

# EXP6: A NEW EQUATION OF STATE LIBRARY FOR HIGH PRESSURE THERMOCHEMISTRY

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We discuss the development of EXP6, a new equation of state library for detonation thermochemistry, shock physics, and high pressure gases. Fluid products such as H<sub>2</sub>O, CO<sub>2</sub>, and N<sub>2</sub>, are treated with an exponential-6 equation of state model. Equation of state parameters are found for EXP6 by matching to a combination of shock data and static compression data. Although matching to shock data is traditional in detonation thermochemistry, we show that our model can match a wider range of data including sound speeds and heat capacities at room temperature. Polar detonation products, such as H<sub>2</sub>O and HF, are treated through a novel "multi-species" representation. This allows the simplicity of the exponential-6 model to be retained while maintaining accuracy for polar fluids.

## INTRODUCTION

There is a continuing need in detonation science<sup>[1,2]</sup> for improved high pressure equations of state. The exponential-6 (exp-6) potential model defines the energy of interaction of a classical fluid composed of identical spherical particles. This model has been used with considerable success to describe the equation of state of many materials over a wide range of pressure and temperature. The definition of an effective spherical system for non-spherical molecules has been discussed within the framework of variational thermodynamic perturbation theory<sup>[3]</sup>. The exp-6 model is particularly necessary in high pressure work, where the flexibility of the potential to model materials of varying stiffness is important.

In the present paper, we apply an accurate and numerically efficient equation of state for the exp-6 fluid based on Zerah and Hansen's hypernetted-mean spherical approximation (HMSA)<sup>[4]</sup> equations and Monte Carlo calculations to detonation, shocks, and static compression. We present a library of

parameters for fluid and condensed high pressure molecules. We call this library "EXP6".

EXP6 supports a wide range of elements and condensed detonation products. We have applied a Murnaghan<sup>[5]</sup> equation of state (EOS) form to a variety of metals, metal oxides and other solids. We have also matched phase transition data for many of these solids. For example, this form has recently been applied to the EOS of carbon<sup>[6]</sup>. Thermal effects in the EOS are included through the dependence of the coefficient of thermal expansion on temperature, which can be directly compared to experiment. We find that we can replicate shock Hugoniot and isothermal compression data for a wide variety of solids with this simple form.

We validate EXP6 through several independent means. We consider the shock Hugoniots of liquids and solids in the "decomposition regime" where thermochemical equilibrium is established. We argue that this regime is reached for most organic materials above 50GPa shock pressures. We also

validate the code against high explosive overdriven shock Hugoniot, and more traditional metrics such as the detonation velocity and pressure. Overall, we find that EXP6 offers a highly accurate representation of high pressure equation of state properties with no empirical fitting to detonation data.

## METHOD

We consider a fluid of particles interacting with the exponential-6 potential energy function. We define  $\epsilon$  to be the depth of the attractive well between particles,  $r_m$  is the position of the potential well minimum, and  $\alpha$  controls the steepness of the repulsive part of the potential. Although the exp-6 potential strictly describes a simple fluid (spherical atoms of identical type), it has also been successfully applied to molecular fluid mixtures[7] through the use of empirical combination rules. We use van der Waals one-fluid rules to relate a mixture of spherical particles to an effective simple fluid. Ree has suggested an improved one-fluid mixture rule for  $\alpha$ [8] that we use here.

We now specify the equation of state used to model detonation products. For the ideal gas portion of the Helmholtz free energy, we use a polyatomic model including electronic, vibrational, and rotational states. Such a model can be conveniently expressed in terms of the heat of formation, standard entropy, and constant pressure heat capacity of each species.

The heat capacities of many product species have been calculated by a direct sum over experimental electronic, vibrational, and rotational states. These calculations were performed to extend the heat capacity model beyond the 6000K upper limit used in the JANAF thermochemical tables. Chebyshev polynomials which accurately reproduce the heat capacities were generated.

