Equation of state of the molecular phase of hydrogen in the solid and liquid states at high pressure

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The parameters are found for the equations of state of molecular hydrogen in the solid and liquid states. The calculated isotherms, shock adiabats, melting curve, and isentropy curves are in good agreement with the experimental data. A new result for the isentropic compression at $\rho = 0.67$ g/cm^3 and $P \sim 1$ Mbar is obtained for the molecular phase of hydrogen.

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INTRODUCTION

In recent years, a number of papers have been published,[1–5] in which the equations of state of the molecular and metallic phases of hydrogen have been studied and the location of the phase transition determined. The results of these researches do not allow us to determine the location of the phase transition precisely, the pressure varying from 0.84[3] to 4.6 Mbar,[1] and the value of the density from 0.46[5] to 1.4 g/cm^3.[1]

Experimental data were given earlier on the isentropic compressibility of hydrogen up to a pressure of ~8 Mbar. It follows from these data that in isentropic compression up to pressures of $P \approx 3$ Mbar and density $\rho = 1$ g/cm^3, the hydrogen remains in the molecular phase. In the present work, the parameters of the equations of state of molecular hydrogen in the solid and liquid states are given. A comparison is also made of the thermodynamic quantities, calculated from these equations of state, with experiment, including static and shock compression, and the melting curve is given. A new result is also given of the measurement of the isentropic compression of the molecular phase of hydrogen for a pressure P = 1 Mbar.

EQUATION OF STATE OF SOLID MOLECULAR HYDROGEN

For the solid phase, we take the equation of state in the form of Mie-Grüneisen:

$$P=P_x(\rho)+{}^9/_8R\rho\gamma(\rho)\Theta(\rho)+3R\rho T\gamma(\rho)D[\Theta(\rho)/T], \tag{1}$$

$$E=E_x(\rho)+{}^9/_8R\Theta(\rho)+3RTD[\Theta(\rho)/T]. \tag{2}$$

The curve of the elastic interaction of molecules is approximated by a relation of the form[7]

$$P_x=\sum a_i\delta^{i/3+1}, \tag{3}$$

where $\delta = \rho/\rho_c$, ρ_c is the density at P = 0 and T = 0, a_i are empirical constants, and x is the index of the elastic components of the equations. The second terms in (1) and (2) describe zero-point oscillations. Here R is the gas constant, $\Theta(\rho)$ is the Debye temperature, and $\gamma(\rho) = d\ln\Theta/d\ln\rho$ is the Grüneisen coefficient. In correspondence with the theory of small oscillations we have

$$\gamma(\rho)=\frac{1}{3}+\frac{1}{2}\frac{d}{d\ln\rho}\ln\left(C_x^2-n\frac{2P_x}{3\rho}\right), \tag{4}$$

where $C_x^2 = dP_x/d\rho$ and n is an empirical parameter. From (4) we easily obtain

$$\Theta(\rho)=\frac{\Theta_0}{C_x(\delta=1)}\delta^{1/3}\left(C_x^2-n\frac{2P_x}{3\rho}\right)^{1/2}. \tag{5}$$

The last terms in (1) and (2) are connected with thermal oscillations. Here $D(\Theta/T)$ is the Debye function.

The applicability of the equation of state in the Mie-Grüneisen form for the description of the solid phase was shown experimentally in [8]. Usually the contribution of the zero-point oscillations to the pressure P_{zp} and the energy E_{zp} is described in conjunction with the elastic interaction curve. However, this turned to be necessary to separate this contribution for hydrogen.[1] The parameters a_i, ρ_c, and n of the elastic-interaction curve were found from the conditions of the description: from the value of the density of the solid phase $\rho = 0.0867$ g/cm^3 for P = 1 bar; from the isotherm at T = 4°K, obtained by Stewart[9], and also from the experimental isentropes found in the present work and in [6]. The numerical values of the parameters of the equation of state found in this fashion are the following: $\rho_c = 0.1335$ g/cm^3, n = 1, $a_1 = -5.57$ kbar, $a_2 = 28.71$ kbar, $a_3 = -70.71$ kbar, $a_4 = 45.57$ kbar. Figure 1 shows the calculated isotherm $P_x + P_{zp}$ in comparison with the experimental one of [9]. The agreement is satisfactory.

