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THE HYDROSTATIC COMPRESSION OF EXPLOSIVES AND DETONATION PRODUCTS TO 10 GPa (100 kbars) AND THEIR CALCULATED SHOCK COMPRESSION: RESULTS FOR PETN, TATB, CO_2 AND H_2O

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Tne isothermal linear and volume compressions of PETN, TATB, CO_2, and H_2O are determined from x-ray diffraction patterns taken at hydrostatic pressures up to 10 GPa. From the compressions the Hugoniots of these materials are calculated assuming that the heat capacity at constant volume and the ratio of the Grüneisen constant to the specific volume both remain constant over the 10 GPa pressure range studied here. The Hugoniots in shock-particle velocity coordinates centered at 0 GPa, 293°K, are

PETN

$U_s = 2.320 + 2.61\ U_p - 0.38\ U_p^2$, $U_p < .8$ km/s, $\rho_o = 1.774$ g/cm^3

$U_s = 2.811 + 1.73\ U_p$, $U_p > .8$ km/s, $\rho_o = 1.774$ g/cm^3

TATB

$U_s = 1.43 + 10.02\ U_p - 10.89\ U_p^2$, $U_p < 0.3$ km/s, $\rho_o = 1.937$ g/cm^3

$U_s = 2.93 + 1.60\ U_p$, $U_p > 0.3$ km/s, $\rho_o = 1.937$ g/cm^3

CO_2 (solid)

$U_s = 1.740 + 1.65\ U_p$, $U_p > 0.7$ km/s, $\rho_o = 1.428$ g/cm^3

H_2O (ice VII)

$U_s = 2.872 + 1.69\ U_p$, $U_p > 0.5$ km/s, $\rho_o = 1.395$ g/cm^3

INTRODUCTION

Many aspects of dynamic compression of explosives have been investigated to better understand the processes of initiation and detonation propagation. Usually these studies involve a careful definition of the explosive's initial state (i.e. porosity, inert content, grain size) and then a determination of its dynamic properties. If the dynamic properties of the explosive's pure components could be defined, then the investigator and the fabricator both may be able to predict the properties of the aggregate. One such property is the shock wave compression on Hugoniots centered at theoretical density. Here we describe an experimental method to determine the isothermal compression of explosives and their detonation products. From these data we can then calculate the shock compression with a reasonable assumption about the equation of state.

EXPERIMENTAL

Primarily, the technique provides x-ray powder diffraction patterns of explosives at well-defined pressures. The design of the apparatus was conceived by Jamieson and Lawson (1) and

was described in detail by Jamieson (2). Recently, the design was modified by Halleck and Olinger (3) to study low Z materials such as explosives, to produce diffraction patterns of increased resolution, and to include a hydrostatic medium that does not support shear permitting the study of weakly bonded materials such as explosives.

The principles of the technique are simple. The explosive to be studied and a pressure calibrating material are placed in an annulus that is relatively transparent to x-rays. This annulus is pressed to high uniaxial stress between two tungsten-carbide flats, called Bridgman anvils, and the diffraction patterns are taken of the trapped materials by directing into them an x-ray beam perpendicular to the axis of stress and recording the pattern on a strip of film surrounding the sample and anvils.

In detail, we use two G. E. grade 999 tungsten carbide Bridgman anvils ground from right circular cylinders 12.3 mm in dia and 13.1 mm high. One end of each anvil has a 4.8 mm dia flat bearing surface in its center and a 30° taper ground from the bearing surface to the sides of the cylinder, thus forming a truncated cone. On one bearing surface an annulus of beryllium foil 0.3 mm thick, 3.8 mm dia, with a 0.3 mm dia hole in its center is mounted with a fast-setting epoxy. The center of the annulus is aligned with the center of the bearing surface. After drying, the excess epoxy is removed from the hole and the sides of the annulus. Into the hole is worked a mixture of fine powdered explosive and pressure indicator, either NaF or NaCl. The powders are not packed, but loosely inserted.

