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COMPRESSION OF SOLIDIFIED GASES TO 20,000 kg/cm² AT LOW TEMPERATURE*

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Abstract—The relative volume decrease as a function of pressure has been measured for solid He, H_2, D_2, and Ne at 4°K, for N_2 and A at 65°K, and for A at 77°K by the direct piston displacement method of BRIDGMAN. The results for He and N_2 are new, while for the other gases earlier work has been confirmed and extended to higher pressure. Solid helium is found to be the most compressible solid yet measured, being reduced in volume by a factor of 2·7 by 20,000 kg/cm² pressure. A suspected phase transition in solid helium and a definite one for nitrogen at 65°K are discussed. The Murnaghan theory of finite strain leads to a convenient representation of all the experimental data. A direct determination of the density of solid argon at 77°K made by W. M. HINDS is also reported.

1. INTRODUCTION

THE present work is a continuation and extension of that performed earlier by the author.[1] The experimental measurement of pressure-volume relations of solidified gases at low temperature is of especial interest to solid state physics because these are among the simplest of dielectric solids. Furthermore it is only at low temperature that theoretical calculations of densities are feasible. For most of the cases considered, 4°K is essentially absolute zero, so that thermal effects should be unimportant. The measurements for solid hydrogen and helium are also of concern to astrophysicists who believe that the planets Jupiter and Saturn may consist nearly entirely of solid hydrogen and helium.[2] The pressures at the centers of these planets (millions of atmospheres) are far beyond the experimentally attainable range, but it is possible to extrapolate experimental measurements made at lower pressures with a fair degree of certainty.

Measurements of relative volume changes have been made up to 20,000 kg/cm² for helium, hydrogen, deuterium, and neon at 4°K, for nitrogen and argon at 65°K, and for argon at 77°K. Inasmuch as no careful theoretical calculations of density as a function of pressure seem to exist for these substances, the present paper is concerned primarily with experimental data with little attempt at theoretical interpretation. It is hoped that these results may serve as a stimulus to further theoretical work.

2. APPARATUS AND TECHNIQUE

The piston displacement method, originally developed by BRIDGMAN,[3] was used in the present work. The new 20,000 kg/cm² apparatus is for the most part simply an enlarged version of the earlier low-temperature equipment[1, 4] so only those features which are different in the present apparatus need be described in detail here. The stainless-steel (Type 304) tension and compression members of the press were once again in the form of hollow concentric cylinders. These were about 30 inches long with wall thickness $\frac{1}{8}$ inch, and were of 2 inch and $1\frac{1}{2}$ inch o.d., respectively. The maximum force transmitted to the compression member by the piston of the hydraulic press was about 7 tons, which corresponds to a pressure of 20,000 kg/cm² over the $\frac{1}{4}$-inch experimental piston tip. The pressure in the hydraulic system was measured and could be maintained constant by means of a dead weight piston gauge to an estimated accuracy of 0·5 per cent. The motion of the upper end of the compression member could be followed as the

pressure was varied to within less than 0·005 mm by means of a micrometer telescope.

As in the past, the technique was to apply a one-sided compressive force directly to the sample of solidified gas contained in a thick-walled cylinder. If measurements of the piston displacement are to give meaningful values of $\Delta V/V_0$, the solid samples must be fairly plastic. Extrusion experiments reported earlier[1] have shown that hydrogen, deuterium, and neon at 4°K, and argon at liquid-nitrogen temperatures, are quite plastic, at least at low pressures. Departures from hydrostatic pressure within the samples will not be large provided that the shear strength of the solid is only a small fraction of the maximum applied pressure.

In the earlier work by the author to 4000 kg/cm²[1] and by SWENSON to 10,000 atm.,[4] the piston tips and sample holders were both made from a heat-treated tool steel. It was found early in the present investigation that cylinders (o.d. 1 inch, i.d. ¼ inch) made from this material containing solid hydrogen burst at pressures of the order of 10,000 kg/cm². The fractures appeared to be extremely brittle. In order to reach 20,000 kg/cm², it was found necessary for the cylinders to use a low-carbon nickel steel, which was more ductile at the low temperature. The best results were obtained with a case-hardenable alloy (AISI 4615) of composition C 0·13–0·18 per cent, Mn 0·45–0·65 per cent, Si 0·20–0·35 per cent, Ni 1·65–2·00 per cent, Mo 0·20–0·30 per cent.[5] The cylinders were heat treated for toughness, but not carburized as there was no advantage in hardening the surface. The piston tips were still made of the hardened Ketos steel to avoid plastic deformation. There was no evidence that the thermal expansivity of these two steels differed by an amount sufficient to spoil the machined fit.

The cylinders were constructed with one closed end. In spite of the greater difficulty in fabrication, this design was essential in the present work because of the need for sealing washers around the moving piston. The open-ended design with two pistons used successfully by SWENSON[4] in his measurements on the alkali metals would double the packing difficulties which are already quite severe with one piston.

The samples were prepared by allowing the gas to condense into the sample holder at low temperature through a 0·035-inch stainless-steel capillary. All except helium at 4°K and nitrogen at 65°K could be frozen at atmospheric pressure. The gases were prevented from leaking out by means of a greased piece of thin brass foil clamped tightly over the top of the cylinder. The brass foil gave a better seal than did the Glassine envelope window used before,[1] and was readily broken by the piston when pressure was applied. To prevent blockage during the filling, a current of 0·5–1·0 ampere was passed through the capillary. The condensation pressure varied between atmospheric and 30 psig (except for He and N₂) which was in all cases above the triple point pressure, so the samples must have passed through the liquid state before freezing.

The preparation of the He samples is worth describing in detail. At 4·2°K the freezing pressure of helium is 143 kg/cm²[6] or 2,040 psi so that at least this much pressure must be applied to the liquid in the sample holder in order to produce solid. As was discovered in the earlier work[1] the most satisfactory packing material at 4°K is metallic potassium. For maximum efficiency in sealing, the unsupported area principle of BRIDGMAN[7] must be utilized. At 4°K potassium flows plastically at a pressure of a few hundred atmospheres; below this pressure it will not seal. A number of attempts were made to solidify liquid helium in the sample holder merely by breaking through the brass seal with the high-pressure piston but the liquid always squirted out before the packing became effective.

