Thermodynamic properties of water at high pressures and temperatures

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The dynamic adiabats of water from initial states with different initial density (porous ice) are investigated in the pressure region 30–500 kilobars, and also the isentropic and double compressibility of water. A thermodynamic description of the results is given.

1. INTRODUCTION

Interest in study of the compressibility and equation of state of water is due first of all to its abundance in nature both as an independent chemical compound and as a component part of numerous natural compounds. Of studies devoted to this question, we will cite here the results of Bridgman,[1] Walsh and Rice,[2,3] Scidmore and Morris,[4] Kuznetsov,[5] Gurtman, Kirsch, and Hastings,[6] and also investigations carried out with participation of the authors of the present work.[7,8] In the articles mentioned, shock compression pressures of 1.1 Mbar were achieved in measurements by absolute methods and ~15 Mbar in comparative measurements. However, all of the measurements had the same major deficiency: In the initial states before the shock compression the density remained practically constant and the possibility of its variation was not utilized. In addition, a decrease of the initial density permits the limits of measurement of thermodynamic parameters to be extended substantially.

Since the maximum pressures at which ice melts amount to 2 kbar, the dynamic adiabats at high pressures, independent of the initial state, are characterized by the compressibility of the liquid phase and by "adiabats of ice" we mean the dynamic adiabats of water, obtained from initial states of the solid modification with various initial densities. Here it is not excluded that in comparatively small regions at low pressures, other modifications of H_2O may be realized in addition to the liquid phase.[1]

In the present investigation the principal attention was devoted to obtaining dynamic adiabats from initial states with different initial densities and using these data to determine the equation of state of water.

Studies of the double compressibility of water and measurement of the velocity of sound in water, reported in the present article, are devoted to solution of the same problem—selection of a demonstrated form of the equation of state.

2. EXPERIMENTAL RESULTS

1. Dynamic compressibility of ice. Investigation of the dynamic compressibility of ice was carried out with the reflection method and the electrical-contact measurement technique.[9] The velocity of the shock wave in the samples was recorded; its intensity was varied in different series of runs as the result of use of a set of explosive systems[10,11] based on acceleration of aluminum and steel plates to various velocities by the products of explosion of powerful high explosives.

The shock wave was conducted to the samples through a screen from the accelerated metal plates. Here the initial states of compression in them were known. This permits us, using the measured value of the wave velocity D, the P-U diagram method,[9] and the conservation laws, to find the remaining compression parameters of the material investigated: U—the mass velocity of the material behind the shock-wave front, and P—the pressure.

$$P=v_{00}^{-1}DU, \quad v=v_{00}(D-U)D^{-1} \qquad (2.1)$$

(v_{00} and v are the specific volumes before and after compression).

The samples investigated were prepared from a sieved powder of ice (the size of the particles did not exceed 300 μ) at a temperature of about −15°C by pressing them to a given density ($\rho_{00} = 1/v_{00}$): 0.35, 0.60, and 0.915 g/cm^3. The experiments were carried out under the same conditions (negative temperatures). In each series of experiments the value of the wave velocity was found from five to eight independent results. The number of recordings, as a rule, was determined by the requirement of obtaining a mean square error in the average value of the wave velocity no greater than ±1.5–2%. The experimental results obtained are shown in Table I.

The functions $D(\rho_{00})$ (Table I) are described by smooth curves which permit calculation of any adiabats of ice in the range of initial density from 1.0 to 0.35 g/cm^3.