The anvil with loaded beryllium annulus is seated on a pedestal that is in turn mounted into the base of a high pressure frame. The high pressure frame is constructed from two thick steel plates held together by steel tie rods and held parallel by precision machined steel tubes surrounding the rods. On the base of the pedestal is mounted the x-ray camera. The camera is cut from a solid brass cylinder 114.6 mm in diameter whose sides and core along the axis have been removed. The top and bottom of the camera on which the film rests are supported by brass pillars through which are mounted the x-ray collimator and exit beam catcher collars. The collimator and beam catcher, when placed in the collars, are directed toward each other along the camera diameter. The x-ray film is mounted over the exit beam collar and is held to the sides of the camera by a light tight steel band under spring tension. An Ni foil is mounted to the camera inside the film radius that serves as a light shield and a x-ray filter for white and CuKβ x-radiation.

The high pressure frame with pedestal, camera and anvil assembly is mounted before an x-ray port of an x-ray generator for x-ray diffraction work. We use the Norelco generator with fine focus Cu x-ray tubes running at 35 kV and 15 ma. Exposure times are 6 to 8 hrs for zero pressure esposures and 12 to 16 hrs for high pressure exposures. The first several patterns of an experiment are taken at zero pressure. These patterns are compared with others taken of the materials using regular powder cameras or are compared with published diffraction patterns. From this comparison correction factors are calculated for uncentered samples and for x-ray cameras that have circumferences different than the normal 360 mm.

Having carefully marked the position of the anvil on the pedestal, the anvil with annulus and sample is removed and a drop of 4:1 mixture of methanol-ethanol is placed on the annulus. This mixture has been found to remain hydrostatic to pressures slightly higher than 10 GPa [100 kbars] (4). The alcohol is worked into the sample hole with a fine needle; this removes air and, if not done carefully, the sample. As the alcohol drys, more drops are added. The anvil is reset into its former position on the pedestal. A commercial hydraulic ram is mounted through the top plate of the high pressure frame. Attached to the end of its piston is another pedestal on which is mounted the other anvil. Alignment and parallelism of the two anvils are the foremost considerations when the high pressure frame is designed. With the alcohol drop on the annulus replenished, the piston is lowered by pumping oil into the ram and the anvils are pressed together against the annulus. The usual starting oil pressure for 10 to 25 ton rams is 1000 psi. The oil pressure ranges normally extend to 6000 to 7000 psi for the 10 ton rams and 4000 to 4500 psi for the 25 ton rams. At the maximum pressures of these ranges the pressure in the sample cavity of the annulus is about 10 GPa, the maximum hydrostatic pressure of the alcohol mixture. Also at these maximum ram pressures, the Be annulus extrudes to the extent where good quality diffraction patterns are difficult to obtain. Once the annulus is under stress, the collimator and beam catcher are adjusted to the level of the annulus

by shimming the camera on its pedestal seat.

The x-ray films show diffraction lines of the explosive, the pressure indicator at a given ram pressure, and the diffraction lines from the beryllium annulus. The latter forms bands on the film because of the annulus' width. The bands obscure diffraction lines from d-spacings between 2.04 to 1.90 Å and 1.79 to 1.67 Å. An exposure is taken for 12 to 16 hours at a constant ram pressure, then the film is developed and the ram pressure is increased several hundred psi for the next exposure. The procedure followed has been to only increase pressure between exposures. The reason for not decreasing pressure is that there is a chance the relieved stress will induce radial cracks in the annulus.

The pressure in the sample region is deduced from the volume of the pressure indicator. The indicator is a substance that exhibits a simple diffraction pattern and whose compression is well known. The two indicators extensively used are NaCl and NaF. Fritz et al. (5) and Weaver et al. (6) have published isothermal compression equations and tables for NaCl which differ by 2 1/2% in pressure in the vicinity of 10 GPa. The P-V relation for NaCl given by Weaver et al. (6) was calculated from thermodynamic parameters derived near ambient conditions. The values given by Fritz et al. (5) were calculated from P,V values along the Hugoniot. Despite their differences, these two studies are the standards for high pressure, x-ray diffraction work. The other indicator, NaF, though less compressible than NaCl, is the most extensively used by us. The P,V correlation for NaF is derived from two sources. Olinger and Jamieson (7) and Spiegelan and Jamieson (8) collected extensive data on the simultaneous compression of NaF and NaCl using high pressure, x-ray diffraction techniques like that described above. The Fritz et al. (5) NaCl pressure scale was used to correlate the NaF volume with pressure. The other ambient temperature, P,V values for NaF were calculated from Hugoniot data by Carter (9). In that study, the P,V values listed do not exactly correspond to values subsequently calculated by Carter and Fritz (10). Apparently an error occurred in calculations, and the pressures listed by Carter (9) are approximately 2% too high. Using either NaF or NaCl, the pressures are deduced from the volumes calculated from their diffraction patterns at high pressures. The pressures correlated with the relative volumes for both these alkali halides are listed in Table 1.

