison in Fig. 5 are the curves for argon and krypton.[8,29] The argon and krypton data are based on Cp and Eqs. (1) and (2).

It is clear that the general behavior of θ/θ_o is very similar to that observed for more classical solids such as argon and krypton. However, there appears to be a small systematic change in θ/θ_o at a given value of T/θ_o with molar volume. Whereas changes in θ_o within the stated limits of error can be made in such a fashion that the θ/θ_o curves for the three molar volumes coincide, it must be considered that 35 to 50% of the errors in θ_o are systematic errors due to the uncertainty in the heat capacity of the empty calorimeter. The remaining random errors, primarily due to the extrapolation of C/T^3 to $T^2 = 0$, are not large enough to permit adjustments in the θ_o values which would cause the θ/θ_o curves to coincide. It thus appears that there is a real increase in θ/θ_o with decreasing molar volume. The fact that anharmonicity effects become smaller at smaller molar volumes tends to suggest that anharmonicity causes a decrease in θ at

relative temperatures below $T/\theta_o \approx 0.1$. At relatively much higher temperatures Beaumont, et al[8] suggested an effect in the opposite direction.

The samples for the measurements at 22.56 cc/M and 18.73 cc/M contained 2% and 6% ortho hydrogen respectively. Possible effects of the ortho hydrogen on the lattice heat capacity cannot be ruled out completely. Such effects are however, believed to be negligible because the reduced Debye thetas are in accord with those for the measurements on 0.2% ortho hydrogen at 19.83 cc/M.

Above $T/\theta_o \approx 0.10$, the Debye thetas at 22.56 cc/M and 18.73 cc/M appear to suddenly decrease excessively fast. Such an effect can be due to several phenomena, and particularly could be an indication of vacancy formation. However, the effect observed here is so small that it may well be due to a slight error in the estimates of C/T^3 from which the θ values were derived. The dotted extensions in Fig. 5 of θ/θ_o below $T/\theta_o = 0.10$ correspond to the dotted high temperature ends of the lines through C/T^3 vs T^2 in Figs. 2 and 3.

Whereas it appears that anharmonic effects on θ/θ_o are small in hydrogen, the effect of anharmonicity on θ_o may well be quite large. It would be interesting to compare the Debye thetas with those predicted by the harmonic approximation, but these calculations are beyond the scope of this work. In the case of argon and krypton such a comparison has

been made.[9] Although it appears that anharmonic effects are present, these effects are relatively small. In hydrogen with a relative zeropoint energy about five times that of argon these effects should show up more clearly.

Two sets of values of Grüneisen gammas were calculated from the measurements at the three molar volumes and are shown in Fig. 6. γ calculated from the heat capacities at 18.73 cc/M and 19.83 cc/M appears to be about 8% smaller than γ calculated from the measurements at 19.83 cc/M and 22.56 cc/M; however the difference is well within the possible error due to the errors in the molar volumes. The temperature dependence of γ is of the same magnitude as that expected for other simple solids.[9]

B. The Thermodynamic Properties of Solid Parahydrogen

There are at this time only very limited thermodynamic data available on solid hydrogen, and except for the C_p measurements by Hill and Lounasmaa[24] there were no reliable data at all on solid parahydrogen previous to this work. Fluid parahydrogen was recently studied very extensively at pressures up to 300 atm[27,30-33] and its properties are now well defined over perhaps larger volume and temperature ranges than those for any other substance. The PVT properties of solid parahydrogen can be expected to differ only slightly from those of solid normal hydrogen. In the liquid state at 14°K, for example, the molar volumes at the vapor pressure differ by only 0.4%.[31] This figure gives

a rough indication of what can be expected when available information on solid hydrogen of a variety of ortho-para compositions is pooled in an attempt to arrive at some conclusions about the PVT properties. A brief review of that available information which is of interest here will now be given.

The molar volume of solid hydrogen was measured by Megaw[28] at 4.2°K from 0 to 100 kg/cm^2. Megaw purified her samples at liquid air temperatures and thus probably had about 50% parahydrogen. Megaw's measurements were later extended to 20,000 kg/cm^2 by Stewart.[34-36] Stewart's samples originally contained 25% parahydrogen. But no doubt the composition changed during the course of the measurements, particularly at the higher pressures, due to the ortho-para conversion.

The molar volume of parahydrogen at the triple point can be estimated with considerable accuracy from other thermodynamic data. The properties of the liquid are now very well known, and the heat of melting was measured by Clusius and Hiller,[25] and again during the course of this work. These data with the help of the Clapeyron equation yield a triple point volume of (23.32 ± 0.01) cc/M and a volume change on melting of (2.86 ± 0.01) cc/M.

The volume change on melting of normal hydrogen was measured by Bartholomé at two temperatures.[26] The volume change on melting would be expected to be affected relatively

little by the para concentration, and Bartholomé's data in conjunction with those by Goodwin and Roder on the liquid[27] can be expected to give the volume of solid parahydrogen at the melting line to ± 0.10 cc/M.

The melting pressure as a function of temperature of normal hydrogen was determined by Mills and Grilly up to 3500 kg/cm^2,[37] and recently the melting pressure of parahydrogen was evaluated by Goodwin and Roder up to 5500 kg/cm^2.[27]

The average compressibility of normal hydrogen between 0 and 230 atm and 6 to 9°K was determined very approximately by Smith and Squire by means of NMR measurements.[38]

Bartholomé and Euken[7] measured the heat capacity at constant volume of parahydrogen; but as discussed earlier, the volume for these measurements is unknown. Hill and Lounasmaa's C_p measurements[24] have already been mentioned. There appears to be no further information pertaining to the thermodynamic properties of solid parahydrogen.

In spite of this scarcity of data, it already was apparent to Megaw[28] that solid hydrogen does not behave like a classical solid. Her PV measurements at 4.2°K showed that the compressibility decreased exceptionally rapidly with increasing pressure. Megaw also considered the fact that both C_p[39] and C_v[7] varied as T^3. Equation (1) then implies that α varies as T if K is independent of T. On the other hand, Grüneisen's Law, Eq. (11), implies that α varies

approximately as T^3. It was thus apparent that the Grüneisen equation of state was not valid for solid hydrogen. Megaw's arguments can now be repeated and extended on the basis of the more extensive and more accurate data presented in this work.

As was shown previously, Eq. (3) with a constant γ is not strictly valid in the case of hydrogen. But the temperature dependence of γ is no more severe than what is expected for other more classical solids,[8,9] and the volume dependence of γ is smaller than the experimental error. If γ were constant, then within the Grüneisen approximation Eq. (11) would also be valid. But comparison of the thermodynamic properties predicted by Eq. (11) with known properties of solid hydrogen will show some severe discrepancies.