The HMSA/MC equation of state was used to describe the excess Helmholtz free energy. An extended Lorentz-Berthelot approximation was used to generate the interaction between unlike species.

$$\begin{aligned}\epsilon_{ij} &= \sqrt{\epsilon_{ii}\epsilon_{jj}} \\ r_{m,ij} &= k_{ij}(r_{m,ii} + r_{m,jj})/2 \\ \alpha_{ij} &= \sqrt{\alpha_{ii}\alpha_{jj}}\end{aligned}$$

The parameter  $k_{ij}$  is a non-additive interaction parameter. In nearly all cases we use  $k_{ij} = 1$ . Our goal is to derive a model for supercritical fluids applicable to a very wide range of states and properties. In order to do so, we have developed an automatic optimization procedure to match a variety of experimental data.

Experimental observables were placed into categories. We took the first category to be the volume along the shock Hugoniot and reshocked states. The second was the temperature along the shock Hugoniot and reshocked states. The third was the volume under static compression. The last category was the sound speed under static compression. For each category, we determined an average error.

The figure of merit is a weighted average of the category errors. We assigned a weight of 40% to shock volumes, 25% to shock temperatures, 25% to static volumes, and 10% to the speed of sound. The optimization procedure is weighted more to shocks than static measurements, although we find below that we reproduce both well. A stochastic optimization algorithm was employed to minimize the figure of merit function. Our final parameters are listed in Table 1. In the following subsections we analyze the performance of the resulting equation of state in reproducing a wide range of experimental measurements. Results for nitrogen are fully discussed in [4]. Although the parameters in that work are slightly different than those used here, the comparison to experiment is similar.

**TABLE I: EXPONENTIAL-6  
POTENTIAL PARAMETERS FOR  
SPECIES CONTAINED IN THE  
SUPERCRITICAL FLUID PHASE.**

Species	$r_m$	$\epsilon$	$\alpha$
Al	2.98	300.0	13.0
Ar	4.07	86.1	13.0
B	2.27	300.0	13.0
BO	4.74	250.0	13.0
C <sub>2</sub> H <sub>2</sub>	4.51	241.8	13.6
C <sub>2</sub> H <sub>4</sub>	4.67	196.2	12.2
C <sub>2</sub> H <sub>6</sub>	4.84	238.5	13.9
Ca	5.07	50.0	13.0
CCl <sub>4</sub>	5.99	650.7	13.6
CClFO	5.07	300.0	13.0
CF <sub>4</sub>	4.67	602.5	14.5
CF <sub>4</sub> O	4.86	200.0	13.0
CFO	4.51	200.0	13.0
CH <sub>2</sub> Cl <sub>2</sub>	5.55	305.8	12.1
CH <sub>2</sub> Cl <sub>2</sub> (a)	5.55	305.8	12.1
CH <sub>2</sub> F <sub>2</sub>	5.03	233.0	11.9
CH <sub>3</sub> OH	4.24	507.2	13.0
CH <sub>4</sub>	4.30	137.8	12.3
CHCl <sub>3</sub> (a)	5.74	301.0	15.3
CHFO	4.50	150.0	13.0
Cl	3.90	130.9	13.0
Cl <sub>2</sub>	4.93	346.7	11.3
CO	4.16	105.5	13.2
CO <sub>2</sub>	4.18	228.3	14.1
D	2.10	50.0	11.0
D <sub>2</sub>	3.49	30.4	11.2
F	3.33	113.0	13.0
F <sub>2</sub>	3.8	92.2	13.0
H	2.10	50.0	11.0
H <sub>2</sub>	3.49	30.4	11.2
H <sub>2</sub> O	3.34	308.8	11.6
H <sub>2</sub> O(a)	3.19	308.8	11.6
HCl	3.84	198.4	13.9

