An experimental equation of state for solid hydrogen at pressures 2–27 kbar and temperatures of 4 and 77 K

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The P-V relations for solid hydrogen of 99.97% purity have been measured with an improved piston displacement method at 4.2 and 77.4 K at pressures up to 27 kbar. The Birch equations, which approximate the results, and values of the molar volume and of the isothermal bulk modulus are given for various pressures.

Over the last decade there has been great interest in studying hydrogen, brought about by the possibility of using hydrogen in power production and by the problem of the transition of molecular hydrogen into the metallic state at megabar pressures. In order to calculate the equation of state of the molecular phase of hydrogen and the thermodynamic functions with sufficient accuracy, the P-V-T relation must be measured at high static pressures. The P-V relation for solid hydrogen has been measured at 4.2 K up to 5 kbar,[1] to 20 kbar[2] and to 25 kbar[3] (piston displacement method), at ~ 17 K to 24 kbar[4] (neutron diffraction method), and also at 77.3 K up to 30 kbar[5] (piston displacement method). For pressures > 2 kbar, the greatest accuracy was obtained in measurements of relative volume, carried out by an improved piston displacement method using a triangular anti-extrusion ring as sealing for the specimen.[3] The measurements were limited to the 4.2 K isotherm. The authors pointed out the impossibility of using their method at temperatures above the triple point.

In the present work, the P-V relations for solid hydrogen have been measured at 4.2 K and the pressure range has been increased in the high-pressure direction, and results of high accuracy have also been obtained at 77 K by an extension of the improved piston displacement method into the temperature region above the triple point. A method was used for this which consists in bypassing the triple point on the high-pressure side on the hydrogen P-T phase diagram, which we tested earlier in measurements on argon.[6] This enabled us for the first time to measure several isotherms of solid hydrogen in one experiment without the loss of accuracy which is unavoidable when using Bridgman unsupported packings, necessary for maintaining the specimen when in the fluid state.

THE EXPERIMENT

The measurements were carried out by an improved piston displacement method in an apparatus, the main com-ponents of which (high-pressure chamber, helium low-temperature press and intensifier for compressing gaseous hydrogen) have been described.[7-9] Two high-pressure chambers with different channel diameters were used (Table I). The cylinder of chamber I was made of R18 steel and that of chamber II of a hard alloy. The use of chambers made of different materials with different channel diameters enables, first, the elimination of systematic errors inherent in each individual chamber and, second, the broadening of the pressure range studied without loss of accuracy.

The initial mark-B hydrogen of 99,97% purity, pre-compressed to 2 kbar by a thermal compressor and a gas intensifier, was fed to the high-pressure chamber cooled to 77 K and maintained at this temperature for ~ 18 h. A solid specimen was formed after liquid helium was siphoned into the cryostat. During an experiment the displacement of the piston of the high-pressure chamber, L, was measured as a function of the applied force, F, on raising and lowering the load and fixing the temperature, over a period of 5–8 h. The method of applying corrections and of evaluating the specimen volume and the pressure in it was, in its main features, similar to that described elsewhere.[2,6,8] The final uncertainty in determining the volume, into which errors in determining the pressure also enter, was ± 0.4%. The chamber was totally immersed in liquid helium during the whole cycle of measurements to obtain a temperature of 4.2 K. For measurements at 77 K, the specimen was compressed to 8 kbar at 4.2 K and the refrigerant was then changed from liquid helium to liquid nitrogen. Eight experiments with different chambers were carried out at 4.2 K in the range 1–27 kbar, and three experiments in chamber II at 77.4 K at pressures of 6–21 kbar. The volume of the solid hydrogen specimen was 0.4–2 cm³.

RESULTS AND DISCUSSION

All the results obtained on any isotherm were normalized to the volume V_N corresponding to some normalizing

TABLE I. Characteristics of the high-pressure chambers.

