Compressibilities of Some Solidified Gases at Low Temperature

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The compressibilities of several solidified gases have been measured by applying a one-sided compression directly to a cylindrical sample, and observing the resulting volume change. Pressure was conveyed to the samples at low temperature by means of long stainless steel compression and tension members. Preliminary extrusion experiments with these solidified gases assured that the pressure applied to the samples was always at least approximately hydrostatic. Compressibility data have been obtained at pressures up to 10 000 kg/cm² for solid hydrogen and deuterium at 4°K, and to 4000 kg/cm² for solid neon at 4°, solid argon at 65° and 77°, and solid krypton at 77°. A single less accurate determination has also been made for solid nitrogen up to 3000 kg/cm².

I. INTRODUCTION

EXPERIMENTAL measurements of compressibilities by the piston displacement method have not previously been feasible at very low temperature because of technical problems involved in the simultaneous production of high hydrostatic pressure and low temperature. The only existing low-temperature compressibility measurements have made use of techniques other than the observation of piston displacement, and have necessarily been confined to relatively low pressures. The two main difficulties heretofore confronting the more direct approach have been (1) the excessive quantity of heat that would be transferred to a liquid helium cooling bath by conduction through the heavy steel parts of conventional high-pressure equipment, and (2) the absence at such temperatures of suitable fluid pressure-transmitting media.

In the present work, the cooling problem was overcome through the use of long cylindrical compression and tension members which were attached to a conventional hydraulic press at room temperature. These could apply compressive force to samples maintained at 4°K. They were made of an 18–8 austenitic stainless steel (Type 304), since these alloys combine unusually high mechanical strength and ductility at low temperature with low thermal conductivity. Forces up to a ton and a half could be applied at 4°K to samples $\frac{1}{4}$ inch in diameter. Once the apparatus had been cooled down, less than 100 cm³ of liquid helium per hour were lost by evaporation from the cryostat.

Even at low pressures there exist no liquids or gases at liquid helium temperatures. Helium itself solidifies at 4.2° at a pressure of only 140 atmospheres. Therefore the usual technique of embedding the samples under investigation in a pressure-transmitting liquid cannot be used. Instead, it is necessary to rely upon solid materials to transmit hydrostatic pressure. Bridgman[1] has encountered and solved this same problem at room temperature during his investigations at pressures of 100 000 kg/cm².

The force applied to the cylindrical samples was, in

the present apparatus, always a one-sided compression. Under these conditions, meaningful compressibility data can be obtained only if the applied uniaxial stress system is effectively translated into a hydrostatic pressure within the solid sample. For this to be the case, the material under investigation must have a very low shear strength. It must be capable of flowing plastically under low applied force so that the shear components of stress within a confined sample are always small compared with the hydrostatic component. Only for such plastic substances can the compressibility be directly calculated from the displacement of the piston with which the one-sided compression is applied.

The most convenient measure of plastic flow strength turned out to be the applied pressure required to cause extrusion of the cylindrical samples through a smaller axial hole. The samples varied between $\frac{1}{4}$ inch and $\frac{1}{2}$ inch in length, while the diameter of the extrusion hole ranged from $\frac{1}{16}$ inch to $\frac{3}{16}$ inch. Extrusion pressures were measured for a number of different materials, sometimes at both liquid nitrogen and liquid helium temperatures. The sample holder used in these measurements is shown in Fig. 1. Several normally solid substances, including some of the alkali metals, were investigated as well as solidified gases.

In all cases, the extrusion pressures were taken to be those at which relatively rapid flow through the hole
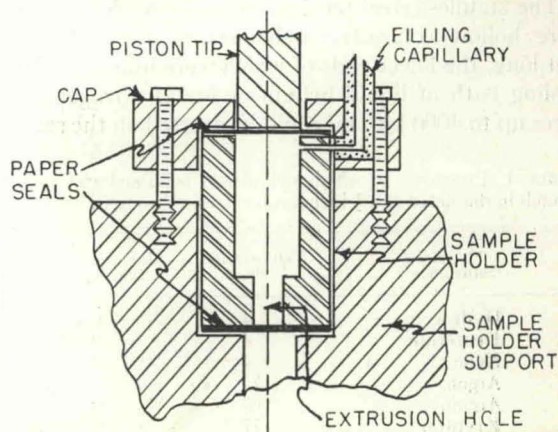

FIG. 1. The apparatus for solidified gas extrusion experiments.