HCN	5.37	358.2	13.6
He	2.97	10.7	13.0
HF	3.27	393.3	13.4
(HF) <sub>2</sub>	4.22	393.3	13.4
(HF) <sub>3</sub>	5.11	393.3	13.4
(HF) <sub>4</sub>	5.79	393.3	13.4
(HF) <sub>5</sub>	6.37	393.3	13.4
(HF) <sub>6</sub>	6.62	393.3	13.4
(HF) <sub>7</sub>	7.17	393.3	13.4
HNCO	4.30	232.0	13.0
K	4.77	850.0	13.0
Li	3.70	71.4	13.0
N	2.43	88.2	11.4
N <sub>2</sub>	4.17	97.1	13.0
N <sub>2</sub> O	4.28	242.8	13.6
Na	4.00	1375.0	13.0
NH <sub>3</sub>	3.72	244.9	12.0
NH <sub>3</sub> (a)	3.72	244.9	12.0
NO	3.71	151.9	13.1
NO <sub>2</sub>	4.27	338.0	13.6
O	2.41	700.0	11.0
O <sub>2</sub>	3.83	121.2	13.6
O <sub>3</sub>	4.41	204.8	13.6
P	4.62	50.0	13.0
P <sub>2</sub>	5.02	200.0	13.0
S	4.31	50.0	13.0
Si	5.62	300.0	13.0
Ti	4.00	100.0	13.0
Xe	4.37	243.1	13.0
Zr	4.50	100.0	13.0

Other workers<sup>[9,10]</sup> have shown that a chemical equilibrium model of hydrocarbons based on an exponential-6 fluid model using Ross's soft-sphere perturbation theory is successful in reproducing the behavior of shocked hydrocarbons. Our model of the supercritical phase includes the species H<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, and C<sub>2</sub>H<sub>4</sub>. We have chosen model parameters so as to match both static compression isotherms and shock measurements wherever possible. The ability to match both types of experiments well increases

confidence in the general applicability of our high pressure equation of state model.

We now specify the sources of experimental data used in the calculations that follow. The shock Hugoniot data for polyvinylchloride (PVC), polychlorotrifluoroethylene (PCTFE),  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ ,  $\text{CCl}_4$ , polyethylene, n-hexane, cyclohexane, benzene, PVF2, and PTFE comes from Marsh[11] and for  $\text{CH}_4$  from Nellis et al.[12]. Shock Hugoniot and shock temperature data for  $\text{H}_2$  comes from a variety of sources[13,14,15]. We use static compression data for  $\text{CH}_2\text{F}_2$ [16],  $\text{HF}$ [17],  $\text{C}_2\text{H}_4$ [18,19],  $\text{CH}_4$ [20,21], and  $\text{C}_2\text{H}_6$ [22,23].

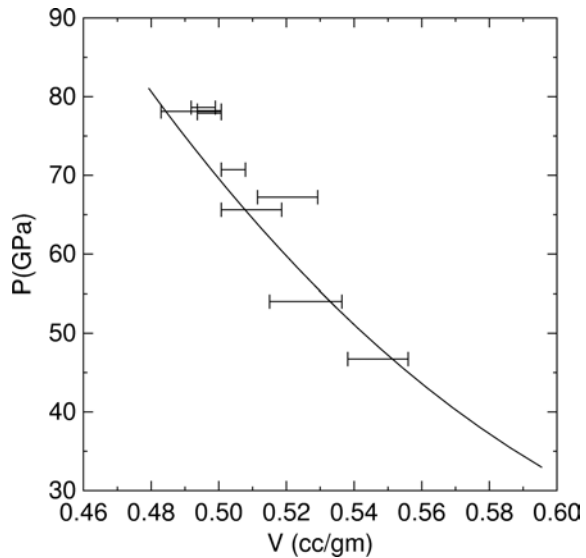
Calibration began with  $\text{H}_2$ , which was matched to measured shock Hugoniot and shock temperatures. The same parameters were used for  $\text{H}_2$  and  $\text{D}_2$ , because of the identical potential energy of interaction of the two isotopes. This served to further constrain the  $\text{H}_2$  equation of state. The parameters used are given in Table I.

