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The Calculation of Hugoniot Adiabatics and Viscosity of Shock Compressed Water

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The Hugoniot adiabatics and viscosity of shock compressed water have been calculated by applying the significant structure theory of water. To consider the effects of pressure and temperature, the sublimation energy has been expressed by the spherically averaged Stillinger-Rahman ST2 potential. Good agreements between theory and experiment are obtained in the whole extreme ranges of shock wave condition up to 100 GPa (1Mbar).

Introduction

Along with the development of techniques for shock wave experiments, physical properties of various materials are known for very high pressures and temperatures. Among them liquid water has been studied continuously in various fields of science because of its abnormalities and importances in biological systems. For shock-compressed water, equation of state, electrical conductivity, temperature, velocity of sound, and viscosity have been measured. High explosives have been used to compress water up to 100 GPa (1 Mbar).¹⁻³ A two-stage light-gas gun has been used to achieve pressures up to 230 GPa (2.3 Mbar).⁴ Soviet workers have used strong explosions (presumably nuclear explosions) to reach pressures of 100-3200 GPa (1-32 Mbar).^{5,7} The temperature accompanying the shock compression ranges from a few 100°C to several eV (1 eV=11600 K).

The pressure-volume^{2,8} and pressure-temperature^{9,10} data of shock compression experiments are available for such wide ranges of pressure and temperature for water. Walsh and Rice² measured the velocities associated with shock waves by applying the conservation relations.^{11,12} The conservation relations for the process are known as Rankine-Hugoniot relations which are

$$P - P_0 = \rho_0 (U_s - U_0) \quad (1)$$

$$V - V_0 (1 - (U_p - U_0)/(U_s - U_0)) \quad (2)$$

$$E - E_0 = \frac{1}{2} (P + P_0) (V_0 - V) \quad (3)$$

where P_0 , ρ_0 , E_0 , and u_0 are the initial pressure, density, specific internal energy, and velocity of material, respectively, $V_0 = 1/\rho_0$ is the initial specific volume, P , V , and E are, respectively, the final shock pressure, specific volume, and specific internal energy, u , is the velocity of shock wave, and u_p is the mass or particle velocity behind the shock front. All of the experimental data from shock compression are convertible into thermodynamic variables using these relations.

Dynamic equation of state data and electrical conductivity for liquid water were obtained in the shock pressure range 30-230 GPa (0.3-2.3 Mbar) using a two-stage light-gas gun by Mitchell and Nellis.⁸ With the assumptions of constant C , and constant $(\partial P/\partial T)_v$, Cowperthwaite and Shaw¹³ explained the temperature of shock compressed water measured near 200 K and 30 GPa by Kormer.⁹ The temperature of shock compressed water have been measured for more wide ranges of temperature and pressure (3300-5200 K and 50-80 GPa) by Lyzenga *et al.*,¹⁰ using a light-gas gun¹⁴ and six channel, time-resolved optical pyrometer.¹⁵ Fairly good agreement between the measured and calculated Hugoniot of water has been obtained by Ree¹⁶ for the temperature range of 1300-3000 K using the perturbation method.

Among various models of liquids, including liquid water as well, the significant structure theory^{17,18} is one of the most

widely applied, and good agreements with experimental data have been obtained using this theory. In this work, pressure dependences of volume, temperature and viscosity¹⁹ of shock compressed water have been calculated by applying the above theory.

Calculation

At extremely high pressure, the liquid water²⁰ is so contracted that closed structures are remained only. Then, the partition function for the solid-like part of liquid water, f_s , reduces to;

$$f_s = \frac{\exp(E_s/RT)}{[1 - \exp(-\theta/T)]^3} \left(1 + n_h \exp\left(\frac{-aE_s}{x-1} \cdot \frac{1}{RT}\right)\right) \times \prod_{i=1}^3 [1 - \exp(-h\nu_i/kT)]^{-1} \quad (4)$$

where E_s is the sublimation energy, θ is the Einstein characteristic temperature, n_h is the number of holes next to a molecule, a is a characteristic constant appearing in the liquid theory we adopted, $x = V/V_s$, and ν_i is the internal vibration frequency of the i th mode of a water molecule. V and V_s are the molar volume of the liquid and that of solid, respectively and the other notations have their usual statistical significance. Knowing the total partition function f as a function of temperature and volume,²¹ we can calculate the internal energy E and pressure P from following equations;