Once a series of x-ray diffraction patterns for an explosive with pressure indicator have been taken, transforming the patterns to P,V values is straightforward. Neither of the two explosives we have studied, PLTN and TATB, has undergone a change in crystal structure up to pressures between 5 and 10 GPa. From extensive x-ray data gathered on these explosives by others, the Miller indices of the diffraction lines of the patterns are well known. The diffraction lines of the pressurized samples are correlated with the ambient diffraction patterns. From the distance between diffraction line pairs, and the factors determined by the diffraction patterns taken of the explosive-indicator mix at ambient conditions, a d-spacing between molecular planes is calculated. (For background to the powder diffraction technique, see Azaroff and Buerger's book, the Powder Method (11).) From the d-spacings and the Miller indices, the length of the unit cell axes and angles between the axes can be calculated. For any crystal system other than cubic, the assistance of a computer least-squares program is desirable or even essential. From the results of such calculations, the volume of the explosive and the pressure indicator can be calculated.

METHOD OF DATA ANALYSIS

The accumulated crystallographic information about the explosive is presented and analyzed in several ways. The cell edges under pressure are usually represented by least-squares polynomials of the relative cell edge compression. It has been observed (12) that explosives undergo large linear changes in the directions corresponding with weak van der Waals bonding. In PLTN all three orthogonal directions have such bonding (12). In TATB, as we shall see, van der Waals bonding occurs in only one direction (also see (13)). The linear compressions may provide important clues about the detonation behavior of an explosive if the explosive is highly oriented, as are some TATB-based materials, or if the explosive contains large crystals of the base explosive.

The volume, too, can be represented by least-squares polynomials, but a more meaningful representation is a form similar to the shock compression Hugoniot

$$U_{st} = c_t + s_t U_{pt} + q U_{pt}^2 \qquad (1)$$

where the t subscript denotes isothermal conditions. Here U_{st} and U_{pt} are obtained from pressure and volume along the isotherm using the analogous Hugoniot conservation relations that apply to shock wave conditions.

$$U_{st} = (P V_o/(1 - V/V_o))^{1/2} \quad (2)$$

$$U_{pt} = (P V_o (1 - V/V_o))^{1/2} \quad (3)$$

$$P = U_{st} U_{pt}/V_o \quad (4)$$

$$V/V_o = (U_{st} - U_{pt})/U_{st} \quad (5)$$

In the isothermal equation (1) c_t is the isothermal bulk sound speed at zero pressure instead of the adiabatic bulk sound speed. Similarly, the second parameter, s_t, is related to the zero pressure, pressure derivative of the isothermal bulk modulus (B'_{ot}) in the same way that the shock second parameter is related to the adiabatic modulus

$$s_t = (B'_{ot} + 1)/4; s = (B'_{os} + 1)/4 \quad (6)$$

If the adiabatic bulk sound speed, c_s, the volume thermal expansion, a_v, and the heat capacity at constant pressure, C_p, are determined for the explosive of interest, then a refined isothermal compression and a shock compression can be calculated. All of these parameters are readily and routinely determined. The zero pressure bulk sound speed, c_s, is the shock U_s intercept at $U_p = 0$. Both c_t and c_v, the heat capacity at constant volume, are calculated from c_s, C_p, and a_v using the following relations

$$C_v = C_p - a_v^2 T c_t^2 \quad (7)$$

and

$$c_t = c_s(C_v/C_p)^{1/2} \quad (8)$$

The calculation is started by assuming $c_t = c_s$ in Eq. (7) and then cycling the results between the two equations until the C_v and c_t values converge. The c_t can be used for the constant in Eq. (1) instead of calculating it from a quadratic fit to the data; this increases the certainty of the other constants.