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[1] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **74**, 425 (1942).

took place. These values were often considerably above the initial yield points. The best pressure transmitters are clearly those materials which extrude rapidly and smoothly at low pressure. Solid hydrogen and deuterium proved to be by far the most satisfactory, with the other solidified gases listed in Table I being somewhat inferior. The most plastic of the normally solid materials investigated at 4°K were the alkali metals, but all of these were poorer than the majority of the gases of Table I. A number of substances which are quite plastic at room temperature were found to harden up greatly at low temperature.

The quoted extrusion pressures, while reproducible to perhaps 10 percent, have little absolute significance. They depend upon several variables, including the sample length and the size of the extrusion hole. However, the relative magnitudes of these pressures, for fixed sample length and hole size, are meaningful as measures of the comparative ability of different substances to transmit hydrostatic pressure.

Compressibility data were taken for each of the solidified gases of Table I at each temperature listed. These were all felt to be sufficiently good pressure transmitters to justify the direct method of measurement, especially since there is evidence that this criterion of complete extrusion is a bit too stringent. The observed extrusion pressures were often higher than the initial yield points by an amount greater than could reasonably be expected from work hardening.

It is worth remarking that, while quite plastic at liquid nitrogen temperatures, the solid argon and krypton samples were shattered instead of being extruded by pressure at 4°K. Solid nitrogen at 4° was also somewhat brittle. All the gases were used directly from storage tanks without prepurification. The presence of a small amount of impurity might be expected to make the samples more brittle at low temperature while having only negligible effect upon their compressibilities.

II. EXPERIMENTAL TECHNIQUE

The stainless steel tension and compression members were hollow concentric cylinders approximately two feet long, the lower ends of which were immersed in the cooling bath of liquid helium or liquid nitrogen. Pressures up to 4000 kg/cm² could be exerted on the samples

TABLE I. Pressures at which cylindrical solidified gas samples, ¼ inch in diameter and ½ inch long, extrude through ⅛-inch hole.

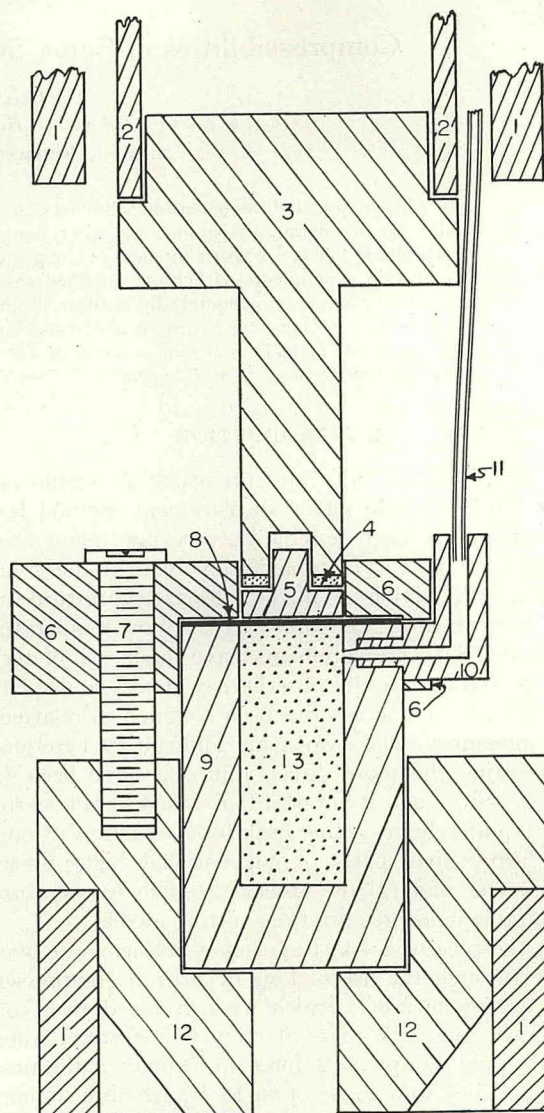| Substance	Temperature °K	Extrusion pressure (kg/cm² ×10⁻³)
Hydrogen	4	0.24
Deuterium	4	0.29
Neon	4	0.67
Argon	77	0.26
Argon	63	0.58
Krypton	77	0.34
Nitrogen	4	0.88

