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UCRL-52190

EQUATION OF STATE OF WATER

Francis H. Ree

December 20, 1976

MASTER

Prepared for U.S. Energy Research & Development
Administration under contract No. W-7405-Eng-48

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Printed in the United States of America
Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161
Price: Printed Copy \$; Microfiche \$3.00

Page Range	Domestic Price	Page Range	Domestic Price
001-025	\$ 3.50	326-350	10.00
026-050	4.00	351-375	10.50
051-075	4.50	376-400	10.75
076-100	5.00	401-425	11.00
101-125	5.50	426-450	11.75
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EQUATION OF STATE OF WATER

Abstract

An equation of state of water is constructed in the density range between 2 g/m^3 and $4 \times 10^2 \text{ Mg/m}^3$ and in the temperature range between 0.025 eV (room temperature) and 25 keV by combining several theoretical codes and experimental data. The liquid-vapor

phase change, ionization process, and chemical equilibrium among dissociation products of water are all considered. Theoretical results and experimental data are compared and several interesting aspects of the thermodynamics of water are discussed.

Introduction

Approximately 2.2×10^{21} kg of water exist in the oceans and within terrestrial rocks. About 36% of this water is contained in rocks as mineral hydrates. Water constitutes the most abundant compound on the surface of the earth. Without water, most living organisms cannot survive. In addition in our modern-day world, an understanding of the physical properties of water is essential to many engineering and industrial applications.

The water contained in rocks has a much lower boiling temperature than that of the rocks themselves and thus the pressure generated from vaporized water can drastically alter the cavity formation from an underground explosion (conventional or nuclear). The high energy released

by the explosion can produce a shock wave of several hundred terapascals which heats the rock-contained water to several kiloelectron volts. This shock compression is usually accompanied by an adiabatic expansion that brings the system to the low-density, gaseous-phase region and, upon further cooling, takes it into the liquid-vapor transition region. The properties of water must be known over a wide range of variables if cavity formation is to be accurately predicted.

An understanding of the properties of water is also essential to another current problem area; namely, safeguarding against a "loss-of-coolant" accident associated with a nuclear reactor. In such a situation, steam and air under pressure, generated as

a result of the loss of coolant, is vented into a pool of cold liquid water, thus relieving the dangerously high pressures. Here, the thermodynamic properties of water are required only over a limited range but, obviously, with great accuracy. The physically important range mainly spans the liquid-vapor transition region but still, the highest densities foreseeable reach several-percent compression.

A material-response code designed to study these water-related problems may require thermodynamic data of water in the range from 2 g/m^3 to

$4 \times 10^2 \text{ Mg/m}^3$ in density (ρ) and from 0.025 eV (room temperature) to 25 keV in temperature (T). Within this range the thermodynamic behavior of water is complex. In addition to normal thermodynamic phase changes, we must consider dissociation and ionization of water molecules. Although water has been studied extensively,¹⁻⁶ available experimental data do not cover the entire ρ -T region required. In this report, we provide a consistent, global equation of state (EOS) for water which encompasses all states of water that may be reached in experimental and working situations.

Construction of the EOS Data Basis

As described earlier, the EOS data are desired for densities from 2 g/m^3 to $4 \times 10^2 \text{ Mg/m}^3$ and for temperatures from 0.025 eV to 25 keV a nearly complete range for any practical application. Understandably, a single theoretical model cannot cover this entire range. Therefore, we have combined several theoretical models, each appropriate over different temperature and density ranges, with available experimental data to develop an EOS that is consistent over this wide range. This procedure has proved to be useful in obtaining the EOS data of various plastics⁷

and of SiO_2 .⁸ Details of the theoretical models and their required approximations have been described in Refs. 7 and 8, as well as in the references quoted therein. Only a brief description of the models relevant to water is necessary for our present purpose.

Figure 1 indicates the five different ρ -T subregions: four theoretical regions plus one experimental region. These are the TIGER, OCCIPITAL, TFCMIX, and MASTER regions, where each name refers to an appropriate theoretical code used in the regions, and the EXPERIMENTAL region,

Fig. 1. The density and temperature regions of the four theoretical codes (TIGER, OCCIPITAL, TFCMIX, and MASTER) plus the experimental data used to obtain the EOS data of water. The data are taken at points shown. There are 45 isotherms as denoted by T_i ($i = 1, 2, \dots, 45$). These are: 0.025, 0.03, 0.035, 0.04, 0.05, 0.07, 0.1, 0.13, 0.15, 0.18, 0.2, 0.25, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 1.0, 1.5, 2.5, 4, 6, 8, 10, 15, 25, 40, 60, 80, 100, 150, 250, 400, 600, 800, 1000, 1500, 2500, 4000, 6000, 8000, 10000, 15000, and 25000 eV.

where the experimental data are employed. In this report we have simply extended the liquid phase to the high-density region where ice is actually a stable phase and therefore, the thermodynamics of ice are treated only approximately.

TIGER REGION

Within this region, the ionization is negligible but, because of the moderately high-temperature and low-density environment encountered here, the EOS data are sensitive to the chemical equilibria of the dissociated species of H_2O as well as of H_2O itself.

The TIGER code calculates the EOS data for a heterogeneous system of

a mixture containing gaseous and condensed components.⁹ The gaseous species chosen in the present calculation are O , O_2 , H , H_2 , OH , and H_2O . In addition, the calculation also includes the liquid H_2O . The pressure for the gaseous mixture is calculated from the BKW (Becker-Kistiakowsky-Wilson) equation.¹⁰ The "covolume" parameters in the BKW equation as well as the enthalpy changes, entropies at room temperature and at standard state, and analytical fits to the specific heat data have been provided by J. Walton and E. Lee¹¹ for our present work. These data are summarized in Table 1. The liquid-state EOS expression of water for TIGER was chosen to be

$$\begin{aligned}
 V(\text{liquid } H_2O) = & 16.94 + 0.03803 T - 2.602 \cdot 10^{-6} T^2 \\
 & + (-1.48 \cdot 10^{-4} + 3.439 \cdot 10^{-8} T + 2.198 \cdot 10^{-11} T^2)P \\
 & + (5.434 \cdot 10^{-10} - 3.037 \cdot 10^{-13} T - 1.342 \cdot 10^{-17} T^2)P^2, \quad (1)
 \end{aligned}$$

where the molar volume V is expressed in units of $10^{-6} \text{ m}^3/\text{mol}$, the temperature T in Kelvins, and the pressure in atmospheres (0.101325 MPa). The above expression correctly reproduces the observed bulk modulus at standard state and room temperature. It was obtained by refitting a semitheoretical EOS expression of Gurtman *et al.*,⁶ which is based on the hydrostatic data of Bridgman

as reported in Ref. 6 and on Rice and Walsh's data deduced from the shock-wave experiments.⁴ Equation (1) is applicable for $T \lesssim 1600 \text{ K}$, $P \lesssim 25 \text{ GPa}$, and $\rho \lesssim 2.2 \text{ Mg/m}^3$. The average error between Eq. (1) and Gurtman *et al.*'s expression⁶ over this range is about 7.5%. However, because a polynomial of Eq. (1) has a rather constrained form which cannot fit the EOS data

Table 1. The parameters in the TIGER code for the equilibrium mixtures of H_2O .^a

	H	O	OH	H_2	O_2	H_2O (gas)	H_2O (liquid)
C_1^b	2.500 E+0	2.251 E+0	4.594 E+0	3.517 E+0	3.247 E+0	7.503 E+0	1.421 E+0
C_2	0	4.450 E-2	1.582 E-1	4.978 E-1	6.613 E-1	2.341 E-1	-2.141 E-1
C_3	0	7.257 E-3	-2.096 E-2	-4.476 E-2	-7.884 E-2	-3.875 E-2	2.691 E-2
C_4	0	-8.006 E-4	7.943 E-4	1.094 E-3	3.120 E-3	1.692 E-3	-1.098 E-3
C_5	0	3.360 E-1	-1.722 E+0	-6.541 E-1	7.757 E-1	-4.192 E+0	-5.221 E-1
C_6	0	-1.431 E-1	8.105 E-1	3.962 E-1	-5.134 E-1	1.707 E+0	1.016 E-1
C_7	0	2.276 E-2	-1.167 E-1	-6.528 E-2	8.697 E-2	-2.303 E-1	-6.440 E-3
$H_{298.15}^\circ$ ^c	52.100	59.559	9.432	0	0	-57.798	
$S_{298.15}^\circ$ ^d	27.392	38.470	43.880	31.210	49.000	45.106	
k^e	76	120	413	180	350	360	

^a Data provided by J. Walton and E. Lee (see Ref. 11).

