THE EQUATION OF STATE OF WATER AT HIGH PRESSURES CALCULATED FROM A STATISTICAL ATOMIC MODEL

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Existing experimental data are sufficient to enable the equation of state of water to be obtained for pressures p up to 10^{11} N/m^2 [1]. The equation of state interpolated from experimental data for this pressure region is found in [2], where an analytic approximation to the solutions of the Thomas–Fermi equation obtained in [3] is used to calculate the thermal contributions to the electron components of energy and pressure. Experimental data for pressures higher than 10^{11} N/m^2 are virtually exhausted by the values given in [4] for $p = 14.25 \cdot 10^{11}$ N/m^2 on the shock adiabat. Thus, it is interesting to calculate the thermodynamic properties of water by direct numerical solution of the equations for a statistical atomic model applicable in the high-pressure region. The thermodynamic properties of water at nonzero temperatures $T \neq 0$ calculated on the basis of Wheeler's model are given in the present paper. The statistical model chosen is that which gives results closest to experimental data at high pressures.

Wheeler's model, which is discussed in [5] for the case of zero temperature, represents the water molecule as consisting of two regions. There is a central sphere occupied by the oxygen atom surrounded by a layer containing the electrons and protons of the hydrogen atoms which form a free electron–nucleon gas. The atomic parameters of oxygen are calculated for $T \neq 0$ and $p \neq 0$ on the basis of a generalized statistical atomic model [3]. The volume of the water molecule is found by treating the proton gas of the outer region as classical and equating its pressure to that due to the electrons of the oxygen atom.

The Thomas–Fermi equation was solved in the present paper by a method developed in [6] which allows the isotherms to be constructed in a natural way. Wheeler's model was used to calculate the isotherms for 19 values of the temperature. These are shown in Fig. 1, where p is the pressure in N/m^2 and n is the number of molecules per cubic meter (1, $T = 1.362 \cdot 10^7$°K; 2, $T = 8.596 \cdot 10^6$°K; 3, $T = 5.425 \cdot 10^6$°K; 4, $T = 3.422 \cdot 10^6$°K; 5, $T = 2.159 \cdot 10^6$°K; 6, $T = 1.362 \cdot 10^6$°K; 7, $T = 8.596 \cdot 10^5$°K; 8, $T = 5.425 \cdot 10^5$°K; 9, $T = 3.422 \cdot 10^5$°K; 10, $T = 2.159 \cdot 10^5$°K; 11, $T = 1.362 \cdot 10^5$°K; 12, $T = 8.596 \cdot 10^4$°K; 13, $T = 5.425 \cdot 10^4$°K; 14, $T = 3.422 \cdot 10^4$°K; 15, $T = 2.159 \cdot 10^4$°K; 16, $T = 1.362 \cdot 10^4$°K; 17, $T = 8.596 \cdot 10^3$°K; 18, $T = 5.425 \cdot 10^3$°K; 19, $T = 342.2$°K). The results for $T = 342.2$°K were used, since they differ negligibly from the results of the cold model ($T = 0$). Lines of constant γ (a–$\gamma = 1.5$; b–$\gamma = 1.55$; c–$\gamma = 1.6$; d–$\gamma = 1.65$; e–$\gamma = 1.7$; f–$\gamma = 1.8$) are also given in Fig. 1. The value of the parameter γ was determined from the formulas

$$\gamma = 1 + \frac{p - p_0}{\varepsilon - \varepsilon_0} v \quad \text{for} \quad v < v_0,$$

$$\gamma = 1 + \frac{p - p_X(v)}{\varepsilon - \varepsilon_X(v)} v \quad \text{for} \quad v > v_0,$$

where v and ε are the volume and total energy of the water molecule, respectively, while p is the total pressure resulting from both the electrons and the surrounding protons, as well as from the motion of the oxygen nuclei. Similarly, p_0, ε_0, and v_0 are the total pressure, energy, and molecular volume for $T = 342.2$°K and normal water density, while $p_X(x)$ and $\varepsilon_X(v)$ are the total pressure and energy of the molecule for $T = 342.2$°K and a molecular volume v. The states satisfying the equation of the shock adiabat were determined by calculating the parameter $L = \frac{1}{2}(p - p_0)(v_0 - v)/(\varepsilon - \varepsilon_0)$ which is equal to unity on the shock adiabat. The values of p and v for which L is unity were found by interpolation. The broken curve in Fig. 1

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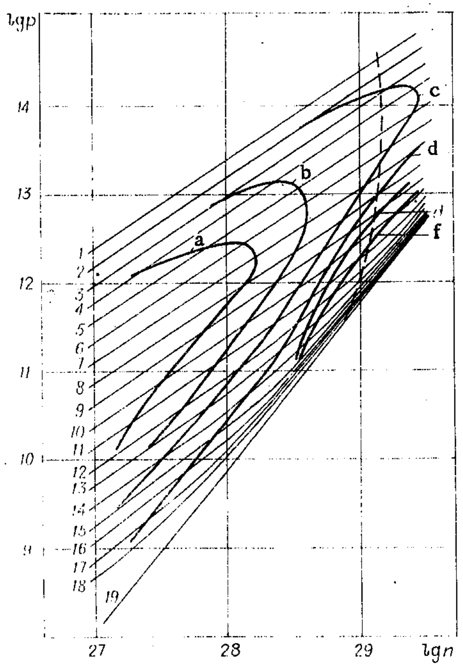