Fig. 1 shows the scheme that proved successful. The packing was placed beneath the seal on the top of the sample holder. The seal was made from a disk of copper 0·010 inch thick which had been annealed before being forced into a conical shape. This heavier seal was needed to withstand the high gas pressure in the sample holder. The capillary ran from the sample holder out to room temperature and into a heavy walled cylinder of several cm³ volume which served as a "pressure booster", and thence to a full helium cylinder. After the apparatus had been assembled, but before it was cooled, helium gas at about 2000 psi was admitted to the sample holder. This served to compact the potassium washer while it was soft. When the apparatus was cooled to 4°K the pressure in the capillary dropped several hundred psi as liquid condensed in the sample holder. Then the capillary was electrically heated (to prevent blocking) and the full helium tank pressure of 2500 psi was admitted. The pressure booster was immersed in liquid nitrogen, the valve between it and the helium cylinder closed, and the pressure booster then transferred to a bath of boiling water. When equilibrium had been attained the pressure in the sample holder was estimated to be 6500 psi, well above the solidification pressure. The heating current was then cut off to allow the helium in the capillary to solidify.

Two pumps connected in parallel were used in the hydraulic system so that the pressure could be raised rapidly. When only one pump was used, the sample was lost between strokes after the copper seal had been broken but before the packing sealed. With two pumps worked by hand 180° out of phase this difficulty was avoided. Once the pressure had successfully been raised to a few thousand atmospheres the sample was never subsequently lost. The friction in the packing was sufficiently large so that the oil pressure could be dropped to zero without loss of the sample.
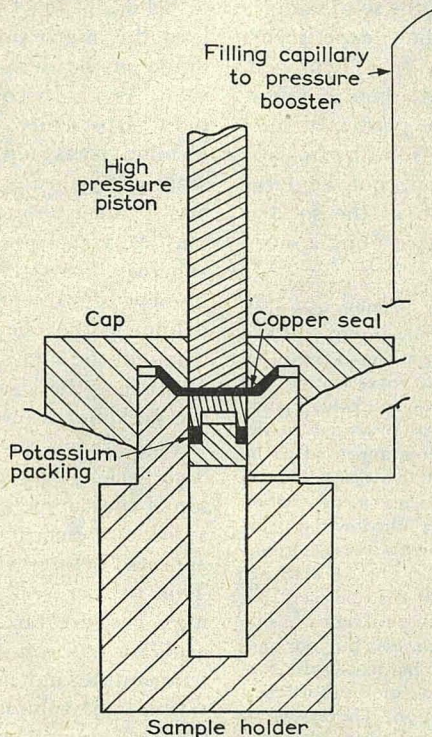

FIG. 1. The solid-helium sample holder.

The same technique as described above was used to produce samples of solid nitrogen at 65°K, for which the solidification pressure is approximately 100 kg/cm². [8]

The low-temperature bath liquid was contained in a conventional all-metal Dewar of five litres' capacity. The surrounding liquid-nitrogen jacket consisted of a commercial (Hofman Laboratories, Inc., Newark, N.J.) 15-litre stainless-steel Dewar. With the pressure apparatus in position, the evaporation rate of helium from the inner Dewar was about one litre of liquid per hour, so that, after losses from initial cooling of the apparatus from 77° to 4°, runs lasting three hours could be made. For runs at 77° and 65° the inner Dewar was filled with liquid nitrogen. The temperature of 65° was obtained by pumping vapor from the bath to 125 to 130 mm of mercury, and could be held constant to ±0·5°K by manual adjustment of a valve in the pumping line.

The technique for taking the data was exactly as previously described. [1, 4] The pressure was rapidly run up to maximum value and released two or three times to insure compaction of the sample. When reproducible telescope readings at maximum pressure were obtained the actual recording of data was started. The pressure was monotonically decreased to zero by removing weights from the dead weight gauge pan in ten to fifteen steps and telescope readings recorded for each value of the pressure. Sufficient time was allowed between readings to maintain isothermal conditions in the sample and to make sure that there was no drift in the telescope readings. At zero pressure the position of a fiducial mark on the observation window was recorded, the telescope refocussed on the compression member, and a set of readings taken with pressure increasing to the maximum value. The initial and final telescope readings for such a run nearly always agreed closely; if they did not the data were rejected. Usually a second run, and occasionally a third, were made before the apparatus was disassembled.

The three important corrections for this type of measurement are:

1. Friction
2. Distortion of the apparatus under pressure
3. Dilation of the sample holder volume from internal pressure.

Friction is the principal factor limiting the accuracy of the results. It is particularly severe at 4°K, and in some of the runs the separation between points of constant telescope reading for increasing and decreasing pressure was as much as 3000 kg/cm², or 15 per cent of the maximum pressure. Most of the friction resides in the sample itself and in the potassium packing; a relatively small amount is contributed by the leather packing in the hydraulic press at room temperature. BRIDGMAN[3] has discussed such friction in connection with his room temperature compressibility measurements and concludes that the most realistic correction is an average between the curves for decreasing and increasing pressure at constant displacement. This was the practice adopted here. Near the two ends of the curve one can no longer interpolate halfway between the smooth curves connecting the experimental points, but must extrapolate parallel to one or the other. See Fig. 2 below. One can have considerable confidence in this procedure if the two curves are parallel, or nearly so, as they were always observed to be. This shows that the friction is nearly constant. In the worst cases the half-height of the hysteresis loop of displacement against pressure was 15 to 20 per cent of the total compression of the sample, so that if the curves are parallel to within 15 per cent to 20 per cent as was always the case, an uncertainty of about 3 per cent is introduced into the final values of $\Delta V/V_0$.