If it is assumed that Eq. (11) is valid, then,

$$\left(\frac{\partial P}{\partial T}\right)_V = \alpha/K = \frac{\gamma C_V}{V}. \tag{14}$$

It is thus possible to integrate relation (14) from low temperatures to the temperature at which melting starts and thereby to determine the pressure change in the solid at constant volume up to the melting point. At 22.56 cc/M and 4°K, the data due to Megaw[28] indicate that the pressure is 8 atm. The integration outlined above yields a pressure change of 27 atm up to the melting point, yielding a pressure of 35 atm at 16.35°K for solid in equilibrium with liquid. The actual melting pressure as determined by Goodwin and

Roder[27] is 82.5 atm, showing a disagreement well outside of experimental error. It must therefore be concluded that Eq. (11) is not valid at 22.56 cc/M.

A similar calculation can be carried out at 19.83 cc/M. The pressure at 4°K is 426 atmospheres. Melting should start at about 27°K, at a pressure of about 560 atm. The pressure change predicted by Eq. (14) and the heat capacity measurements (extrapolated with a Debye θ of 145°K above 20°K) is about 80 atmospheres. Unfortunately the uncertainties in both the sample volume and the temperature at which melting starts are too large to permit any conclusions. But again the predicted pressure change appears low.

Comparison of C_p and C_v leads to the same contradiction between Eqs. (11) and (1) as that discussed by Megaw.

In view of the failure of Grüneisen's Law it will now be attempted to obtain information about the PVT properties of solid parahydrogen by purely thermodynamic means. First the discontinuity in the heat capacity at the beginning of melting at 22.56 cc/M will be discussed, and then the C_p and C_v measurements will be compared. In this latter comparison certain approximations will be necessary, but the approximations are simple and it is well understood what they are.

Lounasmaa[40] showed that the discontinuity in the heat capacity at constant volume at the boundary between a single-phase and a two-phase region is given by

$$\Delta C_V = T \frac{dV}{dT} \left[\left(\frac{\partial P}{\partial T}\right)_V - \frac{dP}{dT} \right] \tag{15}$$

where ΔC_V is always taken to be positive. The partial derivatives refer to the single phase, dV/dT is the volume change of the single phase along the boundary, and dP/dT is the pressure change along the transition. Furthermore the equation

$$\left(\frac{\partial P}{\partial T}\right)_V - \frac{dP}{dT} = - \frac{dV}{dT} \left(\frac{\partial P}{\partial V}\right)_T \tag{16}$$

is also valid. Equations (15) and (16) lead to

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{\Delta C_V}{T(dV/dT)} + \frac{dP}{dT} \tag{17}$$

$$\left(\frac{\partial P}{\partial V}\right)_T = - \frac{\Delta C_V}{T(dV/dT)^2} \tag{18}$$

$$\begin{aligned} \left(\frac{\partial V}{\partial T}\right)_P &= \frac{dV}{dT} + \frac{T}{\Delta C_V} \left(\frac{dV}{dT}\right)^2 \frac{dP}{dT} \\ &= \frac{dV}{dT} - \left(\frac{\partial V}{\partial P}\right)_T \frac{dP}{dT} \end{aligned} \tag{19}$$

for the partial derivatives in terms of the properties along the boundary. Equation (19) was used by Grilly and Mills to derive some properties of α- and γ- He^4.[11] As they pointed out, Eq. (19) can be combined for the solid and the liquid to give

$$\left(\frac{\partial V}{\partial T}\right)_{P,s} = \left(\frac{\partial V}{\partial T}\right)_{P,\ell} - \frac{d\Delta V}{dT} + \left[\left(\frac{\partial V}{\partial P}\right)_{T,\ell} - \left(\frac{\partial V}{\partial P}\right)_{T,s}\right]\frac{dP}{dT} \tag{20}$$

where the subscripts s and ℓ indicate that the derivative refers to the solid or liquid phase, respectively. It is thus possible to obtain the three derivatives for solid hydrogen at the onset of melting. The numerical values used in and derived from the equations are given in Table IV.

It will be noted that $(\partial V/\partial T)_P$ is obtained as a small difference between two large quantities in either of the two equations. It therefore has a rather large error associated with it. Only $(\partial P/\partial V)_T$ can be determined with reasonable accuracy. Nonetheless, comparison with the properties at 4.2°K yields some interesting results.

The compressibility changed little between 4.2 and 16.35°K. Megaw at 100 kg/cm^2 obtained 3.2 x 10^{-4} cm^2/kg.[28] The values at 16.35°K and 82.5 atm is 3.8 x 10^{-4} atm^{-1}. Thus, it appears that at constant pressure K is reasonably temperature independent. This is also in agreement with the approximate value of 2 x 10^{-4} between 0 and 230 atm at 6 to 9°K found by Smith and Squire.[38]

The thermal expansion at 16.35°K and 82.5 atm is essentially zero, with rather wide limits of uncertainty. The largest possible value for $(\partial V/\partial T)_P$ is 0.06 cc/°K. The

TABLE IV

Properties of Solid Parahydrogen at the Melting Line

Variable	Value	Source
T	(16.35 ± 0.02)°K	This work
ΔC	(16.4 ± 0.4) J/M°K	This work
P	82.5 atm	Goodwin and Roder[27]
dP/dT	35.2 atm/°K	Goodwin and Roder[27]
dV/dT	- (0.290 ± 0.03) cc/°K	Goodwin and Roder[27] Bartholomé[26]
$d\Delta V/dT$	- (0.18 ± 0.03) cc/°K	Bartholomé[26]
$(\frac{\partial V}{\partial P})_{T,\ell}$	- (0.0188 ± 0.0001) cc/°K	Goodwin et al[30]
$(\frac{\partial V}{\partial T})_{P,\ell}$	(0.180 ± 0.005) cc/°K	Goodwin et al[30]
$(\frac{\partial P}{\partial V})_{T,s}$	- (118 ± 13) atm/cc	Eq. 18
$(\frac{\partial P}{\partial T})_{V,s}$	(1 ± 5) atm/°K	Eq. 17
$(\frac{\partial V}{\partial T})_{P,s}$	(0.008 ± 0.1) cc/°K	Eq. 19
$(\frac{\partial V}{\partial T})_{P,s}$	(0.00 ± 0.06) cc/°K	Eq. 20

total thermal expansion between 4.2°K and 16.35°K is 0.80 cc. Thus even for the largest possible value of $(\partial V/\partial T)_P$ the 82.5 atm isobar must have a point of inflection, and this implies that α must have a maximum between 4.2 and 16.35°K, and probably between 10°K and 15°K. We shall now proceed to the comparison of the C_p and C_v measurements.

