

# PHASE TRANSITIONS AND COMPRESSIONS OF SOLID CH<sub>4</sub>, CD<sub>4</sub> AND O<sub>2</sub>\*

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**Abstract**—The piston-displacement technique previously described has been applied to a study of phase transitions and isothermal compressibilities of solid CH<sub>4</sub>, CD<sub>4</sub> and O<sub>2</sub> over the pressure range 0–19,000 kg/cm<sup>2</sup> and the temperature range 4–120°K. Phase transitions appear as discontinuities in  $V$  (first order) or in  $(dV/dP)_T$  (second order).

Solid CH<sub>4</sub> and CD<sub>4</sub> both show three phases and one triple point. The transitions appear to be of the second order, with rather large "regions of indifference". There are isotopic differences between the two methanes. At atmospheric pressure CH<sub>4</sub> shows only one of the transitions, at 20.5°K, while CD<sub>4</sub> has both, at 22.1° and 27.2°K. There is at present disagreement between our results for CH<sub>4</sub> and those obtained by STEVENSON.

In the case of solid oxygen, the two well-known transitions have been traced to high pressure. The lower transition is evidently of the second order. The upper first-order transition has a large volume discontinuity. Some difficulty was experienced from ignition of the steel pressure chambers by the solid oxygen under high pressure.

Pressure-volume relations for the three substances have been obtained at various temperatures.

## 1. INTRODUCTION

THE specific-heat anomaly in solid CH<sub>4</sub> at 20.5°K at atmospheric pressure was first observed by CLUSIUS<sup>(1)</sup> in 1929. Since the specific-heat maximum appeared to be finite, it was assumed that this transition was second order. Later work by SCHALLAMACH<sup>(2)</sup>, employing X-ray diffraction, showed that there was no change in the f.c.c. structure of solid methane at 20°K. The transition was assumed to involve a change in the rotational states of the CH<sub>4</sub> molecules. However, proton-resonance measurements by THOMAS *et al.*<sup>(3)</sup> showed that a state of free rotation of the molecules was not realized at 20.5°K, but only at much higher temperature.

KRUIS *et al.*<sup>(4)</sup> investigated the specific heat of solid CD<sub>4</sub> at low temperatures and observed two anomalies, at 22.2 and 27.1°K. These also appeared to be second order. Studies<sup>(5)</sup> of mixtures of CH<sub>4</sub> and CD<sub>4</sub> showed that the upper transition in CD<sub>4</sub> is analogous to the single transition in CH<sub>4</sub>,

and that the lower transition in CD<sub>4</sub> has no equivalent in CH<sub>4</sub> at atmospheric pressure. The lowest-temperature phase in CD<sub>4</sub> is now known to be weakly doubly refracting, so that its structure cannot be strictly f.c.c. The lower transition must therefore be first order, with a very small latent heat of transition.

By means of specific-heat measurements at atmospheric pressure, GIAUQUE and JOHNSTON<sup>(6)</sup> observed two transitions in solid oxygen. Both were believed to be first order, with measured heats of transition 22.4 cal/mole at 23.7°K and 177.6 cal/mole at 43.8°K. However, X-ray studies by VEGARD<sup>(7)</sup> indicate no change in crystal structure at the lower transition, and subsequent thermal measurements by BOROVIK-ROMANOV *et al.*<sup>(8)</sup> also lead to the identification of the lower transition as being of the second order.

The only previous high-pressure work with solid CH<sub>4</sub> appears to be that of TRAPEZNIKOVA and MILJUTIN<sup>(9)</sup>. They measured the specific heat at pressures up to 2000 atm, and found a second transition in CH<sub>4</sub> at elevated pressures, evidently corresponding to the lower transition in CD<sub>4</sub>.

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There appeared to be a triple point in CH<sub>4</sub> near 33°K and 2600 atm. The recent work of STEVENSON<sup>(10)</sup> will be discussed below. The present results for CH<sub>4</sub> represent an extension of results previously presented<sup>(11)</sup> in a preliminary fashion. There has apparently been no previous high-pressure work with solid CD<sub>4</sub>. STEVENSON<sup>(12)</sup> has also obtained high-pressure data for solid O<sub>2</sub>.

