

# INTERPOLATION EQUATION OF STATE FOR WATER AND WATER VAPOR

B. V. Zamyshlyayev and M. G. Menzhulin

Here a procedure is given for the construction of an interpolation equation of state for water, taking into account vaporization, dissociation, and the asymptotic behavior of matter under ultrahigh compression. Well-known equations of state for water [1-3] are restricted to the range of experimental data on dynamic compression ( $p < 1$  Mbar) and general thermodynamic relationships are neglected in their formulation.

We represent the free energy  $F$  of water in an arbitrary state as the free energy  $F_0$  of water in the condensed state with corrections for vaporization, dissociation, hydrogen bonds, and electron excitation. The various forms of internal motion within the molecules are considered to be independent. As was done in [4], we assume that in the condensed state the water molecules have the following forms of motion: three translational and two torsional vibrations, free rotation about the dipole axis, three internal motions of the nuclei in the molecule, and on hydrogen bonds.

Moreover, it is supposed that the torsional oscillations are described by the Debye approximation. The possibility of this has been indicated by a number of authors, and for certain molecules it provides a sufficiently good approximation [5].

For water there is completely satisfactory agreement between the calculated and the actual specific heat  $c_V$  for  $V \approx 1$  cm<sup>3</sup>/g and supercritical temperatures.

Under these assumptions the expression for  $F_0$  has the form

$$F_0 = E_x(V) + \frac{R^*}{\mu} T \ln \left[ \left( \frac{\theta_D}{T} \right)^5 \left( \frac{4\theta_r}{\pi T} \right)^{1/2} \prod_{i=1}^3 \left( 1 - \exp \frac{-\theta_i}{T} \right) \right] \quad (1)$$
$$\theta_r = \frac{h^2}{8\pi^2 J k}$$

Here  $E_x$  is the energy of elastic interaction;  $J$  is the moment of inertia of water about the dipole axis;  $\theta_D$ ,  $\theta_r$ , and  $\theta_i$  are the characteristic temperatures for the Debye degrees of freedom, rotation, and internal oscillations, respectively;  $T$  is the temperature in degrees Kelvin;  $R$  is the universal gas constant;  $\mu$  is the molecular weight;  $h$  is Planck's constant; and  $k$  is Boltzmann's constant.

We introduce a correction to  $F_0$  analogous to that in [6]

$$\Delta F_1 = \frac{5}{2} \frac{R}{\mu} T \ln(1 + z_1)$$

where the coefficient  $\frac{5}{2}$  is chosen to optimize agreement of the equation of state with well-known experimental data on the static compression of water. We find the expression for  $z_1(T, V)$  from the condition that  $F_0 + \Delta F_1$  should go over into the expression for the free energy  $F_0^*$  of water molecules in the ideal-gas state for  $z_1 \gg 1$ .

Under the condition that the various degrees of freedom are independent, we have for water molecules in the ideal-gas state

---

Leningrad. Translated from Zhurnal Prikladnoi Mekhaniki i Tekhnicheskoi Fiziki, No. 3, pp. 113-118, May-June, 1971. Original article submitted November 10, 1970.

© 1973 Consultants Bureau, a division of Plenum Publishing Corporation, 227 West 17th Street, New York, N. Y. 10011. All rights reserved. This article cannot be reproduced for any purpose whatsoever without permission of the publisher. A copy of this article is available from the publisher for \$15.00.

$$F_0^0 = \frac{R}{\mu} T \ln \left[ \left( \frac{h^3}{2\pi mkT} \right)^{3/2} \frac{N}{eV} \left( \frac{\theta_{r1}\theta_{r2}\theta_{r3}}{T^3} \right)^{1/2} \frac{2}{\sqrt{\pi}} \prod_{i=1}^3 \left( 1 - \exp \frac{-\theta_i}{T} \right) \right]$$

Then

$$z_1 = 3.6 \frac{T}{V^{0.4} \theta_D^2} \quad (2)$$

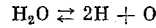
Here  $V$  is the specific volume in  $\text{cm}^3/\text{g}$  and  $N$  is the number of particles in one gram.

One can assume that  $\theta_D$  is a function only of the specific volume. Then the dependence  $\theta_D(V)$  is found from the relationship

$$\theta_D = \theta_{D_0} \exp \left( - \int_{V_0}^V \gamma(V) \frac{dV}{V} \right) \quad (3)$$

Here  $\gamma$  is the Gruneisen constant.

