

## Experimental and Predicted Detonation Parameters for Liquid-Phase H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O Mixtures

Ray Engelke, Stephen A. Sheffield, and Lloyd L. Davis

MS P952, Los Alamos National Laboratory, Los Alamos, New Mexico 87545

Received: March 13, 2000

We report the measured failure diameter and a detonation speed for the liquid explosive mixture 90.5/9.5 wt % H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O confined in thick seamless 304 stainless steel tubing and fired at ca. 30 °C. The detonation speed datum and knowledge of the diameter effect curves of other liquid explosives are used to estimate the infinite-medium (i.e., planewave) detonation speed of this material. Ambient condition sound speed measurements and the universal liquid Hugoniot form are used to obtain the unreacted Hugoniot of the 90.5/9.5 wt % H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O mixture. This Hugoniot and the Rayleigh line obtained from the estimated infinite-medium detonation wave speed are used to predict the von Neumann spike pressure of the material. Estimates of the fully reacted (i.e., products) Hugoniot, the Chapman–Jouguet (CJ) detonation pressure, and CJ detonation speed for other H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O mixtures are obtained using the CHEETAH equilibrium thermochemical code. Predictions of the infinite-medium detonation speed and the von Neumann spike and CJ pressures of 85.0/15.0, 90.0/10.0, 92.5/7.5, 95.0/5.0, 97.5/2.5, and 100.0/0.0 wt % H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O mixtures are also obtained. A general analytical expression is given for the primary shock Hugoniot of any H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O mixture at 22.6 °C.

### I. Introduction

Liquid H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O mixtures are interesting research explosives because of their chemical simplicity—i.e., they are composed of only hydrogen and oxygen atoms, while most explosives of practical interest contain at least three types of atoms from the set of carbon, hydrogen, nitrogen, and oxygen atoms. Recently, more interest has developed concerning the detailed chemical kinetic processes that occur in initiating and detonating condensed-phase energetic materials; these processes are the energy sources responsible for driving the high-pressure mechanical waves that are the primary reason for interest in such materials. Since, in condensed explosives, the physical states reached during detonation are extreme (e.g., pressures of 100 000–400 000 atm and temperatures of ca. 2000–3000 K) such studies are innately difficult. Consequently, it is prudent to begin studies of the chemistry occurring in such processes with materials that are as chemically simple as possible; H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O mixtures fall into this category. Because there is virtually a total absence of measured and predicted detonation properties of such mixtures in the published literature, the following paper has been written to increase the available information. The results presented below should be of value to researchers undertaking basic shock studies of such mixtures; e.g., see the recent work of Proud and Field on high-purity H<sub>2</sub>O<sub>2</sub>.<sup>1</sup> Additionally, the information may be of interest (in terms of safety considerations) to those involved in the commercial use of large quantities of high concentration hydrogen peroxide; e.g., the measured failure diameter value and the fact that such materials are detonable under some circumstances.

### II. Background

Extensive compilations of physical and chemical data on H<sub>2</sub>O<sub>2</sub> are available in refs 2 and 3; none of these data concerns detonation properties.

There have been studies of the detonation of H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O mixtures in the *vapor phase*; see, e.g., ref 4 and references

therein. In contrast to this, very little quantitative published work on the detonation properties of liquid-phase H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O mixtures exists. In the next paragraphs, we give a synopsis of such work known to us.

In ref 5, evidence is presented that liquid 86/14 wt % H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O mixture is detonable. A rough detonation speed of ca. 6000 m/s (measured using a streak camera) is inferred from the data for this mixture. The initial shot temperature and the tube diameter are unspecified, but the confining tube material is specified as steel. Much of the information in this reference pertains to H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O/ alcohol mixtures so it is not relevant to this paper.

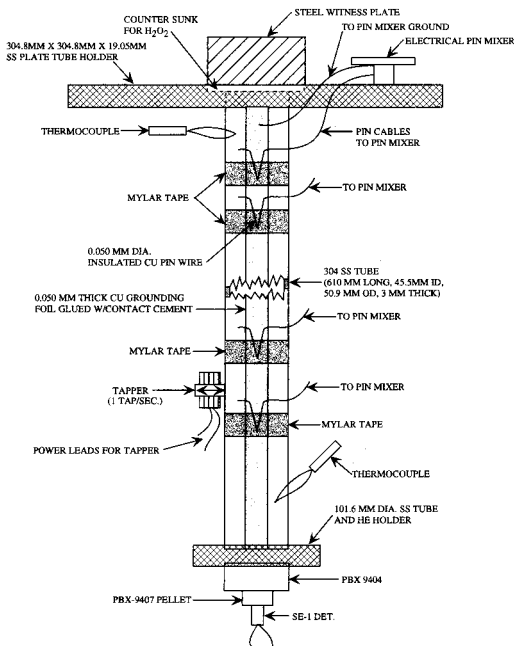
In ref 6, results on the critical diameters of liquid 86.0/14.0 and 90.7/9.3 wt (?) % H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O mixtures confined in 61STS Al tubes with i.d.'s of 26.7, 31.8, and 40.9 mm and at initial temperatures between 25 and 70 °C and are given. The authors conclude that, for the 86% material, the critical diameter is ca. 40.6 mm at 50 °C and 35.6 mm at 70 °C and, for the 90.7% material, the critical diameter decreased from 40.6 mm at 25 °C to 20.3 mm at 70 °C. Rough detonation speed measurements gave speeds in the range 5500–6000 m/s.