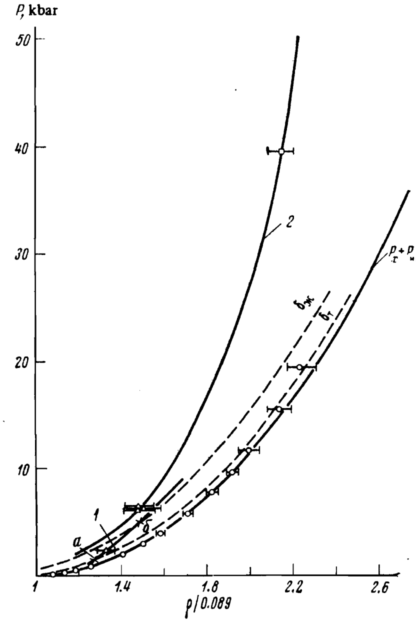

FIG. 1. Comparison of the calculated zero-point isotherms and shock adiabats of hydrogen (curves) with experimental data (points); ○–[9]; △–[14]; m = 1; □–[10], m = 1.255; curve 1–m = 1, calculation according to Eqs. (1), (6); curve 2–m = 1.255, calculation according to Eq. (6).

EQUATION OF STATE OF LIQUID MOLECULAR HYDROGEN

The analysis of the experimental data on shock[10] and isentropic[6] compression of hydrogen has shown that the hydrogen is in the liquid phase over the entire range of densities studied. Therefore, the determination of the equation of state of this phase becomes very urgent. The equation of state of the liquid assumed in this paper

$$P=P_x(\rho)+3R\rho T\frac{\gamma+z/3}{1+z}+3R\rho T_0 a\left(\frac{\delta}{\delta_0}\right)^r, \tag{6}$$

$$E=E_x(\rho)+3RT\frac{1+z/2}{1+z}+3RT_0\left\{c+\frac{a}{r}\left[\left(\frac{\delta}{\delta_0}\right)^r-1\right]\right\} \tag{7}$$

was constructed on the basis of the equation of state of the solid phase, i.e., it has the same elastic interaction curve of the molecules.1) In (6) and (7), the parameter z = $lRT/(C_x^2 - n\cdot 2P_x/3\rho)$ determines the measure of the departure of the thermal properties of the liquid from those of the solid,[11] a, c, r, and l are empirical constants, T_0 and δ_0 are the melting temperature and the relative density of the liquid hydrogen at atmospheric pressure. The last terms in (6) and (7) give the correction to the elastic interaction curve, necessitated by the change in the number of nearest neighbors in the structure of the liquid compared with the structure of the crystal.

The parameters of the equation of state for the liquid phase of molecular hydrogen have the following values: T_0 = 14°K, δ_0 = 0.579, l = 21, a = 9.247, b = 1.8633, c = 1.2593, r = 1. The melting curve was constructed on the basis of the equations of state of the solid and liquid phases for molecular hydrogen. The results of the calculation are shown in Figs. 1 and 2 and in Table I. In Fig. 1, the dashed lines show the region of existence of the solid and liquid phases. In Table I, $\Delta S/R$ is the change in the entropy along the melting curve.

As is seen from Fig. 2, the calculated melting curve is not in bad agreement with the experimental melting curve from [13]. In this same figure, the melting curve calculated from the Simon equation is given by

$$P=P_0+A\{(T/T_0)^c-1\}\ [\text{bar}], \tag{8}$$

here P_0 = 0.98 bar, A = 273 bar, T_0 = 14°K, C = 1.744 and the melting curve is in accord with the Lindeman equation. In the latter case, the melting temperature was calculated as a function of the density with the foregoing parameters of the elastic compression curve, according to the equation

$$T_{\text{melt}}=\text{const}\,(C_x^2-n\cdot 2P_x/3\rho), \tag{9}$$

and then the pressure corresponding to this temperature was determined from Eq. (1).

COMPARISON WITH THE AVAILABLE EXPERIMENTAL DATA

The shock adiabats were calculated according to the equation of state of the liquid phase; these are compared with experimental data in Figs. 1 and 3. The results of the calculations of the shock adiabat with m = 1.255, where m = ρ_c/ρ_0, were investigated experimentally[10] (P = 1 bar and ρ_0 = 0.0709 g/cm^3) are represented in Table II. Figure 2 shows [in the coordinates T(P)] that this shock adiabat as a whole lies in the liquid phase region, never intersecting the melting curve.