The shock compression of the explosive is calculated from Eq. (1) in the following manner. The energy change from the initial volume, V_o, to some volume, V_L, at constant temperature T is

$$E_t\{V_L\} - E_t\{V_o\} = \int_{V_o}^{V_L} (T C_v/V - P_t)dV \quad (9)$$

The brackets, $\{\}$, mean "evaluated at". The subscript, t, again refers to isothermal compression. γ is the Grüneisen constant

$$\gamma = a_v c_s^2/C_p \quad (10)$$

The assumption made here is that both C_v and γ/V remain constant over all conditions of isothermal and shock compression, as long as the explosive does not transform to another phase. A similar energy change along the Hugoniot of the explosive is

$$E_h\{V_L\} - E_h\{V_o\} = \frac{1}{2} P_h\{V_L\}(V_o - V_L) \quad (11)$$

The subscript, h, refers to shock compression. Finally, the energy cycle is completed by calculating the energy difference between V_o on the isotherm and V_L on the Hugoniot. This difference is calculated from the following thermodynamic relation

$$\partial E/\partial P_{T,V} = V/\gamma \quad (12)$$

Since γ/V is assumed constant

$$E_h\{V_L\} - E_t\{V_L\} = (V/\gamma)[P_h\{V_L\} - P_t\{V_L\}] \quad (13)$$

If we set $E_h(V_o) = E_t(V_o)$, then combining Eqs. (9), (11) and (13),

$$P_h\{V_L\} = \quad (14)$$

$$\frac{P_t\{V_L\}(V/\gamma) - \int_{V_o}^{V_L} P_t dV - [1/2/V]C_v(V_L - V_o)}{[(V/\gamma) - 1/2(V_o - V_L)]}$$

The integral in Eq. (14) is solved by numerical integration

$$\int_{V_o}^{V_L} P_t dV = \sum_{r=1}^{L} \frac{P_{tr} + P_{tr-1}}{2}(V_r - V_{r-1}) \quad (15)$$

where

$$V_r = V_o(U_{str} - U_{ptr})/U_{str} \quad (16)$$

and

$$P_{tr} = (1/V_o)U_{str}U_{ptr}. \quad (17)$$

U_s and U_p a. then calculated from P_h (V_L) and v_L.

PETN

The study of the compression of PETN was published earlier (12). However, the NaF pressure scale used was the earlier Carter scale (9) and not the revised scale listed in Table I. In addition, Morris (14) has refined the adiabatic bulk sound speed value (that work appears in this volume). The basic data, V/V_o of PETN correlated with V/V_o of NaF, are listed in the earlier study (12) along with appropriate figures and will not be repeated here. We have listed below the revised volume (U_{st}-U_{pt}) compression and the Hugoniot (U_s-U_p) calculated from Eqs. (18) and (19). The thermodynamic properties of PETN are listed in Table II.

$$U_{st} = 2.233 + 2.737\ U_{pt} - 0.511\ U_{pt}^2, \quad U_{pt} < 1.8\ \text{km/s}, \rho_o = 1.774\ \text{g/cm}^3 \tag{18}$$

$$U_{st} = 2.759 + 1.695\ U_{pt}, \quad U_{pt} > 1.8\ \text{km/s}, \rho_o = 1.774\ \text{g/cm}^3 \tag{19}$$

$$U_s = 2.320 + 2.612\ U_p - 0.379\ U_p^2, \quad U_p < 1.8\ \text{km/s}, \rho_o = 1.774\ \text{g/cm}^3 \tag{20}$$

$$U_s = 2.811 + 1.730\ U_p, \quad U_p > 1.8\ \text{km/s}, \rho_o = 1.774\ \text{g/cm}^3 \tag{21}$$

TABLE I

Relative Volumes of NaCl and NaF as a Function of Pressure at 293°K

Pressure[a] GPa	NaCl[b] V/V_o	NaF[c] V/V_o
0.0	1.00000	1.00000
1.0	0.96268	0.97999
2.0	0.93248	0.96208
3.0	0.90705	0.94588
4.0	0.88506	0.93108
5.0	0.86566	0.91747
6.0	0.84831	0.90488
7.0	0.83259	0.89316
8.0	0.81822	0.88221
9.0	0.80498	0.87193
10.0	0.79270	0.86225
11.0	0.78124	0.85312

a 1 GPa = 10 kilobars.
b A refinement by J. N. Fritz of the V/V_o listing contained in Ref. (5).
c A recalculation by W. J. Carter based on the information contained in Ref. (9).