## 2. EXPERIMENTAL TECHNIQUE

Throughout the present investigation, the piston-displacement technique previously described in detail<sup>(13)</sup> has been used. Volume vs. pressure data have been obtained over the pressure range 0–19,000 kg/cm<sup>2</sup> and the temperature ranges 4–120°K for CH<sub>4</sub>, 4°–90°K for CD<sub>4</sub> and 30°–65°K for O<sub>2</sub>. Pressure is applied by the piston directly to the sample. Plasticity of the solidified gas is relied upon for transmission of the applied uniaxial compressive stress as an approximate hydrostatic pressure. A variable-temperature cryostat of the type designed by SWENSON<sup>(14)</sup> has been employed. Liquid helium was the coolant for temperatures between 4° and 77°K, and liquid nitrogen was used for temperatures above 77°K. The temperature of the sample was determined by means of an indium resistance thermometer of the type suggested by WHITE and WOODS<sup>(15)</sup>. This thermometer will be described in detail elsewhere.<sup>(16)</sup>

Four sizes of sample-holder were used:  $\frac{5}{8}$  in. diameter (stainless steel, Type 304) for pressures of 0–3000 kg/cm<sup>2</sup> (later replaced by a  $\frac{1}{2}$ -in. stainless-steel cylinder, pressure range 0–5000 kg/cm<sup>2</sup>);  $\frac{3}{8}$  in. diameter (AISI 4615 steel, heat-treated), 0–12,000 kg/cm<sup>2</sup>;  $\frac{1}{4}$  in. diameter (AISI 4615 steel, heat-treated), 0–19,000 kg/cm<sup>2</sup>. As before,<sup>(13)</sup> the high-pressure pistons were constructed from heat-treated Ketos tool steel. The larger-diameter cylinders give greater sensitivity at relatively low pressures than is afforded by the  $\frac{1}{4}$ -in. cylinders. All the cylinders used were  $\frac{3}{4}$ –1 in. in depth.

First-order transitions in the sample produce volume discontinuities in the  $V$  vs.  $P$  data, while with a second-order transition the volume is continuous but there is a break in the slope ( $dV/dP$ )<sub>T</sub>. Friction in the sample-holders tends to "round the corners" of either type, and, unless the volume discontinuity is quite large, it is impossible to determine the order of a transition from the  $V$  vs.  $P$  data alone. The friction was reduced by lining the pressure cylinder with 0.005-in. indium foil.

After initial compaction of the sample by one or two applications and releases of pressure, the pressure was decreased from its maximum value to zero in regular steps, and then was likewise increased again to the maximum value. This is the method originated by BRIDGMAN<sup>(17)</sup> for compressibility measurements on solids. At each point, the position of the piston was observed after all drift had stopped. A micrometer slide and telescope were used to follow the motion of a scratch on the upper (room-temperature) end of the stainless-steel compression member. After completion of one or two such "hysteresis loops", the sample was expelled by warming

up the system and applying pressure. The background stretch of the press was then obtained by means of a pressure hysteresis loop with the piston in contact with the bottom of the empty sample-holder. For reasons of economy of liquid helium, these "blank" runs were always carried out at 77°K. The elastic constants of the stainless-steel tension and compression members change very little with temperature in the range of these measurements. The sample length at zero pressure was determined from the blank run, as previously described.<sup>(13)</sup>

The temperature of the sample was controlled by adjustment of a needle valve in the helium-discharge line from the cryostat. Liquid helium was forced through a vacuum-jacketed transfer tube into the heat-exchanger of the cryostat by pressurizing a 25-l. storage Dewar with gaseous helium. The flow rate of the evaporated helium could be monitored with a wet test meter. The temperature, as recorded by the indium resistance thermometer mounted on the bottom of the press in good thermal contact with the sample-holder, was held constant within 0.5°K for periods up to 3 hr.

Data at temperatures above the melting points of the substances were obtained by initially applying pressure at a lower temperature and then allowing the sample to warm up at constant pressure. A hysteresis loop at pressures above the melting pressure was then run.

## 3. RESULTS AND DISCUSSION

### (a) *Methanes*

Phillips Petroleum Company research-grade CH<sub>4</sub> (99.5 per cent or higher purity) was used. The CD<sub>4</sub> was obtained from Tracerlab, Inc., and was stated to be at least 95 per cent CD<sub>4</sub>. No additional purification was carried out in either case.