In Figs. 1 and 2 we have shown the experimental

TABLE I

Parameters and screen material		Average density of samples, g/cm³	D, km/sec	U, km/sec	P, kbar	v_0/v
U, km/sec	P, kbar					
Al 3.97	1159	0.915	9.69	5.67	503	2.205
		0.60	9.52	6.20	354	1.720
		0.35	9.39	6.75	222	1,245
Al 3.65	1009	0.915	9.35	5,24	448	2,081
		0.60	8.86	5.77	307	1.720
		0,35	8.92	6.24	195	1.165
Al 2.32	878.6	0.915	8.52	4,84	377	2.118
		0.60	8.35	5.27	264	1.626
		0.35	8.12	5.72	162	1,184
Al 2.72	661	0.915	7.39	4.04	273	2 018
		0,60	6.97	4.42	186	1.641
		0.35	6.70	4.77	112	1.217
Cu 1,75	1034	0 915	6.12	3,08	172	1.842
Al 1.5	298.6	0.915	5.02	2.36	108	1.726
		0.60	4.44	2.57	68	1.424
		0.35	3.93	2.76	38	1.176
Al 1 14	211	0,915	4.19	1.84	70,5	1.631
Al 0.69	116	0.915	3.27	1.15	34.3	1,411

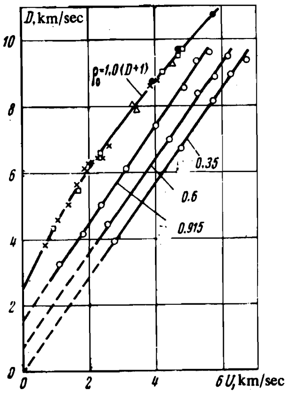

FIG. 1. D-U diagrams of water and ice: ○, ●—experimental points of the present work, □—data of Walsh and Rice, [3] ×—experimental determinations, [7] △—results of Scidmore and Morris, [4] dashed lines—extrapolated parts of the D-U relations. The numbers on the lines are the values of ρ_{00}.

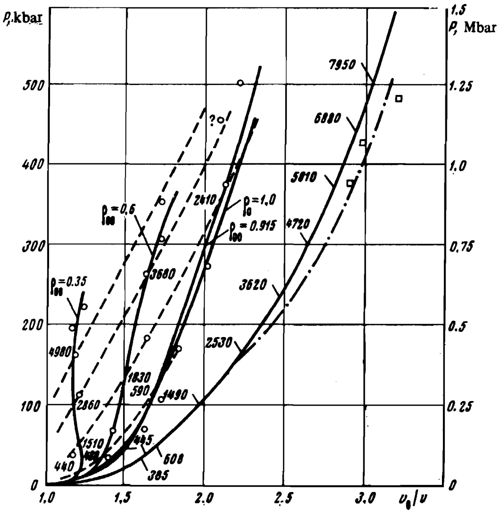

FIG. 2. Shock adiabats and expansion isentropes calculated from the equation of state: solid curves—shock adiabats, dashed curves—expansion isentropes (left scale). On the right are the adiabat of water and the double-compression curve (dot-dash curve—theory, □—experiment) up to pressures of 1.5 Mbar. The numbers on the curves denote the theoretical temperatures in K.

results in coordinates D-U and P-ρ. They correspond to relations of the form

$$D=C_0'+\lambda U, \qquad (2.2)$$

by which each of the sets of experiments for a given initial density could be described. The values of the constants are as follows:

$$C_0'=1.57 \text{ km/sec}, \ \lambda=1.465 \text{ for } \rho_{00}=0.915 \text{ g/cm}^3;$$
$$C_0'=0.74 \text{ km/sec}, \ \lambda=1.425 \text{ for } \rho_{00}=0.60 \text{ g/cm}^3;$$
$$C_0'=0, \qquad \lambda=1.425 \text{ for } \rho_{00}=0.35 \text{ g/cm}^3.$$

2. Double compression of water. Useful information on the thermodynamic properties of water can be obtained also by measurement of its double compressibility,[12,13] i.e., determination of the pressure and density of water compressed by two consecutively passing shock waves. The states arising here are characterized by substantially lower temperatures of heating of the water in comparison with single compression to the same densities. The accuracy of the double-compression method depends directly on the differential in the pressures and mass velocities in the shock adiabats of the barrier and the water. The greater this differential, the more accurately are determined the double-compression parameters being recorded. In the present work we used as a barrier samples of heavy metals—tungsten, copper, tin. The double compression of water was determined for two different initial states. The results obtained are shown in Table II (see also Fig. 2).