In principle it is possible to calculate α^2/K from C_p and C_v by means of Eq. (1). But it was already pointed out that both C_p and C_v must be measured at the same volume. If Eq. (2) is obeyed, it is possible to calculate C_v at the volumes V_T of the C_p measurements from C_v at 22.56 cc/M, provided the volumes of the C_p measurements are known. It was shown earlier that for molar volumes between 18.73 cc and 22.56 cc, Eq. (2) is obeyed within experimental error. In view of the fact that the calculation of $C_v(V_T)$ involves an extrapolation over a maximum of 0.7 cc/M, one would expect that reasonable values of $C_v(V_T)$ can be calculated. Of course the possibility of strong deviations from Eq. (2) near the solid-vapor equilibrium line cannot be entirely ruled out. In order to calculate $C_v(V_T)$, V_T must be known. V_T can be calculated only if α is known. Thus a method of successive approximations was used to calculate α from Eq. (1), assuming first that C_v at 22.56 cc/M is equal to $C_v(V_T)$. The resulting values of α were used to calculate V_T, and a new set of values for α was obtained. The calculation had converged

sufficiently after the fourth approximation. The values of γ used were the ones calculated from C_v at 19.83 cc/M and 22.56 cc/M, and the value for K was the one obtained by Megaw at zero pressure[28] (7.0×10^{-4} atm^{-1}). The final values for α are given in Fig. 7. The predicted triple point volume as calculated from α and Megaw's volume at 4.2°K is 23.27 cc/M, to be compared with the experimental value of 23.32 cc/M.

It is difficult to estimate the accuracy of the values for α obtained by the above calculation because it is not known how reliable the calculation of $C_v(V_T)$ is. It therefore seemed desirable to calculate α by an independent method which involves different approximations. The basic relation between the PVT and the thermal properties is

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{\alpha}{K}. \tag{21}$$

If α/K is independent of V between the volumes of the C_p and C_v measurements, then one can evaluate α/K from

$$\left(\frac{\alpha}{K}\right) = \frac{\Delta S}{\Delta V} \tag{22}$$

where $\Delta V = V_T - V(C_v)$.

Equation (22) is not usable for the calculation of α as it stands because again ΔV is not known. But

$$\Delta V = \Delta V_o + V_o \int_0^T \alpha dT \tag{23}$$

where ΔV_o is the volume difference between the C_p and C_v

measurements at 0°K. Now

$$\Delta V_o \alpha + V_o \alpha \int_0^T \alpha dT = K\Delta S \tag{24}$$

This equation has the solution

$$\alpha = \frac{K\Delta S}{V_o[(\Delta V_o/V_o)^2 + (2K/V_o) \int_0^T \Delta S dT]^{1/2}}. \tag{25}$$

In obtaining Eq. (25) it was assumed that K is independent of T. ΔS and $\int \Delta S dT$ can be obtained from the heat capacity measurements. The value used for K was again the one measured by Megaw[28] at 4.2°K and zero pressure. α was calculated with ΔV_o = 0.00, 0.06, and 0.12 cc/M, and is given in Fig. 7. The predicted triple point volume this time is 23.21 cc/M.

The two methods of calculating α involve partially different assumptions. They both assume that K is independent of T. This assumption is supported by the values of K at 82.5 atm at 4.2°K and 16.35°K. The method employing Eqs. (1) and (2) assumes further only the validity of Eq. (2). The method employing Eq. (25) assumes that α/K is independent of V over the small volume range in question. In view of the rapid change of K with V observed by Megaw this may well be the least reliable assumption. Qualitatively both methods yield the same results for α at high temperatures. At low temperatures, Eq. (25) is very sensitive to errors in ΔV_o, and of course ΔV_o is not known very accurately. α calculated from Eqs. (1) and (2) on the other hand, is not sensitive to

small changes in ΔV_o, and at low temperatures these values for α are perhaps more reliable.

The differences between the predicted triple point volumes and the actual triple point volume are smaller than the possible error in Megaw's volume at 4.2°K for both approximations. Above 4°K, α approaches almost linear behavior. Above 10°K the possibility of a considerable contribution to α from vacancy formation exists. It is thus conceivable that in the absence of vacancies α would rise less rapidly than T, and possibly would even go through a maximum similar to that deduced for the 82 atm isobar. In fact, there is an indication between 9°K and 11°K that α is beginning to rise less rapidly than at lower temperatures. For comparison the qualitative features of α at 82.5 atm are also shown in Fig. 6.

The possible existence of a maximum in α has some interesting thermodynamic consequences. If there is also a maximum in α/K, then at temperatures higher than that of the maximum

$$\frac{\partial^2 S}{\partial V \partial T} = \frac{1}{T}\frac{\partial C_v}{\partial V} < 0 \qquad (26)$$

and thus the Grüneisen γ is negative. Thermodynamically a similar situation exists in the γ-phase of solid He^4,[11] and as yet unpublished detailed measurements of the heat capacity of this phase at several closely spaced volumes do indeed indicate a negative Grüneisen constant. In the case of hydrogen the results reported here show that γ is well behaved

over a large volume range. But the present measurements do not exclude the possibility of unusual behavior over a narrow volume range in the vicinity of 22.5 cc/M. In fact, comparison of the measurements by Bartholomé and Eucken[7] with the present results at 22.56 cc/M supports the idea of a negative γ, as was implied earlier. More detailed measurements on the heat capacity of para hydrogen at large molar volumes are now being undertaken. A more detailed discussion of the implications of these results with regard to the microscopic behavior of solid hydrogen will thus be deferred until these results become available.

Whereas at this time the volume of solid hydrogen is not known under any conditions except at the triple point with an accuracy greater than 0.5%, the best estimates of the PVT properties have been compiled in Fig. 8 in the form of a V-T diagram.

It is interesting to note that Dugdale and Simon[3] used relation (14) to calculate the PVT properties of solid He^4. They determined their integration constant from the melting pressure, and calculated P and $(\partial P/\partial V)_T$ as a function of T down to 0°K. There are no direct low temperature measurements of the volume of solid helium, and the validity of Eq. (14) thus cannot be checked. The results reported here for hydrogen would make such a check extremely desirable, especially since the high pressure work by Stewart on the molar volume of He^4 at 4.2°K[41,42] is based on the data by Dugdale and Simon.