A computerized literature search was made at Los Alamos National Laboratory (LANL) covering work up to 4/1/97. No hits were made when the keyword string H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O and SOUND SPEED and HUGONIOT was searched on. Furthermore, no hits were found when H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O was paired with SOUND SPEED and with HUGONIOT. The only results published after 4/1/97 known to us and related to the work in this paper, are those in ref 1.

This sparseness of data available in the literature motivated publishing the results discussed below.

### III. Results

**(A) Failure Diameter and Detonation Velocity Measurements.** The experimental study was begun by firing a large i.d. rate stick made from a thick seamless 304 stainless steel (SS) tube. It is more normal to determine the failure diameter of a



**Figure 1.** Shot assembly schema for the H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O rate stick. The assembly was entirely heat fitted in order to avoid contact between H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O and welds. Only one of the tapper relays is shown.

material before proceeding to rate measurements. However, in this case, if the rate stick failed, work on the material would have been terminated, since it would not have been feasible to continue studies on a material with such a large failure diameter.

The geometry of the rate stick was as follows: i.d. 45.47 mm, o.d. 50.88 mm, and length 610 mm. A schema of the rate-stick assembly is shown in Figure 1. Note that all the joints in this assembly (and in the failure diameter assemblies to be described below) were heat fits; this was done to avoid passivation problems due to contact of the H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O mixture with welds.

The composition of the H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O mixture to be fired was determined by measuring the mass density of the material and then using the mass density/composition tables in ref 2. The measured density was  $1.390 \pm 0.002$  g/cm<sup>3</sup> at 24.3 °C; this corresponds to the composition 90.5/9.5 wt % H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O.

After extensive efforts at passivating the rate-stick tube to the presence of the H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O mixture, a small amount of chemical reaction was still observed when the 90.5/9.5 wt % H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O mixture was present. This was made evident by the production of gas bubbles at the fluid/metal interface. We will describe the passivation procedures in detail below.

It was observed that light tapping on the exterior of the tube caused the bubbles to disappear. When the tube was tapped, one could see, with appropriate lighting, the machining marks (i.e., a ca. #16 finish) on the bottom piece of the rate stick through the 610 mm of the H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O mixture. Consequently, as shown in Figure 1, two small electric relays ("tappers") were secured on the tube's exterior with hose clamps. They were adjusted so that the tube was tapped at two points at about 1 s intervals during the period when the shot was being fired. Use of this procedure eliminated any visible bubbles in the tube at shot time.

The entire rate-stick assembly was placed inside a Styrofoam box and equilibrated at  $29.0 \pm 0.5$  °C before the shot was fired. The shot was strongly boosted with an SE-1 detonator, a PBX-9407 pellet, and a piece of PBX-9404 50.80 mm diameter by 44.45 mm high. The motion of the detonation wave up the tube

was monitored by 11 2-mil copper-wire pins connected by a pin mixer to a set of raster oscilloscopes, as indicated in Figure 1.

The detonation speed obtained by a least-squares fit to the space-time data from the last 8 pins is  $6.144 \pm 0.003$  mm/ $\mu$ s; the error bar is one standard deviation (std dev).

Next, experiments were performed to determine the failure diameter of the material in the same type of tubing. A rack of four 304 SS tubes was assembled. The experimental diagnostic for propagation or failure of detonation was heavy 304-SS disks placed at the tops of the tubes. A detonation wave was not observed to propagate in any of the tubes; the largest one having an i.d. and o.d. of 31.93 and 38.10 mm, respectively. Tube lengths were 305 mm and boosting was via SE-1 detonators, a PBX-9407 pellet, and 25.4 mm diameter by 25.4 mm high pieces of PBX-9404. A second failure diameter experiment was constructed with larger diameter tubes. A detonation was not propagated in any of the tubes in this second experiment. The geometry parameters for the largest tube in this rack were i.d. 41.00 mm, o.d. 48.26 mm, and length 290 mm. This shot was fired at  $30.6 \pm 1.0$  °C. Boosting was the same as used on the first rack.