The second correction is for the distortion of the apparatus itself under pressure. This must be evaluated with each sample because the compression of the potassium packing varies from run to run depending upon the thickness of the washer. The solidified gas sample is allowed to escape by temporarily warming up the apparatus, and a hysteresis loop then obtained for decreasing and increasing pressure with the piston pressing on the bottom of the sample holder. A reading of the fiducial mark on the window is also taken so that the sample length may be calculated. The friction in this "blank run" is of the order of 500 kg/cm²,

much of it being contributed by the packing. Correction is made in the same manner as when the sample is present. Fig. 2 shows plots of the actual data taken in one of the runs with solid helium.
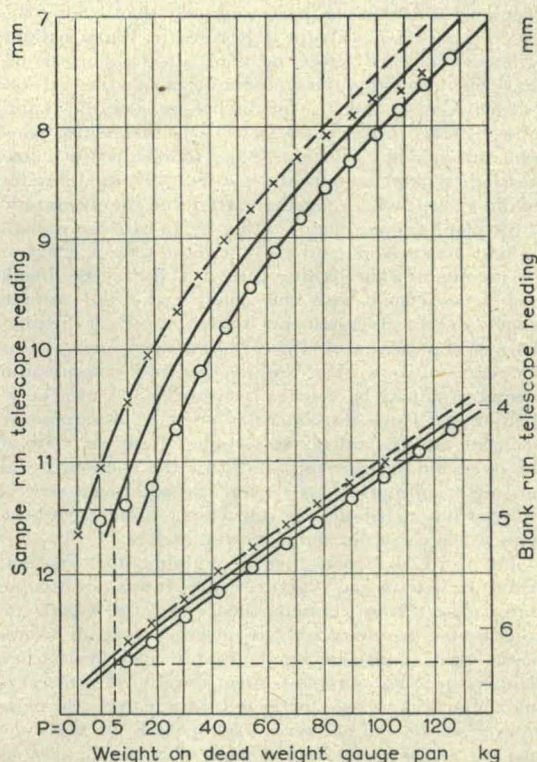

FIG. 2. Experimental data for a typical helium compressibility run, 7 March 1956. The blank run, the friction correction, and the method for obtaining the sample length are shown.

O = Increasing pressure.   X = Decreasing pressure.

The ratio of the blank run displacement to the total displacement with a sample ranged from about 0·3 for the longest H_2, D_2, and He samples up to about 0·6 for short samples. Since this correction can be determined considerably more accurately than can the sample compression itself, the uncertainty introduced into the final results is small.

The length of the sample at any desired pressure could easily be calculated from the telescope readings and from the position of the fiducial mark on the observation window. Whenever the sample was expelled before a blank run, the telescope had to be removed. Upon being replaced it was focussed on the fiducial mark with as nearly as possible the same reading each time to eliminate errors resulting from the direction of travel of the telescope not

being exactly parallel to the length of the compression member. It is believed that the sample length in each case is known to better than ±0.1 mm, or one per cent for average length samples.

From the actual telescope readings this length can be calculated considerably more accurately than 1 per cent, but in some cases with the 4°K runs the liquid helium bath was exhausted before the blank run could be carried out. This means that the temperature inside the cryostat was between 4° and 77° (no higher because the liquid nitrogen level in the outer Dewar was maintained constant throughout). Swenson[4] has found that the compressibility of potassium and the Young's modulus for stainless steel, which together determine the magnitude of the blank run correction, differ by an extremely small amount between 77° and 4°. The most serious effect of not maintaining the temperature of 4° during the blank run is associated with the determination of sample length. Recent measurements by Swenson[9] of the total thermal contraction of Type 304 stainless steel at low temperature show that the tension and compression members should be shorter by roughly 0.1 mm at 4° than at 77° which introduces an error of less than one per cent into the calculated sample length. In view of the larger uncertainty introduced by the friction, it did not seem appropriate to expend the additional several litres of liquid helium per run which would have been required to carry out the blank run at 4°K.

The third correction, that for sample holder dilation, had to be determined experimentally. It was not feasible to calculate it from elasticity theory because of both the complicated geometry and the uncertainty of the values of the elastic constants for the heat-treated steel at low temperature. The sample holders were filled with varying amounts of indium metal and the apparent compressibility of the indium measured at 77°K in the same manner as for the solidified gases. The difference between the apparent compression and Swenson's[10] values for indium at 77° (measured only to 10,000 kg/cm² but assumed to be linear with pressure to 20,000 kg/cm²) was attributed to sample holder dilation. The correction was found to be small in all cases, and the difference between 77° and 4° values should be completely negligible. For $\frac{1}{4}$-inch i.d. sample holders the correction amounted to 1.2 per cent of the base volume for long samples, and fell off almost linearly with length for samples shorter than 11 mm. For the $\frac{5}{16}$-inch i.d. holders the correction was 1.0 per cent at the maximum pressure (12,800 kg/cm²) for long samples, and again fell off linearly with sample length for shorter samples. The uncertainty in this determination is quite high (20 per cent) owing to the smallness of the effect, but the error resulting in the final data is small.

When all the sources of error are considered, it appears that the final experimental data for the relative volume decrease are trustworthy to about 5 per cent. The variance among the several runs made with each substance is about of this order of magnitude.

In most cases runs were made in both the $\frac{1}{4}$-inch and $\frac{5}{16}$-inch sample holders, and the sample lengths varied by a factor of two or more. No trends of the magnitude of the relative compression with either sample diameter or sample length were ever observed. This gives one confidence that hydrostatic pressure was transmitted satisfactorily by all the samples. In addition, some measurements were made on solid argon in a $\frac{5}{8}$-inch i.d. sample holder.

Since small amounts of impurity should have very little effect on the observed compressibilities, no special effort was made to obtain gases of high purity. All gases are believed to have been at least 99.0 per cent pure, which is more than adequate in view of the other limitations.

3. CALCULATION OF THE RESULTS

On account of the large and rapidly changing compressibilities of the solidified gases at low pressure, it was impossible to obtain satisfactory data for $\Delta V/V_0$ at pressures below about 2000 kg/cm². It will be seen from Fig. 2 that the friction correction can be made reliably only at higher pressure, and that extrapolating the corrected (central) curve, which is easy at the high-pressure end, is unsafe at low pressure because of the large curvatures. Therefore the base volume has been taken to be that occupied by the sample at $P = 2043$ kg/cm², corresponding to a weight of 5 kg on the dead weight gauge pan. This point is indicated by the dotted lines in Fig. 2.

Values of the relative volume decreases $\Delta V'/V_0'$ refered to the 2043 kg/cm² base volume are calculated directly from smoothed values of the observed compression of the sample diminished by the blank run correction and the sample holder dilation. The assumption that $\Delta x'/x_0' = \Delta V'/V_0'$, where x' refers to the sample length, is justified only so long as the samples are plastic and are transmitters of hydrostatic pressure, as is presumed throughout.

To obtain more meaningful data it is necessary to extrapolate the averaged and smoothed observed values of $\Delta V'/V_0'$ to give $\Delta V/V_0$, where V_0 is the volume at zero (atmospheric) pressure except as noted below. Where previous compressibility data at lower pressure exist, these can be used as the basis of extrapolation, and an estimate of the consistency of the new results obtained from the smoothness of the fit at $P = 2043$ kg/cm². A second method is to represent the $\Delta V'/V_0'$ data analytically over the range $P = 2043$ kg/cm² to $P = 20,000$ kg/cm², and then to extrapolate algebraically to $P = 0$.