ACKNOWLEDGMENT

The author is indebted to the Bell Telephone Laboratories for secretarial help in the publication of this paper.

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FIGURE CAPTIONS

Figure 1 The Debye theta of copper. The arrows attached to the points by Franck, et. al. approximately indicate the scatter in their experimental points.

Figure 2 The lattice heat capacity of solid hydrogen at zero pressure and at 22.56 cc/M.

Figure 3 The lattice heat capacity of solid hydrogen at 19.83 and 18.73 cc/M.

Figure 4 The anomalous heat capacity of 6.3% ortho hydrogen.
a - original measurements
b - measurements after heating to 20°K

Figure 5 The reduced Debye theta as a function of the reduced temperature for hydrogen, argon and krypton.

Figure 6 The Grüneisen gamma of solid hydrogen as a function of temperature.

Figure 7 The thermal expansion coefficient of solid hydrogen.

Figure 8 The PVT properties of solid hydrogen.

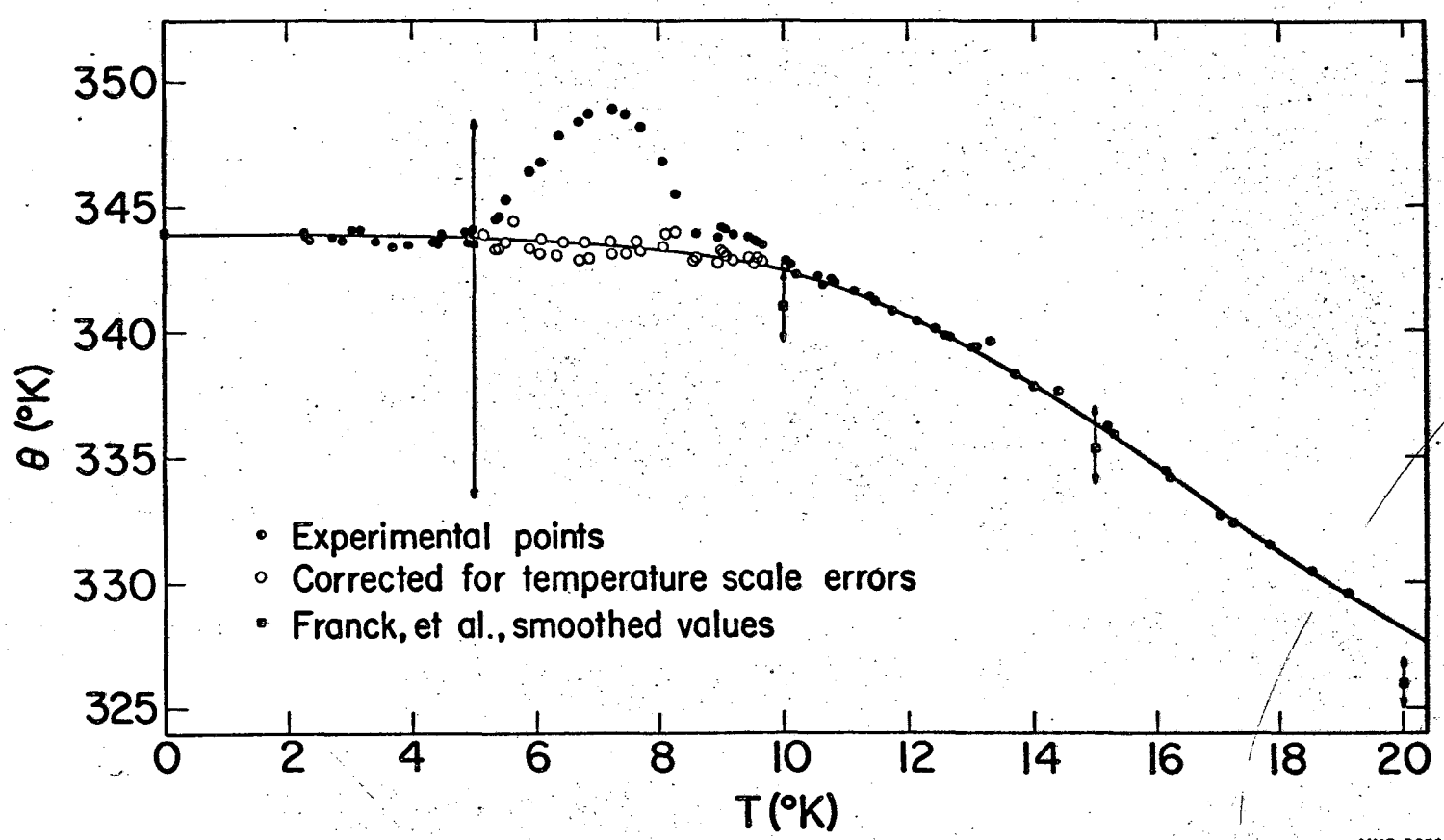
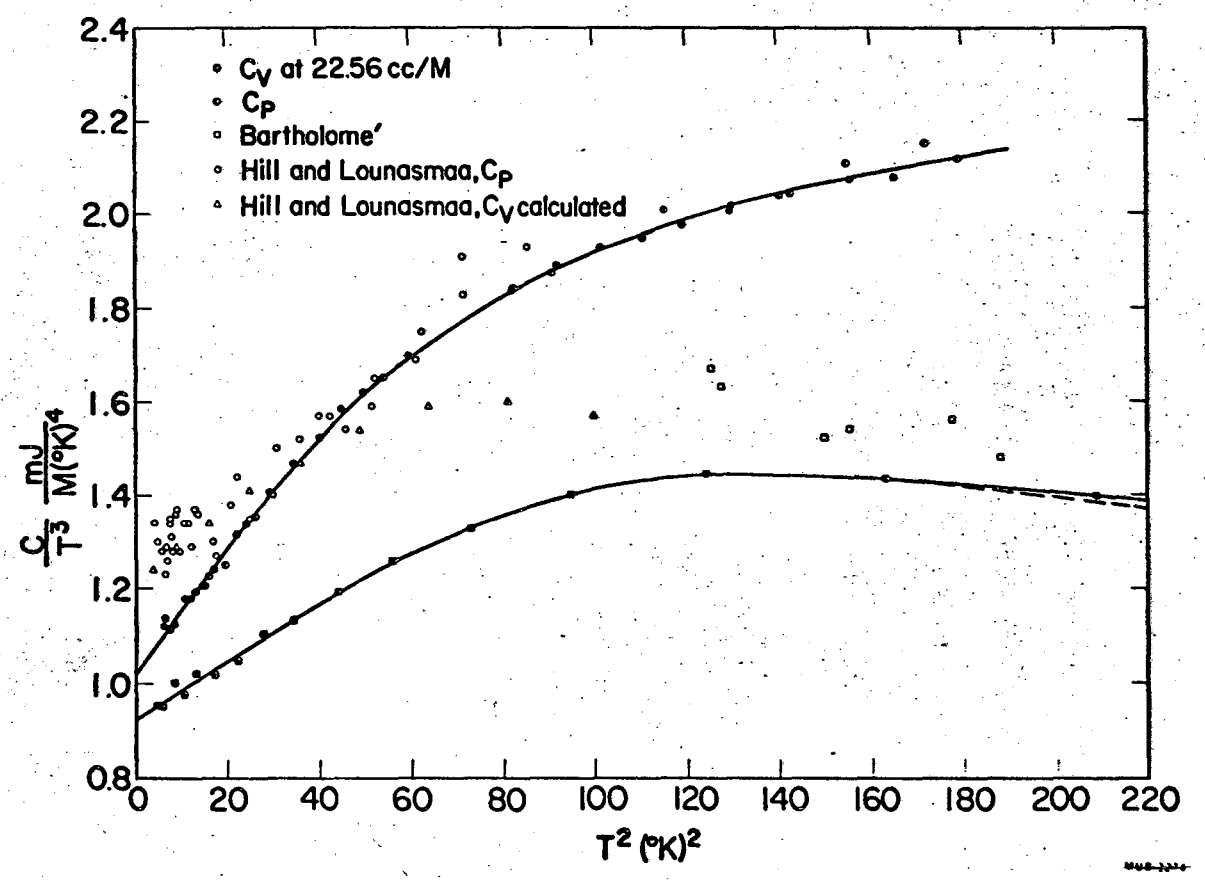