TABLE II

Parameters of incident waves			Material of barrier	Parameters of reflected waves			
D_1, km/sec	U_1, km/sec	P_1, kbar		D_{12}, km/sec	ΔU_{12}, km/sec	P_2, kbar	v_0/v
8.50	4.64	394	Tin	10.16	2.46	943	2.902
			Copper	10.97	2.83	1076	2.98
			Tungsten	10.94	3.41	1215	3.20
7.66	3.93	301	Tungsten	10.27	2.94	922	2.88

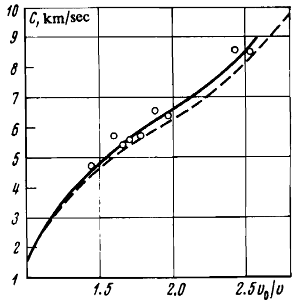

FIG. 3. Comparison of the experimental (solid line, ○—experimental points) and theoretical dependence (dashed curve) of the velocity of sound on the degree of compression of water.

3. Isoentropic compressibility of water.[1)] An independent parameter which can be used to check the correctness of the parameters chosen for the equation of state is the velocity of sound $C^2 = -v^2(\partial P/\partial v)_S$, which characterizes the slope of the isoentrope or the isoentropic compressibility of the material. The methods which have been develops for detection of this quantity[13,14] have permitted the isoentropic compressibility of water to be investigated in the pressure region up to P ~ 600 kbar.

For the most part we used the method of lateral discharge,[2)] based on detection of the deformation of the shock-wave front.

As shown in ref. 14, excellent uniqueness in interpretation of the results is obtained with use of this method for study of media (such as water) which possess low dynamic strength with extremely small shear modulus. In this case the quantities recorded are related directly to the isoentropic modulus of hydrostatic compression $K_S = C^2\rho$. Comparison of theory and experiment is given in Fig. 3.

3. CHOICE OF FORM AND DETERMINATION OF PARAMETERS OF THE EQUATION OF STATE

In constructing the P-v-E equations of state in the high-pressure region, in most studies, including those for water,[5,6] the Gruneisen coefficient (Γ) is introduced as a coefficient of proportionality between the increase of the thermal pressure and the thermal energy density. Usually it is assumed that Γ = const or is a function only of v and for a given v does not depend on the other parameters. This description is valid in the low-temperature region and is supported by theoretical considerations. At high temperatures Γ is, generally speaking, a function of two variables and in this case the assumption Γ = Γ(v) is arbitrary, and a reliable experimental check of this assumption with the existing accuracy of experiments is quite difficult. Therefore, as at low temperatures, the main premise in choice of Γ = Γ(v) is theoretical, and in the high-temperature region it is necessary to use model representations and to check the correctness of the various simplifying assumptions under high-temperature conditions.

For this purpose we used the previously obtained theoretical calculations[15] of the compressibility of dense gases heated to high temperatures. The calculations were carried out with the free volume theory, which gives a correct qualitative description of the properties of dense gases in the region of interest here and permits reliable quantitative predictions of the equations of state in the high-pressure region.[16] According to this theory the energy of elastic interaction, its increase with thermal motion, and other thermodynamic characteristics are calculated with averaging in a specified volume of the potentials of pairing interaction with the surrounding particles. Numerical values of the constants of the pairing interaction potentials for water were found in ref. 15 from its dynamic compressibility. The approximate nature of the free volume theory makes unjustified the use of the complicated computational apparatus of this theory to determine thermodynamic quantities. It is obviously more appropriate in the existing situation to use simplified forms of the equation of state, and here the conclusions of the free volume theory can be used to choose the most realistic assumptions.

The results of calculations for water in the pressure region up to ~1 Mbar and temperatures up to $\sim 10^4$ K were used, in particular, to check the validity of the assumption $\Gamma = \Gamma(v)$. An analysis showed that this assumption in the pressure and temperature range indicated is poorly justified: Γ turns out to be in identical degree strongly dependent both on v and on P (or T) for a fixed value of v.