It has been found by Birch[11] that Bridgman's compressibility data for a large number of substances can be represented very closely in terms of Murnaghan's theory of finite strain. Birch obtains an expression for pressure in terms of the compression ratio V_0/V from the assumption that the elastic energy of the compressed solid can be represented in terms of the square (which alone is retained in ordinary infinitesimal elasticity theory) and the cube of the finite strain. He assumes $\Psi = af^2 + bf^3$ where Ψ is the elastic strain energy and a and b are constants depending only upon the temperature. The finite compressional strain f for hydrostatic pressure, which is always positive, is found from Murnaghan's theory to satisfy the relation $V_0/V = (1+2f)^{3/2}$. One then obtains

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

where $y = (V_0'/V)^{1/3}$, β_0 is the isothermal compressibility $-(1/V_0)(\partial V/\partial P)_T$ evaluated at $P = 0$, and $\xi = -3b/4a$. We also have the relation $3/2\beta_0 = \alpha/3V_0$. In practice it is not convenient to evaluate the parameters a and b directly so that ξ must be found by trial and error. Equation (1) has been used successfully at low temperature by the author to represent the earlier data for solidified gases, and by Swenson[4] for the alkali metals.

When equation (1) is to be used to represent data where V_0 is the volume at some pressure other than zero, it should be modified as follows:

$$P - P_0 = \frac{3}{2\beta_0'}[y'^7 - y'^5][1 - \xi'(y'^2 - 1)] \qquad (2)$$

where $y' = (V_0'/V)^{1/3}$, P_0 is the pressure at which $V = V_0'$, $\beta_0' = -(1/V_0')(\partial V/\partial P)_T$ evaluated at $P = P_0$, and ξ' is an adjustable constant.

The procedure for fitting experimental data to either equation (1) or (2) is to tabulate values of the function $f(y, \xi) = (y^7 - y^5)(1 - \xi(y^2 - 1))$ against pressure for different values of ξ and to choose that value of ξ which gives the best straight line. β_0 is then readily calculated from the slope of the straight line.

Equation (2) can be used to extrapolate $\Delta V'/V_0'$ data to give $\Delta V/V_0$ by finding the value of y' (< 1) which makes $P = 0$. Then $y' = (V_0'/V_0)^{1/3}$ and $V/V_0 = (V/V_0')(V_0'/V_0)$, from which values of $\Delta V/V_0$ can be computed. This method of extrapolation works well for substances whose compressibilities do not change too rapidly with pressure, but it could not be used in the cases of helium, hydrogen, or deuterium, for which half or more of the total compression in 20,000 kg/cm² comes in the first 2000 kg/cm². For these three cases, other experimental data must be used as the basis for the extrapolation.

Once values of $\Delta V/V_0$ have been obtained, one can fit them by trial and error to equation (1). In all seven cases considered in the present investi-

gation, the maximum deviation of the observed pressure from that given by (1) was less than the estimated experimental error.

The most convenient way to calculate the compressibility as a function of pressure is to differentiate equation (1) and use the values of ξ and β_0 found in the original fitting of the relative volume change data. The result is

$$\beta = \frac{2\beta_0}{y^8}[-9\xi y^4 + (7 + 14\xi)y^2 - (5 + 5\xi)]^{-1} \qquad (3)$$

This relation has been used to calculate values of β, from which the *instantaneous* compressibility $\beta_i = -(1/V)(\partial V/\partial P)_T$ can be obtained. The analytical differentiation is more accurate than graphical differentiation, and the uncertainty in the values of β should be roughly 5 per cent, the same as in $\Delta V/V_0$. At low pressure the error may be greater because β is changing rapidly and the fit of the data by equation (1) may not be as good.

Because of the small volume of the sample holders and uncertain temperature gradients along the filling capillary, the present apparatus is not adapted for the direct measurement of densities of the solidified gas samples. Furthermore, a portion of some of the samples may have been lost by extrusion during the initial compaction. Therefore, where molar volume data are given they have been obtained from other sources and may be subject to additional uncertainty.

4. RESULTS AND DISCUSSION

Table 1 presents a summary of the compressibility determinations that were made.

The values for ξ and $3/2\beta_0$ from equation (1) for the seven cases considered are presented in Table 2.

Birch[11] has found that many of Bridgman's results up to $P = 100,000$ kg/cm² are quite closely represented by equation (1) with $\xi = 0$. In addition, Swenson[4] found that sodium, potassium, and rubidium at 4°K satisfy the same relation at pressures up to 10,000 kg/cm². The elastic energy under hydrostatic compression of these substances evidently depends only upon the square of the strain. It appears that the solidified gases behave in a more complicated manner in that all require negative values of ξ. A negative value of ξ means that the constant b in Birch's equation for the

Table 1. *Summary of compressibility runs.* x_{max} *and* x_{min} *represent the lengths of the longest and shortest samples used, measured in each case at* $P = 2043$ *kg/cm²*.

Substance	Temp. °K	$\frac{1}{4}$-inch Holder			$\frac{5}{16}$-inch Holder			0·626-inch Holder		
		Runs	x_{max} mm	x_{min} mm	Runs	x_{max} mm	x_{min} mm	Runs	x_{max} mm	x_{min} mm
Helium	4	5	12·7	5·0	0	—	—	0	—	—
Hydrogen . . .	4	3	11·5	6·6	0	—	—	0	—	—
Deuterium . .	4	3	15·6	12·9	1	14·5	—	0	—	—
Neon	4	3	14·4	5·7	1	17·6	—	0	—	—
Nitrogen . .	65	4	16·4	8·5	1	10·3	—	0	—	—
Argon . . .	65	2	17·2	10·7	2	17·4	17·3	2	21·0	15·7
Argon . . .	77	6	21·5	8·5	1	13·5	—	2	21·3	21·2

Table 2. *Values of* $3/2\beta_0$ *and* ξ *in equation* (1) *which give best fit to experimental compression data.*