$$E = kT^2 \left(\frac{\partial \ln f}{\partial T}\right)_v \\ = \frac{V_s}{V} [-E_s + T \left(\frac{\partial E_s}{\partial T}\right)_v + \frac{6R\theta}{\exp(\theta/T) - 1} + \frac{n_h(\epsilon - T \left(\frac{\partial \epsilon}{\partial T}\right)_v)}{\exp(\epsilon/RT) + n_h}] \\ + 3 \left(1 - \frac{V_s}{V}\right) RT + \sum_{i=1}^3 \frac{Nh\nu_i}{\exp(h\nu_i/kT) - 1} \quad (5)$$

$$P = kT \left(\frac{\partial \ln f}{\partial V}\right)_T \\ = \frac{V_s}{V} \left[\left(\frac{\partial E_s}{\partial V}\right)_T - \frac{6R \left(\frac{\partial \theta}{\partial V}\right)_T}{\exp(\theta/T) - 1} + \frac{RT \left(\frac{\partial n_h}{\partial V}\right)_T - n_h \left(\frac{\partial \epsilon}{\partial V}\right)_T}{\exp(\epsilon/RT) + n_h} \right] \\ + \left(1 - \frac{V_s}{V}\right) \frac{RT}{V} + \frac{V_s}{V} RT \ln(f_s/f_l) \left(\frac{V}{V_s} \left(\frac{\partial V_s}{\partial V}\right)_T - 1\right) \quad (6)$$

where $\epsilon = aE_s/(x-1)$. In order to obtain the temperature and volume dependence of E_s , we used the ST2 potential function.²² The ST2 potential, $\phi_{ST2}(1,2)$,

$$\phi_{ST2}(1,2) = \phi_{LJ}(r) + S(r) \sum_{\alpha,\beta}^4 (-1)^{\alpha+\beta} / r_{\alpha\beta} \quad (7)$$

consists of the Lennard-Jones (LJ) potential,

$$\phi_{LJ}(r) = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right] \quad (8)$$

between two oxygens and the Coulomb interaction of (α, β) pairs of four force centers in each molecule. The latter is modulated by a factor of $S(r)$;

$$S(r) = 0, \text{ if } 0 < r < r_1 \\ = (r - r_1)^2 (3r_u - r_1 - 2r) / (r_u - r_1)^3, \text{ if } r_1 < r < r_u \quad (9)$$

$$= 1, \text{ if } r > r_u$$

where r_1 and r_u are 2.016 and 3.129 Å, respectively. In deriving the expression of E_s , we used the spherically averaged ST2 potential because high temperatures generated by shock-wave simplify the intermolecular potential by prompting water molecules to rotate more freely, and accordingly, many body forces and nonspherical interaction will become less important.¹⁶ The spherically averaged potential $\langle \phi_{ST2} \rangle$ was evaluated by Ree using Monte Carlo method.¹⁶ $\langle \phi_{ST2} \rangle$ is expressed as follows;

$$\langle \phi_{ST2} \rangle = \phi_{LJ} + \Delta \phi_{ST2} \quad (10)$$

where

$$\Delta \phi_{ST2} = -[S(r)]^2 [1.072 \times 10^9 / r^6 + 2.6 \times 10^9 / r^8 \\ - S(r) (5.335 \times 10^{11} / T) \exp(-2.451r)] / T$$

with ϕ_{LJ} and $S(r)$ defined by Eqs. (8) and (9), respectively. Using the spherically averaged ST2 potential $\langle \phi_{ST2} \rangle$, E_s can be obtained as follow²³

$$E_s = E_{LJ} + E_{NB} \quad (11)$$

where

$$E_{LJ} = 6R\epsilon \left(2.409 \left(\frac{N\sigma^3}{V_s}\right)^2 - 1.0109 \left(\frac{N\sigma^3}{V_s}\right)^4\right)$$

and

$$E_{NB} = \frac{R}{T} S(R) [1.072 \times 10^9 / r^6 + 2.6 \times 10^9 / r^8 \\ - S(r) (5.335 \times 10^{11} / T) \exp(-2.451r)]$$

When the pressure is very high, the effect of pressure on the solid-like volume must be considered,²⁴ i.e.,

$$V_s = V_{s0} (1 - \beta \Delta P) \quad (12)$$

where β is the compressibility of closed structured molecules and ΔP is the pressure difference between 1 atm and the applied pressure, P . The volume dependence of the Einstein characteristic temperature θ is evaluated using the Grüneisen parameter γ defined as²⁵;

$$\gamma = - \frac{d(\ln \theta)}{d(\ln V)} \quad (13)$$

Under the condition of shock compression, the value of γ of water ranges from 0.5 to 1.5. The effect of the volume dependence on θ is small compared to other terms in Eq. (6) so that γ has been treated as a constant by setting it equal to 1.0.

