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Compression and Densities of Four Solidified Hydrocarbons and Carbon Tetrafluoride at 77°K*

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The piston displacement method of Bridgman has been used to measure the volume changes and compressibilities of solid ethane, ethylene, propane, propylene, and carbon tetrafluoride from 0 to 20 000 kg/cm² at 77°K. The only polymorphic phase change observed is a first-order transition at $P = 180 \pm 80$ kg/cm² at 77° in CF_4. The densities of these solidified gases at 77° have been measured at atmospheric pressure by direct condensation into a volumetric flask. The accompanying pressure drop in a storage tank of known volume is observed.

I. INTRODUCTION

THE present work makes use of methods previously described in detail.[1,2] There is no change in the low-temperature pressure apparatus[1] which was used for the compression measurements, but a new gas reservoir has been built for the density measurements. Preliminary extrusion experiments were carried out to verify that these solidified gases were soft enough to transmit the applied uniaxial compression as a hydrostatic pressure. At 77°K, the order of plasticity from softest to hardest was as follows: carbon tetrafluoride, ethylene, ethane, propylene, propane. It is felt that the pressure is transmitted satisfactorily in all except possibly solid propane. It showed signs of being somewhat brittle.

The hydrocarbons used were Phillips Petroleum Research grade (supposedly better than 99.7% purity). The sample of CF_4, approximately 99.8% pure, was supplied through the kindness of Dr. R. M. Joyce of the Du Pont Experimental Station, Wilmington, Delaware.

II. COMPRESSION DATA

As in the earlier work,[1] piston displacement readings were taken for increasing and decreasing pressure and a "hysteresis loop" plotted. The friction correction was made by averaging the pressure at constant displacement. Corrections were also made for the stretching of the pressure apparatus and for the dilation of the sample holder. Measurements were made in $\frac{1}{4}$-inch and $\frac{5}{16}$-inch cylinders. The results for the five solidified gases are given in Table I. The molar volumes at zero pressure were computed from the density measurements described below.

For the hydrocarbons the friction in the apparatus was quite high. This made the data for the lower 10% of the pressure range somewhat unreliable. The observed compressions for pressures above 2000 kg/cm² were fitted empirically to a relation[3] derived from the Murnaghan theory of finite strain. This relation was then extrapolated to zero pressure. This procedure introduces some uncertainty into the low pressure results, particularly the compressibilities, but should have little effect on the accuracy of the over-all compressions at higher pressure. There is no evidence that any of the four hydrocarbons have phase transitions in the observed pressure range. A transition below 2000 kg/cm² would of course invalidate such an extrapolation. The extrapolations were subsequently checked by direct measurements of the compression in a larger sample holder $\frac{5}{8}$-in. in diameter, in which the maximum pressure obtainable was 3025 kg/cm². The estimated

TABLE I. Compressions of solidified gases 77°K.

Substance	Ethane $\xi = -9.0$		Ethylene $\xi = -6.0$		Propane $\xi = -5.5$		Propylene $\xi = -3.5$		Carbon tetrafluoride $\xi = -5.0$[a]	
Pressure kg/cm²	Molar volume cm³	$10^5\beta$ cm²/kg	Molar volume cm³	$10^5\beta$ cm²/kg	Molar volume cm³	$10^5\beta$ cm²/kg	Molar volume cm³	$10^5\beta$ cm²/kg	Molar volume cm³	$10^5\beta$ cm²/kg
0	42.2	2.9	38.3	4.7	57.8	2.3	52.2	3.0	45.3	...
180	...	...	...	...	...	...	...	...	45.1	...
180	...	...	...	...	...	...	...	...	42.9	2.8
1000	...	...	...	...	...	...	...	...	41.9	2.3
2000	40.1	2.0	36.0	2.5	55.5	1.6	49.6	2.0	41.1	1.8
4000	38.8	1.5	34.5	1.8	54.3	1.2	48.0	1.6	39.9	1.2
8000	36.7	1.0	32.6	1.2	52.0	0.9	45.4	1.1	38.2	0.9
12 000	35.4	0.8	31.4	0.9	50.3	0.7	43.9	0.9	36.9	0.7
16 000	34.5	0.6	30.7	0.8	49.1	0.6	42.3	0.7	36.0	0.6
20 000	33.7	0.5	29.9	0.7	48.0	0.5	41.2	0.6	35.1	0.5

[a] Valid for $P > 180$ kg/cm².

[1] J. W. Stewart, J. Phys. Chem. Solids **1**, 146 (1956).
[2] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **74**, 425 (1942).
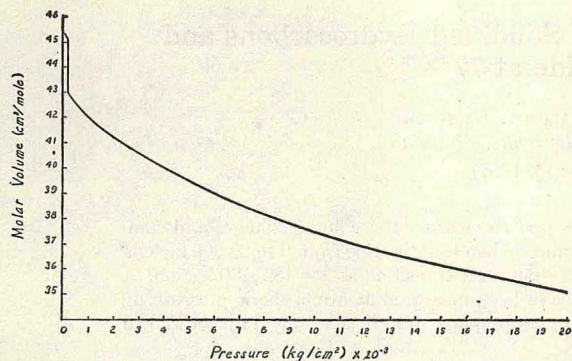[3] F. Birch, J. Geophys. Research **56**, 227 (1952).