Substance	Temp °K	ξ	$10^4 \times 3/2\beta_0$ kg/cm²	Remarks
Helium . . .	4	$-2\cdot3\pm0\cdot1$	0·131	$P_0 = 143$ kg/cm² at melting curve
Hydrogen . . .	4	$-1\cdot9\pm0\cdot1$	0·306	
Deuterium . .	4	$-1\cdot6\pm0\cdot2$	0·496	
Neon . . .	4	$-4\cdot0\pm0\cdot5$	1·52	
Nitrogen . .	65	$-2\cdot3\pm0\cdot1$	1·91	$P < 10{,}200$ kg/cm². $P_0 = 100$ kg/cm
		$-0\cdot7\pm0\cdot1$	(2·86)	$P > 10{,}200$ kg/cm². $P_0 = -1380$ kg/cm²
				Phase transition at $10{,}200 \pm 800$ kg/cm²
Argon . . .	65	$-4\cdot9\pm0\cdot5$	2·40	
Argon . . .	77	$-6\cdot5\pm0\cdot5$	1·63	

strain energy must be positive, since a is necessarily positive, which means that these substances are too "hard" when compared with "normal" substances which have $\xi = 0$. Their compressibilities decrease more rapidly with pressure than would be the case for a "normal" substance. However, it should be emphasized that equation (1) has no direct theoretical significance in terms of an interatomic force model and is thus merely a convenient analytical representation for the experimental data.

We now pass to a detailed presentation of the data and a separate discussion for each of the solidified gases. Table 3 presents all the data for 4°K, while the results for nitrogen and argon are given in Table 4. In both tables the original experimental data for the volume change relative to the volume at $P = 2043$ kg/cm² are given, since these results are not subject to possible errors

resulting from extrapolation to zero pressure. The instantaneous compressibilities β_i are believed to be more meaningful for comparison than $\beta = -(1/V_0)(\partial V/\partial P)_T$.

Helium. Oil-free grade "A" commercial helium such as can be handled by the Collins liquefier without a cold trap was used. Because of the elaborate seal necessary to hold the samples, the friction for these runs tended to be greater than for the others, so the overall accuracy of the results may be poorer. Unlike the other solidified gases which have been shown[1] by extrusion measurements to be fairly plastic, there is no direct evidence on how effective a transmitter of hydrostatic pressure solid helium is. On account of the sealing difficulties, it has not yet been possible to carry out extrusion experiments, or even to prepare samples in the $\frac{5}{16}$-inch sample holder. However, the $\frac{1}{4}$-inch

Table 3. Compressions at 4°K.

Pres- sure kg/ cm²	HELIUM				HYDROGEN				DEUTERIUM				NEON			
	$\frac{\Delta V'}{V_0'}$	$\frac{V}{V_0}$	M.V. cm³	$\frac{10^5 \beta_i}{\text{cm}^2/\text{kg}}$	$\frac{\Delta V'}{V_0'}$	$\frac{V}{V_0}$	M.V. cm³	$\frac{10^5 \beta_i}{\text{cm}^2/\text{kg}}$	$\frac{\Delta V'}{V_0'}$	$\frac{V}{V_0}$	M.V. cm³	$\frac{10^5 \beta_i}{\text{cm}^2/\text{kg}}$	$\frac{\Delta V'}{V_0'}$	$\frac{V}{V_0}$	M.V. c.m³	$\frac{10^5 \beta_i}{\text{cm}^2/\text{kg}}$
P_0 or 0	—	1·000	17·1	115	—	1·000	22·65	49	—	1·000	19·56	30	—	1·000	14·0	10
200	—	·924	15·8	77	—	·928	21·0	31	—	·948	18·5	22	—	·982	13·7	—
400	—	·846	14·5	41	—	·883	20·0	23	—	·911	17·8	18	—	·966	13·5	—
600	—	·792	13·5	29	—	·847	19·2	19	—	·882	17·2	15	—	·952	13·3	—
1000	—	·722	12·4	19	—	·794	18·0	14	—	·840	16·4	12	—	·927	13·0	5·3
2043	0	·625	10·7	9·8	0	·711	16·1	8·1	0	·764	14·9	7·3	0	·882	12·3	3·8
3000	·079	·579	9·9	7·0	·065	·667	15·1	6·1	·061	·715	14·0	5·5	·032	·858	12·0	—
4000	·134	·544	9·3	5·5	·110	·632	14·3	4·8	·103	·680	13·3	4·5	·055	·832	11·6	2·6
6000	·205	·497	8·5	3·8	·181	·583	13·2	3·5	·173	·632	12·4	3·3	·100	·797	11·1	2·0
8000	·256	·466	8·0	2·9	·227	·549	12·4	2·7	·215	·597	11·7	2·6	·130	·770	10·8	1·7
10,000	·295	·440	7·5	2·4	·266	·523	11·8	2·3	·253	·571	11·2	2·2	·156	·747	10·4	1·41
12,000	·325	·421	7·2	2·0	·297	·500	11·3	1·9	·281	·549	10·7	1·9	·178	·728	10·2	1·23
16,000	·370	·392	6·7	1·5	·343	·467	10·6	1·4	·325	·514	10·0	1·4	·213	·696	9·7	·98
20,000	·403	·373	6·4	1·3	·376	·445	10·1	1·2	·358	·485	9·5	1·2	·240	·669	9·4	·81

samples used varied in length by a factor of $2\frac{1}{2}$ with no systematic trend in the observed compression. Therefore it is felt quite strongly that solid helium is sufficiently plastic so that this method of measurement is valid.

The only means at hand for extrapolating the $\Delta V'/V'_0$ data to the melting pressure at 4°K was by means of the isochores given by DUGDALE and SIMON.[6] They made no direct compressibility determinations but were able to calculate thermodynamically molar volumes as functions of pressure and temperature from their measurements of the specific heat at constant volume at various densities and knowledge of the melting parameters. Values of molar volume at 4·2K were read off their diagram for different pressures between the melting pressure and 2200 kg/cm². Their value of V at 2043 kg/cm² (obtained by interpolation) was used for the basis of the extrapolation. It is quite gratifying that their curve for V below 2043 kg/cm² fits smoothly onto ours for higher pressure when the extrapolation is made in this manner. A good fit to the Murnaghan relation, equation (1), is obtained right across the junction of the two sets of data. The compressibilities as calculated from (3) for pressures below 2043 kg/cm² agree well with those for 0°K given by DUGDALE and SIMON.