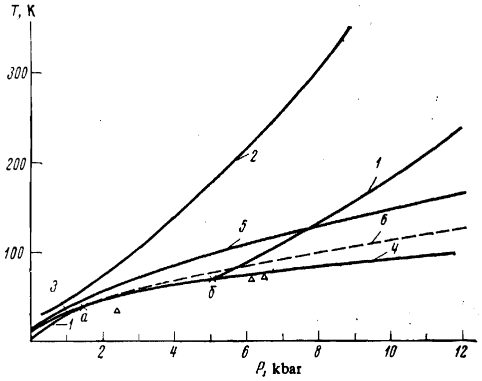

FIG. 2. Shock adiabats and melting curves of hydrogen: curve 1—corresponds to curve 1 in Fig. 1; 2—corresponds to curve 2 in Fig. 1; 3—experimental up to 60°K from [13]; 4—melting curve according to Eqs. (1), (6); 5—melting curve according to Lindeman; △—calculation from [14]; 6—calculation according to the Simon formula.

TABLE 1

T, K	P, kbar	δ_{lig}	δ_T	$\frac{\Delta S}{R}$	$\frac{\Delta V}{V}$, %	z	$\frac{dT}{dP}$, deg/kbar
14	0	0.579	0.650	1.01	12	1.33	34
42	1.5	0.777	0.862	1.92	11	1.15	12.3
70	4.8	0.989	1.069	2.19	8	0.84	6.5
140	26.3	1.58	1.65	2.48	4.6	0.51	2.1
280	169	2.91	2.99	2.6	2.5	0.30	0.59
700	2440	7.67	7.74	2.4	1.0	0.14	0.10
910	4660	9.8	9.9	2.4	0.8	0.12	0.06

TABLE 2

$\delta=\rho/0.1335$	z	T, K	P, kbar	$\delta=\rho/0.1335$	z	T, K	P, kbar
0.898	2.16	130	3.8	1.44	10.6	2340	41
1.08	3.64	390	9.6	1.60	17.2	4820	75
1.28	6.63	1100	22	1.70	25.4	8370	121

It is seen from Fig. 1 that the agreement of the calculated adiabat with the experimental data of [10] is excellent. This is not surprising, since the point of that paper for P ≈ 40 kbar was taken into account in estimating the parameters of the equation of state of the liquid phase. The experimental data on the shock compression of solid hydrogen at T_0 = 4°K and ρ = 0.089 g/cm^3 [14] are shown in the same figure. The corresponding calculated shock adiabat of hydrogen with m = 1 first passes into the solid phase, intersects the region of coexistence and passes into the liquid phase at P = 5 kbar and ρ = 0.133 g/cm^3. It passes somewhat below the experimental points, within the limits of the measurement error. Possibly a somewhat lower value of the Grüneisen coefficient for the solid phase was used in the calculation: $\gamma(\rho_0$ = 0.089 g/cm$^3) \approx 3.4$.

The point a in Fig. 1 is the place of entry of the calculated shock adiabat into the region of coexistence from the solid phase, and point b is the place of entry into the liquid phase. Figure 2 shows the calculated shock adiabat 1, in the coordinates T(P), corresponding to [14]. The points a and b correspond to Fig. 1. The calculated temperatures from [14] are shown by triangles in Fig. 2.

The calculated shock adiabats for single and double compressions are compared in Fig. 3 with the experimental values measured in [15]. The authors of [15], studying the compressibility of liquid deuterium, obtained data for its single (P ~ 200 kbar) and double (P ~ 960 kbar) shock compression. The density of deuterium measured in [15] is reduced by a factor of two

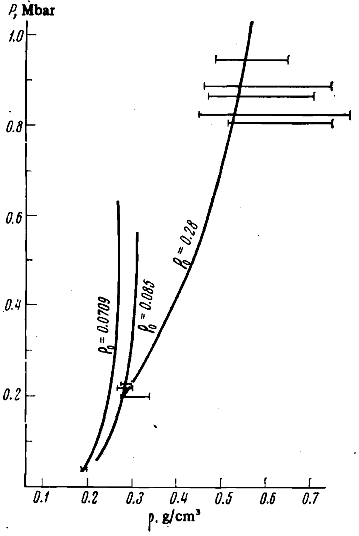

FIG. 3. Comparison of the calculated shock adiabats for single and double compressions with experiment: $\rho_0 = 0.0709$ corresponds to the experiment of [10]; $\rho_0 = 0.085$ corresponds to the experiment of [15] for a single compression; $\rho_0 = 0.28$ corresponds to the experiment of [15] for a double compression.