^b $C_p(T)/R \equiv C_1 + C_2\theta + C_3\theta^2 + C_4\theta^3 + C_5\theta^{-1} + C_6\theta^{-2} + C_7\theta^{-3}$; $\theta \equiv T/1000$.

^c Heat of formation in kcal/mol at standard state and 298.15 K (see Ref. 12).

^d Entropy in cal/mol/K at standard state and 298.15 (see Ref. 12).

^e Covolume in the BKW equation (Ref. 10) in $\text{K}^{0.5} \cdot \text{cm}^3/\text{mol}$.

over a large range of pressure, the deviation between the two approaches can become as large as 17%.

The TIGER region included in our data basis has an approximately rectangular shape in ρ and T coordinates with ρ between 2 g/m^3 and 2.5 Mg/m^3 and T between 0.1 and 1.0 eV . We chose the upper temperature boundary so that ionization contributions would be negligible. The lower temperature boundary was set so that the available experimental data could be used below it. Comparison of the EOS data between the TIGER calculation and the experimental data below 0.1 eV will be presented in a later section of this work. Note that the upper left-hand corner (low- ρ and high- T portion) of the TIGER region in Fig. 1 was trimmed and replaced by the OCCIPITAL generated data because the ionization becomes significant in this area. When the density exceeds the upper end (2.5 Mg/m^3) of the TIGER region, the nonideal (repulsive) contribution to the pressure in the BKW equation produces an undesirably large pressure. Thus, the TIGER data beyond 2.5 Mg/m^3 were not used. The energy of formation of liquid H_2O at standard state and room temperature is 15.6 kJ/g ($15.6 \text{ GPa}\cdot\text{m}^3/\text{Mg}$).¹² The internal energy (E) values in the present work are referred from this standard state.

OCCIPITAL REGION

Here, H_2O is assumed to be completely dissociated into ions, electrons, and neutral atomic hydrogen and oxygen. The concentrations of these species are obtained from the Saha equation.¹³ Thermodynamic properties are calculated by assuming that the dissociated species behave like an ideal gas. The OCCIPITAL code used here is provided by Cortez and Lacey.¹⁴ We used it to generate the EOS data in the region of ρ approximately less than 0.1 Mg/m^3 and T greater than 0.8 eV . The lower right corner (corresponding to the high- ρ , low- T portion) of the OCCIPITAL region was not included in the final data basis because contribution from the partially ionized molecular species may be important in this region. A constant, 53.57 MJ/g , is added to the OCCIPITAL-generated E (which is relative to the separated un-ionized states at $T = 0 \text{ K}$) to refer it to the standard state used in the present work.

MASTER AND TFCMIX REGIONS

The thermodynamic properties in these regions are evaluated by the Thomas-Fermi Theory with several corrections.¹⁵ These are Kirzhnits' correction¹⁶ to account for the wave nature of electrons and the electron exchange contribution plus Warren's

correction¹⁷ for the thermal contribution of nuclei. In addition, a mixture model is used in which the volume and energy of H₂O are assumed to be the sums of the volumes and energies of individual atomic species of oxygen and hydrogen in a 1-to-2 ratio at constant temperature and electron pressure. The internal energies were shifted in the same manner as the OCCIPITAL energies to refer to the standard state.

The TFCMIX region corresponds approximately to $\rho \gtrsim 0.1$ to 1.0 Mg/m^3 and $T \geq 40 \text{ eV}$. Below 40 eV, electronic correlations and atomic shell

structures become important. To correct these deficiencies phenomenologically, the MASTER code¹⁸ generates a new O-K isotherm. The lower-pressure portion of the new O-K isotherm was obtained from the Grüneisen model,

$$P_H - P_O = (\gamma/V) (E_H - E_O), \quad (2)$$

by solving for the O-K quantities, E_O , and $P_O = -\partial E_O / \partial V$. The experimentally determined Hugoniot quantities (P_H and E_H) and the Grüneisen γ expressed as a polynomial in V , where also used such that

$$\begin{aligned} \gamma = & -239.703 + 3081.87 V - 16345.9 V^2 + 46506.6 V^3 - 76706.8 V^4 \\ & + 73499.3 V^5 - 37987.4 V^6 + 8192.56 V^7, \end{aligned} \quad (3)$$

where V is in units of m^3/Mg .

Equation (3) agrees within 10%, over V between 0.45 and $1.0018 \text{ m}^3/\text{Mg}$, to the expression of Gurtman et al.⁶ who estimated γ from the static and Hugoniot data. Such agreement can be considered satisfactory because the

uncertainty in the experimental data is at least as great. The Hugoniot quantities P_H and E_H in Eq. (2) are obtained from the Rankine-Hugoniot relation using the shock velocity (U_s) vs particle velocity (U_p) relation (in km/s):

$$U_s = 1.4829 + 2.1057 U_p - 0.1744 U_p^2 + 0.010085 U_p^3. \quad (4)$$

This accurately represents the experimental data of Walsh and Rice¹⁹ and of Skidmore and Morris to $U_p \approx 8.7 \text{ km/s}$ or $U_s \approx 13 \text{ km/s}$ as compiled

by Van Thiel et al.²⁰ MASTER uses the constant volume specific heat (C_v) of $3R/\bar{A}$ ($\bar{A}$ = average atomic weight = $18.015/3$) to shift E_O to the

energy reference used in the present work.

The 0-K isotherm from the Mie-Grüneisen model is used only for $P \leq 15$ GPa, corresponding to the Hugoniot pressure of 39 GPa or to 54 vol % compression. This is unfortunate because Hugoniot data are available to 0.1 TPa. However, this choice was necessary because the Grüneisen γ expression [Eq. (3)] becomes unreliable for $V \leq 0.45 \text{ m}^3/\text{Mg}$.

The higher-pressure portion of the new 0-K isotherm ($P \geq 20$ TPa) was assumed to be the same as the 0-K isotherm of the TFCMIX code. In the intermediate range of P (i.e., between 15 GPa and 20 TPa), a smooth interpolation was made to join the lower and the upper portions of the 0-K isotherm. The other finite-T isotherms were obtained by rescaling the TFCMIX isotherms, adding at each density a quantity that is equal to the difference between the new 0-K isotherm and the TFCMIX 0-K isotherm.

EXPERIMENTAL REGION

This region is approximately rectangular in shape and is bounded by $T \leq 0.08$ to 0.1 eV and $\rho \leq 1.0$ to 1.25 Mg/m^3 . Three different experimental sources are used here; Schmidt's steam table³, Burnham *et al.*'s static compression data³, and Bridgman's work as reported in Refs. 4 and 6.

The pressures at $\rho = 1.25 \text{ Mg/m}^3$ and $T = 0.025, 0.03, \text{ and } 0.04$ eV are obtained by graphically extrapolating or interpolating Bridgman's data. The corresponding energies are calculated by assuming that C_v is equal to $3.27 \text{ J/g}\cdot\text{K}$. The assumption of a constant C_v in the ρ - T range described above has been discussed by Gurtman *et al.*⁶ who concluded that the above value for C_v is reasonable. The thermodynamic data up to 0.1 GPa were taken directly from the steam table while those above 0.1 GPa were obtained by Burnham *et al.*²¹ from the following two empirical polynomials:

$$PV = \sum_{j=0}^9 \sum_{i=0}^{9-j} a_{ij} T^i P^j, \quad (5)$$

$$PV = \sum_{j=0}^8 \sum_{i=0}^{8-j} a_{ij} T^i P^{-j}, \quad (6)$$

depending on different ranges of T and P . Numerical values of 55 a_{ij} coefficients in Eq. (5) and 45 in Eq. (6) that can reproduce the experimental specific volume data to 1 GPa and 1173 K within 0.3% are given by Burnham *et al.*³ They have also used a polynomial similar to Eq. (5) to extrapolate the data to 1373 K and to 1 GPa; this data was also included in our present work.

DATA REDUCTION

To generate the EOS data over an entire ρ -T plane in Fig. 1, the EOS data from each of the theoretical codes described above are generated over a sufficiently large region. Next, each region must be trimmed until the energy and pressure isotherms and isochores from the neighboring regions appear to be a smooth continuation of each other. Figure 2 illustrates the final "trimmed-down" isotherms of pressure and energy, respectively, for the ρ -T data points in Figure 1.

The "hole" regions in Fig. 1 where the theories become unreliable must be filled by a suitable interpolation. There are essentially three different hole regions in Fig. 1. The degree of difficulty of filling the holes is directly related to the extent of deviation from the ideal-gas behavior. As can be seen in Fig. 2, the easiest region to interpolate is the one bounded by the OCCIPITAL and the TFCMIX regions as well as between the OCCIPITAL and the MASTER regions for $T \geq 2.5$ eV.