Using the rate-stick result and the fact that the 41.00 mm i.d. tube failed to support a detonation shows that the failure diameter for the 90.5/9.5 wt % H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O confined in 304 SS is  $43.2 \pm 2.2$  mm at  $29.8 \pm 0.8$  °C, where the error bars are ranges. Given that the thickness of the 304 SS tubes was 2.7 mm or greater, it is likely that the confinement thickness was effectively infinite; i.e., increasing the tube thickness further would not have changed the results.

Perhaps, it is worthwhile to describe the most extensive passivation procedure used on the 304 SS tube. The tubes were (1) submerged in trichloroethylene for 15 min at 77 °C, (2) submerged in 75 g/L NaOH for 2 h at 80 °C, (3) water rinsed, (4) submerged in 50 vol % HNO<sub>3</sub> for 1 h at ambient temperature, (5) rinsed at ambient temperature in deionized water, (6) dried in oil free air, and (7) filled with 90.5/9.5 wt % H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O and left at ambient temperature for 30 days. After this process there was still some residual chemical activity between the liquid mixture and the stainless steel; this necessitated the use of the tappers. If further work is done on this material, the tubes will be electropolished before step (7) described above.

**(B) Sound Speed as a Function of Composition.** The sound speeds in the H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O mixtures were measured using an apparatus assembled for the specific purpose of measuring sound speed in liquids. It consists of an ultrasonic thickness measuring system (Panametrics Ultrasonic Gauge model 5228) designed to measure the thickness of a material with a known sound speed; the sound speed is dialed in and the thickness is displayed. A 6 mm diameter pitch/catch ultrasonic transducer (Panasonic No. A112S) was used to produce and detect the sound waves. The transducer was attached to an electronic height gauge (Mititoyo Digimatic Indicator model ID-150E with a resolution of 1  $\mu$ m) so that an independent reading of the thickness could be obtained. A container for the liquid was made from Teflon and Vistal (a multicrystalline high-density sapphire). A rectangular cavity (15 mm by 36 mm) was cut into a 12 mm thick Teflon piece epoxied to the Vistal disk (57 mm diameter by 11 mm thick). The Vistal provides a large impedance mismatch with the liquid so the sound waves are efficiently reflected from the liquid/Vistal interface back into the transducer.

The cavity was filled about half full with the H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O mixture and the height gauge/transducer assembly was zeroed by allowing the transducer to bottom out on the Vistal. A sound

**TABLE 1: Sound Speeds ( $c_0$ ) and Mass Densities for  $\text{H}_2\text{O}_2/\text{H}_2\text{O}$  Mixtures**

wt % $\text{H}_2\text{O}_2$	set points <sup>a</sup> $c_0$ (mm/ $\mu\text{s}$ )	corrected $c_0$ (mm/ $\mu\text{s}$ )	temp ( $^\circ\text{C}$ ) <sup>b</sup>	fitted $c_0$ (mm/ $\mu\text{s}$ )	density ( $\text{g}/\text{cm}^3$ ) <sup>c</sup>
0.0	1.450–1.455	1.489	20.2	1.488	0.9971
10.0	1.465–1.470	1.503	22.4	1.501	1.0326
20.0	1.480–1.490	1.518	22.0	1.525	1.0698
30.0	1.500–1.510	1.559	23.0	1.556	1.1087
40.0	1.550–1.555	1.596	24.0	1.590	1.1495
50.0	1.590–1.595	1.624	24.1	1.624	1.1924
60.0	1.610–1.615	1.655	23.2	1.658	1.2375
70.0	1.650–1.660	1.692	21.6	1.691	1.2850
80.0 <sup>d</sup>	1.670–1.690	1.721	22.9	1.722	1.3350
90.0 <sup>d</sup>	1.680–1.700	1.751	22.4	1.750	1.3879
100.0				1.775	1.4436

<sup>a</sup> Range of set point values used on the Panametrics gauge at each composition. <sup>b</sup> Temperature at which the sound speed measurement was made. <sup>c</sup> Reference 2 mass density data corrected to 22.6  $^\circ\text{C}$ . <sup>d</sup> Sound speed measurements on this composition were more difficult because of increased reactivity of the mixture.

speed set point was determined by adjusting the sound speed on the Panametrics gauge until the displayed thickness agreed with the height gauge thickness reading at a height somewhere between 3 and 5 mm. The transducer was then moved up and down in the cavity at heights between 2 and 7 mm with readings of both the height gauge and Panasonic gauge taken at each position; usually, about 10 readings at each set point. For each mixture there were usually two to four sets of readings taken at different set points (differing by only a small amount, 0.01–0.02 mm/ $\mu\text{s}$ ). Because there are systematic errors in the measurement method, the height readings from both the gauges were the same in only one region of heights. These data were then subjected to a data reduction method to reduce this error.<sup>7</sup> The Panametrics gauge set point and the corrected sound speed data are given in Table 1, along with the temperatures at which the measurements were made.