Next parameters for  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ , and  $\text{C}_2\text{H}_4$  were determined by matching a combination of static and shock compression data for the materials,  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_2\text{H}_4$ , benzene, n-hexane, and cyclohexane. We found agreement to within roughly 1% between the measured and calculated equation of state properties.

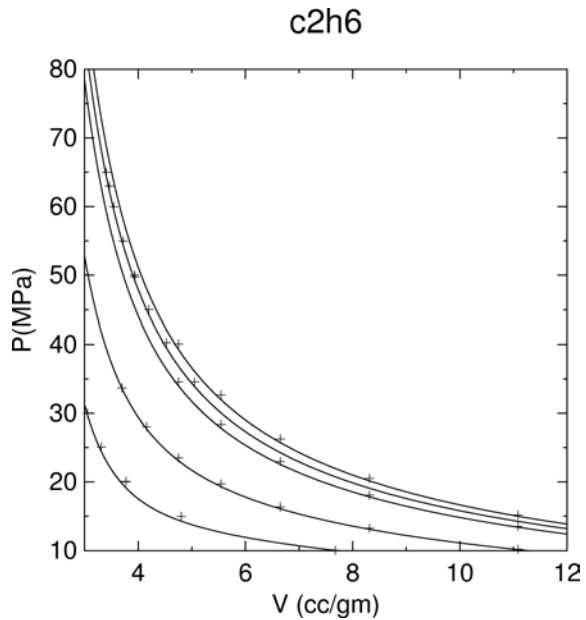
In Figure 1 we show the shock Hugoniot of polybutene as calculated with the current modeling system. We find good agreement with reshock experiments up to 210 GPa in this material as well. In Figure 2 we compare calculated and experimental isotherms of  $\text{C}_2\text{H}_6$ . Note that a high level of accuracy is found even at moderate (MPa) pressures.

We next discuss the fluorocarbon model. To our knowledge, high pressure equation of state measurements have not been performed on  $\text{F}_2$ . We use exp-6 parameters for  $\text{F}_2$  estimated by Zerilli and Jones[24]. We considered the shock behavior of PTFE in order to determine parameters for  $\text{CF}_4$ .

We predict that PTFE decomposes into a fluid phase composed mostly of  $\text{CF}_4$ , and carbon in the diamond phase. We found an unusually high value of the potential steepness parameter  $\alpha$ . We note that Zerilli



**FIGURE 1. MEASUREMENTS OF THE REACTIVE SHOCK HUGONIOT OF POLYBUTENE (ERROR BARS) ARE COMPARED TO CALCULATIONS OF THE PRESENT MODEL (LINE)**

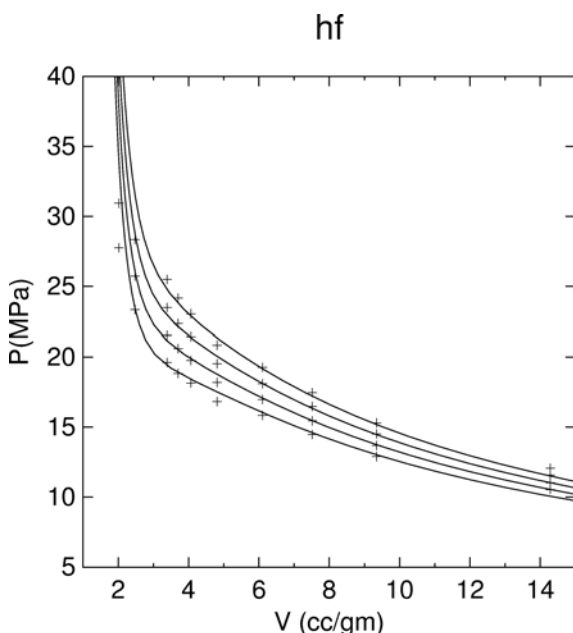


**FIGURE 2. MEASUREMENTS OF THE ISOTHERMS OF  $\text{C}_2\text{H}_6$  AT 400, 473, 573, AND 600K (POINTS) ARE COMPARED TO CALCULATIONS OF THE PRESENT MODEL (LINES)**