The hole region most difficult to interpolate occurs in density between 1.25 Mg/m^3 and 4 Mg/m^3 . This region joins the EXPERIMENTAL and the MASTER regions and is difficult to interpolate because the energy and the pressure are strongly increasing

functions of density. The interpolations within this region are done iteratively until satisfactory data can be obtained.

The third hole region lies in temperature between 0.15 and 1.5 eV. It connects the TIGER and the MASTER as well as the low-T (≤ 1.5 eV) OCCIPITAL data and the MASTER data. This region has a relatively large hole and is difficult to interpolate along each isotherm. The interpolations within this region are done bivariantly (in both ρ and T) after interpolating the first two hole regions that sandwich this third region.

The final EOS data are composed in a tabular form at 80 ρ -points and 45 T-points, comprising the total 3600 data points. The ρ -grids used are multiples of 1, 1.25, 1.5, 2, 2.5, 3, 4, 5, 6, and 8 between 2 g/m^3 and 400 Mg/m^3 (except for $\rho = 3 \times 10^{-6}$, 5×10^{-6} , 8×10^{-6} , 1.5×10^{-5} , 50, 80, 100, 125, 200, 250, and 300 Mg/m^3). The T-grids are multiples of 1, 1.5, 2.5, 4, 6 and 8 between 2.5×10^{-2} and 2.5×10^4 eV (except for $T = 0.06$, and 0.08 eV). In addition, the isochores at $\rho = 0.6309, 0.9, 1.02, 1.04, 1.08, 1.14$, and 1.18 Mg/m^3 as well as the isotherms at $T = 0.03, 0.035, 0.05, 0.07, 0.13, 0.18, 0.2, 0.3, 0.5$, and 0.7 eV are included to

Fig. 2. The pressure (a) and energy (b) isotherms of water over the data basis shown in Fig. 1.

obtain the more detailed structure of the EOS data. The final pressure energy isotherms are shown in Fig. 3. Tables 2 and 3 list the values of P and E, respectively, at selected T and ρ . This data is

abstracted from the EOS table which is too large to be included in this report.²² The present EOS table is constructed to be used with the LLL hydrocodes such as MEG, GREDEL, and CORONET.

Discussions

SHAPES OF THE EOS DATA

The critical point of water occurs at $T_c = 647.3$ K, $P = 21.408$ MPa, and $\rho = 0.305$ Mg/m³. Within the liquid-vapor two-phase region, the internal energy along an isotherm initially decreases steeply with density and then levels off until the liquid end of the transition region is reached. In the pure liquid region, the energy decreases again to $\rho = 1.2$ Mg/m³, above which the energy increases because of the repulsive interaction among the H₂O molecules (Fig. 3b). At temperatures between 0.1 and 150 eV, (the upper T corresponds to a nearly complete ionization of an oxygen atom, possibly excepting the last two, most tightly bound electrons), the influence of the ionization processes on the EOS behavior is significant as is evidenced by the ramped stairstep character in the energy isotherms in Fig. 3b.

Figure 4 shows the P vs E plots along isotherms ranging from room

temperature to 773.15 K in the interval of 20 K. The data shown here correspond to those within the EXPERIMENTAL region. The stairstep character in the P vs E isotherms corresponds to the liquid-vapor phase changes. At the transition, the energy drops from the higher (gaseous) values to the lower (liquid) values while the pressure obviously must remain constant. Figure 5 illustrates the corresponding P vs ρ isotherms.

ANALYTICAL REPRESENTATIONS OF THE EOS DATA

Many available material-response codes accept the EOS information only in an analytical form. For such codes, the EOS table developed in this study must be fitted into an appropriate analytical form. To fit the entire EOS table by a single expression with a limited number of parameters is a very difficult task. Therefore, a single analytical form is used here

Fig. 3. The EOS data of water from the EOS table obtained in this study: (a) pressure isotherms, (b) energy isotherms.

Table 2. Values of P at selected values of T and ρ (abstracted from the complete EOS table²²).

		PRESSURE (TPA)									
DENSITY	TEMPERATURE (eV)										
MG/M**3		2.50E-02	3.50E-02	5.00E-02	7.00E-02	1.00E-01	1.50E-01	2.50E-01	3.00E-01	4.00E-01	5.00E-01
1.00E-05	1.353E-09	1.075E-09	2.679E-09	3.751E-09	5.358E-09	8.049E-09	1.709E-08	3.161E-08	6.223E-08	8.004E-08	
1.00E-04	2.340E-09	1.071E-08	2.677E-08	3.750E-08	5.361E-08	8.045E-08	1.405E-07	2.266E-07	5.279E-07	7.758E-07	
1.00E-03	2.340E-09	1.042E-07	2.662E-07	3.741E-07	5.390E-07	8.079E-07	1.405E-06	1.880E-06	3.788E-06	6.564E-06	
2.50E-02	2.340E-09	2.970E-07	5.639E-06	8.814E-06	1.402E-05	2.202E-05	3.670E-05	4.548E-05	7.158E-05	1.122E-04	
6.00E-02	2.340E-09	2.970E-07	9.511E-06	1.948E-05	3.153E-05	5.215E-05	9.052E-05	1.125E-04	1.75E-04	2.702E-04	
1.00E-01	2.340E-09	2.970E-07	9.500E-06	2.970E-05	5.067E-05	8.874E-05	1.606E-04	2.003E-04	3.108E-04	4.676E-04	
1.50E-01	2.340E-09	2.970E-07	9.523E-06	4.023E-05	7.469E-05	1.392E-04	2.633E-04	3.296E-04	5.079E-04	7.468E-04	
2.50E-01	2.340E-09	2.970E-07	9.518E-06	5.734E-05	1.250E-04	2.585E-04	5.245E-04	6.615E-04	1.009E-03	1.425E-03	
6.00E-01	2.340E-09	2.970E-07	9.597E-06	1.627E-04	4.207E-04	9.743E-04	2.215E-03	2.808E-03	4.125E-03	5.264E-03	
8.00E-01	2.340E-09	2.971E-07	8.206E-05	4.033E-04	8.503E-04	1.762E-03	3.939E-03	4.946E-03	7.083E-03	8.655E-03	
1.00E+00	7.064E-08	1.642E-04	5.439E-04	1.045E-03	1.715E-03	3.081E-03	6.552E-03	8.102E-03	1.128E-02	1.333E-02	
1.04E+00	9.951E-05	2.915E-04	7.175E-04	1.240E-03	1.965E-03	3.449E-03	7.267E-03	8.955E-03	1.239E-02	1.451E-02	
1.14E+00	4.621E-04	7.683E-04	1.376E-03	1.851E-03	2.733E-03	4.532E-03	9.302E-03	1.136E-02	1.549E-02	1.787E-02	
1.25E+00	1.170E-03	1.450E-03	2.481E-03	2.758E-03	3.846E-03	5.925E-03	1.162E-02	1.405E-02	1.887E-02	2.145E-02	
1.50E+00	4.799E-03	5.181E-03	6.306E-03	6.714E-03	8.025E-03	1.035E-02	1.720E-02	1.998E-02	2.536E-02	2.877E-02	
2.00E+00	1.838E-02	1.906E-02	2.042E-02	2.122E-02	2.316E-02	2.610E-02	3.623E-02	3.995E-02	4.677E-02	5.190E-02	
4.00E+00	1.822E-01	1.832E-01	1.846E-01	1.866E-01	1.894E-01	1.942E-01	2.037E-01	2.085E-01	2.179E-01	2.271E-01	
6.00E+00	7.204E-01	7.224E-01	7.249E-01	7.271E-01	7.319E-01	7.393E-01	7.540E-01	7.610E-01	7.747E-01	7.888E-01	
1.00E+01	3.174E+00	3.176E+00	3.178E+00	3.185E+00	3.192E+00	3.204E+00	3.228E+00	3.240E+00	3.264E+00	3.287E+00	
1.50E+01	8.692E+00	8.697E+00	8.700E+00	8.707E+00	8.719E+00	8.738E+00	8.771E+00	8.788E+00	8.826E+00	8.864E+00	
2.50E+01	2.637E+01	2.638E+01	2.639E+01	2.641E+01	2.642E+01	2.645E+01	2.651E+01	2.654E+01	2.659E+01	2.665E+01	
1.50E+02	8.859E+02	8.860E+02	8.858E+02	8.860E+02	8.860E+02	8.865E+02	8.868E+02	8.870E+02	8.875E+02	8.878E+02	