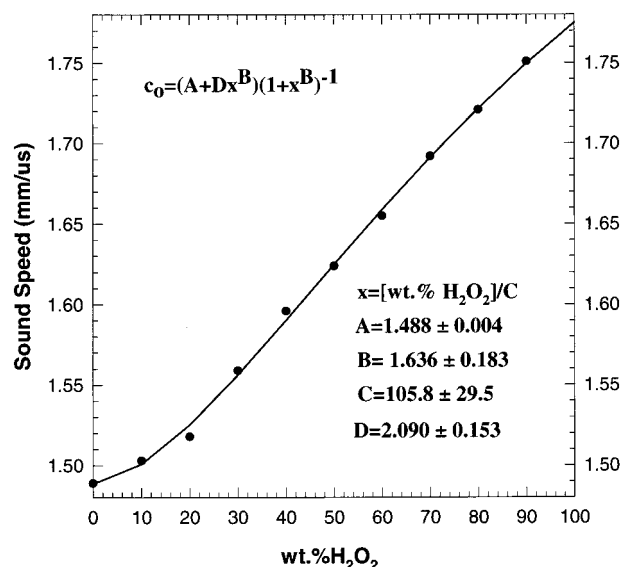
To represent the sound speed data at any composition, the corrected values of sound speed were least-squares fit to the analytic (sigmoid) form

$$c_0 = (A + Dx^B)/(1 + x^B) \quad (1)$$

where  $x = [\text{wt } \% \text{H}_2\text{O}]/C$  and  $A$ ,  $B$ ,  $C$ , and  $D$  are fitting parameters. The resultant parameter values are  $A = 1.488 \pm 0.004$  mm/ $\mu\text{s}$ ,  $B = 1.636 \pm 0.183$ ,  $C = 105.8 \pm 29.5$ , and  $D = 2.090 \pm 0.153$  mm/ $\mu\text{s}$ ; the error bars are std devs. The experimental data and the fitted curve are shown in Figure 2. The mean and std dev of the temperatures at which the sound speed data were taken was  $22.6 \pm 1.2$   $^\circ\text{C}$ . Therefore, we take the fit shown in Figure 2 to be representative of  $\text{H}_2\text{O}_2/\text{H}_2\text{O}$  mixtures at this temperature.

**(C) Mass Density as a Function of Composition.** To generate the primary shock Hugoniot (see below) for any  $\text{H}_2\text{O}_2/\text{H}_2\text{O}$  composition, we need the mass density ( $\equiv \rho_0$ ) of such compositions. We used the mass density vs composition tables from ref 2 for this purpose. Since the sound-speed data vs composition correspond to 22.6  $^\circ\text{C}$ , we wished to generate a mass density fitting form at this same temperature. We used the 25  $^\circ\text{C}$  data of ref 2 and corrected it to 22.6  $^\circ\text{C}$  by a linear density vs temperature correction (computed for each composition) obtained from the ref 2 density/composition tables for 0 and 25  $^\circ\text{C}$ .

The resultant mass densities (at 22.6  $^\circ\text{C}$ ) as a function of composition are given in Table 1. These densities were least-squares fitted to a quadratic of the form



**Figure 2.** Measured sound speeds for  $\text{H}_2\text{O}_2/\text{H}_2\text{O}$  mixtures as a function of the wt % of  $\text{H}_2\text{O}_2$ . A sigmoid-curve least-squares fit is also shown, along with the fit parameters and their error bars (std devs).

$$\rho_0 = A + B[\%] + C[\%]^2 \quad (2)$$

where  $[\%] = \text{wt } \% \text{H}_2\text{O}_2$ . The resultant fitting parameters are  $A = 0.9991 \pm 0.0001$ ,  $B = (3.369 \pm 0.003) \times 10^{-3}$ , and  $C = (1.058 \pm 0.003) \times 10^{-5}$ , where the units of  $A$ ,  $B$ , and  $C$  are  $\text{g}/\text{cm}^3$  and the error bars are std devs. The  $\rho_0$  data and the least-squares fit are shown on Figure 3.