TABLE II

Thermodynamic Properties of PETN at 293°K, 0 GPa

ρ_o = 1.774 g/cm^3	Ref. (12)
c_s = 2.32 km/s	Ref. (14)
c_t = 2.23 km/s	
α_v = 2.3[illegible] x 10^{-4}/K°	Ref. (15)
C_p = 1.03 J/gK°	Ref. (16)
C_v = 1.0 J/gK°	
γ = 1.15	

TATB

The symmetry of TATB is much lower than that of PETN (triclinic with 6 parameters to determine as compared to tetragonal with only 2 parameters to determine). [For details on the crystal structure, see Ref. (17)]. The large TATB molecule is flat and shaped like a hexagon in the plane defined by the a and b axes. It is hydrogen bonded to 6 molecules in hexagonal close-packed array. The molecules bonded in this manner form sheets. The resulting symmetry in the a-b plane is nearly hexagonal (a/b = 0.998, γ = 119.9°). The sheets are bonded to one another by weak van der Waals bonds. A point in one sheet is shifted from a position directly over the corresponding point in the sheet beneath it so that the cell edge that connects these points, the c axis, forms an angle of 91.82° (β) with the a axis and an angle of 108.58° (α) with the b axis. The two assumptions we used to determine the cell parameters from high pressure diffraction patterns are 1) a/b remains constant under pressure and 2) a point on one sheet of molecules remains over the same relative position on the sheet below it. From this assumption the following relations are derived. If c_a is the projection of the c axis on the a axis at zero pressure and c_b is the projection of the c axis on the b axis at zero pressure, then the angles between c and a (β) and c and b (α) at high pressure are

$$\alpha_p = \text{arc cosine } (-\underline{c}_b \times (\underline{b}_p/\underline{b}_o)/\underline{c}_p) \tag{22}$$

$$\beta_p = \text{arc cosine } (-\underline{c}_a \times (\underline{a}_p/\underline{a}_o)/\underline{c}_p) \tag{23}$$

$$\gamma_p = \gamma_o \text{ (because of the first assumption)} \tag{24}$$

The subscript,o, in the above expressions

TABLE III

Crystallographic Cell Parameters of TATB

NaF[T] (V/V_o)	Pressure[*] (GPa)	a[*] (Å)	b[§] (Å)	c[*] (Å)	α[§] (deg)	β[§] (deg)	γ[§] (deg)
1.0000	0.00	9.010[+]	9.028[+]	6.812[+]	108.6[+]	91.8[+]	120.0[+]
0.9965 (09)	0.17 (.05)	9.016 (.009)	9.034	6.807 (.017)	108.6	91.8	120.0
0.9826 (12)	0.87 (.07)	8.986 (.021)	9.004	6.492 (.020)	109.5	91.9	120.0
0.9774 (10)	1.41 (.06)	8.958 (.018)	8.976	6.461 (.014)	109.5	91.9	120.0
0.9597 (09)	2.14 (.08)	8.944 (.009)	8.962	6.376 (.011)	109.8	91.9	120.0
0.9507 (15)	2.69 (.10)	8.877 (.017)	8.895	6.289 (.013)	109.9	91.9	120.0
0.9374 (14)	3.56 (.09)	8.846 (.016)	8.864	6.205 (.012)	110.1	92.0	120.0
0.9029 (11)	6.47 (.10)	8.752 (.018)	8.770	6.039 (.015)	110.4	92.0	120.0
0.8929 (15)	7.02 (.13)	8.678 (.005)	8.695	5.951 (.001)	110.6	92.0	120.0

[T] Deviation x 10^4 in parenthesis
[*] Deviation in parenthesis
[§] Calculated from a and c
[+] Ref. (17)

denotes zero pressure, and the subscript, p, denotes pressure p.

At low pressures (0.1 to 3.0 GPa) as many as ten diffraction lines were measureable; at high pressure these were reduced to four. The 4 θ values measured were used to determine the two independent cell parameter variables, a and c (reduced from 6 to 2 by the above two assumptions.) The pressure was indicated by the diffraction pattern of NaF which was mixed with the TATB sample. Table III lists the cell parameters and pressures determined from the high pressure patterns. The isothermal compression fits of the two independent variables and the U_{st}-U_{pt} fits are

$$a/a_o = 1 - 2.084 \times 10^{-3}p - 1.071 \times 10^{-3}p^2 + 9.344 \times 10^{-5}p^3 \quad (25)$$

$$c/c_o = 1 - 4.931 \times 10^{-2}p + 9.495 \times 10^{-3}p^2 - 7.202 \times 10^{-4}p^3 \quad (26)$$