		PRESSURE (TPA)									
DENSITY	TEMPERATURE (eV)										
MG/M**3		7.00E-01	1.00E+00	1.50E+00	2.50E+00	4.00E+00	1.00E+01	2.50E+01	1.00E+02	1.00E+03	1.00E+04
1.00E-05	1.125E-07	1.725E-07	3.828E-07	7.920E-07	1.444E-06	5.070E-06	1.457E-05	6.943E-05	6.965E-04	6.965E-03	
1.00E-04	1.122E-06	1.646E-06	3.049E-06	7.416E-06	1.331E-05	4.483E-05	1.432E-04	6.880E-04	6.963E-03	6.965E-02	
1.00E-03	1.093E-05	1.515E-05	2.647E-05	6.179E-05	1.205E-04	3.931E-04	1.383E-03	6.631E-03	6.959E-02	6.965E-01	
2.50E-02	2.211E-04	3.530E-04	5.814E-04	1.192E-03	2.355E-03	8.263E-03	3.074E-02	1.492E-01	1.734E+00	1.741E+01	
6.00E-02	5.224E-04	8.290E-04	1.423E-03	2.778E-03	5.385E-03	1.849E-02	6.864E-02	3.473E-01	4.152E+00	4.178E+01	
1.00E-01	8.857E-04	1.396E-03	2.290E-03	4.511E-03	8.820E-03	2.947E-02	1.082E-01	5.692E-01	6.909E+00	6.963E+01	
1.50E-01	1.381E-03	2.159E-03	3.679E-03	6.871E-03	1.311E-02	5.065E-02	1.544E-01	8.465E-01	1.035E+01	1.044E+02	
2.50E-01	2.523E-03	3.885E-03	6.198E-03	1.144E-02	2.171E-02	8.012E-02	2.555E-01	1.405E+00	1.722E+01	1.741E+02	
6.00E-01	8.169E-03	1.193E-02	1.855E-02	2.963E-02	5.211E-02	1.872E-01	6.084E-01	3.356E+00	4.124E+01	4.176E+02	
8.00E-01	1.258E-02	1.781E-02	2.574E-02	4.027E-02	6.963E-02	2.477E-01	8.048E-01	4.453E+00	5.496E+01	5.569E+02	
1.00E+00	1.822E-02	2.457E-02	3.397E-02	5.124E-02	8.723E-02	2.815E-01	9.985E-01	5.534E+00	6.867E+01	6.963E+02	
1.04E+00	1.967E-02	2.678E-02	3.609E-02	5.355E-02	9.075E-02	2.938E-01	1.037E+00	5.748E+00	7.141E+01	7.242E+02	
1.14E+00	2.359E-02	3.159E-02	4.192E-02	5.954E-02	9.357E-02	3.335E-01	1.132E+00	6.281E+00	7.826E+01	7.938E+02	
1.25E+00	2.756E-02	3.627E-02	4.829E-02	6.650E-02	1.093E-01	3.705E-01	1.235E+00	6.863E+00	8.580E+01	8.703E+02	
1.50E+00	3.726E-02	4.747E-02	5.988E-02	8.381E-02	1.315E-01	4.467E-01	1.467E+00	8.178E+00	1.029E+02	1.044E+03	
2.00E+00	6.557E-02	7.758E-02	8.887E-02	1.249E-01	1.785E-01	5.842E-01	1.929E+00	1.079E+01	1.369E+02	1.391E+03	
4.00E+00	2.453E-01	2.651E-01	3.078E-01	3.937E-01	5.145E-01	1.223E+00	3.783E+00	2.116E+01	2.725E+02	2.783E+03	
6.00E+00	8.163E-01	8.576E-01	9.272E-01	1.054E+00	1.232E+00	2.200E+00	5.850E+00	3.143E+01	4.075E+02	4.173E+03	
1.00E+01	3.335E+00	3.483E+00	3.521E+00	3.770E+00	4.076E+00	5.520E+00	1.105E+01	5.235E+01	6.762E+02	6.951E+03	
1.50E+01	8.936E+00	9.038E+00	9.216E+00	9.577E+00	1.011E+01	1.216E+01	1.970E+01	7.934E+01	1.010E+03	1.043E+04	
2.50E+01	2.678E+01	2.696E+01	2.725E+01	2.784E+01	2.880E+01	3.220E+01	4.325E+01	1.363E+02	1.675E+03	1.737E+04	
1.50E+02	8.882E+02	8.894E+02	8.913E+02	8.950E+02	9.001E+02	9.219E+02	9.762E+02	1.351E+03	9.947E+03	1.040E+05	

Table 3. Values of E at selected values of T and ρ (abstracted from the complete EOS table²²).

DENSITY : TEMPERATURE (eV)		ENERGY (MJ/G)									
MG/M**3		2.50E-02	3.50E-02	5.00E-02	7.00E-02	1.00E-01	1.50E-01	2.50E-01	3.00E-01	4.00E-01	5.00E-01
1.00E-05	2.298E-03	2.459E-03	2.719E-03	3.094E-03	3.729E-03	5.009E-03	1.532E-02	3.460E-02	6.030E-02	6.478E-02	
1.00E-04	3.802E-04	2.457E-03	2.718E-03	3.094E-03	3.729E-03	4.983E-03	1.084E-02	2.037E-02	4.970E-02	6.263E-02	
1.00E-03	2.565E-05	2.461E-03	2.725E-03	3.102E-03	3.730E-03	4.972E-03	9.094E-03	1.392E-02	3.248E-02	5.199E-02	
2.50E-02	-8.885E-06	5.929E-04	2.604E-03	3.035E-03	3.743E-03	4.954E-03	8.135E-03	1.063E-02	1.886E-02	3.038E-02	
6.00E-02	-9.874E-06	5.168E-04	2.291E-03	2.947E-03	3.691E-03	4.786E-03	7.639E-03	1.001E-02	1.773E-02	2.838E-02	
1.00E-01	-1.015E-05	4.947E-04	1.847E-03	2.851E-03	3.614E-03	4.672E-03	7.409E-03	9.698E-03	1.705E-02	2.712E-02	
1.50E-01	-1.028E-05	4.839E-04	1.628E-03	2.740E-03	3.521E-03	4.573E-03	7.270E-03	9.506E-03	1.663E-02	2.610E-02	
2.50E-01	-1.039E-05	4.750E-04	1.450E-03	2.544E-03	3.357E-03	4.442E-03	7.176E-03	9.364E-03	1.617E-02	2.483E-02	
6.00E-01	-1.049E-05	4.674E-04	1.294E-03	2.053E-03	2.881E-03	4.247E-03	7.512E-03	9.702E-03	1.602E-02	2.292E-02	
8.00E-01	-1.050E-05	4.661E-04	1.160E-03	1.813E-03	2.671E-03	4.248E-03	7.928E-03	1.045E-02	1.633E-02	2.251E-02	
1.00E+00	-1.071E-05	4.165E-04	9.660E-04	1.684E-03	2.670E-03	4.501E-03	8.687E-03	1.097E-02	1.711E-02	2.273E-02	
1.04E+00	-1.631E-05	3.932E-04	9.365E-04	1.693E-03	2.693E-03	4.589E-03	8.906E-03	1.121E-02	1.736E-02	2.287E-02	
1.14E+00	-4.102E-05	3.477E-04	9.225E-04	1.752E-03	2.775E-03	4.841E-03	9.497E-03	1.184E-02	1.802E-02	2.330E-02	
1.25E+00	8.090E-05	3.442E-04	1.016E-03	1.840E-03	2.900E-03	5.122E-03	1.008E-02	1.248E-02	1.869E-02	2.374E-02	
1.50E+00	2.560E-04	5.885E-04	1.267E-03	2.043E-03	3.111E-03	5.570E-03	1.083E-02	1.330E-02	1.942E-02	2.449E-02	
2.00E+00	1.554E-03	2.023E-03	2.696E-03	3.344E-03	4.397E-03	7.282E-03	1.302E-02	1.555E-02	2.131E-02	2.630E-02	
4.00E+00	1.400E-02	1.449E-02	1.521E-02	1.616E-02	1.760E-02	1.998E-02	2.470E-02	2.705E-02	3.170E-02	3.638E-02	
6.00E+00	4.545E-02	4.569E-02	4.663E-02	4.761E-02	4.905E-02	5.143E-02	5.619E-02	5.856E-02	6.327E-02	6.794E-02	
1.00E+01	1.512E-01	1.516E-01	1.524E-01	1.534E-01	1.548E-01	1.572E-01	1.619E-01	1.643E-01	1.691E-01	1.739E-01	
1.50E+01	3.293E-01	3.298E-01	3.305E-01	3.316E-01	3.329E-01	3.353E-01	3.401E-01	3.425E-01	3.473E-01	3.521E-01	
2.50E+01	7.391E-01	7.397E-01	7.402E-01	7.413E-01	7.428E-01	7.451E-01	7.499E-01	7.523E-01	7.570E-01	7.618E-01	
1.50E+02	5.923E+00	5.924E+00	5.924E+00	5.926E+00	5.927E+00	5.929E+00	5.934E+00	5.936E+00	5.941E+00	5.946E+00	