and Jones[24] also obtained a very steep potential for  $\text{CF}_4$  by spherically averaging a Lennard-Jones potential.

HF is known to strongly associate[25], in the gaseous, liquid, and fluid phases. We have determined a simple HF association model that matches both high and low pressure data.

There is insufficient experimental data on HF to uniquely determine the exp-6 parameters of each associated species. Instead, we use the following simple scaling rules to relate the properties of the clusters to that of HF.



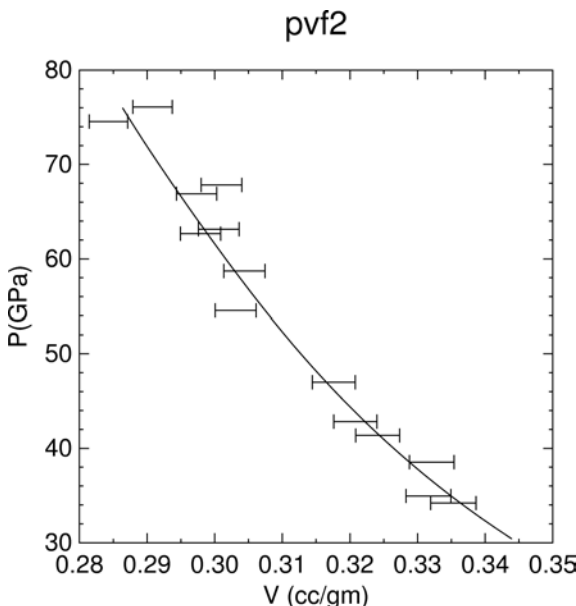
**FIGURE 3. MEASUREMENTS OF THE ISOTHERMS OF HF AT 543, 553, 563, AND 573K (POINTS) ARE COMPARED TO CALCULATIONS OF THE PRESENT MODEL (LINES)**

The motivation for the cluster model is to determine the simplest possible model that will match both the low pressure static compression of supercritical HF, and the shock Hugoniot of PVF2. The current model succeeds in this regard, although we cannot claim that the description of individual cluster species is quantitatively accurate. We have found that it is possible to match the shock Hugoniot of PVF2 without the association model, but the static

compression requires an explicit treatment of association. We decided to limit our model to only those clusters described by JANAF.

We show the calculated isotherms of HF in Figure 3. The calculated shock Hugoniot of PVF2 is shown in Figure 4. In our calculations PVF2 dissociates to HF and carbon. The HF model is seen to work equally well in the experimental pressure range of 0.01 to 75 GPa.

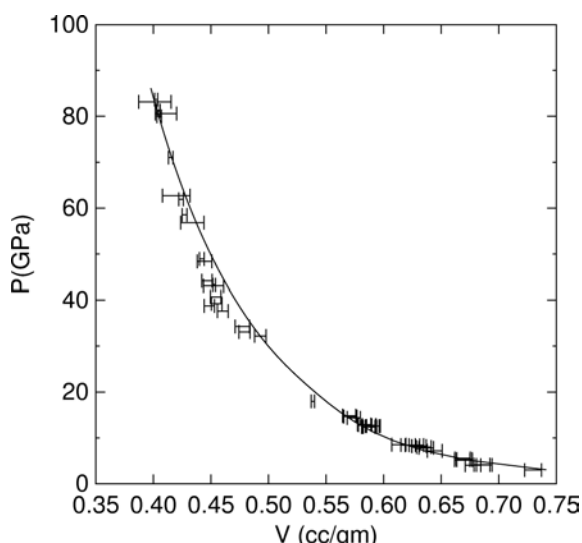
There is more shock data available on chlorocarbons than the fluorocarbons. This allows for more extensive testing of the validity of the present model. We note that Dremov and Modestov[26] have reported effective exponential-6 parameters for chlorinated methanes. We find their parameters to be inaccurate when used within the current modeling framework, which uses the recently developed HMSA/MC equation of state[4], and a product set including hydrocarbons and condensed carbon.