To make an approximate estimate of the effect of dissociation on the thermodynamic functions of water we study the reaction



We represent the correction to the free energy due to dissociation in the form

$$\Delta F_2 = - \frac{1}{2} \frac{R}{\mu} T \ln (1 + z_2) \quad (4)$$

We find the dependence  $z_2(V, T)$  from the condition that the expression  $F_0 + \Delta F_1 + \Delta F_2$  should go over into that for the free energy of water vapor in the fully dissociated ideal-gas state for  $z_2 \gg 1$ . In particular, for  $z_1 \gg 1$  we obtain

$$z_2 = \frac{7.4 \cdot 10^{19}}{T^3} V^4 \exp \frac{-2U}{kT} \quad (U/k = 1.106 \cdot 10^4 \text{ }^\circ\text{K})$$

Here  $U$  is the energy of dissociation of a water molecule.

The coefficient  $1/2$  in Eq. (4) is chosen in order to fulfill the condition  $z_{2\text{max}} \gg 1$  behind a shock front and to optimize the approximate relationship (4) as a correction calculated according to the principle of minimization of free energy. In this case, for temperatures  $T \geq 7.4 \cdot 10^4 \text{ }^\circ\text{K}$  water is represented as an ideal-gas mixture of atoms of oxygen and hydrogen for all states coming within the restriction of the shock adiabat.

The components of the thermodynamic functions of water due to the hydrogen bonds can be estimated from data on the specific heat and enthalpy of water [4, 7] and the value of the critical temperature  $T_* = 647^\circ\text{K}$  at which all hydrogen bonds are completely broken. As a first approximation we assume that in the absence of vaporization ( $z_1 = 0$ ) the number of hydrogen bonds is a function of temperature alone. Then that part of the specific heat due to the hydrogen bonds is found as the difference between the total specific heat  $c_V(1, T)$  at  $V = 1 \text{ cm}^3/\text{g}$  and the specific heat determined on the basis of expression (1) and the relationship

$$c_V = - \frac{\partial}{\partial T} \left[ T^2 \frac{\partial F}{\partial T} \right]$$

The value of the specific heat  $c_{V\text{OH}}(1, T)$ , estimated in this way, can be approximated by the relationship

$$c_{V\text{OH}}(1, T) = \frac{R}{\mu} (6.8 - 1.05 \cdot 10^{-2} T)$$

From this we obtain the following expression for the free energy due to the hydrogen bonds, with  $z_1 = 0$ :

$$F_{\text{OH}}(1, T) = \frac{R}{\mu} \left( -15.6 \lg T + 5.25 \cdot 10^{-2} T - \frac{2.2 \cdot 10^8}{T} + 44 \right) T$$

Clearly, the probability  $W$  of the existence of hydrogen bonds is largest for  $z_1 = 0$  and decreases with increasing  $z_1$ . For arbitrary values of  $z_1$  we may assume that  $F_{OH}$  is proportional to the probability  $W$  of the existence of hydrogen bonds

$$F_{OH} = WF_{OH}(1, T)$$

where  $W$  can be assumed to be of the form  $W = 1/(1 + z_1)$ .

From this we obtain, neglecting second-order terms,

$$E_{OH} = \frac{R}{\mu} \frac{6.8T - 5.25 \cdot 10^{-3}T^2 - 2.2 \cdot 10^3}{1 + z_1}$$

$$c_{VOH} = \frac{c_{VOH}(1, T)}{1 + z_1} \quad (T < T_*)$$

The hydrogen bonds have practically no effect on the pressure.

Thus, we have the following relationships for the thermodynamic functions of water:

$$F = E_x + \frac{R}{\mu} T \ln \left[ \left( \frac{\theta_D}{T} \right)^5 \left( \frac{4\theta_r}{\pi T} \right)^{1/2} \prod_{i=1}^3 \left( 1 - \exp \frac{-\theta_i}{T} \right) (1 + z_1)^{1/2} (1 + z_2)^{-1/2} \right] + F_{OH} + F_e \quad (5)$$

$$p = p_x(V) + \frac{R}{\mu} \frac{T}{V} \left( \frac{5\gamma + z_1}{1 + z_1} + 2 \frac{z_2}{1 + z_2} \right) + p_e \quad (6)$$

$$E = E_x(V) + \frac{R}{\mu} T \left( 5.5 - 2.5 \frac{z_1}{1 + z_1} - \frac{3}{2} \frac{z_2}{1 + z_2} + \sum_{i=1}^3 \frac{\theta_i/T}{\exp \theta_i/T - 1} \right) + \frac{z_2}{1 + z_2} U + E_{OH} + E_e$$