DENSITY : TEMPERATURE (eV)		ENERGY (MJ/G)									
MG/M**3		7.00E-01	1.00E+00	1.50E+00	2.50E+00	4.00E+00	1.00E+01	2.50E+01	1.00E+02	1.00E+03	1.00E+04
1.00E-05	7.804E-02	9.552E-02	2.449E-01	3.911E-01	6.503E-01	2.352E+00	4.704E+00	2.153E+01	1.156E+02	1.056E+03	
1.00E-04	6.984E-02	8.375E-02	1.634E-01	3.617E-01	5.447E-01	1.734E+00	4.657E+00	2.113E+01	1.156E+02	1.056E+03	
1.00E-03	6.804E-02	7.511E-02	1.196E-01	2.849E-01	4.572E-01	1.333E+00	4.513E+00	1.931E+01	1.155E+02	1.056E+03	
2.50E-02	5.260E-02	6.918E-02	5.816E-02	1.835E-01	3.304E-01	9.611E-01	3.697E+00	1.413E+01	1.152E+02	1.056E+03	
6.00E-02	4.897E-02	6.455E-02	9.192E-02	1.616E-01	2.854E-01	8.669E-01	3.231E+00	1.287E+01	1.150E+02	1.056E+03	
1.00E-01	4.653E-02	6.147E-02	8.785E-02	1.484E-01	2.596E-01	8.138E-01	2.909E+00	1.226E+01	1.148E+02	1.056E+03	
1.50E-01	4.448E-02	5.891E-02	8.406E-02	1.383E-01	2.404E-01	7.516E-01	2.655E+00	1.195E+01	1.145E+02	1.059E+03	
2.50E-01	4.173E-02	5.556E-02	7.970E-02	1.268E-01	2.182E-01	7.037E-01	2.390E+00	1.176E+01	1.149E+02	1.059E+03	
6.00E-01	3.668E-02	4.966E-02	7.097E-02	1.096E-01	1.869E-01	6.196E-01	2.110E+00	1.151E+01	1.146E+02	1.059E+03	
8.00E-01	3.499E-02	4.777E-02	6.812E-02	1.051E-01	1.786E-01	5.921E-01	2.029E+00	1.135E+01	1.144E+02	1.058E+03	
1.00E+00	3.424E-02	4.702E-02	6.654E-02	1.018E-01	1.728E-01	5.719E-01	1.958E+00	1.117E+01	1.142E+02	1.058E+03	
1.04E+00	3.422E-02	4.702E-02	6.634E-02	1.012E-01	1.718E-01	5.701E-01	1.947E+00	1.113E+01	1.142E+02	1.058E+03	
1.14E+00	3.427E-02	4.716E-02	6.595E-02	9.980E-02	1.697E-01	5.683E-01	1.924E+00	1.104E+01	1.140E+02	1.058E+03	
1.25E+00	3.432E-02	4.732E-02	6.560E-02	9.859E-02	1.676E-01	5.680E-01	1.904E+00	1.094E+01	1.139E+02	1.058E+03	
1.50E+00	3.469E-02	4.729E-02	6.475E-02	9.746E-02	1.639E-01	5.641E-01	1.871E+00	1.073E+01	1.137E+02	1.058E+03	
2.00E+00	3.560E-02	4.721E-02	6.285E-02	1.000E-01	1.594E-01	5.373E-01	1.820E+00	1.040E+01	1.133E+02	1.058E+03	
4.00E+00	4.578E-02	5.688E-02	7.579E-02	1.139E-01	1.695E-01	4.878E-01	1.653E+00	9.666E+00	1.121E+02	1.057E+03	
6.00E+00	7.726E-02	9.168E-02	1.149E-01	1.531E-01	2.059E-01	4.899E-01	1.568E+00	9.264E+00	1.113E+02	1.057E+03	
1.00E+01	1.833E-01	1.971E-01	2.210E-01	2.686E-01	3.246E-01	5.728E-01	1.529E+00	8.820E+00	1.100E+02	1.055E+03	
1.50E+01	3.615E-01	3.754E-01	3.988E-01	4.470E-01	5.141E-01	7.467E-01	1.600E+00	8.509E+00	1.090E+02	1.055E+03	
2.50E+01	7.714E-01	7.858E-01	8.089E-01	8.550E-01	9.313E-01	1.168E+00	1.901E+00	8.288E+00	1.075E+02	1.054E+03	
1.50E+02	5.956E+00	5.969E+00	5.994E+00	6.041E+00	6.111E+00	6.390E+00	7.028E+00	1.112E+01	1.015E+02	1.049E+03	

Fig. 4. The pressure vs energy isotherms over the steam region . There are 25 equally spaced isotherms from 293.15 to 773.15 K.

Fig. 5. The pressure vs density isotherms corresponding to the temperatures in Fig. 4.

to describe the different ρ -T subregions by assigning different values

to the parameters in the expression. The form selected for this purpose is:

$$P = (1 + a\mu) \frac{G_1 + G_2 \epsilon + G_3 \epsilon^2 + G_4 \epsilon^3}{G_5 + G_6 \epsilon + G_7 \epsilon^2}, \quad (7)$$

and

$$G_i = \sum_{j=0}^3 A_{ij} \mu^j, \quad (8)$$

where P is in TPa, $\mu \equiv \rho/\rho_0 - 1$, ϵ (TPa) $\equiv E \rho_0$, and $\rho_0 = 0.998 \text{ Mg/m}^3$ (density at 298.15 K and standard pressure).

Coefficients A_{ij} for two analytical expressions are presented in Tables 4

and 5 for the compression and expansion (mainly steam) regions of the water EOS, respectively. During the determination of A_{ij} , certain A_{ij} 's are frozen at specified values. In Table 4, these frozen values are $A_{10} = 0$ to yield $P = 0$ at $\mu = \epsilon = 0$ as well as $A_{11} = 0.00219$ and $A_{50} = 1.0$ to correctly predict the bulk modulus at ρ_0 and $\epsilon = 0$. In Table 5

Table 4. Numerical values of constants A_{ij} in the analytical expression [Eq. (7) with $a = 1$] used to fit the EOS data of water.^a

i	A_{i0}	A_{i1}	A_{i2}	A_{i3}
1	0	2.190 E-3	1.544 E-1	2.160 E-1
2	-1.340 E-2	2.809 E+1	1.990 E+2	-1.114 E+1
3	1.493 E+3	3.016 E+4	7.418 E+3	3.184 E+3
4	9.166 E+4	7.468 E+5	7.742 E+4	4.722 E+3
5	1.000 E+0	6.723 E+1	-6.347 E+1	3.331 E+1
6	1.625 E+3	3.274 E+4	-2.819 E+3	-1.842 E+3
7	1.931 E+5	1.545 E+6	8.734 E+4	6.006 E+3

^aRange of applicability: $0.025 \leq T \leq 10 \text{ eV}$ and $0.998 \leq \rho \leq 40 \text{ Mg/m}^3$ and $P \leq 10^{-2} \text{ MPa}$. Note that P and ϵ in Eq. (7) are expressed in TPa.

Table 5. Numerical values of constants A_{ij} in the analytical expression [Eq. (7) with $a = 0$] used to fit the EOS data of water in the principally liquid-vapor equilibrium range.^a

i	A_{i0}	A_{i1}	A_{i2}	A_{i3}
1	1.0000000 E-7	-5.0893660 E-8	5.2838201 E-4	-3.9363072 E-2
2	-4.7273258 E-2	-9.0003238 E+0	-1.0696594 E+2	-9.5511199 E+3
3	-1.1611630 E+4	4.0721008 E+6	6.3079416 E+7	-1.1724779 E+9
4	7.2916356 E+9	3.6361684 E+10	-6.9116429 E+12	-8.4530829 E+13
5	1.0000000 E+0	-6.7953918 E+2	3.0285599 E+4	-1.4200691 E+7
6	-1.7224963 E+6	1.4444637 E+8	-2.4477486 E+10	2.3300340 E+11
7	4.2460639 E+11	1.1937554 E+13	4.0117326 E+14	-9.3774594 E+14

^a The range of applicability: $293.15 \leq T < 493.15$ K, $0.699 \leq \rho \leq 1.002$ Mg/m³, and $2.2 \times 10^{-3} \leq P \leq 3.0$ MPa. Note that P and ϵ in Eq. (7) are in TPa.