	Chamber I	Chamber II
Channel diameter, cm	1.222	0.630
Pressure range, kbar	1–8.4	1.5–27
Friction, % of maximum force	2–3	2–4

TABLE II. Values of the parameters of the Birch equation and of the mean square error δ, for 4.2 and 77.4 K.

	4,2 K	77,4 K
P_0, kbar	1	4.953
A_1, kbar	11.523	32.480
A_2, kbar	10.310	18.674
δ, cm^3/mole	0.019	0.013

pressure P_N. The normalized results of all the experiments at a given temperature were analyzed together by the method of least squares. The Birch equation[10] in the form

$$P(V) = P_0 + y^5 \sum_{n=1}^{2} A_n (y^2 - 1)^n, \qquad (1)$$

was used, where

$$y = [V(P_0)/V(P)]^{1/3}.$$

Values of the parameters for Eq. (1) and the least squares error are given in Table II for 4,2 and 77.4 K. The value of V ($P = 3$ kbar) $= 15.24$ cm^3/mole, obtained for p-H$_2$ on the "zero" isotherm by different methods,[4,11] was used to determine the molar volumes at 4.2 K; for 77.4 K the value of the molar volume of solid hydrogen on the melting line, V_{ms} (77.4 K) $= 14.24$ cm^3/mole, was used.[12] Values of the molar volume and of the isothermal bulk modulus, $B \equiv -V(\partial P/\partial V)$, calculated by Eq. (1) are given in Table III.

The P-V relations for solid hydrogen at helium temperature (the "zero" isotherm) have been measured before.[1–4] The results of Anderson and Swenson,[3] obtained by an improved piston displacement method, have the highest accuracy in determining the relative value of the volume (0.1–0.3%). In this work identical results were obtained for a single p-H$_2$ specimen as for several specimens for which the o-H$_2$ concentration was, according to the author's estimated, 75–50%. The merits of measurements by the neutron diffraction method,[4] carried out on p-H$_2$ in the range 0.02–24 kbar, are in obtaining absolute values of molar volumes and the high accuracy of measurements in the range of pressures < 0.5 kbar.

In the present work the initial hydrogen had the equilibrium ortho-para composition at room temperature (the fraction of o-H$_2$ $C_1 = 0.75$). According to our estimates, the fraction of ortho molecules in a solid hydrogen specimen, as a result of conversion at low temperature and under pressure, was not more than 0.55. A calculation, carried out on the basis of an expression given by Driessen et al.,[13] showed that the quadrupole pressure, produced by the attraction of ortho molecules, changes the values of relative volumes obtained in our experiments at $2 < P < 27$ kbar and 4 K by less than 0.15%, and on the 77 K isotherm by less than 0.01%. Within the limits of experimental error, therfore, the results obtained can be regarded as $V(P)$ for p-H$_2$.

The departures of published results for the "zero" isotherm of hydrogen relative to the results of the present work are shown in Fig. 1. The ordinate axis gives the departure $(V_L - V)/V$, where V_L are the results found in the literature and V are our results. For convenience in comparison, all the results in Figs. 1 and 2 are shown in the form of relative volumes (divided by the basic value of the volume corresponding respectively, to $P = 3$ and 10 kbar), i.e., in the form in which results are obtained in the present work and in other measurements by the piston displacement method. As can be seen from Fig. 1, our results at 4 K agree within limits of 0.2% with the results of measurements carried out both on p-H$_2$,[3,4] and on specimens containing o-H$_2$. The "zero" isotherm obtained by Driessen and Silvera[14] by putting together various experimental results, differs appreciably at $P > 10$ kbar from the results of the present work and of the 4 K isotherm[3] on the basis of which it was constructed.