#### **(D) Predicted Shock Hugoniots for $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ Mixtures.**

The principal shock Hugoniot of a material is the locus of all final thermodynamic states reachable by a single shock from a given initial state.<sup>8</sup> In ref 9a, it is shown that a “universal” form for the Hugoniots of liquids is

$$U_S = c_0[1.37 - 0.37 \exp(-2u_p/c_0)] + 1.62u_p \quad (3)$$

where  $U_S$  and  $u_p$  are the shock and resultant particle speeds in the fluid and  $c_0$  is the *ambient condition* sound speed in the fluid. We have shown that eq 3 accurately represents the actual  $U_S - u_p$  relationship found by direct measurement of  $U_S$  and  $u_p$  in a variety of liquids.<sup>9b</sup>

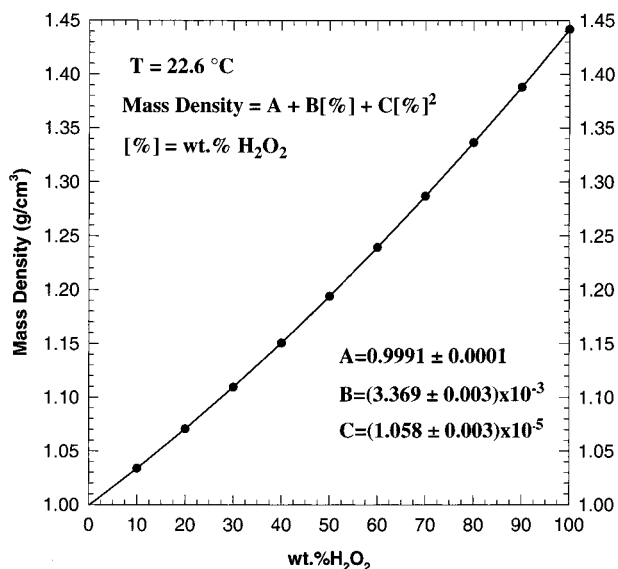
If the sound speed values in the  $\text{H}_2\text{O}_2/\text{H}_2\text{O}$  mixtures represented by eq 1 are used in eq 3, one obtains the  $U_S - u_p$  Hugoniot of any  $\text{H}_2\text{O}_2/\text{H}_2\text{O}$  composition at 22.6  $^\circ\text{C}$ .

The momentum conservation condition across a shock is

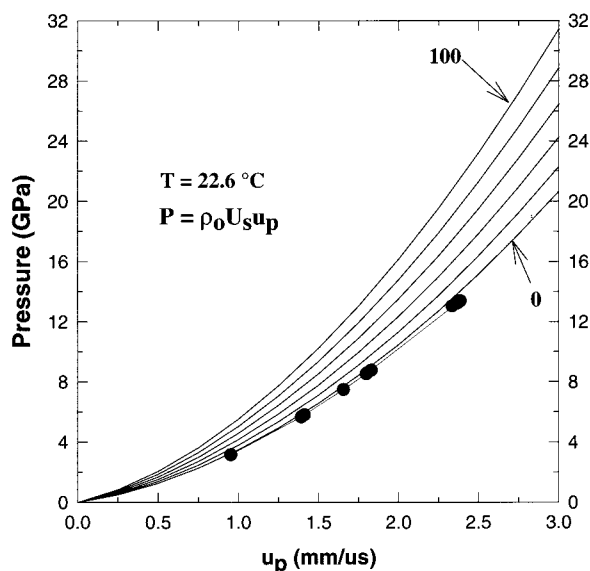
$$P = \rho_0 U_S u_p \quad (4)$$

Therefore, use of eqs 1–3 in eq 4 gives the pressure on the principal shock Hugoniot of  $\text{H}_2\text{O}_2/\text{H}_2\text{O}$  mixtures as a function of the particle speed produced by the shock for *any*  $\text{H}_2\text{O}_2/\text{H}_2\text{O}$  mixture with initial temperature 22.6  $^\circ\text{C}$ . A selection of six such predicted Hugoniots is shown on Figure 4. The black circles near the water Hugoniot on this figure are experimental data points for water;<sup>10</sup> the water data give an idea of the accuracy of the Hugoniot pressure predictions for the other compositions.