350
345
340
335
330
325
θ (°K)
0
2
4
6
8
10
12
14
16
18
20
T (°K)
• Experimental points
○ Corrected for temperature scale errors
▪ Franck, et al., smoothed values
MUB-2073

FIG. 1



MUB-2074

FIG. 2

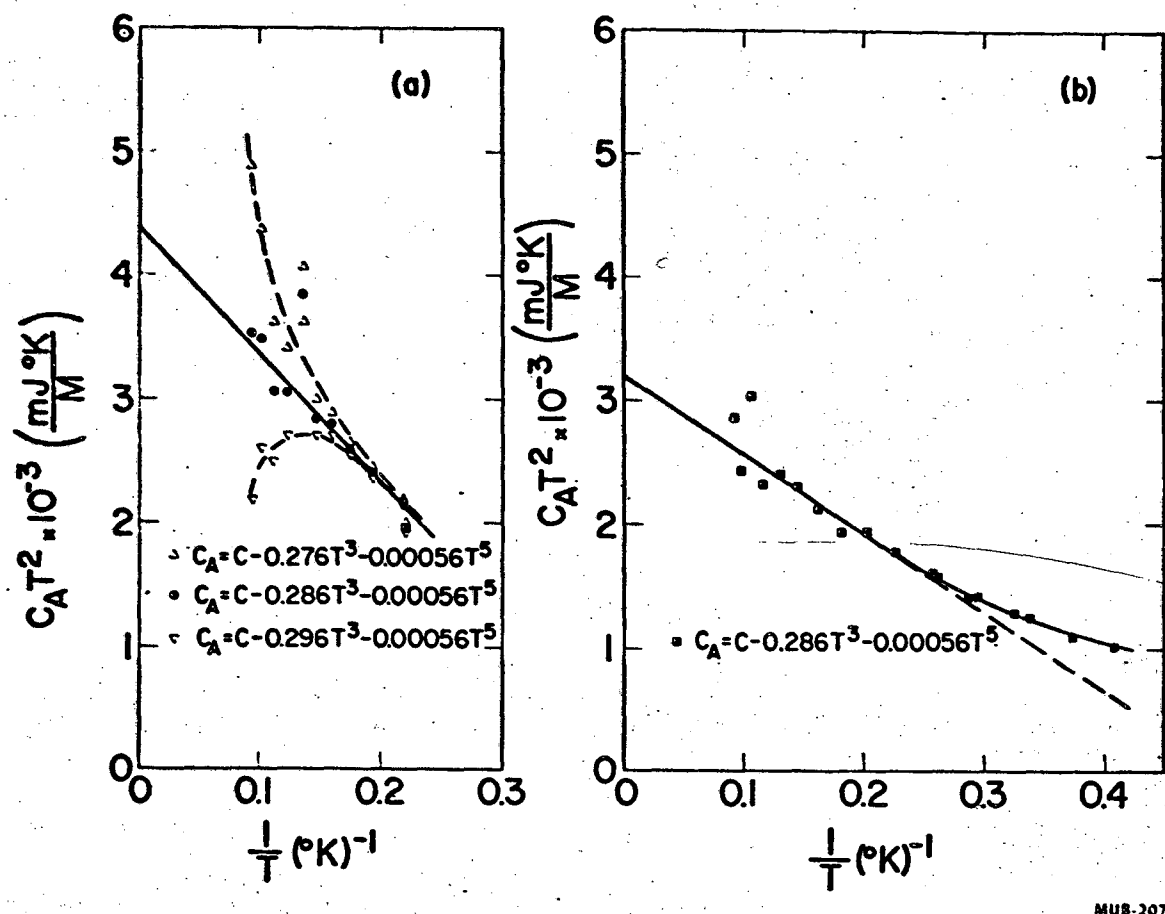
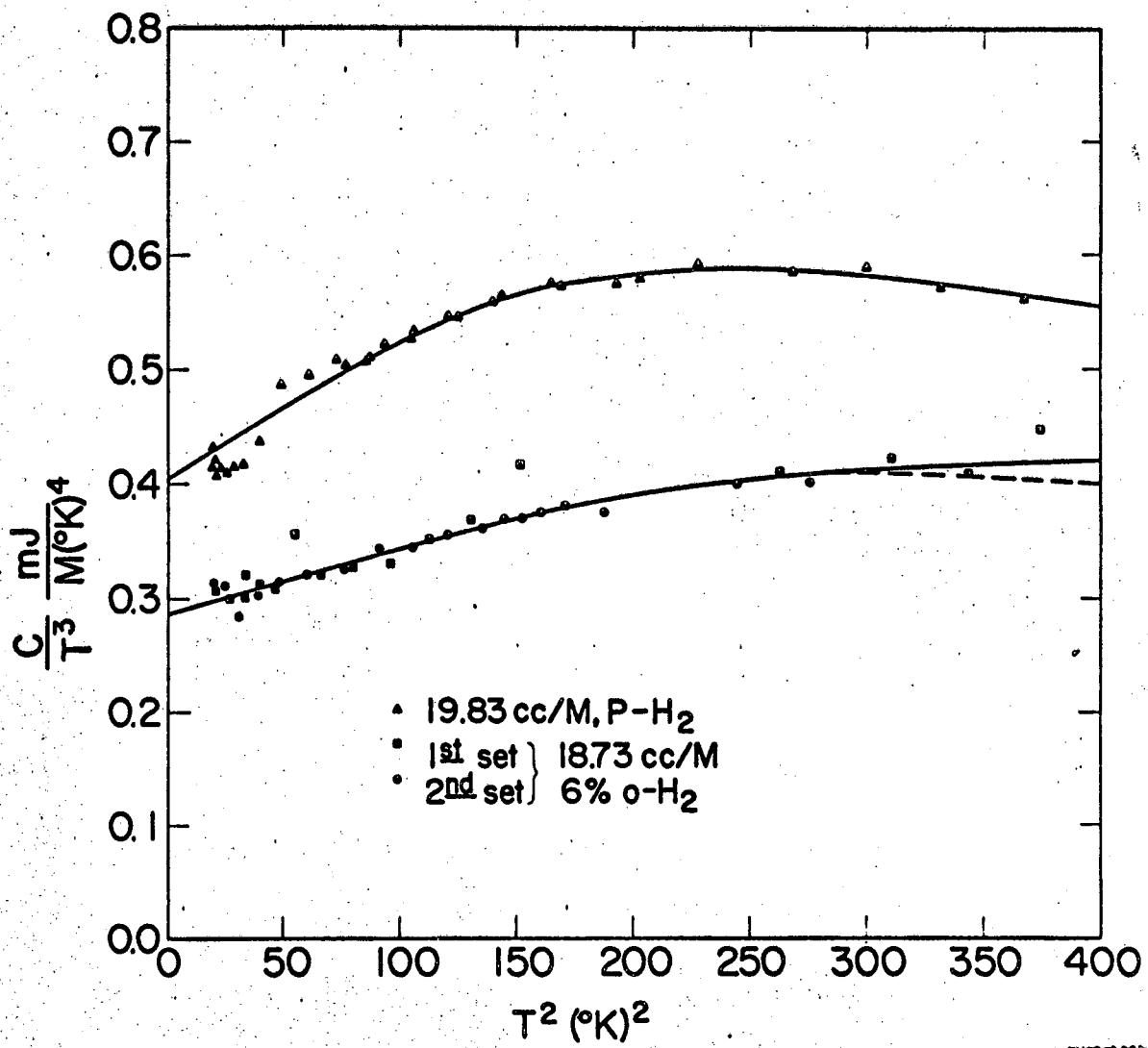