FIG. 2. The apparatus for compressibility measurements at low temperature. 1. Tension member. 2. Compression member. 3, 4, 5. Experimental piston tip with potassium packing washer. 8. Sealing paper. 9. Sample holder. 10, 11. Filling capillary. 12. Sample holder support. 13. Solidified gas sample.

at low temperature by means of a piston tip ¼ inch in diameter. The piston tips and sample holders were made of hardened steel or beryllium copper. The highest pressures attainable were limited by buckling of the long slender compression member rather than by the ultimate strength of any part of the equipment, although, to reduce heat influxes, all designs were close to yield strength. The external diameter of the compression member was ¾ inch and its wall thickness 0.06 inch.

Force was applied to the upper end of the compression member (always at room temperature) by means of the piston of a hydraulic press, which was driven by oil under pressure. This pressure was generated with a hand pump, and was accurately measured by means
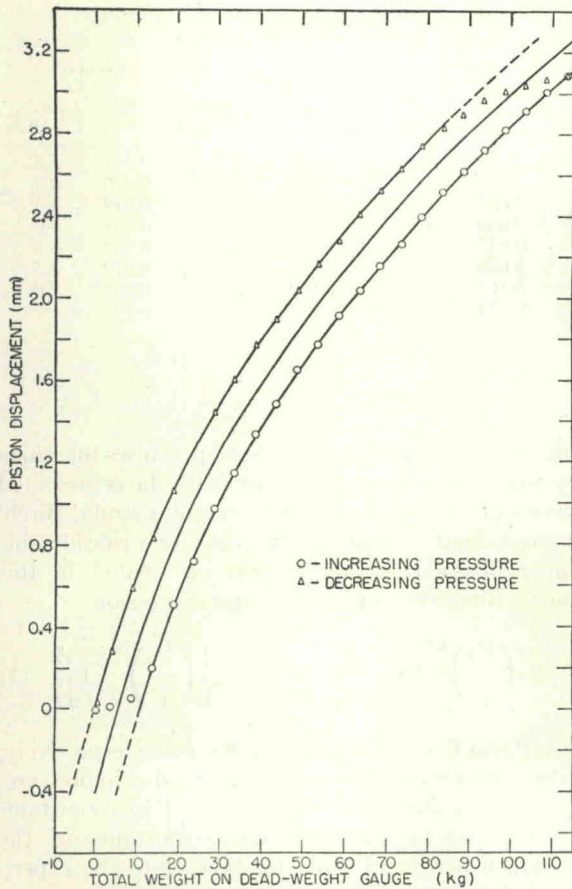
FIG. 3. Plot of piston displacement against sample pressure for a typical compressibility run (solid deuterium sample). (One kilogram on dead-weight gauge corresponds to pressure of 37.8 kg/cm².)

of a dead-weight piston gauge. The use of a dead-weight gauge also made it possible to hold the pressure on the sample at a constant value for a period of minutes. The maximum sample pressure of 4000 kg/cm² corresponded to an oil pressure of about 5000 lb/in.²

Values of the displacement under pressure of the experimental piston at 4° were deduced from observations of the position of a fine scratch machined near the top of the compression member. This scratch was visible through a window in the wall of the hydraulic press. Readings reproducible within a few thousandths of a millimeter could be made by means of a small traveling microscope.

The cryostat was of all-metal construction, based upon the original design of Henry and Dolecek.[2] The inner helium pot, of 1.5 liters capacity, was separated from the liquid nitrogen space by a vacuum jacket, while a second separate vacuum jacket insulated the liquid nitrogen from room temperature. The heat influxes were sufficiently small so that, at 4°K, runs lasting more than six hours could be made on one filling.