$A_{10} = 10^{-7}$ and $A_{50} = 1.0$ are fixed to produce the correct standard pressure at $\epsilon = 0$. The A_{ij} parameters given in Table 4 can be used for T between 0.025 and 10 eV and for ρ between ρ_0 and 40 Mg/m³ (corresponding to $P \leq 80$ TPa). Summing $|P(\text{analytical fit})/P(\text{data point}) - 1|$ over 549 data points at $P > 0.1$ MPa, the average error is 2.6%. The expression given in Table 5 is developed for the reactor-safeguarding analysis and therefore, is applicable only within a small density ($0.7 \rho_0 - 1.004 \rho_0$) and temperature (293.15 - 493.15 K) range corresponding to $P \leq 3$ MPa. Here, the average error over 368 data points is 7.5%. The above-mentioned ρ - T range includes the high-density

portion of the liquid-vapor region where P , at a fixed value of T , is flat and independent of density. The ρ - T range also includes the purely liquid portion where P increases abruptly. Strictly speaking, any analytical expression for P cannot "turn the corner" as abruptly as is observed in the real isotherms. Nevertheless, the expression given in Table 5 can approximately satisfy such a requirement.

PRINCIPAL HUGONIOT

Hugoniots of water with an initial state at room temperature and standard pressure have been measured by Walsh and Rice¹⁹ to 42 GPa and by Skidmore and Morris to about 110 GPa (see

Ref. 20). The experimental Hugoniot data are plotted in Fig. 6 for U_p vs U_s and ρ vs P . The corresponding Hugoniots derived from our present work are also shown. The

theoretical Hugoniot was obtained by solving for ρ which satisfies the Rankine-Hugoniot relation along each isotherm in the EOS table, i.e.,

$$H = E - E_{oh} - (P + P_{oh}) (V_{oh} - V)/2 = 0, \quad (9)$$

where the initial point (E_{oh} , P_{oh} , V_{oh}) corresponds to $E_{oh} = P_{oh} = 0$ and $V_{oh} = V_o = 1.002 \text{ m}^3/\text{Mg}$. The theoretical Hugoniot follows very closely Walsh and Rice's experimental points¹⁹ to about 13 GPa. Above this point (especially above 100 GPa), the experimental points have large uncertainties. Both the experimental and

theoretical points can be considered to agree within the experimental uncertainties. There is a lack of experimental data between 4 and 8 km/s in U_p or between 42 and 100 GPa in P . Hugoniot experiments to obtain these necessary data are being prepared by Nellis and Shaner.²³ Such experiments will provide data with which to test

Fig. 6. The principal Hugoniot of steam: (a) U_s vs U_p and (b) P vs ρ . Open circles are experimental data of Walsh and Rice¹⁹, solid circles are data of Skidmore and Morris²⁰, and the curve represents our calculations.

the adequacy of our present work. The available experimental data near 1.4 to 3 Mg/m³ lie well within the hole region that connects the EXPERIMENTAL and MASTER regions (see Fig. 1). The satisfactory agreement between the theoretical and experimental data, therefore, indicates that the procedure used to interpolate the EOS data in this most difficult hole region was apparently successful.

HUGONIOT OF STEAM: HIGH-PRESSURE PORTION

To our knowledge, experimental shock-wave data on steam are not available in the literature. This is unfortunate because steam undergoes an enormous volume change under shock compression. This in turn produces a large increase in internal energy and results in a high temperature. Accordingly, if accurate Hugoniot measurements are made, they would offer a valuable tool with which to probe the thermodynamic behavior of water in the chemically reacting region and possibly in the partially ionizing regime for higher-pressure experiments. Such experiments could be conducted with a two-stage gas gun. Preliminary feasibility studies on such experiments are in progress by Gust and Shaner.²⁴

To estimate the magnitudes of dynamic and thermodynamic variables

achieved along such Hugoniots, we have conducted Hugoniot calculations using our water EOS table. Three different initial states are considered. These points lie on the saturated-vapor line at $T_{oh} = 0.0339$, 0.0470, and 0.0522 eV (corresponding respectively to $P_{oh} = 0.2$, 0.5, and 2 MPa or, equivalently, to $V_{oh} = 885.4$, 374.7, and 99.54 m³/Mg). Plots of T vs ρ , P vs ρ , and U_s vs U_p along the Hugoniots are shown in Fig. 7. Compressions achieved in the initial portions ($\lesssim 0.1$ eV) of the Hugoniots in Fig. 7 (a,b) are mainly associated with the PΔV work and the excitation of the rotational degrees of freedom. The subsequent compressions to about 0.3 eV (Fig. 7c) result from the excitation of the internal vibrations of H₂O molecules that soak up the energy and reduce the temperature increase. At higher temperatures, the stored vibrational energy becomes so large that H₂O molecules break apart partially or completely, thereby forming mixtures of reacting species in a chemical equilibrium. Maximum compressions achieved in the present problems are eleven- to fourteen-fold greater than the initial densities. Temperatures at these points are about 0.5 eV and the values of Grüneisen γ are 0.15 to 0.2. To experimentally realize such compressions, it is necessary to generate a shock wave in

Fig. 7. Hugoniot of steam with the initial state lying on the saturated-vapor line at $P_{oh} = 0.2, 0.5$, and 2 MPa (or equivalently at $T_{oh} = 0.0339, 0.0470$, and 0.0522 eV) and represented by lines 1, 2, and 3, respectively: (a) T vs ρ , (b) P vs ρ , and (c) U_s vs U_p .

water with $U_s \approx 7.7$ to 8.4 km/s (corresponding to $U_p \approx 7.0$ to 7.8 km/s). The slopes of $(\partial P / \partial \rho)_H$ change sign beyond these compressions because the temperatures attained are high enough for the reacting species to begin to exhibit more ideal-gaslike

behavior. At sufficiently high T , the volume compressions approach the ideal-gas value of $1/4$ of the initial volumes.

The relative abundances of the chemical species along the Hugoniot trajectory, starting at $P_{oh} = 0.2$ MPa,

are shown in Fig. 8. At T of 0.3 to 0.4 eV, H_2O molecules dissociate into molecular hydrogen (H_2) and hydroxyl (OH) radical that is highly reactive and usually occurs as a transient intermediate. At even higher temperatures up to 1.0 eV, other dissociation products (H , O , O_2) appear significantly. However, above $T \geq 1.0$ eV, only hydrogen and oxygen atoms exist in any significant amount.

HUGONIOT OF STEAM: LOW-PRESSURE PORTION

Another region where shock Hugoniots exhibit interesting behavior

is located at temperatures below 0.1 eV, in the steam "dome" region where the liquid-vapor transition occurs. Within this region, accurate thermodynamic data are available from the steam table as well as from calorimetric and hydrostatic measurements. Comparison of dynamic and static data in the liquid-vapor transition region provides information on rate effects associated with the formation and evaporation of liquid droplets. Present shock-tube techniques are sufficiently advanced so that it may be possible to actually perform such experiments.

Fig. 8. Relative abundance of the chemical species that occur along the Hugoniot trajectory shown in Fig. 7 (initial point $P_{oh} = 0.2$ MPa).

Within the two-phase region, two energetic processes essentially control the trajectory of a Hugoniot. These are the PΔV work that is associated with the volume compression and the energy release during the condensation of steam. Depending on the location of the initial state, one process can predominate over the other to determine the subsequent trajectory. The PΔV-work process dominates if E is appreciably larger than E_{oh} and if E is approximately balanced by the PΔV term in Eq. (9). The energy-release process becomes important when the initial state (V_{oh} , T_{oh}) lies close to the saturated-vapor line. In this case, E_{oh} is relatively larger than the corresponding energy on the pure liquid side. The Hugoniot compression induces the partial condensation of steam, thereby releasing the energy stored in the vapor. Here, the Hugoniot condition [Eq. (9)] is essentially satisfied by a near cancellation of E_{oh} and E in Eq. (9); the contribution of the PΔV term affects the Hugoniot solution in only a minor way.