Solid helium is seen to be the most compressible of all solids, as has long been suspected. The main reason for this is its large zero-point energy which causes its volume at zero pressure to be much larger than it otherwise would be. This is the cause of the very rapid decrease of compressibility with pressure—by a factor of ten in the first 2000 kg/cm², and by almost another factor of ten at $P = 20,000$ kg/cm². At the higher pressures where the elastic energy of compression is large compared to the zero-point energy, the compressibility is almost exactly the same as for hydrogen and deuterium, and less than double that for neon and argon (at 77°K). If one takes for the zero-point energy its value on the melting curve at 0°K of 50 cal/mole,[12] one finds that the work of compression becomes of the same order of magnitude at a pressure of about 1000 kg/cm². The very rapid decrease of compressibility with pressure appears to slow down near $P = 6000$ kg/cm², at which point the total work of compression is roughly six times the zero point energy. At 20,000 kg/cm² the elastic energy is seventeen times the initial zero-point energy. This calculation is of only qualitative significance because the Debye θ and therefore the zero-point energy increase sharply with decreasing volume,[6] but it would appear that the compressibility at the top of the pressure range

should not be greatly influenced by the zero-point energy.

When the helium data were first analysed there was a strong suspicion that there was a phase change in the solid at a pressure of 10,000 to 11,000 kg/cm². It appeared that two values of the constants ξ and β_0 of equation (1) were needed to fit the data below and above this pressure. Subsequent examination in which equation (1) was applied to each of the runs separately showed that not all of them exhibited signs of a transition. The friction is so large that a sudden change in the compressibility or even a small volume discontinuity would be smeared over a wide pressure range and practically unobservable. The known transition in solid nitrogen, to be discussed below, was barely discernible in the data for that substance and friction was less severe in the nitrogen runs than with the helium. The present experimental data are not sufficient to confirm or deny the existence of a transition in the neighborhood of 10,000 kg/cm². Because of this doubt as to the reality of the transition, only one value of ξ was used to represent the data. The fit at $P = 20,000$ kg/cm² is still within experimental error. Further measurements are contemplated.

The question is of particular interest because of the first order transition in the solid found at higher temperature by DUGDALE and SIMON.[6] Their transition line intersects the melting curve at $T = 14.9°K$, but the initial slope is definitely towards higher temperature with higher pressure. It is unlikely that there could be a third phase at the lower temperature because an inert substance like helium must crystallize in a close-packed structure and there are only the two possibilities. DUGDALE and SIMON believe that their transition is from close-packed hexagonal to close-packed cubic. Therefore, if this transition is to occur at 4°, the equilibrium line between the two phases must bend back on itself. At the melting curve the volume change in the transition (calculated from the Clapeyron equation and measured thermal quantities) was found to be only 4×10^{-4} cm³ or of the order of one part in 30,000. Even in the absence of friction this could never be observed as a volume discontinuity with a piston displacement apparatus. The best one could hope for would be a break in the compressibility as calculated from the $\Delta V/V_0$ data.

Theoretical calculations by BARRON and DOMB[13] on the relative stability of the two close-packed lattices have indicated that there should be a first-order transition at absolute zero from close-packed hexagonal to close-packed cubic at high pressure. In the case of helium they find that the transition should start out from the melting curve at 15°K as observed by DUGDALE and SIMON, but that at higher pressure it should reverse its direction and

go to lower temperature. BARRON and DOMB conclude that the energy difference between the two lattices is always very small (of the order of 0.01 per cent), so that the volume change at the transition should be correspondingly small. At 4°K their calculations indicate a transition at a molar volume of 4.5 cm³; the suspected effect in the present data occurs at 7.4 cm³/mole. The discrepancy is large, but the computations are subject to error because of the extremely small energy difference involved. If the data of Table 3 are extrapolated using equation (1), a molar volume of 4.5 cm³ is found to correspond to a pressure of 75,000 kg/cm². Conclusive experimental verification of this effect must await a means for substantially reducing friction in solidified gas samples at 4°K, and possibly also extension of the measurements to higher pressure.

Hydrogen and Deuterium. Standard commercial hydrogen was used. The deuterium was supplied by the Stuart Oxygen Company with a purity of better than 99.5 per cent. The present results confirm the earlier ones[1] very closely. It was necessary to use the value of $\Delta V/V_0$ at $P = 2043$ kg/cm² that had been obtained before[1] to carry out the extrapolation of the present $\Delta V/V'_0$ data to zero pressure. When this is done the new $\Delta V/V_0$ data agree almost perfectly with the old over the entire pressure range of the latter, which was 0 to 10,000 kg/cm² for both hydrogen and deuterium. The constants in equation (1) needed to fit the new data up to 20,000 kg/cm² are the same as before, so that the new results could have been obtained simply by extrapolating the old.

Only three runs, all with $\frac{1}{4}$-inch samples, were deemed necessary for hydrogen because of the excellent agreement both among themselves and with the earlier results. There is evidence that the plasticity of solid hydrogen continues to be very high at high pressure both from the mode of bursting of the tool-steel sample holders used at the beginning of this investigation and the extremely rapid extrusion and loss of sample that occur in the absence of packing.

The values of the molar volumes of hydrogen and deuterium at zero pressure used in Table 3 were obtained by MEGAW.[14]

Zero point energy again plays a predominant role in the very high initial compressibilities of H_2 and D_2, as well as in the rapid decrease of compressibility at high pressure. At high pressure the molar volumes of H_2 and D_2 approach each other but they still differ by 6 per cent at 20,000 kg/cm². This means that the zero-point energies still play

a role as otherwise the molar volumes should be the same. Of course the zero-point energy increases to some extent with pressure, but not so fast as the compressional energy so that the relative importance of the zero-point energy diminishes as the pressure is raised.

It is interesting to note that at $P = 20,000$ kg/cm² the energies of compression of H_2 and D_2 are both of the order of 30 per cent larger than for helium in spite of the larger compression of the latter. This comes about because of the larger

initial molar volumes of hydrogen and deuterium and because of the greater relative decrease of the compressibility of helium at pressures near the top of the range.