The thermal part of the electron components  $E_e$  and  $p_e$  of the equations of state (5) and (6) can be estimated in an approximate way by making use of Latter's solution of the Thomas-Fermi equations [8], the approximation being fulfilled, for instance, in [9]. Regarding water as made up of cells in which a negative charge of  $10e$  ( $e$  being the charge of an electron) is smeared out uniformly, we obtain

$$p_e = \frac{4.71 \cdot 10^{-4} T^2}{1.235 V^{1/2} + T V \cdot 10^{-5}} \left( 1 + \frac{V^{1/2}}{1.02 + 7.69 \cdot 10^{-10} T^{3/2} V} \right)^{-1} \text{ atm} \quad (7)$$

$$E_e = p_e V \left[ \frac{3}{2} + \frac{(0.358 T^{3/2} + 1.825 \cdot 10^4 V^{1/2})}{T^{1/2} + 2.94 \cdot 10^8 - 25.1 T V} \right] \text{ kg} \cdot \text{cm}^2 / \text{g} \quad (8)$$

The function  $\gamma(V)$  can be worked out from data on the static and dynamic compression of water, taking account of its asymptotic values  $\gamma = 2/3$  for  $V \rightarrow \infty$  and  $V \rightarrow 0$ . The value  $\gamma = 2/3$  for  $V \rightarrow 0$  follows from the properties of matter at ultrahigh compression, described by the Thomas-Fermi model, which yields the asymptotic relationship  $P_x \sim V^{-5/3}$ . The quantity  $p_x$  and its derivatives determined the Gruneisen constant according to the Landau-Slater and the Dugdale-Macdonald theories and the theory of a free region. Calculations by any of these theories lead to the value  $\gamma = 2/3$  for  $V \rightarrow 0$ .

Experimental data on the static compression of water have been approximated with great accuracy by Juza [10], for instance, by an expression of the form given in [11, p. 233],

$$p = \frac{RT}{\mu V} \Phi(V) + \frac{a(V, T)}{V^2} \quad (9)$$

In the case where  $a(V, T)$  depends only on  $V$ , Eq. (5) coincides exactly with (9) for  $z_1 \ll 1$ .

Accordingly, we can assume that  $\gamma = 1/5 \Phi$  and that the temperature dependence of  $a(V, T)$  is compensated by the quantity  $z_1$ .

The form of the dependence  $\gamma(V)$  can be assumed for  $V \leq 1 \text{ cm}^3/\text{g}$ . States with  $V > 1 \text{ cm}^3/\text{g}$  correspond to high temperature, for which the pressure is not determined by the Debye degrees of freedom alone, and the simple relationship  $\gamma = 1/5 \Phi$  is no longer valid.

For  $V > 1$  we can introduce an interpolation function whose magnitude and first derivative coincide with those of  $\frac{1}{5}\Phi$  at the point  $V = 1 \text{ cm}^3/\text{g}$  and whose asymptotic value is  $\gamma = \frac{2}{3}$  for  $V \rightarrow \infty$ .

A series of values of  $\gamma(V)$  for  $V > 0.49 \text{ cm}^3/\text{g}$  can be obtained from experimental data on reflection of shock waves [12].

Introducing an interpolation function, coinciding in magnitude and the value of its first derivative with  $\frac{1}{5}\Phi$  at  $V = 0.59 \text{ cm}^3/\text{g}$  and having the asymptotic value  $\gamma = \frac{2}{3}$  for  $V \rightarrow 0$ , we obtain a function  $\gamma(V)$  for  $V < 0.59 \text{ cm}^3/\text{g}$  which describes the experimental data of [12] in a satisfactory way.

Thus, we have

$$\begin{aligned} \gamma(V) &= \frac{2}{3} + \frac{1}{12V^{13.1}} & (V < 1 \text{ cm}^3/\text{g}) \\ \gamma(V) &= \frac{1}{5} \left( 1 + \frac{1.09008}{V} + \frac{0.835352}{V^2} + \frac{0.45304}{V^3} + \frac{0.396896}{V^4} - \frac{0.0155648}{V^{13}} + \frac{0.00363725}{V^{15}} \right) & (0.59 < V \leq 1 \text{ cm}^3/\text{g}) \\ \gamma(V) &= \frac{2}{3} + 4.618V^{4.125} & (V \leq 0.59 \text{ cm}^3/\text{g}) \end{aligned} \quad (10)$$

And so the thermal components of the thermodynamic functions are completely determined.

The elastic components  $p_X(V)$  and  $E_X(V)$  can be determined from experimental data on static and dynamic compression of water and water vapor. In the range of static pressures  $p_X$  can be determined in the following way.