**FIGURE 4. MEASUREMENTS OF THE SHOCK HUGONIOT OF PVF2 (ERROR BARS) ARE COMPARED TO CALCULATIONS OF THE PRESENT MODEL (LINE)**

Parameters for fluid  $\text{CCl}_4$  were matched to the shock Hugoniot of liquid  $\text{CCl}_4$ .

H<sub>2</sub>O is a major detonation product. The hydrogen-bonded tetrahedral structure of water, however, is not naturally represented by a simple exp-6 potential model. We find that an effective two-species model is effective in representing the equation of state of supercritical water over a wide range of conditions. In the two-species model, we represent water by two species in chemical equilibrium: non-associated water (H<sub>2</sub>O) and associated water: H<sub>2</sub>O(a). The non-associated water has standard state parameters given by gaseous water. In associated water, however, standard state parameters are chosen closer to that of liquid water: the standard enthalpy and entropy are both less than that of gaseous water.

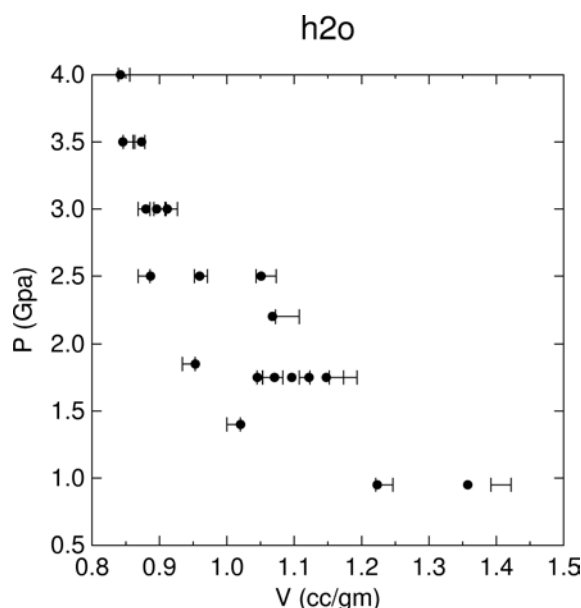


**FIGURE 5: MEASUREMENTS OF THE SHOCK HUGONIOT OF H<sub>2</sub>O (ERROR BARS) ARE COMPARED TO CALCULATIONS OF THE PRESENT MODEL (LINE)**

In the limit of high temperatures and low density, chemical equilibrium favors the non-associated species. For temperatures close to the critical temperature, associated water is favored. This models the increasingly strong nature of the interactions between water molecules as hydrogen bonding is established in the fluid.

In Figure 5 we compare our model to the shock Hugoniot of liquid water. Good agreement is seen. In particular, we successfully reproduce the low-density tail of the shock Hugoniot while using the

(correct) energy of formation for liquid water in the shock Hugoniot relations ( $E_0$ ). In this region a single exp-6 species fails to accurately model the experimental data. In fact, solutions to the Hugoniot equation do not exist for low compressions with a single species model. In Figure 6 we compare the predictions of the EXP6 model for H<sub>2</sub>O to experimental PVT data taken between 1600 and 500K [27]. The model is in good agreement with experiment, even in the difficult region near the critical temperature.