The same method was used to check another assumption, namely, that the derivative $P(\partial v/\partial E)_P$ is a function only of pressure, i.e.,

$$P\left(\frac{\partial v}{\partial E}\right)_P = \eta(P), \tag{3.1}$$

which is equivalent to the assumption made by Rice and Walsh.[3] It turned out that in the high-pressure region it is possible to assume that Eq. (3.1) is valid with high accuracy.

Using Eq. (3.1), the equation of state in P-v-E coordinates can be written in the form

$$E(P,v)-E_1(P)=\frac{P}{\eta(P)}[v-v_1(P)], \tag{3.2}$$

where $E_1(v)$ and $v_1(P)$ are dependences on some "reference" curve, for which it is natural to take the well studied experimental shock adiabat of water.[2,4,7] Here it is assumed that on all dynamic adiabats, states of the liquid phase are realized. The adiabat of water in D-U coordinates is well described by the function

$$D=C_0+\lambda_1 U+\lambda_2 U^2, \tag{3.3}$$

which gives in P-v variables the shock adiabat in parametric form:

$$v_1=v_0\left(1-\frac{U}{C_0+\lambda_1 U+\lambda_2 U^2}\right), \quad P=\frac{U}{v_0}(C_0+\lambda_1 U+\lambda_2 U^2). \tag{3.4}$$

In addition to the conservation law

$$E_1(P)=E_0+{}^1\!/_2 P[v_0-v_1(P)] \tag{3.5}$$

Eqs. (3.4) and (3.5) determine the functions $v_1(P)$ and $E_1(P)$ entering in Eq. (3.2).

The values of the constants in Eq. (3.3) which best satisfy the experimental data are as follows:

$$C_0=1.50\ \mathrm{km/sec},\ \lambda_1=2.0,\quad \lambda_2=-0.107\ \mathrm{sec/km}\quad (0<U\leqslant 4.0\ \mathrm{km/sec});$$
$$C_0=3.2\ \mathrm{km/sec},\quad \lambda_1=1.144,\quad \lambda_2=0\qquad (U\geqslant 4.0\ \mathrm{km/sec}).$$

According to Eq. (3.2) the adiabats of porous material and the adiabats of double compression are written in the form

$$v-v_1(P)=\frac{\eta(P)\{2E_0+P_2[v_{00}-v_1(P)]-P(v_0-v_2)\}}{\eta(P)(P+P_2)+2P}. \tag{3.6}$$

For the double-compression adiabat $E_0 = 0$, $v_{00} = v_0$; P_2 and v_2 are the coordinates of the initial point for the second adiabat.

For the adiabat of a porous material we have $P_2 = 0$, $v_2 = v_{00}$, and $E_0 = \Delta H$, where $\Delta H = -4.4 \times 10^{10}$ erg/g is the change in enthalpy in transition of the material from one state (ice, t = –15°C) to another state (water, t = +20°C) at atmospheric pressure.

Together with Eq. (3.2), the condition of isoentropy $dE = -Pdv$ leads to a differential equation for determination of the isentrope:

$$\frac{dH}{dP}-\frac{\eta}{P(1+\eta)}H=\frac{2+\eta}{2(1+\eta)}v_1(P)-\frac{\eta}{1+\eta}\left(\frac{E_0}{P}+\frac{v_0}{2}\right) \tag{3.7}$$

($H = E + Pv$ is the enthalpy; E_0 and v_0 are the initial values of the quantities in the initial state of the shock adiabat of water). The temperatures on the isentropes are determined by the obvious relation

$$T=T_0\exp\left[\int\limits_{P_0}^{P}\frac{\eta(P)}{1+\eta(P)}\frac{dP}{P}\right], \tag{3.8}$$

if the temperature (T_0) at any point on the isentrope is known (for $P = P_0$).