From Eqs. 3, 5, and 6, Hugoniot adiabatics can be obtained by the numerical iteration method. The initial state for experimental Hugoniot data corresponds to 1 atm and 295.8 K with $V_0 = 18.059 \text{ cm}^3$ and $E_0 = -41.478 \text{ kJ/mole}$. The value E_0 was determined from the enthalpy and heat capacity data of liquid water and its vapor.

From the calculated results of pressure, volume, and

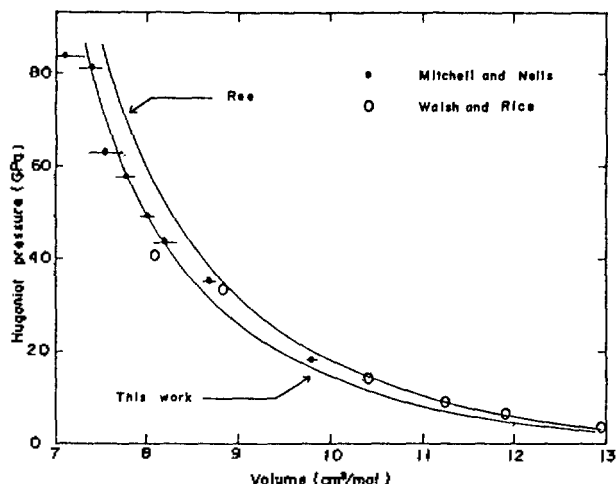


Figure 1. Theoretical and experimental Hugoniot of H_2O . Other theoretical results are taken from ref. 16. Experimental data are taken from the works of Mitchell and Nellis (Ref. 8) and of Walsh and Rice (Ref. 2).

temperature for shock compressed water, one can obtain the following viscosity equation,²⁴

$$\eta = [(\pi m k T)^{1/2} N l_r / 2 (V - V_s) \chi] \exp[-a' V_s Z \phi / 2 k T (V - V_s)] \quad (14)$$

where N is Avogadro's number, l_r is a free distance between nearest neighbor, χ is a transmission coefficient, a' is a proportionality constant, Z is the number of nearest molecules, and ϕ is the intermolecular potential which is given by Eq. 10. The free distance l_r is given as

$$l_r = 2[(\sqrt{2} V_s / N)^{1/3} - \sigma] \quad (15)$$

and the collision diameter δ is related to

$$\sigma \approx (b/4N)^{1/3} \approx (V_c/12N)^{1/3}$$

where b is van der Waals' constant and V_c is the critical molar volume which is 55.44 cm³/mole for water.

Results and Discussion

The calculated results of Hugoniot adiabatics are shown in Figure 1 and 2. Also plotted are the experimental data and other calculated results.¹⁶ As we can see from Figure 1 and 2, the theoretical Hugoniot pressure obtained by this work is predicted well in the pressure region greater than 40 GPa which corresponds to the volume of liquid water smaller than 8.2 cm³/mole. In the pressure region of small than 40 GPa, the theory underestimates the pressure and temperature by about 10%. Ree¹⁶ has evaluated the Hugoniot of water using perturbation theory. Above 3000 K, his result overestimates shock pressures and temperatures by 10% to 20%. More favorable agreements with experiment were obtained by this work than other works. Since Lyzenga *et al.*¹⁰ found that substantial variation of Grüneise parameter γ have only small effect on the calculated temperatures, we approximated the value of γ as a constant.

The results for the viscosity of shock compressed water are plotted with experimental values in Figure 3. In the previous study of Hamann *et al.*,²⁶ they failed to predict the viscosity