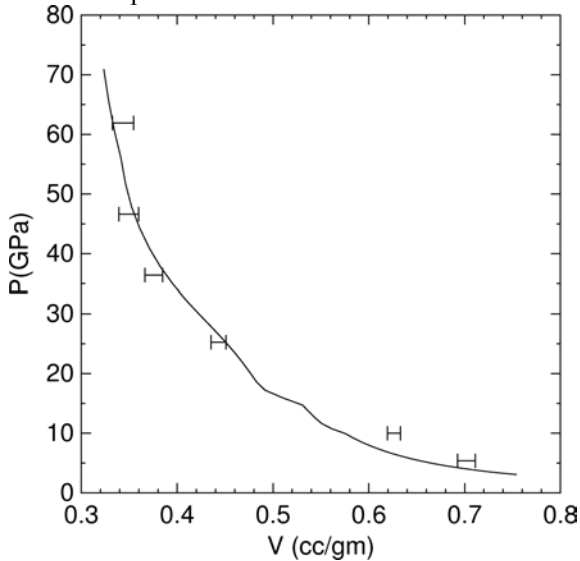


**FIGURE 6: PVT MEASUREMENTS OF WATER BETWEEN 500 AND 1600K (ERROR BARS) ARE COMPARED TO CALCULATIONS OF THE PRESENT MODEL (POINTS).**

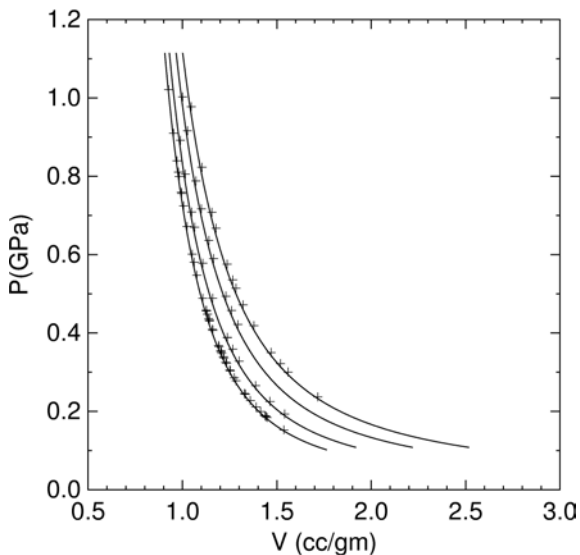
Most commercially used explosives and propellants have roughly a 1:1 carbon/oxygen ratio. Thus, CO is expected to be a major detonation product. The modeling of CO presents some challenges. The shock Hugoniot of CO reaches very high temperatures. In order to model this accurately, we calculated extended  $C_p$  functions for CO, O<sub>2</sub> and CO<sub>2</sub> valid up to 20,000K. A comparison between our calculated shock Hugoniot and the experimental shock Hugoniot of CO is shown in Figure 7.

The accurate modeling of the CO shock Hugoniot

required the specification of non-additive pair interaction parameters between O and CO<sub>2</sub>. We set  $k_{\text{CO}_2,\text{O}} = 0.897$ . This is the only non-additive interaction parameter used in EXP6.