Neon. The neon used was the Linde Air Co. research grade from a small cylinder. The extrapolation to zero pressure was made with the aid of the Murnaghan formula, equation (1). The compressibility changes slowly enough at low pressure so that this method is reliable. The $\Delta V/V_0$ data
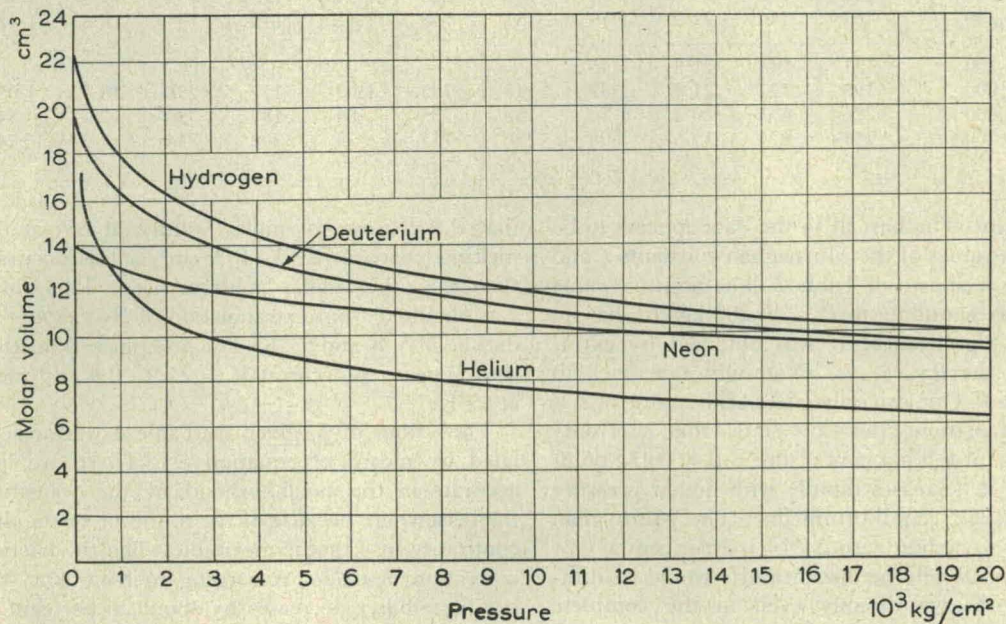

FIG. 3. The molar volumes of helium, hydrogen, deuterium and neon at 4°K.

agree satisfactorily with the older results[1] up to $P = 4000$ kg/cm². The molar volumes have been calculated from a value for the density of $1 \cdot 443$ gm/cm³ given by PARTINGTON.[15] Except at low pressure the molar volume of neon is larger than that of helium because the Ne atom is larger than the He atom. The reversal below $P = 700$ kg/cm² is a consequence of the helium zero-point energy.

Nitrogen. Air Reduction Co. oil-pumped dry nitrogen was used. The measurements with nitrogen served as a rehearsal for helium since at 65° a

pressure of 100 kg/cm² must be applied to liquid nitrogen to solidify it. The extrapolation below $P = 2043$ kg/cm² was made with the aid of equation (1). The compressibility appears to change slowly enough at low pressure so that this should be valid.

The principal interest in the results is the confirmation at higher temperature of the phase transition found in solid nitrogen by SWENSON.[16] All of the runs at 65°K show evidence of a sudden change in compressibility, which, after friction has been eliminated, occurs at $P = 10,200\pm$

Table 4. Compressions of Nitrogen and Argon

Pressure kg/cm²	Nitrogen 65°				Argon 65°			Argon 77°K			
	$\dfrac{\Delta V'}{V_0'}$	$\dfrac{V}{V_0}$	M.V. cm³	$10^5 \times \beta_i$ cm²/kg	$\dfrac{\Delta V'}{V_0'}$	$\dfrac{V}{V_0}$	$10^5 \times \beta_i$ cm²/kg	$\dfrac{\Delta V'}{V_0'}$	$\dfrac{V}{V_0}$	M.V. cm³	$10^5 \times \beta_i$ cm²/kg
P_0 or 0	—	1·000	29·3	7·9	—	1·000	6·2	—	1·000	24·3	9·2
500	—	·970	28·4	6·4	—	·975	4·9	—	·964	23·4	6·0
1000	—	·941	27·6	5·2	—	·954	4·0	—	·939	22·8	4·7
2043	0	·897	26·3	3·9	0	·920	3·0	0	·901	21·9	3·3
4000	·059	·841	24·6	2·8	·046	·877	2·1	·051	·853	20·7	2·2
6000	·105	·802	23·5	2·1	·082	·845	1·63	·089	·820	19·9	1·68
8000	·138	·772	22·6	1·77	·108	·820	1·34	·115	·795	19·3	1·40
10,200	·167	·746	21·9	1·50	·131	·798	1·15	·140	·774	18·8	1·18
10,200	·171	·744	21·8	1·45	—	—	—	—	—	—	—
12,000	·190	·727	21·3	1·32	·148	·783	1·03	·157	·758	18·4	1·05
16,000	·226	·693	20·3	1·10	·180	·755	·84	·189	·730	17·7	·84
19,000	·251	·671	19·5	·98	·200	·737	·74	·208	·714	17·3	·74

800 kg/cm². The best fit to the data appears to be with two values of the Murnaghan constants ξ and $3/2\beta_0$, as is shown in Table 2. The negative value of P_0 corresponding to $P > 10,200$ kg/cm² has no physical significance. It was obtained by extrapolating the $f(y, \xi)$ vs. P straight line back to $f(y, \xi) = 0$. One can only guess at the value of ΔV at the transition. SWENSON states that it is only 0·21 cm³, or 0·8 per cent at the α–β–γ triple point and that it decreases rapidly with higher pressure along the β–γ equilibrium line. The Murnaghan fit seems to be best with $\Delta V = 0·3$ per cent at 65°. Such a small volume discontinuity would be difficult to observe directly even in the complete absence of friction. At lower temperatures SWENSON had less friction because he used no packing, but this would not be possible at 65° where the sample is initially liquid.

In the earlier work,[1] a single rough determination of β was made for solid nitrogen at 4°K. The agreement with the present results is poor both because of the large difference in temperature and the fact that solid N_2 appears to be somewhat brittle at 4°. No sign of SWENSON's α–γ transition was noted then because it would have occurred very close to the top of the pressure range (at 4°, $P = 3500$ kg/cm²) where the friction correction is uncertain.

There is considerable diversity in published values for the density of solid nitrogen [8, 16] so that the estimate of molar volume at 65° at the melting curve of $29·3 \pm 0·3$ cm³ is less accurate than the other molar volumes used. This value was obtained from extrapolation of SWENSON's[16] data at 39·5°K and 53°K. The β–γ phase transition thus appears to occur at $V = 21·9 \pm 0·4$ cm³/mole at 65°K.