From the tabulated data of [7] and Bridgman's experimental data on isochors [13], a number of values of  $T$  and the total pressure  $p$  were chosen. With use of the relationships (2), (3), (5), and (10) it is an easy matter to determine the thermal component of the pressure  $p_{\text{tm}}$  corresponding to selected values of  $V$  and  $T$ . Then the elastic component  $p_X$  is found as the difference between the total and the thermal pressures. The values of  $p_X$  found in this way agree well among themselves over a wide range of measurements of the overall pressure. Data corresponding to the calculations are given in Table 1. These characterize the convergence of values of  $p_X$  for various values of  $p$  and, consequently, the overall error in the equation of state as well.

In the domain of dynamic experiments  $p_X$  and  $E_X$  are found from the relationships

$$\begin{aligned} p_x &= p_\Gamma - p_T, & E_\Gamma - E_0 &= \frac{1}{2}(p_\Gamma + p_0)(V_0 - V_\Gamma) \\ E_x &= -\int p_x dV, & E_\Gamma &= E_x + E_T \end{aligned}$$

where the subscript  $\Gamma$  indicates that values of the parameters of the medium are to be taken at a point immediately behind the shock front and the subscript  $T$  indicates the thermal component of the corresponding parameter.

Experimental data on shock compression of water are well approximated by the following relationships between the velocity  $N$  of the shock front and the particle velocity  $v$ :

$$\begin{aligned} N &= c_0 + 2v & (v < 890 \text{ m/sec}) \\ N &= 1.16c_0 + 1.73v & (890 < v < 1840 \text{ m/sec}) \\ N &= 1.73c_0 + 1.28v & (1840 < v < 13\,000 \text{ m/sec}) \end{aligned} \quad (11)$$

TABLE 1.

$v, \text{ cm}^3/\text{g}$	$p/p_x, \text{ atm}$		
0.74	25600/10400	26600/10500	—
0.76	13400/7450	15100/7350	16600/7440
0.86	6000/—1500	6500/—1520	9700/—1300
0.90	3000/—3040	3500/—3090	4000/—3130
1.0	20/—4980	300/—5200	2300/—5190
1.2	250/—6600	850/—6700	—
3	245/—2530	300/—2550	1000/—2600
5	457/—1250	500/—1240	1000/—1260
10	220/—460	280/—470	—
100	22/—8.8	34/—8.4	55/—8.0

Here  $c_0$  is the sound speed in the undisturbed medium.

Under ultrahigh compression a nuclear gas may be considered to be ideal, and the electron component is determined by relationships (7) and (8). Then the shock adiabat for water is easily calculated for this domain of pressures. Results of the corresponding calculations are well approximated by relationships (11) in the range  $2.53 \cdot 10^4 < v < 1.5 \cdot 10^5 \text{ m/sec}$ , and also by the dependence

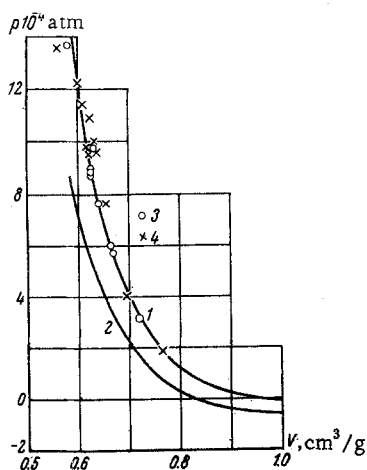


Fig. 1

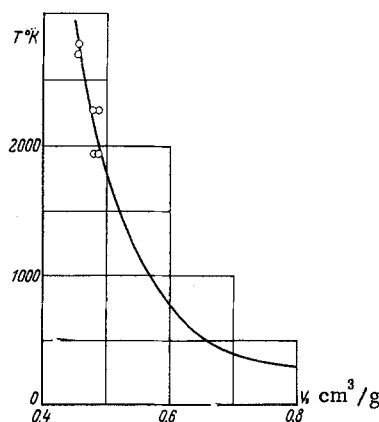


Fig. 2

$$dV = -3.32c_0 + 1.33v \text{ m/sec for } v > 1.5 \cdot 10^5 \text{ m/sec} \quad (12)$$

As equations (11) describe both the experimental and the calculated results, they can evidently be used for interpolation of the shock adiabat for water throughout the entire intermediate range.

In the calculation of  $p_x$  and  $E_x$  the interaction of all the particles — nuclei and electrons — is taken into account simultaneously. Figure 1 shows values of  $p_x$  (curve 2) and the shock adiabat (curve 1) calculated in this way, and also experimental data on shock compression of water from [12, 14] (points 3 and 4, respectively).