FIG. 1. The molar volume of carbon tetrafluoride at 77°K.

TABLE II. Densities and molar volumes at $P=1$ atmos, $T=77°$K.

Substance	Density g/cm³	Molar volume cm³
Ethane	0.713±0.002	42.2±0.1
Ethylene	0.732±0.002	38.3±0.1
Propane	0.763±0.004	57.8±0.3
Propylene	0.806±0.003	52.2±0.2
Carbon tetrafluoride	1.943±0.007	45.3±0.2

accuracy of the observed relative compression $\Delta V/V_0$ is ±5% to 10% of its value. As before, the compressibilities $\beta = -(1/V)(\partial V/\partial P)_T$ were calculated by differentiation of the Murnaghan relation

$$P = \frac{3}{2\beta_0}[y^7 - y^5][1 - \xi(y^2 - 1)].$$

Here β_0 is the compressibility at zero pressure, y is the cube root of the ratio of the volume V_0 at $P=0$ to the volume V at pressure P, and ξ is an adjustable constant. The fit of the current results to this formula is not as close as in the cases of the six solidified gases He, H_2, D_2, Ne, N_2, and A previously considered.[1] The values of ξ for the present group of solidified gases are negative and unduly large, which means that the compressibilities decrease much faster with increasing pressure than is "normal."[3] However, it must be remembered that the Murnaghan relation has only empirical significance.

The data for CF_4 could not be extrapolated in the above manner because this substance exhibits a very conspicuous first-order phase transition. Fortunately, the friction was less than for the hydrocarbons. Low-pressure data could be obtained directly with the $\frac{5}{8}$-inch sample holder, in which an abrupt discontinuity in volume was observed for both increasing and decreasing pressure. Observations of the transition pressure were made at three temperatures with the following results: $T=65±0.5°$K, no transition; $T=77±0.5°$, $P=180±80$ kg/cm²; $T=84±0.5°$K, $P=820±80$ kg/cm². Eucken and Schroeder[4] observed this transition by means of specific heat measurements at atmospheric pressure at $T=76.2°$K. From all these data the slope dP/dT was found. Since the entropy change for the transition at 76.2°K is also given by Eucken and Schroeder, ΔV can be calculated from the Clapeyron equation. This volume change is thus computed to be 1.7 cm³ per mole, while the ΔV as measured with the present apparatus is 2.2 cm³ per mole (Table I, Fig. 1). The calculated value depends strongly upon the observed

transition pressures at 77° and 84°. On account of friction, these are considerably less accurate than the ΔV measurement. It is hoped to trace this transition to higher temperature and pressure with a variable temperature cryostat now under construction.

Figure 1 shows the molar volume of solid CF_4 as a function of pressure at 77°K.

III. DENSITY MEASUREMENTS

No satisfactory data on the densities of these solidified gases at 77°K appear to exist in the literature. Measurements have been made with essentially the technique previously used in the case of solid argon.[1] Gas is allowed to condense into a 5-ml volumetric flask maintained at 77°K by a bath of liquid nitrogen. The mass of condensate is determined from the pressure drop of gas at room temperature contained in a storage tank and connecting capillaries of accurately known volume.

Unlike argon these gases all necessarily pass through the liquid state because of their low triple point pressures. Care had to be taken that the liquid froze solid throughout the volume of the flask, and that it did not draw away from the walls. The narrow capillary used resulted in slow condensation, 20 to 30 minutes being required to fill the 5-ml flask. This nearly always resulted in homogeneous freezing. However, some trouble was experienced with propane and propylene from supercooling until a few particles of chalk dust were placed in the flask. In all cases, the solid consisted of a translucent mass of small crystals. The observed pressure drops for a number of runs were reproducible, and if visual observation of the flask showed voids in the solid, that particular run was discarded. Ethane and ethylene had to be distilled at 77°K before being admitted to the storage tank. Without such distillation, bubbles were observed escaping from the solid as it froze.

The mass of gas condensing was determined from the pressure drop in the storage tank. This was of the order of 20 to 30 cm Hg. The mass of gas in the tank before condensation and after condensation could readily be determined from the equation

$$PV = nRT\left(1 + \frac{B(T)}{V}\right).$$

The second virial coefficient $B(T)$ was determined from values given in the literature. P, V, and T were meas-

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[4] A. Eucken and F. Schroeder, Z. physik. Chem. B41, 307 (1938).

ured, and the number of moles, n, was calculated. The gas in the storage tank was originally at approximately one atmosphere, at which relatively low pressure it was unnecessary to consider virial coefficients higher than the second. Values of $B(T)$ for the four hydrocarbons are given by Hirschfelder, McClure, and Weeks,[5] and for CF₄ by MacCormack and Schneider.[6] The densities quoted in Table II are based on eight or more determinations for each substance.

[5] Hirschfelder, McClure, and Weeks, J. Chem. Phys. **10**, 201 (1942).
[6] K. E. MacCormack and W. G. Schneider, J. Chem. Phys. **19**, 845 (1951).