The values of β_i given in Table 4 were calculated by means of equation (3). These are less accurate in the neighborhood of the transition than elsewhere because of the rounding of the discontinuity in β that is inevitable when the friction correction is made. According to SWENSON, the compressibility decreases by about 20 per cent as the transition is crossed in the direction of increasing pressure. Table 4 shows a discontinuous decrease of less than 5 per cent which is without doubt too small. Compressibilities determined graphically from the slope of the V/V_0 vs. P curve above and below the transition differ by 12 per cent.

Argon. Commercial argon was used, so this was probably the least pure of all the gases, of the order of 99·0 per cent. Determinations of compression were made at both 65° and 77° because the compressibility at low pressure appears to depend strongly upon temperature in this temperature range. At both temperatures extrapolation to $P = 0$ was made by means of the Murnaghan

relation. The resulting $\Delta V/V_0$ data agree satisfactorily with the earlier work[1] as do the values of ξ and $3/2\beta_0$.

BARKER and DOBBS[17] have recently completed measurements of the adiabatic compressibility of solid argon by means of an ultrasonic interferometer. They measured both longitudinal and transverse wave velocities in polycrystalline samples of solid argon which had been slowly condensed from the gaseous phase below the triple point pressure. These measurements improved upon the earlier results by the same investigators[18] in which only longitudinal velocities had been measured. This method yields values of the compressibility only at zero pressure. BARKER and DOBBS combine their values of the adiabatic compressibility with other data to calculate the initial isothermal compressibility β_0 at different temperatures. At 65°K they obtain $\beta_0 = 5·2 \times 10^{-5}$ cm²/kg, while Table 4 gives $\beta_0 = 6·2 \times 10^{-5}$ cm²/kg. At 77° the values are $6·0 \times 10^{-5}$ cm²/kg and $9·2 \times 10^{-5}$ cm²/kg, respectively. Allowing for an extra 5 per cent error introduced into our values of β_0 by the extrapolation we see that the results at 65° no longer disagree badly, but that there remains a serious discrepancy at 77°.

BARKER and DOBBS believe that the discrepancy may be caused by incomplete compaction of the samples used in the piston displacement measurements. These were prepared by condensation through the liquid state, and were initially quite open in their structure as was shown by the irreversible volume decrease (of the order of 20 per cent) during the initial compaction. However, the reproducibility of the telescope readings, and particularly the fact that the data with maximum pressure 19,000 kg/cm² agree so well with those for which $P_{max} = 4000$ kg/cm²[1] make it highly improbable that the samples are porous. If some pores had remained at 4000 kg/cm² the higher pressure should have been more effective in closing them without affecting the reproducibility of either set of data. If our compressibilities have been too high for this reason, the present results for β should have been lower than the previous ones. This is not the case.

To verify that no large error was introduced through the extrapolation to low pressure, a separate series of runs was made for argon at both 65° and 77° in a large stainless-steel sample holder of inner diameter 0·626 inch. The maximum pressure reached with this holder is 3000 kg/cm², and extrapolation need be made only below $P = 325$ kg/cm². Over the range 325–3000 kg/cm² the agreement with the results in Table 4 was satisfactory. Equation (1) was used to extrapolate over the short range $P = 325$ kg/cm² to $P = 0$. A graphical estimate for β_0, which is subject to large error, yielded values

higher than those in Table 4. A more meaningful graphical determination of β at low pressure can be made at $P = 325$ kg/cm² where the friction correction should be reliable. This gives $\beta = 5·8 \times 10^{-5}$ cm²/kg at 65°K and $6·4 \times 10^{-5}$ cm²/kg at 77°. These values can be regarded as lower limits for β_0 so that it would appear that the results of BARKER and DOBBS may be a bit too low.

Another possible source of the discrepancy arises from uncertainty as to the density of solid argon, which needs to be known in the computation of compressibility from the measured sonic velocities. Capt. W. M. HINDS in this laboratory has made a determination of the density at 77°K[19] in order to check the previous values.[17] His method was to allow argon to condense from a 40-litre gas holder at room temperature into a 5 ml Pyrex volumetric flask. The mass of gas in the gas holder before and after condensation was determined from the initial and final pressures, the volume of the gas holder, and the temperature. The volume of the gas holder was determined to 0·1 per cent by direct measurement. The virial coefficients of argon gas[20] were used in the calculation of mass. The Pyrex flask was gradually lowered into a bath of liquid nitrogen so that solid formed in uniform laminae beginning at the bottom of the flask. The rate of growth was of the order of 0·1 mm/min, which is comparable to that obtained by BARKER and DOBBS during the growth of their samples. HINDS' solid was always transparent and uniform in appearance, although great care had to be exercised to prevent the formation of bubbles. It was thus believed to be non-porous. A total of 28 runs were made, some with a starting pressure above the triple point (516·8 mm Hg), and others below. The total pressure drop in the gas holder during condensation was about 100 mm Hg.

The results for the density clustered into two groups, depending upon whether the solid had formed from the liquid, or directly from the gas. The density was found to be $1·644 \pm 0·006$ gm/cm³ if the solid had frozen from liquid, and $1·627 \pm 0·006$ gm/cm³ for starting pressures below the triple point. In general, the higher the starting pressure, the higher was the observed density. The temperature may be taken to be $77·0 \pm 0·5$°K, with slight variations caused by impurities in the nitrogen bath that was used.

For comparison with the densities of BARKER and DOBBS, we should take $\rho = 1·627$ gm/cm³, as in their experiment the argon did not pass through the liquid phase. At 77°, they use the value $\rho = 1·616$ gm/cm³, so that the agreement at this temperature is certainly satisfactory considering the rather large experimental errors in some of the older density measurements that were used to obtain the above figure. The discrepancy between the current β_0 and that of BARKER and DOBBS is thus not to be explained by an error in density.

Even if our extrapolation below $P = 325$ kg/cm² were incorrect, and the result of BARKER and DOBBS therefore not significantly too low, the values of V/V_0 in Table 4 would be affected very little. The only part of the pressure-volume

relation that would be wrong would be at the extreme lower end. A separate experiment to obtain a precise value of the initial compressibility by direct means would be highly desirable.

Since the samples were all frozen from the liquid, the molar volumes at 77° in Table 4 are based upon $\beta = 1 \cdot 644$ gm/cm³. No molar volumes are given at 65° because of the uncertainty in the density. If BARKER and DOBBS's value is used, one obtains the inconsistent result that $V_{65} > V_{77}$ at $P = 19,000$ kg/cm². This could be due to a small error in either the densities or the compressibility data.

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