Approximate formulas for  $p_x$  (in atmospheres) can be represented in the form

$$p_x = -\frac{1.26 \cdot 10^4}{V^{1.44}} \quad (V > 20 \text{ cm}^3/\text{g})$$

$$p_x = \frac{4.8 \cdot 10^4 (1 - V/0.837)}{V^{1/2} [1 - 1.7(1 - V/0.837)]^2} \quad (0.8 < V \leq 20 \text{ cm}^3/\text{g})$$

$$p_x = 1.25701 - \frac{2.63114 \cdot 10^6}{V} + \frac{1.75451 \cdot 10^6}{V^2} - \frac{3.6183 \cdot 10^9}{V^3} \quad (0.6 < V \leq 0.8 \text{ cm}^3/\text{g})$$

$$p_x = \frac{5.31 \cdot 10^3}{V^{5.04}} \quad (V \leq 0.6 \text{ cm}^3/\text{g})$$

Having obtained the thermodynamic functions of water, one can make approximate calculations of the vaporization, dissociation, and electron excitation. Within the range of the experimental data on static compression of water the error in pressure in the equation of state obtained here does not exceed a few percent.

Estimates of errors in the thermodynamic functions in the domain of ultrahigh pressures are impossible since, at the present time, neither experimental nor rigorous theoretical results on the thermodynamic properties of water in this domain are available.

However, satisfaction of all asymptotic transitions and an estimate of the shock adiabat that takes account of the asymptotic laws of the behavior of water evidently ensures an accuracy sufficient for practical calculations in this domain as well. In particular, this is attested to by the good agreement between experimental data on the temperature behind a shock front from [15] and the curve, constructed on the basis of calculation, in Fig. 2.

#### LITERATURE CITED

1. M. H. Rice and J. M. Walsh, "Equation of state of water to 250 kilobars," *J. Chem. Phys.*, **26**, No. 4 (1957).
2. N. M. Kuznetsov, "Equation of state and specific heat of water over a wide range of the thermodynamic parameters," *Zh. Prikl. Mekhan. i Tekh. Fiz.*, No. 1 (1961).
3. R. A. Papetti and M. Fujisaki, "The Rice and Walsh equation of state for water: discussion, limitations, and extensions," *J. Appl. Phys.*, **39**, No. 12 (1968).

4. G. Nemethy and H. A. Scheraga, "Structure of water and hydrophobic bonding in proteins. I. A model for the thermodynamic properties of liquid water," *J. Chem. Phys.*, 36, No. 12 (1962).
5. Ch'ien Hsueh-sien, *Physical Mechanics* [in Russian], Mir, Moscow (1965).
6. S. B. Kormer, A. I. Funtikov, V. D. Urlin, and A. N. Kolesnikova, "Dynamic compression of porous metals and an equation of state with variable specific heat for high temperatures," *Zh. Éksp. i Teor. Fiz.*, 42, No. 3 (1962).
7. M. P. Bukalovich, *Thermophysical Properties of Water and Water Vapor* [in Russian], Mashinostroenie, Moscow (1967).
8. R. Latter, "Temperature behavior of the Thomas-Fermi statistical model for atoms," *Phys. Rev.*, 99, No. 6 (1955).
9. S. V. Bobrovskii, V. M. Gogolev, and B. V. Zamyshlyaev, "Construction of approximate shock adiabats for solid bodies in the hydrodynamic domain," *Dokl. Akad. Nauk SSSR*, 184, No. 3 (1969).
10. J. Juza, "An equation of state for water and steam," in: *Advances in Thermophysical Properties at Extreme Temperature and Pressure*, Amer. Soc. Mech. Engrs., New York (1965).
11. J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids*, Wiley New York (1954).
12. J. Walsh and M. H. Rice, "Dynamic compression of liquids from measurements on strong shock waves," *J. Chem. Phys.*, 26, No. 4 (1957).
13. P. V. Bridgman, "Most recent work in the high-pressure domain," *Usp. Fiz. Nauk*, 31, No. 1 (1947).
14. L. V. Al'tshuler, A. A. Bakanova, and R. F. Trunin, "Phase changes in water under compression by strong shock waves," *Dokl. Akad. Nauk SSSR*, 121, No. 1 (1958).
15. S. B. Kormer, "Optical investigations of properties of shock-compressed, condensed dielectrics," *Usp. Fiz. Nauk*, 94, No. 4 (1968).