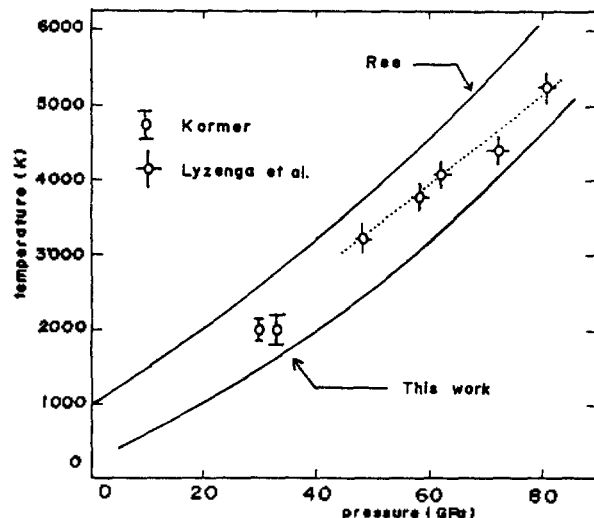


Figure 2. H_2O shock temperatures. Other theoretical results are taken from ref. 16. Experimental data are taken from the works of Kormer (Ref. 9) and of Lyzenga *et al.* (Ref. 10).

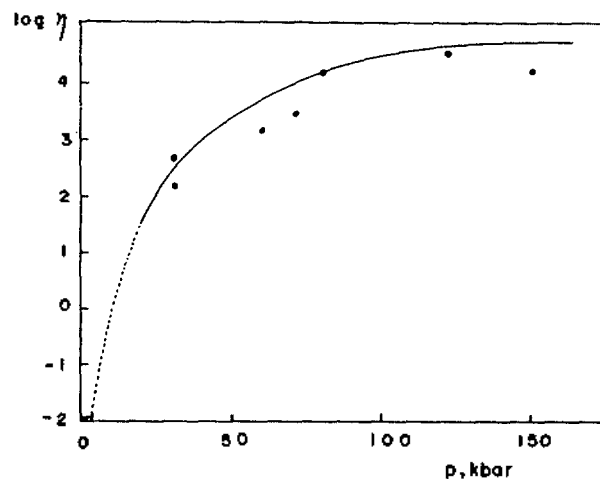


Figure 3. Viscosity of shock compressed H_2O . Experimental data are taken from the works of Mineev *et al.* (Ref. 27) and Al'tshuler *et al.* (Ref. 19).

of shock compressed water by applying Enskog's hard spherical model and molecular dynamics. Experimentally,²⁷ the viscosity increases by a factor of more than 10⁶, but their prediction was less than 10². They explained that the discrepancy between their theoretical results and experimental data was due to some experimental difficulties which might have affected the analysis of viscosity data. However, Al'tshuler *et al.*¹⁹ have reported higher pressure experiment and confirmed Mineev's experimental data²⁷ again. Above 70 kbar in pressure, the viscosity of shock compressed water remains nearly constant until at least 150 kbar. The agreement between our results and experimental data are good.

The above results lead us to conclude that, (i) the spherically averaged potential function was a good choice to express the intermolecular interaction of shock compressed water, (ii) the inclusion of pressure dependence on solid-like volume, V_s , was essential, and (iii) the neglect of open-structure term in the partition function was a good approximation under the shock wave experiment.

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A Facile Reduction of Acid Anhydrides with Borane in the Presence of Lithium Chloride in Tetrahydrofuran

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Carboxylic acid anhydrides are rapidly reduced with borane-lithium chloride (1:0.1) system to give corresponding alcohols (diols in the case of cyclic anhydride) quantitatively in tetrahydrofuran at room temperature. This reagent tolerates aromatic acid ester, nitro, and halide functional groups, however competitively reduces aliphatic ester and nitrile groups.

Introduction

The partial reduction of cyclic acid anhydrides to the corresponding lactones can be effected readily with various metal hydrides such as NaBH_4 , LiAlH_4 , DIBAL and $n\text{-BuLi}$, LiEt_2BH , and LiSi_3BH . However the complete reduction of acid anhydrides to the corresponding alcohols (diols in the case of cyclic anhydride) has been effected with LiAlH_4 almost exclusively. Rate and stoichiometry studies revealed that $\text{Li}(\text{CH}_3\text{O})_3\text{AlH}$ and AlH_3 could be even better reducing agents, however, these are very powerful reducing agents, and many functional groups are not expected to tolerate these strong hydrides.

Sometime ago, we have observed that the rate and stoichiometry of phthalic anhydride reduction with borane could be dramatically accelerated by the addition of 10 mol percent of lithium chloride.⁹ Since borane is a much milder and more selective reducing agent than the aluminohydrides, we have decided to explore more in detail the reduction of acid anhydrides with $\text{BH}_3\text{-LiCl}$ (1:0.1) system.

Results and Discussion

First, we examined the reduction of glutaric anhydride with borane and borane-dimethyl sulfide (BMS) at room temperature, and also in the presence of 10 mol percent of