**(E) Cheetah Calculations of the Detonation State.** Estimates of the detonation parameters of the  $\text{H}_2\text{O}_2/\text{H}_2\text{O}$  mixtures were made using the Cheetah 2.0 code developed at Lawrence Livermore National Laboratory.<sup>11</sup> CHEETAH is an equilibrium thermochemical code used to estimate detonation parameters for explosives, as well as parameters for other conditions (such as a constant volume explosion). It solves the thermodynamic

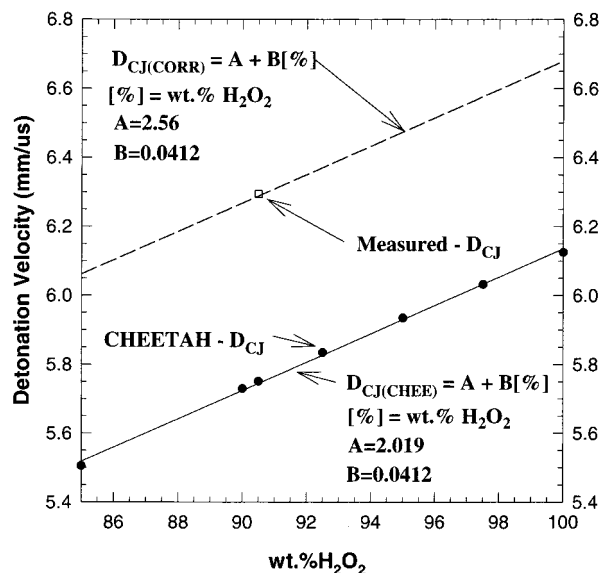


**Figure 3.** Mass density of H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O mixtures as a function of the wt % of H<sub>2</sub>O<sub>2</sub>. A quadratic fit of the data is also shown, along with the fit parameters and their error bars (std devs).



**Figure 4.** Predicted Hugoniot curves for H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O mixtures containing 0, 20, 40, 60, 80, and 100 wt % H<sub>2</sub>O<sub>2</sub> at 22.6 °C. Experimental points for pure H<sub>2</sub>O are also shown as filled circles with a line through them.

equations governing product species to find the equilibrium chemical composition. One inputs the chemical makeup of the molecule or mixture of interest, along with the heat(s) of formation and the various densities of the constituents. Then the desired condition is selected (in our case CJ detonation) and the code calculates the equilibrium condition (CJ values in our case) using a particular library of chemical data for the product species. Several product species libraries are available (i.e., BKWC, BKWS, JCZS, etc.); these contain the thermochemical data for the product species. Each library has a different set of data that mirrors the preferences of the workers that use it. Because very little equation of state data are available for H<sub>2</sub>O<sub>2</sub> and the products are mostly H<sub>2</sub>O (which is quite polar and therefore difficult to calculate), none of the libraries provide a good prediction of the measured detonation speed for the 90.5/9.5 wt % H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O mixture reported above. The best estimates were provided by the BKWS library developed at Sandia National Laboratory.<sup>12</sup> Calculations were made for 85.0/15.0, 90.0/10.0, 90.5/9.5, 92.5/7.5, 95.0/5.0, 97.5/2.5, and 100 wt %



**Figure 5.** The lower points are the calculated CJ detonation speeds for H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O mixtures at an initial temperature of 23 °C, as obtained with the CHEETAH code using the BKWS products library; a least-squares line has been fit through the points. The square point is the temperature and infinite diameter corrected experimental datum. The dashed line through the experimental point is a translation (holding the slope constant) of the lower line, providing an estimate of the expected detonation speed as a function of composition.

H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O mixtures; the CHEETAH detonation speeds are shown in Figure 5. The measured speed adjusted to the correct initial temperature and infinite diameter (see below) is also shown (6.294 mm/μs). The (corrected) experimental detonation speed is 9% higher than the CHEETAH calculation of 5.75 mm/μs, a rather large difference.

To more accurately estimate the detonation speed for the other compositions, we fit a line to the CHEETAH values and then translated it, maintaining the same slope, so that it went through the (corrected) experimental detonation speed of the 90.5/9.5 wt % H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O mixture. This translated line is shown as a dashed line in Figure 5; the linear fit parameters are also given. On the basis of this fit 100% H<sub>2</sub>O<sub>2</sub> would be expected to have a detonation speed of nearly 6.7 mm/μs and an 85.0/15.0 wt % H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O mixture a speed of about 6.0 mm/μs. This is in reasonable agreement with the information given in ref 6.

**(F) Predicted von-Neumann Spike and CJ Pressures.** Given eq 4 and an infinite-medium (i.e., planewave) detonation speed for an H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O composition, one can predict the von-Neumann spike detonation pressure for the material.

The measured detonation speed for the 90.5/9.5 wt % H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O composition discussed above is not the infinite-medium value and, also, it was obtained at 29.0 °C; therefore, corrections to it are necessary, if one is to make a prediction of the spike pressure. First, we attempt to correct for the diameter-effect deficit present in the measured value; our measured speed was obtained quite close to the failure diameter ( $\equiv D_f$ ), the rate-stick tube i.d. being 45.5 mm and  $D_f$  being  $43.2 \pm 2.2$  mm.