The behavior under pressure of the solid CD<sub>4</sub> and CH<sub>4</sub> was rather peculiar. The transitions were always much more conspicuous on the decreasing-pressure side of the hysteresis loop than on the increasing-pressure side. The break in slope on the decreasing side was accompanied by unusually large drift of the piston, which continued for 15 or 20 min after a change of pressure had been made. The drift first appeared several decrements of pressure above the apparent transition point, and increased in magnitude and duration at each point until the transition was complete. As the pressure was further reduced, there was no drift of the piston until very low pressures were reached. On account of friction, all the solidified gas samples studied so far have shown some drift of the piston at the extreme low-pressure end of the decreasing-pressure leg of the hysteresis loop.

On the increasing-pressure side of the  $V$  vs.  $P$  loop, it was difficult to distinguish breaks in slope



from frictional irregularities in the piston motion. There was little or no drift as the transition was approached from the low-pressure side. The size of feasible pressure increments could not be reduced below a minimum value. The piston motion became jerky if the increments were made too small, with a tendency for alternate points to lie on a smooth curve. These effects are believed to be caused by frictional "hanging up" of the piston on the wall of the cylinder, arising from the finite shear strength of the solidified samples.

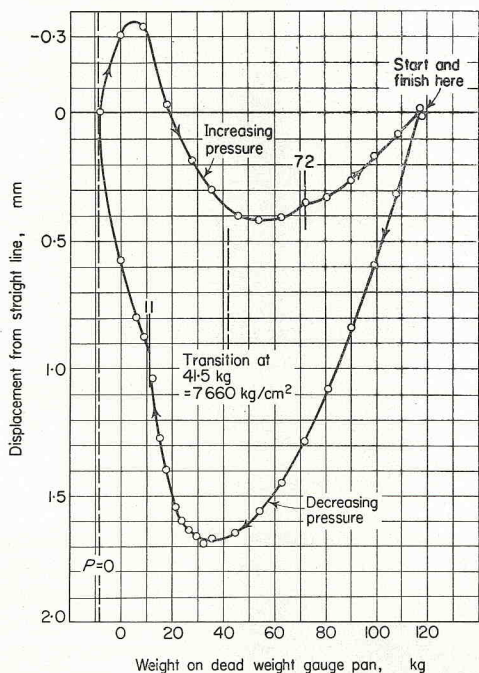


FIG. 1. "Hysteresis" loop for locating phase transitions in solid  $\text{CH}_4$ . A straight line was drawn connecting the maximum and zero pressure points on a plot of piston position vs. weight on dead-weight gauge pan. The ordinate on the graph shown here is the difference between the piston position corresponding to the actual point and that corresponding to the linear relation. The abscissae are essentially pressure; 1 kg on the dead-weight gauge pan is equivalent to  $154 \text{ kg/cm}^2$  sample pressure for the  $\frac{1}{8}$ -in. sample-holders. The run shown is for solid  $\text{CH}_4$  at  $57^\circ\text{K}$ .

The transitions appear more clearly if the data are plotted against pressure as differences between the observed piston position and a straight line drawn between the maximum and zero pressure

points. This increases the scale of the irregularities in piston motion over those appearing in a direct  $V$  vs.  $P$  plot. A typical plot of this kind is shown in Fig. 1. The transition pressure is taken as the arithmetic mean of the pressures of the breaks in the decreasing- and increasing-pressure curves.

The phase diagram for solid  $\text{CH}_4$  is shown in Fig. 2, and that for  $\text{CD}_4$  in Fig. 3. In the case of  $\text{CH}_4$ , the present results disagree in part with those of TRAPEZNIKOVA and MILJUTIN<sup>(9)</sup> and of STEVENSON<sup>(10)</sup>. Agreement is perfect with TRAPEZNIKOVA and MILJUTIN for the I—II transition, but the present II—III curve lies at a substantially higher pressure than those of either TRAPEZNIKOVA and MILJUTIN or STEVENSON. The reason for this discrepancy is not known. It is felt that our observed points for the II—III transition are more accurate than those at higher pressure.