The sample holder rested on a support which was

[2] W. Henry and R. Dolecek, Rev. Sci. Instr. 21, 496 (1950).

inserted in a slot milled near the bottom of the stainless steel tension member. The experimental piston tip was attached to the bottom of the compression member (Fig. 2).

The solidified gas samples were prepared by direct condensation into the sample holder through the capillary tube. This was connected with a supply of the appropriate gas at room temperature. The solidified samples as prepared in this manner were all $\frac{1}{4}$ inch in diameter and about $\frac{1}{2}$ inch long. During the condensation process, leakage of gas around the piston was prevented by the sealing paper (a Glassine envelope window). As soon as pressure was applied, the piston easily broke through the paper and pressed directly upon the solidified sample. During the filling care had to be exercised that the capillary did not become blocked with solid. This required holding the apparatus at precisely the correct level in the cryostat.

The same technique was used to prepare the gas samples for the extrusion experiments which have been described above. During the filling, the extrusion hole was also covered by a paper seal (Fig. 1). When extrusion started, the extruded plug readily punched a hole through the lower paper.

The actual compressibility measurements were made by a method due originally to Bridgman.[1] It was assumed, as indicated by the results of the extrusion measurements for these substances, that the applied uniaxial compression was translated into a purely hydrostatic pressure. After each gas had been condensed into the sample holder of Fig. 2, readings of piston displacement versus pressure were taken for increasing and decreasing pressure. In order to obtain reproducible results, however, one first had to raise the pressure rapidly to its maximum value. This irreversibly compacted the samples, which had always frozen loosely. Once this compaction had been completed, the piston displacement versus pressure curves became quite reproducible from run to run. The considerable friction in the apparatus always resulted in a "hysteresis loop" of piston displacement versus pressure, such as is shown in Fig. 3. Usually two or three complete cycles could be obtained with each sample. The size of the steps by which the sample pressure was changed between readings made no significant difference in the results. The increments varied between about 50 kg/cm² and 400 kg/cm².

"Blank" runs with no sample in the sample holder

TABLE II. Values of K_0 and ξ for solidified gases.

Substance	Temperature °K	K_0 kg/cm²×10⁻³	ξ
Hydrogen	4	2.1	−1.9±0.1
Deuterium	4	3.3	−1.6±0.1
Neon	4	10.7	−4.3±0.5
Argon	65	16.1	−4.7±0.3
Argon	77	11.5	−6.5±0.5
Krypton	77	18.2	−5.1±0.2

TABLE III. Pressure-volume relations and isothermal compressibilities (in $cm^2/kg \times 10^5$) for some solidified gases.

Pressure kg/cm^2	Hydrogen 4°K $-\dfrac{\Delta V}{V_0}$	$-\dfrac{1}{V_0}\left(\dfrac{\partial V}{\partial P}\right)_T$	Deuterium 4°K $-\dfrac{\Delta V}{V_0}$	$-\dfrac{1}{V_0}\left(\dfrac{\partial V}{\partial P}\right)_T$	Neon 4°K $-\dfrac{\Delta V}{V_0}$	$-\dfrac{1}{V_0}\left(\dfrac{\partial V}{\partial P}\right)_T$	Argon 65°K $-\dfrac{\Delta V}{V_0}$	$-\dfrac{1}{V_0}\left(\dfrac{\partial V}{\partial P}\right)_T$	Argon 77°K $-\dfrac{\Delta V}{V_0}$	$-\dfrac{1}{V_0}\left(\dfrac{\partial V}{\partial P}\right)_T$	Krypton 77°K $-\dfrac{\Delta V}{V_0}$	$-\dfrac{1}{V_0}\left(\dfrac{\partial V}{\partial P}\right)_T$
0	0	48	0	30	0	9.4	0	6.2	0	8.7	0	5.5
200	0.075	28	0.055	20	0.016	8.0	0.011	5.5	0.017	7.0	0.010	4.9
400	0.120	19	0.091	16	0.031	6.9	0.021	5.0	0.030	5.9	0.019	4.4
600	0.156	15	0.118	13	0.044	6.1	0.030	4.5	0.041	5.2	0.028	4.0
1000	0.206	10.7	0.162	10.0	0.064	5.0	0.047	3.8	0.059	4.2	0.042	3.4
2000	0.287	5.8	0.237	5.5	0.107	3.4	0.080	2.8	0.093	3.0	0.072	2.5
3000	0.337	4.0	0.284	4.0	0.136	2.6	0.105	2.2	0.119	2.3	0.095	2.0
4000	0.370	3.0	0.318	3.0	0.158	2.2	0.124	1.9	0.140	1.9	0.113	1.7
6000	0.418	2.0	0.368	2.0								
8000	0.451	1.5	0.402	1.5								
10 000	0.477	1.2	0.426	1.2								