For sufficiently high pressures $P \gtrsim 300$ kbar the value $\eta(P) \simeq 0.2$ follows from calculations according to the free volume theory. However, at low pressures the function $\eta(P)$ is substantially nonconstant. In the pressure region ~100 kbar, calculations according to the free volume theory predict a maximum of $\eta(P)$, and at lower pressures $\eta(P)$ begins to decrease. A decrease in $\eta(P)$ at low pressures also follows from the thermodynamic identity

$$\eta(P)=\frac{P\Gamma(v)}{\rho C^2-P\Gamma(v)}, \tag{3.9}$$

which is easily obtained if we take into account the definition of η from Eq. (3.1) and $\Gamma = v(\partial P/\partial E)_V$. It can be seen from this identity that for $P \to 0$ we have $\eta \sim P$, since at low pressures for a condensed medium $\rho C^2 \gg P(\Gamma \approx 1)$. The value of

$$\left.\frac{d\eta}{dP}\right|_{P=0}=\frac{\Gamma}{\rho C^2}=\frac{\alpha_0\rho_0}{C_{v0}}$$

($\alpha_0 = 2.09 \times 10^{-4}\ \mathrm{deg}^{-1}$ is the volume expansion coefficient, $C_{V0} = 4.18 \times 10^7$ J/deg is the heat capacity under normal conditions) is found to be $d\eta/dP|_{P=0} = 5\ \mathrm{Mbar}^{-1}$.

In transition of the system to the state of an ideal gas, we have $\eta_{id} = \Gamma_{id} = \gamma - 1$ (γ is the exponent of the Poisson adiabat), which follows directly from Eq. (3.9).

The coefficients in the function $\eta(P)$, which was given in the form

$$\eta(P)=a(1-e^{-\alpha P})+bPe^{-\beta P}, \tag{3.10}$$

were determined with account of the location in the P-v plane of the experimental points for porous ice (ρ_{00} = 0.35 and 0.6 g/cm^3), and also of the points on the

TABLE III

T, 10^3 K	H, 10^{-10} erg/g	T, 10^3 K	H, 10^{-10} erg/g	T, 10^3 K	H, 10^{-10} erg/g
0.35	4.60	2.5	13.35	5.0	24.45
0.4	4.75	3.0	15.80	5.5	25.90
0.5	5.10	3.5	18.25	6.0	27.10
1.0	6.90	4.0	20.60	6.5	28.05
1.5	8.85	4.5	22.65	7.0	28.60
2.0	11.00				

Note. H = 0 for P = 1 atm, T = 293 K.

TABLE IV

P, kbar	v_1, cm³/g	T_1, K	v_2, cm³/g	T_2, K	v_3, cm³/g	T_3, K	v_4, cm³/g	T_4, K	v_5, cm³/g	T_5, K	v_6, cm³/g	T_6, K
10	0.8317	300	0.8682	428	1.0144	1286	1.1899	2143	1.3809	3000	1.5225	3856
20	0.7817	313	0.8003	447	0.9402	1342	1.1080	2237	1.2908	3132	1.4550	4027
40	0.7038	338	0.7260	483	0.8546	1448	1.1090	2416	1.1771	3382	1.3280	4348
60	0.6631	361	0.6789	516	0.7979	1548	0.9406	2581	1.0959	3613	1.2354	4645
100	0.6012	402	0.6149	575	0.7176	1725	0.8407	2875	0.9748	4026	1.0951	5176
200	0.519	484	0.5192	691	0.5924	2073	0.6802	3454	0.7757	4836	0.8616	6218
300	0.452	542	0.4594	774	0.5123	2322	0.5758	3871	0.6449	5419	0.7009	6967
400	0.412	584	0.4173	834	0.4556	2503	0.5016	4172	0.5516	5840	0.5965	7509
500	0.387	615	0.3904	878	0.4181	2634	0.4514	4390	0.4877	6146	0.5202	7902
700	0.356	653	0.3580	933	0.3729	2799	0.3908	4665	0.4103	6531	0.4278	8396
900	0.337	674	0.3378	963	0.3465	2893	0.3570	4817	0.3684	6744	0.3786	8671
1100	0.321	688	0.3222	982	0.3280	2947	0.3349	4912	0.3413	6876	0.3492	8841
1300	0.308	697	0.3089	995	0.3132	2986	0.3183	4977	0.3239	6968	0.3290	8959
1500	0.297	704	0.2978	1006	0.3014	3017	0.3050	5029	0.3096	7040	0.3137	9051