To rigorously study the situations described above, we employed the experimental data^{2,3} and examined the possible Hugoniot trajectories originating from three different volumes, $V_{oh} = 1000, 10$, and $3.333 \text{ m}^3/\text{Mg}$, and from four different temperatures,

$T_{oh} = 0.0511, 0.0373, 0.0321$, and 0.0253 eV (corresponding to 593.15, 433.15, 373.15, and 293.15 K).

Hugoniot plots of T vs ρ , P vs ρ , and U_s vs U_p are shown in Fig. 9 for $V_{oh} = 1000 \text{ m}^3/\text{Mg}$. The corresponding data for $V_{oh} = 10$ and $3.333 \text{ m}^3/\text{Mg}$ are shown in Figs. 10 and 11, respectively. The initial states in Fig. 9 [(V_{oh} , T_{oh}) = (1000, 0.0511) and (1000, 0.0373)] lie in the pure-vapor phase. The other initial states in Figs. 9-11 belong to the coexistence region. Several interesting features are revealed by these figures:

- (1) If the initial state of a Hugoniot lies within the two-phase region and if its density is not close to the saturation density of vapor, the Hugoniot locus enters immediately into the pure-liquid-water phase. (See curve 4 in Fig. 9b, curves 2 and 3 in Figs. 10b and 11b).
- (2) The Hugoniots belonging to those with the lowest initial density (namely, Hugoniots 3 and 4 in Fig. 9b) subsequently reenter the two-phase region at a higher pressure. Eventually, they exit the coexistence region through the vapor side. Those Hugoniots belonging to (1) with the intermediate initial density (namely, those in Fig. 10b) stay

Fig. 9. Low-temperature Hugoniots of steam starting at $V_{\text{oh}} = 1000 \text{ m}^3/\text{Mg}$ and at initial temperatures of 0.0522, 0.0373, 0.0321, and 0.0253 eV (Hugoniots 1, 2, 3, and 4, respectively): (a) T vs ρ , (b) P vs ρ , and (c) U_s vs U_p . The initial states of Hugoniots 1 and 2 lie outside the liquid-vapor transition region while the initial states of Hugoniots 3 and 4 lie inside the transition region. Note that some isotherms (dotted lines) are superimposed in (b) to indicate the Hugoniot trajectories. Portions of the Hugoniots in (b) indicated by dash-dotted lines are obtained by interpolation between the high-pressure points and the initial points.

within the liquid phase, eventually bending back toward lower densities at a pressure above the critical-point pressure and thereby completely bypassing the two-phase region. Those Hugoniots with the highest initial

density (Fig. 11b) behave "normally" as the pressure increases with increasing density.

The Hugoniot in (1) penetrates deeply into the pure-liquid phase if the initial temperature is low or if the initial density is high. In fact,

(a) Density — Mg/m^3

(b) Density — Mg/m^3

(c) U_p — km/s

Fig. 10. Low-temperature Hugoniots of steam starting at $V_{oh} = 10 \text{ m}^3/\text{Mg}$ and at initial temperatures of 0.0522, 0.0373, and 0.0321 eV (Hugoniots 1, 2, and 3, respectively): (a) T vs ρ , (b) P vs ρ , and (c) U_s vs U_p . All initial states lie within the two-phase region. Note that some isotherms (dotted lines) are superimposed in (b) to indicate the Hugoniot trajectories. Portions of the Hugoniots in (b) indicated by dash-dotted lines are obtained by interpolation between the high-pressure points and the initial points.

the Hugoniot states that immediately follow the initial states [$(T_{oh} = 0.025 \text{ eV}$ and $V_{oh} = 10 \text{ m}^3/\text{Mg})$ and $(T_{oh} = 0.025 \text{ eV}$ and $3.333 \text{ m}^3/\text{Mg})$] penetrate so deeply into the pure-liquid region that they exceed the boundary of the experimental data which ends at $\rho = 1.2 \text{ Mg/m}^3$ (i.e. 20%

compression of water at standard state at room temperature). Therefore, we were not able to present these Hugoniots in Figs. 10 and 11.

The peculiar behavior described in (1) is not difficult to understand. The vapor pressure can be extremely small, behaving like $\sim \exp(-\text{constant}/$

Fig. 11. Low-temperature Hugoniots of steam starting at $V_{oh} = 3.333 \text{ m}^3/\text{Mg}$ and at temperatures of 0.0522, 0.0373, and 0.0321 eV (Hugoniots 1, 2, and 3, respectively): (a) T vs ρ , (b) P vs ρ , and (c) U_s vs U_p . All initial states lie within the two-phase region. Note that some isotherms (dotted lines) are superimposed in (b) to indicate the Hugoniot trajectories. Portions of the Hugoniots in (b) indicated by dash-dotted lines are obtained by interpolation between the high-pressure points and the initial points.

T) at low T and is independent of ρ . Moreover, within the two-phase range, E also is nearly a constant along an isotherm if $V_{oh} \ll V_g$. Therefore, $E - E_{oh}$ is nearly constant but is much larger than the $P\Delta V$ term in the

Hugoniot relation within the two-phase region even for those states that immediately follow the initial states. The Hugoniot relation is essentially a balance between the $E - E_{oh}$ and $P\Delta V$ terms in Eq. 9 and

this is realized only when the steam condenses completely into liquid, where P can vary sensitively with ρ . Because the difference between the saturated volumes of liquid and vapor can become enormously large at low temperature, the initial condition $V_{oh} \ll V_g$ required to observe the situation described in (1) can be met in a large portion of the coexistence region. However, if the initial state is located near the gaseous end of the coexistence region, the energy release during the condensation process dominates over the $P\Delta V$ work process. In this case, the pressure increases with the density inside and immediately outside the steam dome and the Hugoniot trajectory never completely extends to the liquid phase.

Extrapolation to higher temperatures of all Hugoniots in Fig. 9 leads to an ultimate compression of about eight times the initial state. Under the ideal-gas assumption, which is reasonable in this case, the Grüneisen γ at such a compression is equal to $2/[(\rho/\rho_0)-1]$, or about $2/7$. This value lies close to the value of $\gamma = 1/3$ when only the translational and rotational degrees in H_2O molecules are fully excited. The lowest vibrational frequency of a water molecule is known to be 1954 cm^{-1} or 0.2 eV .²⁵ This is consistent with our result that the internal molecular vibrations are only slightly excited at 0.1 eV .

Figure 12 shows the P - T phase diagram of water and the four

Fig. 12. Hugoniot trajectories of P vs T starting at a point (101.3 kPa and 373.15 K) lying on the phase boundary. The initial volumes are $V_{oh} = 1000, 100, 10, \text{ and } 3.33 \text{ m}^3/\text{Mg}$ for Hugoniots 1, 2, 3, and 4, respectively.

Hugoniot trajectories originating from a common (P,T) point on the liquid-vapor phase line at $T = 373.15$ K ($P = 103.3$ kPa). The initial volumes of the Hugoniots are $V_{oh} = 1000, 100, 10,$ and $3.333 \text{ m}^3/\text{Mg}$. This figure clearly demonstrates that a wide range of thermodynamic states can be achieved by performing Hugoniot experiments that start from the phase line.

Figure 9c shows that U_s of the high-temperature Hugoniots (1 and 2) initially decreases with increasing U_p . It is difficult, at present, to understand the exact cause of the peculiar behavior. However, it is possible that the numerical procedure employed in the calculation might be the cause of this anomalous behavior.

BEHAVIOR OF THE TIGER DATA

As mentioned earlier, we did not use the TIGER-generated EOS data below 0.1 eV at low density because experimental data were available in this region. Within this region, the dissociation of H_2O molecules is not important and the thermodynamic behavior is essentially determined by the behavior of H_2O molecules. To locate the range of applicability of the TIGER data, we made the TIGER calculation and compared the computational results with the experimental data. This is shown in Fig. 13

for pressure and energy along seven different isotherms. We note that the TIGER-generated data deviate from the experimental data when the density exceeds approximately 0.01 Mg/m^3 . This implies that the TIGER data become unreliable as soon as the nonideal effect begins to contribute to the EOS data. There is a simple explanation for this. The BKW equation for pressure used in the TIGER code contains the contribution from the repulsive intermolecular forces but neglects the contribution from the attractive intermolecular forces. The repulsive interactions typically are stronger and of shorter range than are the attractive forces. Thus, at the relatively low temperature and density considered here, the attractive contribution actually dominates the repulsive forces if the density lies below 0.01 Mg/m^3 . However, at temperatures above 0.1 eV where the TIGER data are actually used, the influence of the attractive interactions is progressively diminished. Therefore, the range of applicability of the TIGER data can be extended to higher densities.