We make a correction to this detonation speed by noting that for liquid nitromethane fired in brass confinement, the measured detonation speed deficit between the planewave value and failure is 1.8%.<sup>13</sup> The analogous number for liquid TNT fired in Al confinement is 2.3%.<sup>14</sup> We, therefore, suggest that a correction obtained by increasing the measured detonation speed for the 90.5/9.5 wt % H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O by 2% will produce a speed close to the planewave value. The planewave speed obtained in this way is 6.267 mm/μs. A temperature correction of this value to 22.6

**TABLE 2: Detonation Parameters for H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O Mixtures**

wt % H <sub>2</sub> O <sub>2</sub>	calc $D_{CJ}$ (mm/ $\mu$ s) <sup>a</sup>	corrected $D_{CJ}$ (mm/ $\mu$ s) <sup>b</sup>	est spike $P$ (kbar)	calc $P_{CJ}$ (kbar) <sup>a</sup>	corrected $P_{CJ}$ (kbar) <sup>c</sup>
85.0	5.50	6.06	190	79	95
90.0	5.73	6.27	210	89	106
90.5	5.75	6.29	212	90	107
92.5	5.83	6.37	220	94	112
95.0	5.93	6.48	232	99	118
97.5	6.03	6.58	244	104	124
100.0	6.12	6.68	255	109	130

<sup>a</sup> Calculated using the equilibrium thermodynamic CHEETAH code. <sup>b</sup> Corrected using the measured detonation speed as explained in text. <sup>c</sup> Corrected using the constant gamma relationship as explained in text.

°C is still necessary. We made a rough temperature correction by using the measured liquid nitromethane value<sup>15</sup> of 4.23 (m/s)/°C. This yields a temperature correction of 27 m/s when the temperature is reduced from 29.0 to 22.6 °C. Therefore, the infinite medium detonation speed of the 90.5/9.5 wt % H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O mixture at 22.6 °C is estimated to be 6.294 mm/ $\mu$ s.

From eq 2, the mass density of the 90.5/9.5 wt % H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O mixture at 22.6 °C is 1.391 g/cm<sup>3</sup>. Iteratively solving eq 3 to find a value of  $u_p$  consistent with the planewave detonation speed of 6.294 mm/ $\mu$ s, one finds that  $u_p = 2.430$  mm/ $\mu$ s. The von-Neumann spike pressure under these conditions can now be found from eq 4 and is  $P_{\text{spike}} = 212$  kbar.

Since the CHEETAH calculations underestimate the detonation speed by about 9%, the CJ detonation pressures are also underestimated. However, the magnitude of the underestimate is more difficult to determine because no  $P_{CJ}$  has been measured; i.e., there is no measured value to use to make an adjustment as there was for detonation speed. We used a relationship between  $P_{CJ}$  and  $D_{CJ}$ , which applies for a constant Gruneisen  $\gamma^8$  equation of state, i.e.,

$$P_{CJ} = \rho_0 \frac{D_{CJ}^2}{\gamma + 1} \quad (5)$$

to make a correction to the calculated  $P_{CJ}$  values. If  $\gamma$  is assumed to be constant, the CHEETAH values can be adjusted using the following expression

$$P_{CJ}^{\text{CORR}} = P_{CJ}^{\text{CHEE}} \left\{ \frac{D_{CJ}^{\text{CORR}}}{D_{CJ}^{\text{CHEE}}} \right\}^2 \quad (6)$$

where CORR and CHEE indicate corrected and CHEETAH values, respectively. The corrected  $P_{CJ}$  values obtained in this way are given in Table 2. The correction raises the  $P_{CJ}$  values ca. 20% above the CHEETAH code values.

#### IV. Discussion and Conclusions

Note that the von-Neumann spike pressures estimated for the H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O mixtures are about twice the CJ pressures ( $P_{\text{spike}}/P_{CJ} \approx 2$ ). This ratio is typically 1.3–1.5 for many condensed phase explosives.<sup>16,17</sup> For example, the spike pressure in nitromethane is about 200 kbar and the CJ pressure about 130 kbar, giving a ratio of 1.54. It can be shown that for a constant  $\gamma$  explosive, the spike pressure is exactly twice the CJ pressure for any value of  $\gamma$ . The experimentally based estimates in this paper indicate that a pressure ratio of about 2 may be correct for H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O mixtures; this suggests such mixtures may have reaction-zone structures distinct from that of most other condensed phase explosives.