had to be made in order to obtain the distortion under pressure of the apparatus itself. Correction for friction was made by averaging (horizontally) between the curves for increasing and decreasing pressure. This gave rise to the central curve of Fig. 3. The length of the sample under zero pressure (after initial compaction) could be determined quite accurately from a comparison of piston positions during the actual run and the blank run. After the corrections had been applied, the relative change of volume $(-\Delta V/V_0)$ was calculated as a function of pressure with an estimated experimental error of less than 5 percent.

For neon, argon, krypton, and nitrogen, the measurements were carried up to about 4000 kg/cm^2, while, as has previously been described,[3] hydrogen and deuterium have been investigated to 10 000 kg/cm^2, using for some of the runs a larger similar apparatus constructed by Dr. C. A. Swenson at Massachusetts Institute of Technology.

III. RESULTS AND DISCUSSION

The relative volume changes and compressibilities for five solidified gases are given in Table III. The results for solid hydrogen and solid deuterium have previously been discussed.[3] The unstable extrusion of these two solids through the small annular space between the piston and the cylinder wall which, during the earlier measurements, often resulted in the complete loss of the samples was eliminated through the use of a Bridgman-type unsupported area packing made of metallic potassium[3] (Fig. 2). Potassium at 4° was found to be soft enough to flow and seal around the piston before the highly plastic H$_2$ or D$_2$ could start to extrude. Once such extrusion does start, it proceeds rapidly to completion because the heat released when a small amount of the solid escapes past the piston is considerably more than sufficient to warm up and melt the extruded H$_2$ or D$_2$. The solidified rare gases and solid nitrogen showed no such tendency to be extruded, and so did not require any packing.

As in the case of hydrogen and deuterium,[3] the pressure-volume relations for the solidified rare gases

neon, argon, and krypton at the temperatures for which they were determined can conveniently be represented in terms of Murnaghan's theory of finite strain. Birch[4] has pointed out that Bridgman's data for a considerable number of solid substances can be treated in this manner. Birch develops the general expression

$$P = \tfrac{3}{2} K_0 \left(\frac{V_0}{V}\right)^{5/3} \left\{ \left(\frac{V_0}{V}\right)^{\frac{2}{3}} - 1 \right\} \left\{ 1 - \xi \left[\left(\frac{V_0}{V}\right)^{\frac{2}{3}} - 1 \right] \right\}, \quad (1)$$

where P and V are the pressure and volume respectively, K_0 the reciprocal of the compressibility at zero pressure, and V_0 the volume at zero pressure. ξ is a constant, involving the higher-order elastic constants of the material, which is adjusted for best fit to the experimental data. It has been found that $\xi = 0$ for many metals.[4] However, each of the solidified gases of the present investigation requires the use of nonzero values of ξ in order to represent the experimental results. Table II gives those values of K_0 and ξ which best fit the data. In all cases the fit turns out to be quite good.

The isothermal compressibilities, $-(1/V_0)(\partial V/\partial P)_T$, as functions of pressure may most readily be obtained by differentiation of Eq. (1), using the values of K_0 and ξ from Table II. Table III gives the relative volume changes and compressibilities at different pressures.

The compressibilities of solid hydrogen and deuterium are higher than those for any solid previously measured. The solidified rare gases have compressibilities of the same order of magnitude as those of the alkali metals, which are still large values for solids in general.

In Table IV is given the compressibility of solid nitrogen at 4°K as a function of pressure, as determined with the present apparatus. These results may be considerably less accurate than the others because of the observed brittleness of nitrogen.