In the present work, no evidence was found of the fourth phase ( $\delta$ ), stable at high pressure and low temperature, reported by STEVENSON<sup>(10)</sup>. A careful search was made for this, but no irregularities in the piston motion consistent enough to be associated with a phase transition were observed. There is evidence that solid  $\text{CH}_4$  becomes increasingly brittle in this region of the  $PT$  plane. When the pressure was changed, the piston moved in jerks accompanied by crunching sounds. Except for the lack of consistency between data at neighboring temperatures, it would be possible to mistake this behavior for a phase transition. Where the sample is brittle, the applied uniaxial compressive stress is not transmitted throughout as hydrostatic pressure, and the stress system in the sample is complicated. The compressibility and phase-transition data then have doubtful validity.

Previous extrusion experiments in this laboratory have shown that solid  $\text{CH}_4$  is quite plastic near atmospheric pressure at  $77^\circ\text{K}$ . A pressure of  $800 \text{ kg/cm}^2$  applied to a solid sample in a  $\frac{1}{4}$ -in. cylinder extruded the sample smoothly through a coaxial  $\frac{1}{8}$ -in. hole in the bottom of the cylinder. However, as the temperature is lowered, solid methane becomes increasingly brittle.

At higher temperatures, the present disagreement with STEVENSON on the location of the I—III transition curve appears to arise from the fact that he was there working near the top of his available pressure range, where the transition data are quite inaccurate.



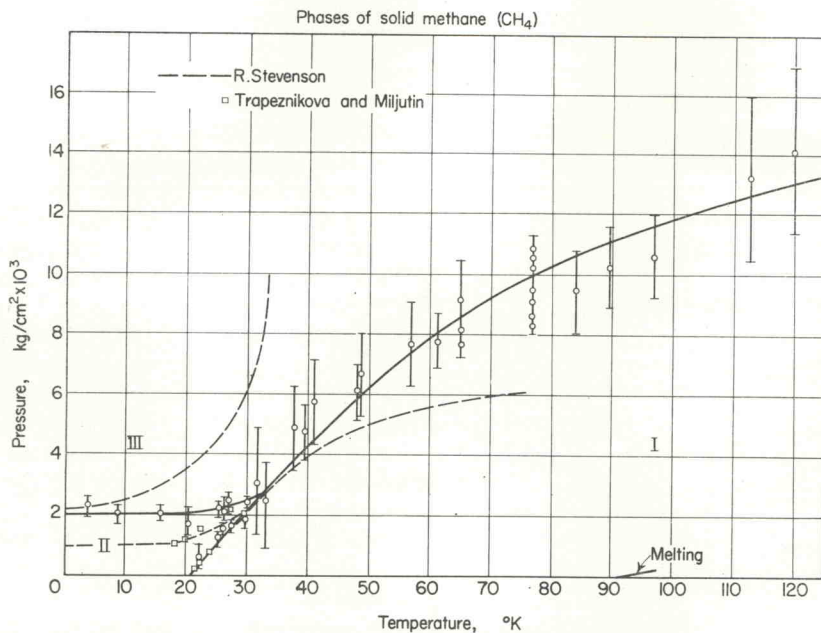


FIG. 2. Phase diagram for solid CH<sub>4</sub>. The results of earlier investigators are shown.

All three sets of data lead to very nearly the same I—II—III triple-point parameters, namely 33°K and 2700 kg/cm<sup>2</sup>. In Fig. 2 the I—II and I—III transitions are shown as a continuous straight line through the triple point. From a consideration of thermodynamic potentials, it can be shown that at a triple point the transition line dividing the regions of stability of the *i*th phase and the *j*th phase must, when projected through the triple point, enter the region of stability of the *k*th phase. This theorem applies to transitions of all orders. Thus the I—III line cannot bend away from the temperature axis at the triple point (Fig. 2).

Presumably because of greater impurity content, the CD<sub>4</sub> transitions appeared less distinctly than those for CH<sub>4</sub>. BRIDGMAN<sup>(18)</sup> has pointed out that the corners of transitions when plotted on a *V* vs. *P* diagram are rounded by the presence of impurity. In contrast to the situation in CH<sub>4</sub>, both transitions in CD<sub>4</sub> occur at atmospheric pressure. Otherwise the two phase diagrams are qualitatively similar. At a given temperature, the transition pressure for CD<sub>4</sub> is lower than the corresponding pressure for CH<sub>4</sub>. The triple-point parameters for CD<sub>4</sub> are 40°K and 3000 kg/cm<sup>2</sup>. These are less

accurately known than is the case for CH<sub>4</sub>. There is no evidence in the present data for a fourth phase in CD<sub>4</sub> analogous to STEVENSON's  $\delta$  in CH<sub>4</sub>.