(a)
(b)
$C_A T^2 \times 10^{-3} \left(\frac{mJ\,°K}{M}\right)$
$\frac{1}{T}$ (°K)$^{-1}$
$C_A = C - 0.276T^3 - 0.00056T^5$
$C_A = C - 0.286T^3 - 0.00056T^5$
$C_A = C - 0.296T^3 - 0.00056T^5$
$C_A = C - 0.286T^3 - 0.00056T^5$
MUB-2070

FIG. 4



MUB-2072

FIG. 3

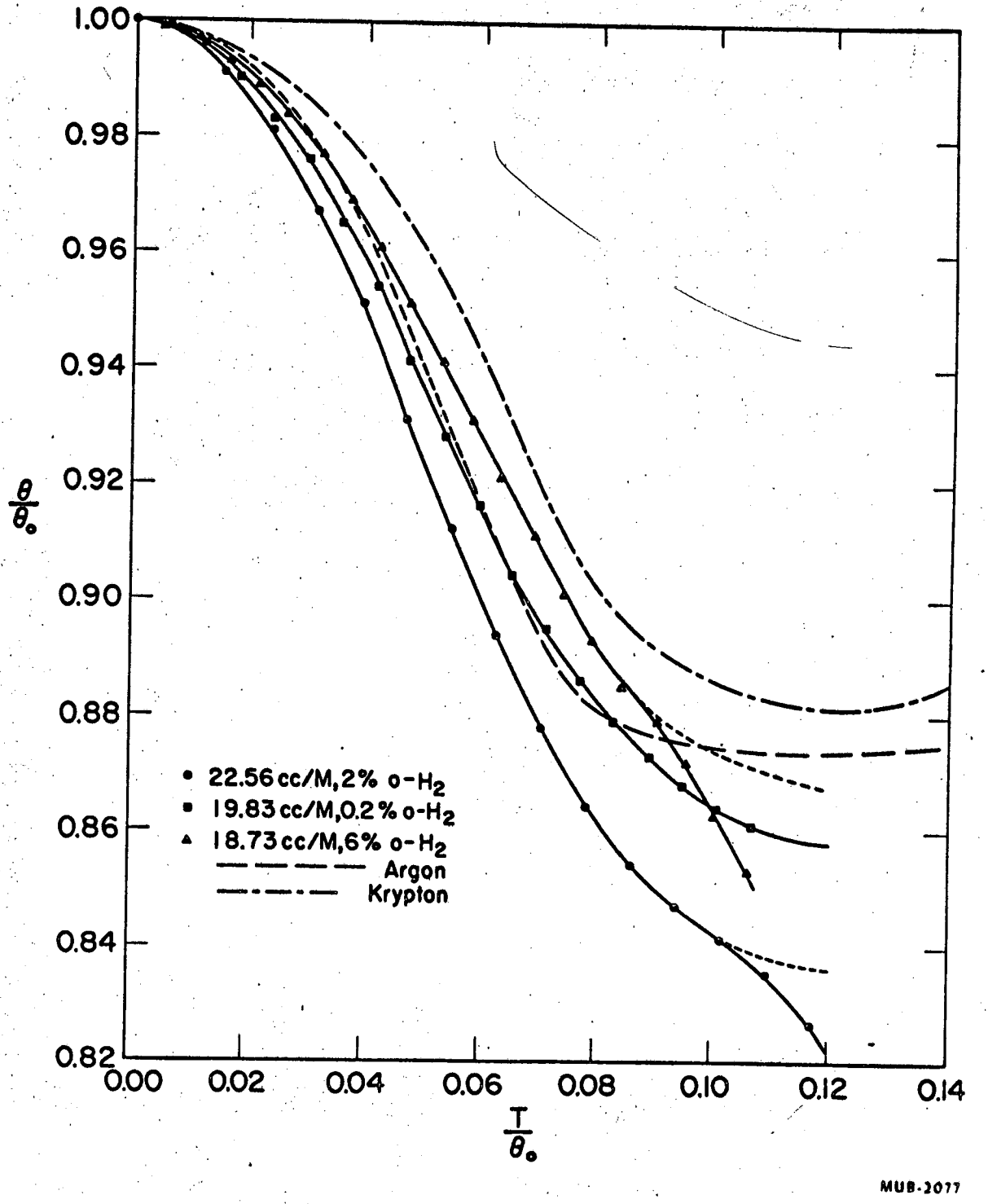

1.00
0.98
0.96
0.94
0.92
0.90
0.88
0.86
0.84
0.82
θ/θ₀
0.00
0.02
0.04
0.06
0.08
0.10
0.12
0.14
T/θ₀
• 22.56 cc/M, 2% o-H₂
▪ 19.83 cc/M, 0.2% o-H₂
▲ 18.73 cc/M, 6% o-H₂
Argon
Krypton
MUB-2077