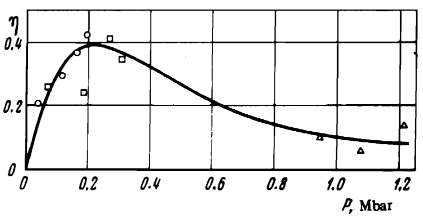

FIG. 4

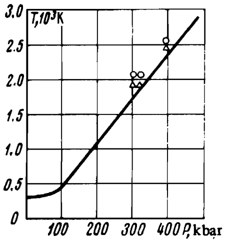

FIG. 5

FIG. 4. Dependence of the coefficient η on pressure: solid curve—calculation with Eq. (3.10), ○, □—experimental points found from the dynamic adiabat of water and ice with ρ_{00} = 0.35 and 0.60 g/cm³, △—from the double-compression adiabat of water.

FIG. 5. Comparison of theoretical values of the temperature of water (solid curve) with the experimental data (○, △) of Kormer. [17]

double-compression adiabats relative to the shock adiabat of water. The description of the experimental values $\eta_{\exp}$, calculated from Eq. (3.6), by the function (3.10) with the determined coefficients a = 0.7, b = 4.4095 Mbar^{-1}, α = 8.436 Mbar^{-1}, β = 4.8202 Mbar^{-1} is shown in Fig. 4.

The location of the adiabats calculated from Eq. (3.6) for ice (ρ_{00} = 0.35, 0.6, and 0.915 g/cm³) and the double-compression adiabats with the assumed dependence $\eta(P)$ is shown in Fig. 2.

To determine the temperatures from Eqs. (3.7) and (3.8), it is necessary to know the initial values H(T, P) along some line. As initial conditions in solution of Eq. (3.7), we used the results of the calculations of ref. 16, from which we determined the values H(T) for P = 50 kbar, which are shown in Table III.

This description of the experimental data was used to calculate the grid of isentropes in P-v coordinates and to determine the temperatures on them. The theoretical values are given in Table IV. From the results of these calculations we also found the velocities of sound and the temperatures behind the shock-wave front in water.

4. DISCUSSION OF RESULTS

With known P-T-v functions on the isentropes, it is easy to determine the isothermal P-v curves. Comparison of these curves with the isothermal data of Bridgman[1] corresponding to t_0 = 75, 125, and 175°C shows that the difference in their relative position amounts to 2–4% in the specific volumes.

In Fig. 5 the calculated temperatures on the adiabat of water are compared with the experimental determinations of Kormer.[17] The figure illustrates the satisfactory agreement (~10%) of the theoretical and experimental data for this region of the P-T diagram. This independent comparison is a confirmation of the correctness of choice of the form and constants of the equation of state. Another parameter which monitors the correctness of this choice is the direct comparison of the theoretical values of the velocity of sound C with the corresponding experimentally determined values. The comparison is given in Fig. 3. As in the preceding case, the satisfactory agreement with independent experimental data indicates the adequate reliability of the results obtained.

Thus, verification of the equation of state of water by means of various experimentally determined parameters indicates the sufficiently good joint description of the thermodynamic properties of water over a wide range of variation of pressure and temperature.

The authors take this occasion to express their indebtedness to L. V. Al'tshuler, who took part in the investigations of isoentropic compression of water, for his constant interest in this work and for helpful discussions.

[1)] These investigations were carried out by the authors of the present article jointly with L. V. Al'tshuler.

[2)] In two experiments we also used the "overtaking" discharge method.

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