Fig. 1

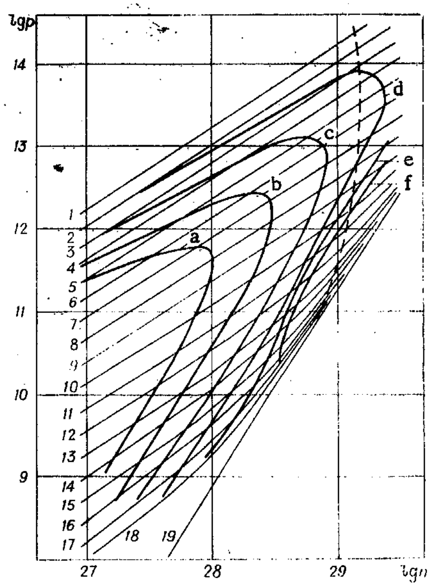

Fig. 2

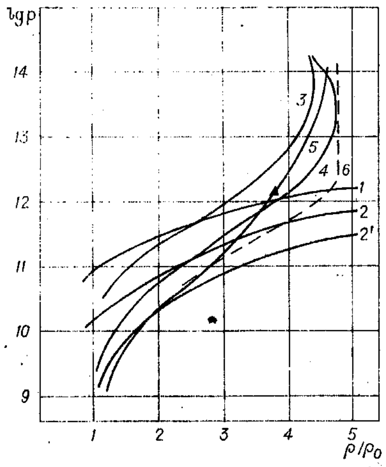

Fig. 3

TABLE 1

T, K	ρ/ρ_0	$p\cdot10^{-11}$, N/m²	γ
5,425·10³	2,27	0,94	
8,596	2,37	1,06	
1,362·10⁴	2,52	1,33	2,33
2,159	2,65	1,67	2,18
5,425	3,15	3.83	1,91
8,596	3,51	6.16	1,80
1,362·10⁵	3,88	10.6	1,72
5,425	4,56	57,4	1,56
1,362·10⁶	4,74	186	1,53
2,159	4,74	339	1,53
3,422	4,68	575	1,54
5,425	4,58	955	1,56
8,596	4,40	1480	1.58
1,362·10⁷	4,34	2370	1,60

TABLE 2

T, K	ρ/ρ_0	$p\cdot10^{-11}$, N/m²	γ
5.425·10³	2,54	3,99	2,29
1,362·10⁴	2,63	4,96	2,20
2,159	2,75	5,89	2.14
3,422	2,88	7,43	2,06
5,425	3.06	9,93	1,96
8,596	3,28	14,2	1.87
1.362·10⁵	3,60	22,1	1,80
8.596	4.20	163	1,62
1,362·10⁶	4,32	288	1,60
2,159	4,36	479	1,59
3,422	4.40	794	1,58
5,425	4.32	1320	1,60
8.596	4,28	2090	1,61
1,362·10⁷	4,22	3390	1,62

shows the shock adiabat obtained in this way. A generalized statistical model of the oxygen atom was taken as another possible model for describing the behavior of water at high pressures. Figure 2 gives 19 calculated isotherms (the values of temperature are the same as those in Fig. 1). The shock adiabat is shown as a broken curve in the same figure and the lines of constant γ (a$-\gamma = 1.4$; b$-\gamma = 1.45$; c$-\gamma = 1.5$; d$-\gamma = 1.55$; e$-\gamma = 1.6$; f$-\gamma = 1.65$), determined from (1), are also given. A summary of data on the shock adiabats (curves 3-5) is given in Fig. 3. Cold compression curves 1, H_2O; 2, O without exchange; 2', O with exchange [5]) are given in the same figure which allows the contribution of the thermal pressure components to be estimated. Curve 3 (Fig. 3) gives the calculations from Wheeler's model, and curve 4 the calculations for the oxygen atom; curve 5 is an extrapolation to pressures above the experimental point $14.25\cdot10^{11}$ N/m² [4], and curve 6 gives the calculations from [1]. A series of shock adiabats numerically calculated for different T, p, and ρ/ρ_0, where ρ_0 is the normal density of water, is given in Tables 1 and 2 for the oxygen model and Wheeler's model, respectively. It can be seen that the experimental point from [4] lies closest to our calculations for oxygen, while for lower pressures these calculations are even closer to the experimental curve compared with curve 3.

The statistical model of the oxygen atom can be used for $p \gtrsim 10^{12}$ N/m² to describe the shock compression of water, as comparison with experiment shows, and it appears to be preferable to Wheeler's model. Wheeler's model, which involves more complicated calculations, leads to pressures considerably in excess of the experimental values and so it would seem inadvisable to use it in the present conditions.

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