We have used a measured detonation speed for a 90.5/9.5 wt % H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O mixture and measured sound speeds for a number of H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O mixtures as a basis for estimating detonation properties. Using the universal liquid Hugoniot and equilibrium thermochemical results from the CHEETAH code, detonation property estimates are made for 85.0/15.0 to 100.0/0.0 wt % H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O mixtures. Neat H<sub>2</sub>O<sub>2</sub> is predicted to have a detonation speed of 6.68 km/s and a CJ pressure of 130 kbar.

The measured failure diameter of the 90.5/9.5 wt % H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O mixture confined in thick 304SS tubes and fired at 29.8 ± 0.8 °C is 43.2 ± 2.2 mm, where the error bars is a range. The measured detonation speed of this mixture fired in a thick-walled 304 SS 45.47 mm i.d. tube at 29.0 ± 0.5 °C is 6.144 ± 0.003 mm/ $\mu$ s. This value corrected to infinite medium and to an initial temperature of 22.6 °C is 6.294 mm/ $\mu$ s.

**Acknowledgment.** We thank Charles Mader of Los Alamos National Laboratory (LANL) for BKW calculations that showed stainless steel tubes could be used to confine the liquid 90.5/9.5 wt % H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O mixture for the detonation velocity and critical diameter experiments. Richard Martinez of LANL is thanked for drawing Figure 1. Melvin Baer and Michael Hobbs of Sandia National Laboratories provided valuable discussions regarding the use of the CHEETAH code and the various libraries available; they also made preliminary calculations of the CJ state of H<sub>2</sub>O<sub>2</sub>.

#### References and Notes

- (1) Proud, W. G.; Field, J. E. In *Shock Compression of Condensed Matter—1999*; Furnish, M. D., Chhabildas, L. C., Hixson, R. S., Eds.; AIP Conference Proceedings 505; American Institute of Physics: New York, 2000; p 937.
- (2) *Hydrogen Peroxide Physical Properties Data Book, Bulletin No. 67*; Dierdorff, L. H., Jr., Ed.; Becco Chemical Division, FMC Corp.: New York, 1954.
- (3) Schumb, W. C.; Satterfield, C. N.; Wentworth, R. L. *Hydrogen Peroxide*; Rheinhold Publishing Corp.: New York, 1955.
- (4) Campbell, G. A.; Rutledge, P. V. *J. Chem. E. Symp. Ser.* **1972**, *37*, No. 33.
- (5) Haeuselner, E. *Explosivstoffe* **1953**, *NR 6/7*, 64.
- (6) Bureau of Mines Staff, *U. S. Bureau Mines Inform. Circ.* No. 8387 **1968**.
- (7) Ferm, E. N. Private communication, Los Alamos National Laboratory, 1999.
- (8) Engelke, R.; Sheffield, S. A. *High-Pressure Shock Compression of Solid III*; Davison, L., Sahinpoor, M., Eds.; Springer-Verlag: New York, 1998; Chapter 7.
- (9) (a) Woolfolk, R. W.; Cowperthwaite, M.; Shaw, R. *Thermochim. Acta* **1973**, *5*, 409. (b) Sheffield, S. A.; Alcon, R. R., In *Shock Compression of Condensed Matter—1989*; Schmidt, S. C., Johnson, J. N., Davison, L. W., Eds.; North-Holland, Elsevier Science Publishers B. V.: Amsterdam, The Netherlands, 1990; p 683.
- (10) Marsh, S. P., Ed. *LASL Shock Hugoniot Data*; University of California Press: Berkeley, 1980; pp 573–574.
- (11) Fried, L. E.; Howard, W. M.; Souers, P. C. *Cheetah 2.0 User's Manual*; UCRL-MA-117541 Rev. 5; Lawrence Livermore National Laboratory: Livermore, CA, 1998.
- (12) Hobbs, M. L.; Baer, M. R. *Proceedings of the Tenth International Detonation Symposium*; Office of Naval Research Report ONR 33395-12; ONR: Washington, DC, 1995; p 409.
- (13) Campbell, A. W.; Engelke, R. *Proceeding of the Sixth Symposium on Detonation (Intl.)*; Edwards, D. J., Ed.; ONR: Washington, DC, 1976; p 642.
- (14) Igel, E. A.; Seely, L. B. *Second ONR Symposium on Detonation*; Office of Naval Research: Washington, DC, 1955; p 320.
- (15) Campbell, A. W.; Malin, M. E.; Holland, T. E. *Second ONR Symposium on Detonation*; Office of Naval Research: Washington, DC, 1955; p 336.
- (16) Sheffield, S. A.; Bloomquist, D. D.; Tarver, C. M. *J. Chem. Phys.* **1984**, *80*, 3831 and references therein.
- (17) Al'tshuler, L. V.; Doronin, G. S.; Zhuchenko, V. S. *Combustion, Explosion, Shock Waves* **1989**, *25* (2), 209.