FIG. 5

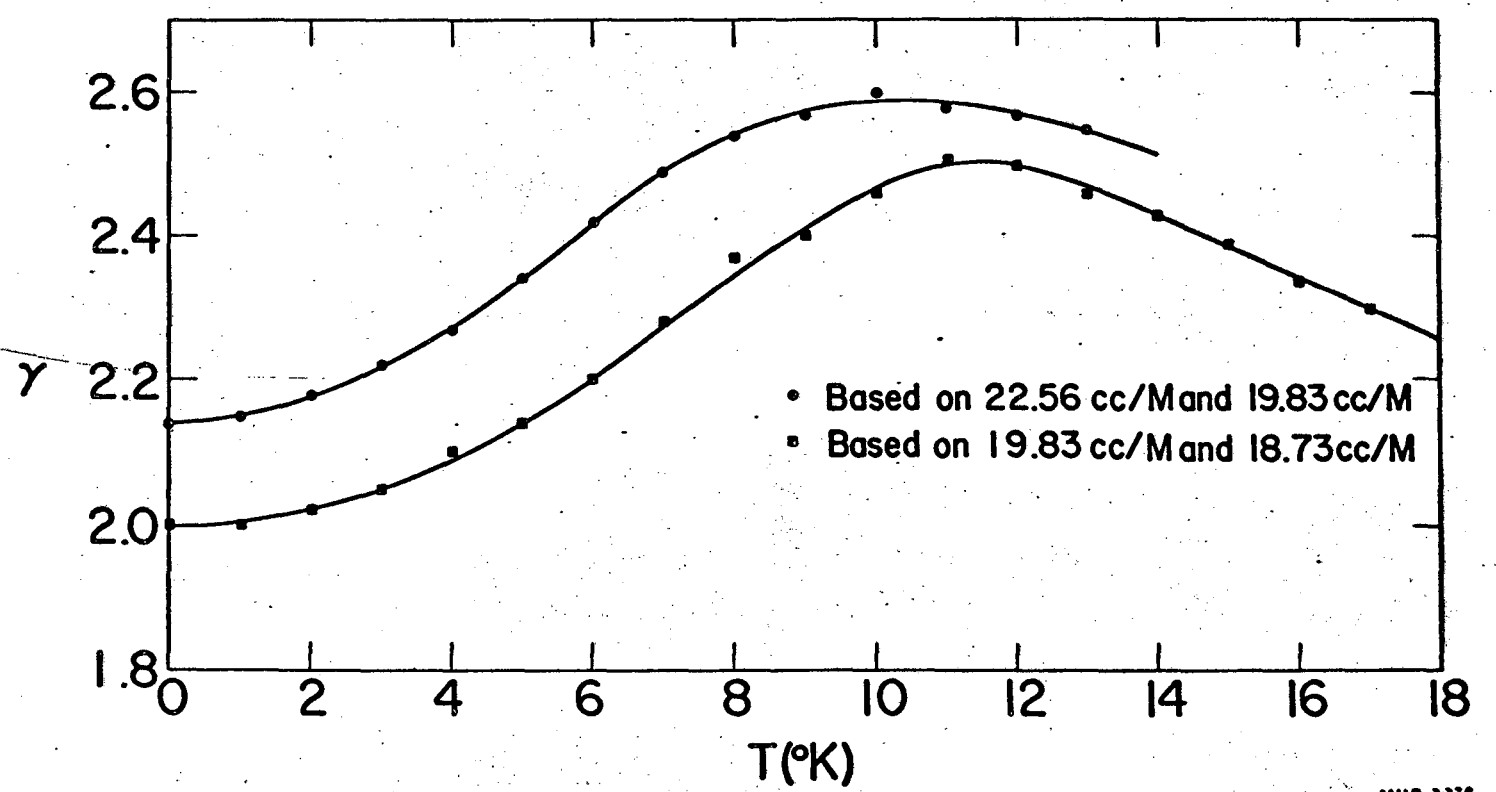


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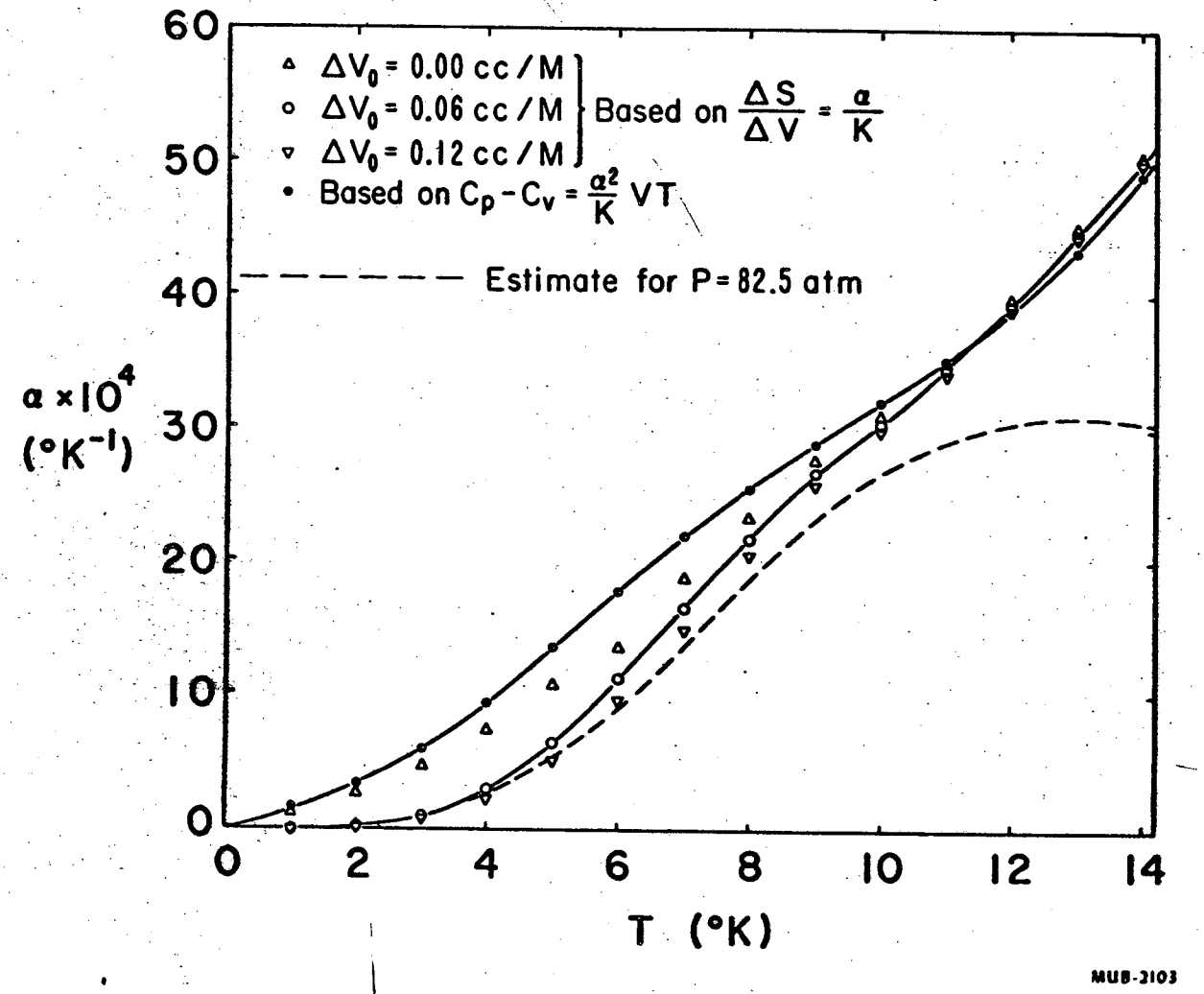
FIG. 6

MUB-2078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50
40
30
20
10
0
0
2
4
6
8
10
12
14
T (°K)