Measurements of the P-V relation for solid H$_2$ at higher temperatures have only been carried out for 77.4 K (Ref. 5). In this work a piston displacement method with a Bridgman

TABLE III. Smoothed values of molar volumes V and of the isothermal bulk moduli B for solid hydrogen.

| P, kbar	4 K V, cm^3/mole	4 K B, kbar	77 K V, cm^3/mole	77 K B, kbar	P, kbar	4 K V, cm^3/mole	4 K B, kbar	77 K V, cm^3/mole	77 K B, kbar
2	16.31	12.58	–	–	14	11.14	61.24	11.24	60.09
3	15.24	17.12	–	–	16	10.81	68.82	10.89	67.98
4	14.47	21.47	–	–	18	10.51	76.33	10.60	75.75
5	13.86	25.70	14.21	21.88	20	10.25	83.78	10.33	83.43
6	13.37	29.84	13.64	26.53	22	10.02	91.18	10.10	91.03
8	12.60	37.92	12.78	35.38	24	9.81	98.54	–	–
10	12.01	45.82	12.15	43.85	26	9.62	105.86	–	–
12	11.54	53.58	11.65	52.06					
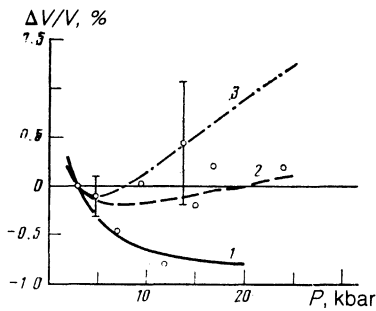
FIG. 1. Comparison of results for the "zero" isotherm for solid hydrogen. Departures are shown relative to the results of the present work: curve 1) piston displacement, 4 K (Ref. 2); 2) piston displacement, 4 K (Ref. 3); 3) equation of state "zero" isotherm;[14] O) experimental neutron diffraction points;[4] the line of best fit to these points differs by < 0.05% from curve 2 for $P > 3$ kbar and is therefore not shown.
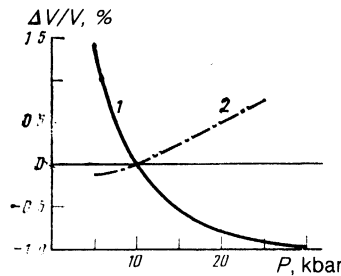

FIG. 2. Comparison of results for the 77 K isotherm of solid hydrogen. Departures are shown relative to the results of the present work at 77 K. All results have been normalized as $V(P)/V$ ($P = 10$ kbar). Curve 1) piston displacement, 77 K (Ref. 5); 2) calculated from the equation of state.[14]

unsupported packing of the specimen was used, and the uncertainty in measurement of volumes was $\pm 1\%$.

The merits of the present measurements at 77 K are the appreciable reduction in errors of measurements and also the fact that the measurements at 4 and 77 K were carried out in each experiment on one and the same specimen. This increases the reliability and the matching of the results. The departure of published experimental results for the 77 K isotherm and of the results of calculating the 77 K isotherm from the equation of state, taken from Driessen and Silvera,[14] are shown in Fig. 2, relative to the results of the present work. The departure of the results of Kechin et al.[5] somewhat exceeds the total experimental uncertainty. The departure of the 77 K isotherm, calculated from the equation of state,[14] becomes appreciable for $P > 15$ kbar.

Results have been published for the higher pressure region of measurements of the density of solid H_2 in diamond intensifies at $T = 295$ K up to 200 kbar[15] and at 5 K up to 370 kbar,[16] and also results of measuring the adiabatic equation of state ($T < 100$ K) of solid H_2 up to 150 kbar.[17] The disagreements between the results of these works[15-17] are appreciable, and a further refinement of the equation of state for $P > 100$ kbar is called for. On extrapolating our experimental isotherms into the region of 100 kbar, compatibility is observed in the extrapolation of both isotherms ($P_{77K}(V) < P_{4K}(V)$) and there is agreement with the experimental results of van Straaten et al.[16] At $V = 8$ and 7

cm^3/mole, calculation according to Eq. (1) gives values of 53.6 and 89.0 kbar, close to the values (54.1 and 87.8 kbar), given by van Straaten et al.[16]

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