$$U_{st} = 1.40 + 10.32\ U_{pt} - 11.76\ U_{pt}^2,$$

$$U_{pt} < 0.3 \text{ km/s}, \rho_o = 1.937 \text{ g/cm}^3 \quad (27)$$

$$U_{st} = 2.92 + 1.59\ U_{pt},$$

$$U_{pt} > 0.3 \text{ km/s}, \rho_o = 1.937 \text{ g/cm}^3 \quad (28)$$

From the isothermal compression data and thermodynamic parameters listed in Table IV, the shock compression Hugoniots are calculated to be

$$U_s = 1.43 + 10.02\ U_p - 10.89\ U_p^2,$$

$$U_p < 0.3 \text{ km/s}, \rho_o = 1.937 \text{ g/cm}^3 \quad (29)$$

$$U_s = 2.95 + 1.60\ U_p,$$

$$U_p > 0.3 \text{ km/s}, \rho_o = 1.937 \text{ g/cm}^3 \quad (30)$$

The U_s-U_p slope, 1.60, calculated for the TATB Hugoniot in the higher U_p region is smaller than found by either Coleburn and Liddard (18), 2.52, or by Craig (18), 2.50, but is of the same magnitude as for many other explosives. For PETN the quadratic fit of the calculated U_s-U_p Hugoniot was necessary to fit the compression data up to 5.5 GPa. As we stated earlier, PETN has van der Waals bonding in all directions. For TATB, however, where van der Waals bonds are in only one direction, the linear fit is adequate for U_s-U_p data above 2.0 GPa. One other item to be noted is that the Grüneisen constant calculated here (0.20) is considerably smaller than the constant reported in Dorbratt's compendium (18), 1.60. The small Grüneisen constant is due to the small bulk sound speed (1.45 km/s) and small volume thermal expansion (9.9×10^{-5}/k°). Though both may be slightly higher because of porosity effects for the former and accuracy for the latter, the Grüneisen constant is probably no larger than 0.4.

CO_2

The work on CO_2 had to be done on the solid form, of course, so that the CO_2 would yield diffraction patterns.

TABLE IV

Thermodynamic Properties of TATB at 293°K, 0 GPa

ρ_o = 1.937 g/cm^3	Ref. (17)
c_s = 1.43 km/s	Ref. (19)
c_v = 1.40 km/s	
α_v = 9.95 x 10^{-5}/K°	Ref. (20)
C_p = 1.00 J/gK°	Ref. (21)
C_v = 0.96 J/gK°	
γ = 0.20	

The anvil on which was mounted the beryllium annulus containing NaF was cooled by circulating liquid nitrogen around its base. Once cooled, commercial dry ice was scraped on the edge of the annulus, and a small pile of fine CO_2 chips accumulated above the annulus hole. The upper anvil, at room temperature, was lowered onto the pile of CO_2 as quickly as possible, luckily trapping some CO_2 in the hole of the annulus with the NaF. No alcohol was added because the experiment would have been more difficult and there was no proof that CO_2 was not miscible in the alcohol. The specific volumes of CO_2 at 293°K at pressures from 3 to 10 GPa are listed in Table V.

A Hugoniot for solid CO_2 centered at ambient conditions can be calculated if estimates of the specific volume, V_o, thermal expansion, α_v, and heat capacity, C_p, for these conditions can be made. In 1926 Maas and Barnes (22) made a very thorough study of the thermodynamic properties of solid and liquid

TABLE V

Specific Volume Data for CO_2 at Pressures to 10 GPA, 293°K

V_o (cm^3/g)	Pressure (GPa)
0.4965 ± .0007	3.30 ± 0.14
0.4638 ± .0006	5.52 ± 0.17
0.4529 ± .0006	6.68 ± 0.14
0.4462 ± .0006	7.18 ± 0.04
0.4433 ± .0010	7.70 ± 0.12
0.4403 ± .0005	7.89 ± 0.13
0.4357 ± .0007	8.67 ± 0.09
0.4290 ± .0007	9.83 ± 0.07
0.4263 ± .0008	9.99 ± 0.19

TABLE VI

Thermodynamic Properties of CO_2 (solid) at 293°K, 0 GPa

ρ_o = 1.489 g/cm^3	Ref. (23)
c_s = 1.74 km/s	
c_t = 1.62 km/s	Ref. (24)
α_v = 5.41 x 10^{-4}/K°	Ref. (23)
C_p = 1.77 J/gK°	Ref. (25)
C_v = 1.54 J/gK°	
γ = 0.93	