α × 10^4 (°K^-1)
ΔV0 = 0.00 cc/M
ΔV0 = 0.06 cc/M
ΔV0 = 0.12 cc/M
Based on ΔS/ΔV = α/K
Based on Cp - Cv = α²/K VT
Estimate for P = 82.5 atm
MUB-2103

FIG. 7

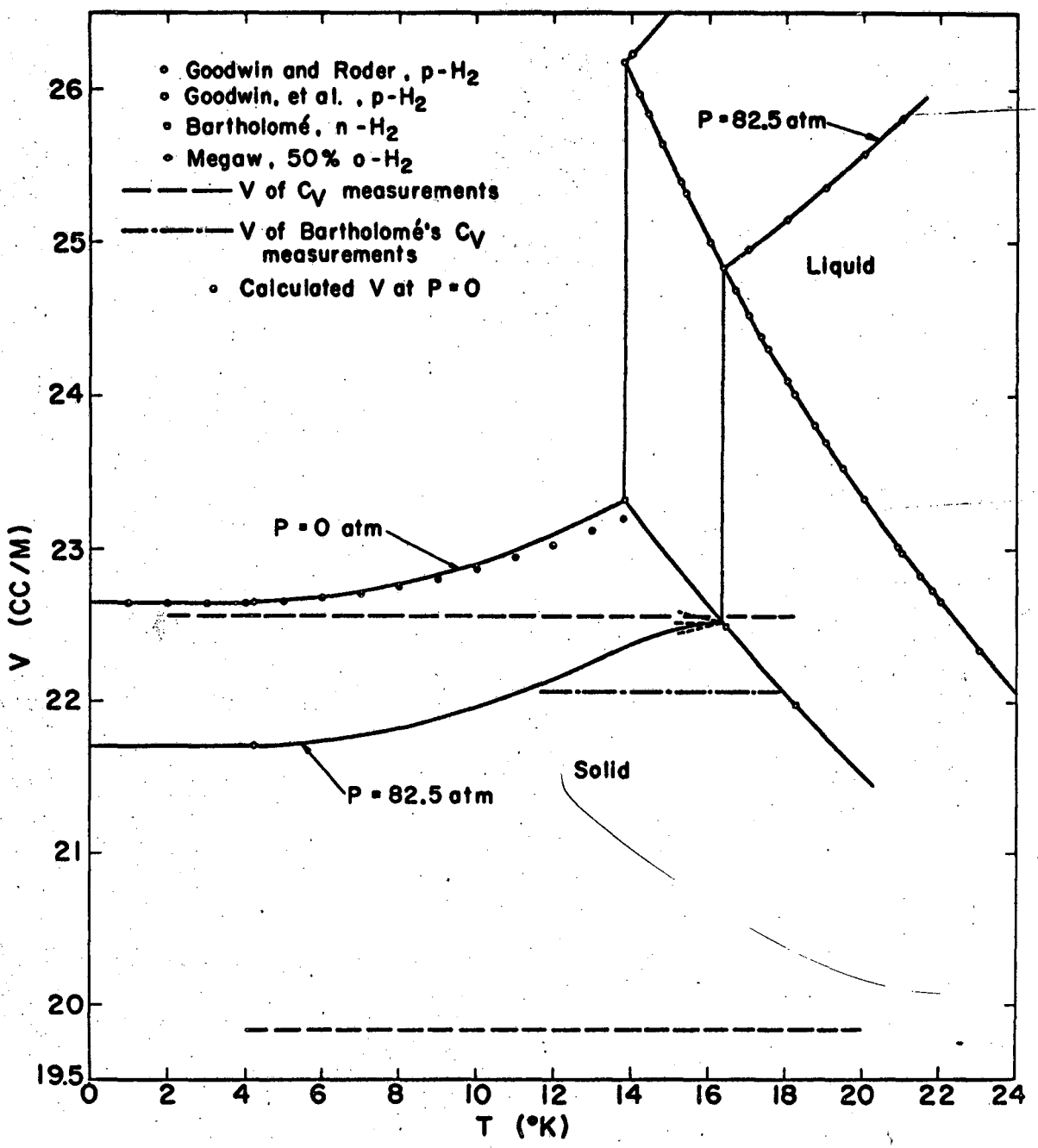

FIG. 8

MUB-2067

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