Figure 13a shows that the TIGER-generated data produce a grossly distorted steam dome at high temperature, overestimating the critical pressure by about 100 times and the critical temperature by about 2 times.

Fig. 13. Comparison of TIGER (broken line) and EXPERIMENTAL (solid lines) data below 0.1 eV: (a) P vs ρ isotherms and (b) E vs ρ isotherms. Note that the EOS table constructed for this report does not use the TIGER data shown here. Isotherms 1 through 7 begin at the following respective initial temperatures: 313.15, 413.15, 513.15, 593.15, 673.15, 853.15, and 1033.15 K.

This deviation again results from the repulsive interaction in the BKW equation. Thermodynamically, the repulsion in the BKW equation increases the free energy of the gaseous phase with respect to that of liquid water. The theoretical system adjusts by forming more condensed species than that actually present. Consequently, the liquid phase remains stable beyond the observed critical point and the two-phase region in the TIGER calculation is extended to higher temperature. On the other hand, the attractive interactions

tend to lower the free energy, therefore reducing the repulsive contribution to the free energy. Thus, to describe the low-temperature behavior of water, the BKW equation in the TIGER code should be modified to take proper account of the attractive contribution.

The higher-order thermodynamic quantities predicted from the TIGER calculation also warrant study.

Figure 14 shows the specific heat at constant volume (C_v) vs ρ at fixed values of T to 0.1 eV. Below $T = 0.07$ eV, the C_v isotherms exhibit a

Fig. 14. Isotherms of higher-order thermodynamic quantities of water as calculated from the TIGER code: (a) constant volume specific heat vs ρ and (b) $P(\partial V/\partial E)_P$ vs ρ . Isotherms 1 through 9 begin at the following respective initial temperatures: 0.025, 0.035, 0.05, 0.07, 0.15, 0.2, 0.4, 0.8, and 1.0 eV.

discontinuity at the two-phase boundary. At higher T , the C_v isotherms reach a maximum in density. This behavior occurs because water in this range dissociates into lower molecular weight species.

The quantity η shown in Fig. 14b is defined as

$$\eta = P(\partial V/\partial E)_P, \quad (10)$$

and measures the $P\Delta V$ work necessary to increase the energy of the system by a unit amount along an isobar. This quantity can be measured by isobaric experiments.²⁶ Quantity η becomes exactly equal to the usual

Grüneisen γ [$\equiv V(\partial P/\partial E)_V$] in the low-density limit. Both quantities closely follow each other over the ρ - T region studied in Fig. 14b.

Within the two-phase region, η can be shown to be exactly related to the temperature derivative of the vapor pressure. That is,

$$\eta^{-1} = \frac{d \ln P}{d \ln T} - 1. \quad (11)$$

Hence, η is strictly independent of ρ as can be seen in the isotherms (1-4) in Fig. 14b. This independence is not generally true for the Grüneisen γ . At fixed ρ , η decreases at

low T but increases at higher T . This is an expected behavior of a reacting gas as it undergoes a phase change. An extensive variation of η (and γ) over T and ρ in Fig. 14 shows that a simple ρ -dependent (but T -independent) approximation of γ used in a phenomenological EOS theory will become poor indeed. Likewise, Fig 14a shows that an often-used approximation of a constancy of C_v no longer applies in this range.

MIXTURE OF SiO_2 AND H_2O

To gain a qualitative insight into the thermodynamic behavior of a mixture containing H_2O , we chose a binary system containing 90 wt% SiO_2 and

10 wt% H_2O . This weight percentage is representative of some naturally occurring hydrous minerals. The TIGER code was used to calculate the EOS data. The pressure isotherms to 1.0 eV are shown in Fig. 15a. Figure 15b presents an expanded view of the high- ρ , high- T portion of Fig. 15a. For $T \geq 0.07$ eV, the calculation includes the following species: gaseous Si , Si_2 , Si_3 , O , O_2 , H , H_2 , SiO , SiO_2 , OH , SiOH , $\text{Si}(\text{OH})_2$, SiH , and SiH_4 , liquid Si , SiO_2 , and H_2O , plus solid Si , and SiO_2 . In addition to those chemical species considered earlier in this work and in Ref. 8, gaseous SiOH , $\text{Si}(\text{OH})_2$, SiH and SiH_4 are also included in this work

Fig. 15. The pressure isotherms of a mixed system composed of 90 wt% SiO_2 and 10 wt% H_2O . The high-temperature and high-density portion of the isotherms indicated by thick lines in (a) is expanded in (b). Various possible phase changes are shown by broken lines: gaseous SiO_2 -liquid SiO_2 ----, liquid SiO_2 -solid SiO_2 - · -, and gaseous H_2O -liquid H_2O - · · -.

because the possibility of exchange reactions between SiO_2 and H_2O molecules cannot yet be ruled out. These potential reactions, however, do not contribute appreciably to the EOS data shown in Fig. 15. The isotherms in Fig. 15 below $T = 0.07$ eV are those of the TIGER data of pure water. However, the density of water is shifted to account for the fact that the mixture system contains only 10 wt% H_2O . This is a reasonable procedure because only solid SiO_2 exists below $T < 0.07$ eV and its contribution to the pressure at low density ($\sim 2.2 \text{ Mg/m}^3$) is negligible. This approximation was verified at $T = 0.07$ eV; a very accurate 0.07 eV - isotherm was reproduced.

The isotherms in Fig. 15 display a complex behavior. This results from the large difference in the boiling points of SiO_2 and H_2O . The isotherms can be classified into four distinct regions plus three connecting transition regions. These are (1) gaseous SiO_2 + gaseous H_2O , (2) liquid SiO_2 + gaseous H_2O , (3) solid SiO_2 + gaseous H_2O , and (4) solid H_2O + liquid H_2O . Region (1) corresponds to the high-T, low- ρ portion in Fig. 15 while region (4) corresponds to the low-T, high- ρ portion. Within regions (1), (2), and (3) as well as within the transition regions, temperature is so high that water can

exist only as vapor. Because SiO_2 has been precipitated out in regions (2) and (3), the pressure of the system is essentially that of water vapor. The flat tieline observed in isotherms of the pure- SiO_2 system⁸ at the liquid-vapor and the liquid-solid transition regions does not appear in regions (2) and (3). Instead, the tieline is replaced by an isotherm with a small positive slope. The present system is basically a two-component system composed of SiO_2 and H_2O . For such a system, the Gibbs-phase rule states that the two independent thermodynamic variables, P and T , are required to specify the phase change. The same argument also holds true for the transition region of water that connects regions (3) and (4). In this case, however, the contribution of solid SiO_2 to the pressure is so low (except at the high- ρ end of the transition region) that the system acts as if it is undergoing a first-order phase change.

It is interesting that, in Fig. 15b, the liquid phase of water remains stable to at least 0.18 eV, considerably higher than the critical temperature (~ 0.1 eV) of pure water as predicted from the TIGER data. Apparently, the presence of condensed SiO_2 alters the boiling temperature under pressure. A more detailed analysis of this mixed system would

require the construction of a phase diagram of a binary mixture of SiO_2 and H_2O with variable concentrations at high pressure. Because the TIGER code was used, the numerical values

quoted above are overestimated. However, at present there is no reason to doubt the theoretical prediction that the liquid region of water will be greatly enhanced in the binary system.

Conclusion

The EOS table in this work was constructed from a combination of several theoretical models and experimental data and is applicable over a large region of density and temperature. We believe that the table represents a reasonable EOS behavior within this range.

There are two areas of improvement that should be considered further. The first area concerns the chemical-reaction region as calculated by the TIGER code. A substantial improvement could be made here by adopting a better theoretical model for gaseous mixtures. The model should include the contribution from the attractive intermolecular forces. This would allow the extension of the calculation to low temperature. The second area of improvement relates to the hole

region that connects the experimental data and the MASTER data (see Fig. 1). The missing data could be filled in with a theoretical code such as GRAY.^{27,28} The parameters in GRAY must be optimized to agree with the experimental data. For water, this is not a trivial task because H_2O has several internal degrees of freedom. An alternative approach would be to employ perturbation theories of fluids that have been developed recently.²⁹ These theories have been successfully applied to simple systems and can be extended to apply to water. Because water is one of the simpler polyatomic systems and because the intermolecular potential of water has been investigated extensively,^{30,31} such a first-principle approach will yield a clear understanding of high-pressure behavior of water.

Acknowledgments

I thank R. Grover, H. Graboske, J. Shaner, and D. Young for informative discussions during the course of this work. J. Walton and E. Lee

generated the input parameters necessary for the TIGER code. Technical assistance was provided by E. Collins, S. Link, and B. Hodge.

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