The experimental uncertainties in the transition pressures are of the order of the smallest pressure increment that could be applied without irregular piston motion. The transitions observed in the larger holders have a smaller absolute error than those observed in the smaller, higher-pressure, holders. The relative uncertainties are nearly the same. The large spread in transition pressures observed at 77°K is not understood. Some of the earlier values<sup>(11)</sup> are now believed to be too high and have been assigned smaller weight in the location of the transition curves.

The spread between the transition points observed with increasing and decreasing pressure is considerably greater than the friction. With a closely fitting piston and indium liner, the half-width of the friction hysteresis loop was of the order of 5 per cent of the maximum pressure. The width of the "region of indifference" was at least as large as the friction, but showed no obvious dependence upon temperature, pressure, sample length or sample-holder diameter. In general, the

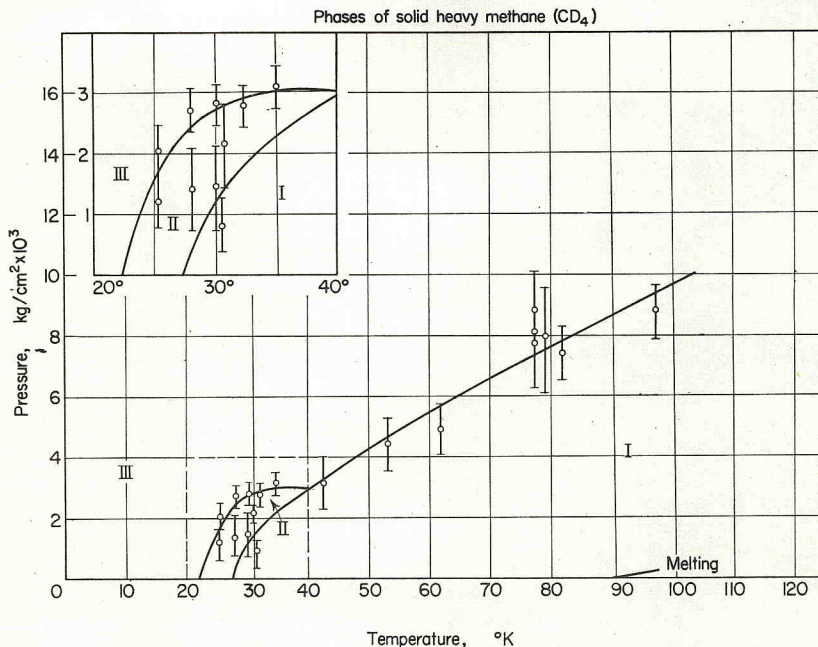


FIG. 3. Phase diagram for solid CD<sub>4</sub>. The inset shows the lower portion of the diagram at twice the scale of the main plot.

friction tends to be less with a small length-to-diameter ratio for the sample. On the other hand, the magnitude of the piston displacement then becomes inconveniently small, so that one does not gain in accuracy by reducing the sample length below a certain value. The samples used in this investigation had length-to-diameter ratios of between 1.0 and 2.0.

A total of 36 runs was made with CH<sub>4</sub> and 18 with CD<sub>4</sub>. One to four separate runs were made with each sample, the most common number being two.

The pressure-volume relations for CH<sub>4</sub> and CD<sub>4</sub> at 77°K are shown in Table 1. The method of calculation is the same as that described previously.<sup>(13)</sup> The observed difference between  $\Delta V/V_0$  for CH<sub>4</sub> and for CD<sub>4</sub> is less than the estimated 5 per cent precision of measurement. One might expect CD<sub>4</sub> to be slightly less compressible than CH<sub>4</sub>, particularly at low pressure, because of the smaller zero-point energy of CD<sub>4</sub>. Owing to the width of the regions of indifference, the difference in compressibility at the transitions cannot be

determined accurately. One must extrapolate the experimental curves from each side of the transition so that they meet without a discontinuity in volume. In all cases it is observed that the compressibility of the high-pressure phase is greater than that of the low-pressure phase at the transition point.