The only previous experimental measurements of the compressibilities of solid hydrogen and deuterium are those of Miss Megaw[5] for pressures up to 100 kg/cm^2. The present results are in satisfactory agreement with

[3] J. W. Stewart and C. A. Swenson, Phys. Rev. 94, 1069 (1954).

[4] F. Birch, J. Geophys. Research 57, 227 (1952).
[5] H. D. Megaw, Phil. Mag. 28, 129 (1939).

TABLE IV. Isothermal compressibility of solid nitrogen at 4°K.

Pressure kg/cm²	$-\frac{1}{V_0}\left(\frac{\partial V}{\partial P}\right)_T$ cm²/kg $\times 10^5$
0	5.2
1000	2.9
2000	2.2
3000	1.9

these over the limited range of pressures where comparison can be made. At zero pressure, her values for the compressibilities are: H_2, $(68\pm15)\times10^{-5}$ cm²/kg, and D_2, $(45\pm20)\times10^{-5}$ cm²/kg. At 100 kg/cm² pressure, she obtains for H_2, 32×10^{-5} cm²/kg, and for D_2, 21×10^{-5} cm²/kg.

Barker, Dobbs, and Jones[6] have determined the adiabatic compressibility of argon at zero pressure at 78°K and 60°K by measuring the velocity of ultrasonic longitudinal waves in the solid. Even allowing for a possible 20 percent difference between the adiabatic and isothermal compressibilities of solid argon, one still finds that the results of Barker et al. are nearly 50 percent lower than the current ones. The compressibilities as calculated from ultrasonic data are somewhat uncertain because a value for Poisson's ratio had to be estimated, there being no experimental value for solid argon.

It should be emphasized that Murnaghan's theory of finite strain, while a convenient means for representing compressibility data, is not a real "theory" in the stricter sense through which quantitative correlation with other properties of the solidified gases could be obtained.

A few theoretical calculations of the pressure-volume-temperature relations have been made for the solidified rare gases, particularly for argon. The most promising, that recently performed by Henkel,[7] which is based upon actual determination of the energy eigenvalues, appears to agree quite closely with the present experimental compressibilities below 1000 kg/cm². His calculations do not extend to higher pressure.

Two older theories, those of Kane[8] and Rice,[9] lead to calculated compressibilities which disagree rather badly with the experimental values. Kane's results for neon, argon, and krypton, which are obtained from an

assumed interatomic potential function of the van der Waal type, tend to be higher than the experimental data, while the somewhat more empirical results of Rice for argon are considerably too low. The calculations of Kane, however, indicate that the variations with pressure and temperature of the compressibilities of neon, argon, and krypton should be in roughly the same proportions as were actually observed.

There exists no detailed theoretical calculation for the compressibilities of solid hydrogen and deuterium. These are more difficult cases than the solidified rare gases because they do not possess a closed-shell structure. It can be said that solid hydrogen has a greater initial compressibility than solid deuterium because of its larger zero-point energy. The very rapid decrease of compressibility with pressure for both hydrogen and deuterium is also a consequence of the high zero-point energies, which cause the volumes at zero pressure to be larger than they otherwise would be. As the pressure is raised, the energy of compression eventually become much greater than the zero-point energy of either H_2 or D_2. Thus the compressibilities at high pressures are more nearly alike. However, because of the quite appreciable difference between the initial molar volumes, it is fortuitous that the compressibilities as defined herein become exactly the same within the experimental range of pressures. At zero pressure,[5] solid H_2 at 4° has a molar volume of 22.65 cm³ per mole, and solid D_2, 19.56 cm³ per mole. From the data of Table III, it is found[3] that, at the highest observed pressures, the molar volume of hydrogen remains greater than that of deuterium.

In the cases of the solidified rare gases, the decrease of compressibility with increasing atomic weight is consistent with the greater ion core repulsion exhibited by the heavier atoms.

Further measurements of compressibilities of solidified gases at higher pressures are now in progress.

IV. ACKNOWLEDGMENTS

[6] Barker, Dobbs, and Jones, Phil. Mag. 44, 1182 (1953).
[7] J. Henkel (to be published).
[8] G. Kane, J. Chem. Phys. 7, 603 (1939).
[9] O. Rice, J. Chem. Phys. 12, 289 (1944).