CO_2. From their solid CO_2 density measurements between 88°K and 186°K (above 186° their measurements deviated suddenly from a linear V-T behavior) and specific heat content measurements between 90°K and 212°K, the values for density and specific heat content were extrapolated to 293°K. The extrapolations were linear for density, quadratic for heat content; α_v and C_p were calculated from the slopes at 293°K. These values are listed in Table VI. Using the V_o value ($1/\rho_o$ = 0.6720 cm^3/g), a U_{st} U_{pt} fit to the data in Table V is

$$U_{st} = 1.623 + 1.71\ U_{pt},$$

$$U_{pt} > 0.7 \text{ km/s}, \rho_o = 1.488 \text{ g/cm}^3 \quad (31)$$

Using Eq. (31) and the thermodynamic quantities listed in Table VI, the calculated Hugoniot for solid CO_2 starting at 293°K is

$$U_s = 1.740 + 1.65\ U_p,$$

$$U_p > 0.7 \text{ km/s}, \rho_o = 1.488 \text{ g/cm}^3 \quad (32)$$

Solid CO_2, like the explosives discussed above, is composed of CO_2 molecules bonded to one another by van der Waals bonds. Therefore, like PETN and TATB, the U_{st}-U_{pt} and U_s-U_p equations are quadratic at low pressures and thus the c_t and c_s are lower than given in Eqs. (31) and (32). The present data does not permit an estimate of the quadratic coefficients, and the fits are only accurate above U_{pt} and U_p values of 0.7 km/s.

H_2O

As with CO_2, the study of H_2O was on a solid form, specifically ice VII, the stable phase of H_2O above 2.5 GPa at 298°K. Data for the compression of

ice VII was presented earlier (26) using the experimental technique described here. However, aluminum was used as the pressure indicator, and the pressures correlated with aluminum's relative volumes have been found to be 5% to 4% larger up to 10 GPa (27) than given in that work (26). Therefore, the pressures were revised and the results are presented here. The listings of the relative volumes of aluminum and ice VII are found in the earlier work; the isothermal compression used here for aluminum is

$$U_{st} = 5.290 + 1.388\ U_{pt},$$
$$\rho_o = 2.701\ g/cm^3 \qquad (33)$$

The ambient specific volume of ice VII is chosen so that the U_{st}-U_{pt} equation (Eq. (1) above) is linear; that volume is 0.717 cm^3/g. The subsequent linear equation for ice VII is

$$U_{st} = 2.872 + 1.685\ U_{pt},$$
$$\rightarrow U_{p_t} > 0.5\ km/s, \rho_o = 1.395\ g/cm^3 \qquad (34)$$

In order to calculate the Hugoniot of ice VII centered at ambient conditions, assumptions about the specific heat capacity and thermal expansion of ice VII must be made. Normal ice, ice Ih, has a structure only slightly different from the structure of low temperature ice at zero pressure, ice Ic. Their densities, too, are nearly the same. Therefore, we assume that both structures have the same specific heat capacities and thermal expansions. The ice VII structure consists of two interpenetrating but not interconnecting ice Ic frameworks, and thus it is not unreasonable to expect molecular vibrations and relative bond length expansions to be nearly the same between the two structures. Therefore we assume the specific heat capacities and thermal expansions to be the same. Including the isothermal bulk sound speed calculated for Eq. (34) above, the thermodynamic properties of ice VII at ambient conditions are listed in Table VII. Combining these with the isothermal compression, Eq. (34), the ice VII Hugoniot, centered at ambient conditions, is calculated to be

$$U_s = 2.920 + 1.678\ U_p,$$
$$U_p > 0.5\ km/s, \rho_o = 1.395\ g/cm^3 \qquad (35)$$

TABLE VII

Thermodynamic Properties of H_2O (ice VII) 293°K, 0 GPa

$\rho_o = 1.397\ g/cm^3$	Ref. (28)
$c_s = 2.32\ km/s$	
$c_t = 2.87\ km/s$	Ref. (29)
$\alpha_v = 1.7 \times 10^{-4}/K^o$	Ref. (30)
$C_p = 2.09\ J/gK^o$	Ref. (30)
$\gamma = 0.69$	

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