The molar volume data for solid CH<sub>4</sub> given in Table 1 are based upon a value of  $0.507 \pm 0.004$  g/cm<sup>3</sup> for the density at 77°K, obtained in this laboratory by LAROCK<sup>(19)</sup>. Since no accurate measurement of the density of solid CD<sub>4</sub> seems to have been made, no molar volumes are given.

In the previous determinations of *PV* isotherms for solidified gases,<sup>(13,20)</sup> the Murnaghan theory of finite strain was found to be quite useful for empirical fitting of the experimental data. However, because of the phase transitions, no attempt has been made to apply this theory to the present compressibility data. At a given temperature, different values of the two adjustable constants would be needed for each phase. It was not felt that this representation would be particularly useful.



Table 1. Compression data for solids CH<sub>4</sub>, CD<sub>4</sub> and O<sub>2</sub>

Pressure (kg/cm <sup>2</sup> )	CH <sub>4</sub> 77°K, ρ = 0.507 g/cm <sup>3</sup>		CD <sub>4</sub> 77°K	32°K	O <sub>2</sub> 51°K, ρ = 1.36 g/cm <sup>3</sup>	
	Mol. vol. (cm <sup>3</sup> )	-ΔV/V <sub>0</sub>	-ΔV/V <sub>0</sub>	-ΔV/V <sub>0</sub>	Mol. vol. (cm <sup>3</sup> )	-ΔV/V <sub>0</sub>
0	31.6	0	0	0	23.5	0
1000	29.9	0.054	0.049	0.032	—	—
1100	—	—	—	—	22.2	0.054*
1100	—	—	—	—	21.2	0.096*
2000	28.8	0.090	0.083	0.058	20.6	0.122
2500	—	—	—	0.067*	—	—
4000	27.1	0.141	0.133	0.097	19.6	0.167
6000	25.9	0.179	0.169	0.128	18.8	0.198
7400	—	—	0.187*	—	—	—
7900	—	—	—	—	18.4	0.219*
8000	25.0	0.208	0.196	0.151	—	—
10,000	24.3	0.230*	0.221	0.170	17.8	0.241
12,000	23.7	0.251	0.242	0.187	17.4	0.258
14,000	23.1	0.268	0.260	—	17.1	0.272
16,000	22.7	0.281	0.274	—	16.8	0.283
19,000	22.2	0.299	0.292	—	16.5	0.298

\* Phase transition.

### (b) Oxygen

Linde Company oxygen (U.S.P.) was used without additional purification. Judging by the sharpness of the transitions, the purity must have been quite high. Both transitions, the purity must have been quite high. Both transitions were evident on both the decreasing- and increasing-pressure legs of the hysteresis loop. Fig. 4 shows the phase diagram for solid oxygen. The present results agree closely with those of STEVENSON<sup>(12)</sup>.

A previous extrusion experiment similar to that described above for CH<sub>4</sub> showed that solid oxygen is brittle at 4°K. However, it appears to transmit hydrostatic pressure satisfactorily at temperatures above 30°K.

The lower-temperature transition (β-γ, Fig. 4) is assumed to be of the second order. The discontinuity in piston motion for this transition was very small, and because of friction it is not possible to distinguish between a small volume change and a jump in  $(dV/dP)_T$ . The compressibility of phase γ is greater than that of phase β at the transition pressures observed (7900 kg/cm<sup>2</sup> at 51°K, 2500 kg/cm<sup>2</sup> at 32°K). The differences between the

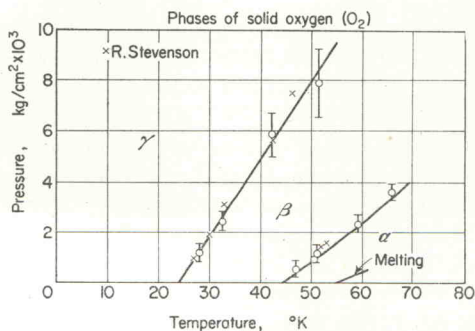


FIG. 4. Phase diagram for solid O<sub>2</sub>.

compressibilities appear to be smaller than is the case with the second-order transitions of the solid methanes.

The α-β transition shows a large volume change, and is certainly first-order. X-ray data<sup>(7)</sup> show that, in the α phase, pairs of O<sub>2</sub> molecules are arranged with their centers in a f.c.c. array. In the β phase the structure is either trigonal or rhombohedral. The γ phase was found to have the same structure as the β phase.