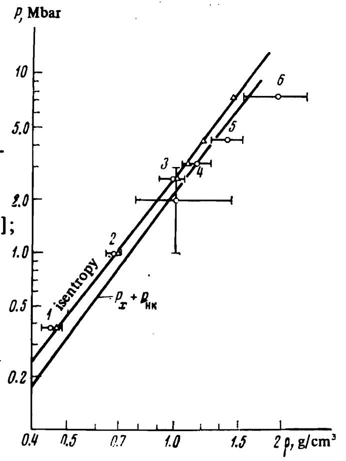

FIG. 4. Comparison of the calculated and experimental data on the isentropic compression of hydrogen: 1, 2, 3, 4, 5, 6—experiments from [6]; 2—experiment of the present work; ○—experiment from [16].

TABLE 3

ρ_{exp}, g/cm³	ρ_{calc}, g/cm³	P_{calc}, Mbar	T_{calc}, K	z	S/R
0.45±0.03	0.47	0.37	3100	2.34	6.6
0.67±0.03	0.69	1.00	4200	1.61	6.8
0.98±0.08	1.01	2.63	5600	1.14	7.0
1,15±0.1	1.09	3.24	6000	1.08	7.3
1,4±0.14	1.19	4.40	6500	1.01	7.5
1.95±0.39	1.40	8	9100	1.0	7.8

in Fig. 3 in order to bring it into correspondence with the equation of state of hydrogen-protium. Strictly speaking, such an operation is not entirely correct. This is connected with the existing difference in the equation of state of the hydrogen isotopes at low pressure. The experimental isotherms of H_2 and D_2 are given in [9] for T = 4°K up to P = 20 kbar. It follows from these data that the compressibility of D_2 in the region considered is somewhat less than the compressibility of H_2, approaching it with increase in the pressure. Thus, whereas at P = 0 the molar volume of H_2 was 16% larger than for D_2, at P = 20 kbar this difference amounted to only 6%. One of the reasons for the difference is the contribution of the zero-point oscillations, the relative role of which decreases with increase in the pressure. It is therefore reasonable to assume that the difference in the compressibilities of H_2 and D_2 becomes insignificant at still higher pressures.

As is seen from Fig. 3, the agreement between the shock adiabats calculated in the present work and the experimental values is excellent. The calculated values of the temperatures behind the shock wave are given in [15]: T = 4500°K for P = 200 kbar and T = 7000°K for P = 900 kbar. The calculated temperatures in the present work are higher by a factor of two. This is evidently connected with the fact that the value of the specific heat in [15] was taken to be the same as for a solid, i.e., $C_V = 3R$, whereas according to the equation of state of the liquid phase used by us $C_V = (3/2)R$ in the range of temperatures much higher than the melting curve.

To describe more accurately the behavior of the molecular phase of hydrogen by the method used in [6], an experiment was carried out on isentropic compression. As can be seen from Fig. 4, the result ($\rho = 0.67$ g/cm³ and P = 1 Mbar) is in excellent agreement with the previously calculated isentrope. The triangles in Fig. 4 indicate the density and pressure, obtained from the gasdynamic calculation on a high-speed computer with use of Eqs. (1)–(7). In this same figure we show the experimental result from [16], in which the hydrogen was compressed isentropically in a magnetic field. Within the limits of rather large scatter of both the pressure and the density, indicated in [16], this experimental point (average value of $\rho = 1$ g/cm³ and P = 2 Mbar) does not contradict our data.

The values of the entropy, the calculated and experimental values of the densities and pressures, and the parameter z are given in Table III.

The considerations given show that all the existing experimental data for the pressure range up to 3 Mbar on both the shock and isentropic compression of hydrogen and deuterium are well described by the equations of state of the solid and liquid phases of molecular hydrogen given above. This allows us to assume that the obtained $P_X(\rho)$ dependence of the molecular phase of hydrogen is sufficiently reliable.

In this connection, the contrasting estimates of the pressure of the phase transition made in [15] according to the data of [6], where the states of the hydrogen were investigated experimentally up to densities exceeding the region of the phase transition, are not persuasive. In the recently published work of Ross[17] (one of the co-authors of [15]) he assumes that the lower limit of the appearance of the metallic phase at 0°K is the pressure of 2.2 Mbar.

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1) The form and the methods of estimating the parameters of the equation of state of the liquid phase were similar to those used in [8,11,12].

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