The volume changes observed for the  $\alpha$ - $\beta$  transition were  $1.09 \pm 0.05$  cm<sup>3</sup>/mole at 47° and  $0.98 \pm 0.05$  cm<sup>3</sup>/mole at 51°K. Less accurate values, which appear to be smaller, were obtained at 59° and 66°K. The latter two were not converted to cm<sup>3</sup>/mole, because the pressure hysteresis loop could not be carried to zero pressure at temperatures above the melting point of oxygen. A linear extrapolation of the results at 47° and 51°K leads to  $\Delta V = 1.18 \pm 0.06$  cm<sup>3</sup>/mole at 43.8°K, the temperature of the transition at atmospheric pressure.

Using GIAUQUE's<sup>(6)</sup> value for the latent heat of the transition ( $177.6 \pm 0.5$  cal/mole) and the slope,  $dP/dT$ , of the  $\alpha$ - $\beta$  transition line (determined from Fig. 4) in Clapeyron's equation, we calculate  $\Delta V = 1.16 \pm 0.14$  cm<sup>3</sup>/mole. The agreement is excellent.

The density of solid oxygen at 51°K was calculated from an extrapolation to the melting point of values of the density of the liquid as a function of temperature given by VAN ITTERBECK<sup>(21)</sup> and from the volume change at fusion (54.3°) determined from Clapeyron's equation. GIAUQUE's<sup>(6)</sup> value of the latent heat of fusion (106 cal/mole) and LISMAN's<sup>(22)</sup> determination of  $dP/dT$  based upon melting-curve measurements to 170 kg/cm<sup>2</sup> were used. The value adopted for the density at 51°K was  $1.36 \pm 0.01$  g/cm<sup>3</sup>. From this the molar volumes in Table 1 were determined.

In some of the oxygen runs trouble was experienced from chemical reaction at high pressure of the solid oxygen samples with the steel pressure cylinder. Once such a reaction started, it proceeded explosively, and pressure was quickly lost as the sample vaporized and leaked past the piston. This happened on three separate occasions, as follows: (1) 41°K, 12,000 kg/cm<sup>2</sup>, on initial increase of pressure; (2) 51°K, 16,000 kg/cm<sup>2</sup>, as pressure was being increased for the third time on that particular sample (after a successful run had been completed); (3) 70°K, 19,000 kg/cm<sup>2</sup>, sample warming up at constant pressure. In each case, as the oxygen escaped, a channel was melted in the piston and cylinder. This combustion could usually be prevented by the indium liner. On the first occasion no liner was used; on the latter two occasions it presumably was torn. One might suppose that it would be impossible to initiate this spontaneous reaction at reproducible temperatures and pressures,

since it presumably requires sufficient activation energy to be supplied by the compression at one spot on the wall of the pressure chamber. This would vary with friction.

#### 4. CONCLUSION

The exact nature of the phase transitions of methane is not yet understood theoretically. They are believed to involve changes in rotational states of the molecules in the solid crystal, although there must also be a slight change in the crystal structure in the lower-temperature transition of solid CD<sub>4</sub> to account for the anisotropy of phase III. The same might well be true for the II—III transition of CH<sub>4</sub>. No studies of the refractive properties of phase III of CH<sub>4</sub> have been made. JAMES and KEENAN<sup>(23)</sup> have carried out a classical statistical-mechanical calculation for CD<sub>4</sub> at atmospheric pressure, based upon octopole—octopole interaction between the molecules. This accounts reasonably well for the observed two transition temperatures. This theory is not yet applicable to CH<sub>4</sub>, for which quantum effects are more important. Neither does it apply to CD<sub>4</sub> under pressure, because lattice compressibility is neglected. It is the author's understanding that further calculations to take account of these effects are in progress at the present time.

Further experimental studies of the solid methanes under pressure would be highly desirable. In particular, specific-heat measurements, nuclear magnetic-resonance measurements and perhaps neutron-diffraction measurements should be carried out at as high a pressure as possible. In order to improve materially upon the present accuracy of the piston-displacement technique, it will be necessary to embed the solid methane in a medium which transmits hydrostatic pressure. Solid hydrogen could be used at the lower temperatures. Gaseous helium would be suitable over the entire range if only relatively low pressures were desired.

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