**FIGURE 7: MEASUREMENTS OF THE SHOCK HUGONIOT OF CO (ERROR BARS) ARE COMPARED TO CALCULATIONS (LINE)**  
CO



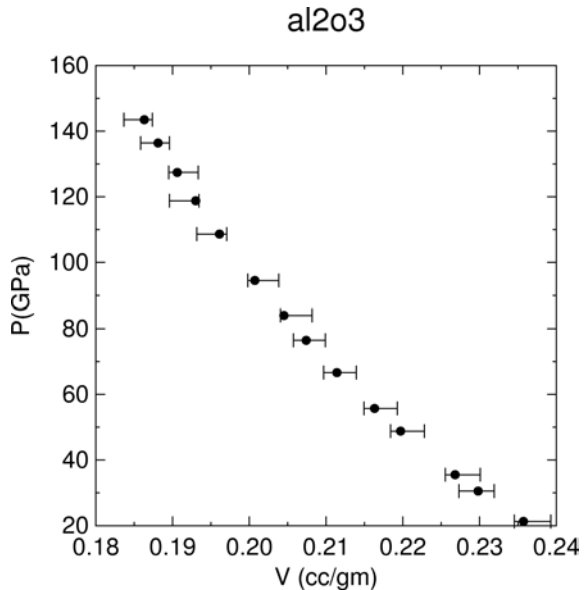
**FIGURE 8. MEASUREMENTS OF THE ISOTHERMS OF CO (CROSSES) AT 308K, 373K, 473K, AND 573K ARE COMPARED TO CALCULATIONS (LINES)**

We have also calibrated the CO model to static compression data. In Figure 8 we compare isotherms of CO to experimental data. Good agreement is found.

## CONDENSED EQUATIONS OF STATE

We used the Murnaghan equation of state model described in [5] for all condensed materials except for carbon. The parameters for the equation of states of these materials is given in Table II.

Carbon is also a major detonation product. A successful thermochemical library must include an accurate equation of state for carbon. Our carbon equation of state [6] is based on an explicit functional form for  $G(P,T)$ . It is more often the case that the pressure of a system is known than its volume. This makes a  $(P,T)$  equation of state very convenient in practical application.



**FIGURE 9. MEASUREMENTS OF THE SHOCK HUGONIOT OF AL<sub>2</sub>O<sub>3</sub> (ERROR BARS) ARE COMPARED TO CALCULATIONS (DOTS).**

Aluminum is a major ingredient in many detonation products. It reacts to form primarily Al<sub>2</sub>O<sub>3</sub> in detonations. We have derived multiphase models for

Al and Al<sub>2</sub>O<sub>3</sub> based on the Murnaghan equation of state. Parameters are given in Table II. We show the shock Hugoniot of Al<sub>2</sub>O<sub>3</sub> as an example in Figure 9.

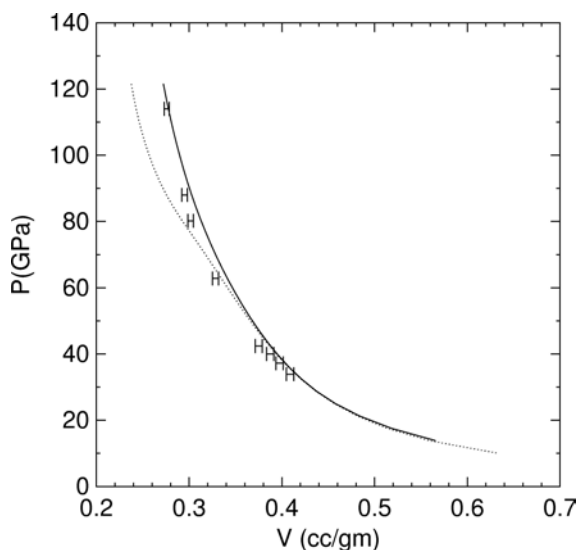
**Table II: Murnaghan equation of state parameters for condensed species.**

Species	V <sub>0</sub>	α	B <sub>0</sub>	B <sub>0</sub> '
Al(s)	10.00	6.90e-05	1.34e-06	4.0
Al(l)	11.36		1.50e-06	3.8
Al <sub>2</sub> O <sub>3</sub> (s)	25.68	1.62e-05	3.58e-07	3.0
Al <sub>2</sub> O <sub>3</sub> (l)	32.02		1.40e-06	4.5
Al <sub>2</sub> SiO <sub>5</sub>	49.90		5.00e-07	3.0
Al <sub>6</sub> O <sub>13</sub> Si <sub>2</sub>	135.00		2.00e-06	5.6
AlN	12.58		4.96e-07	3.7
B	4.62		4.34e-07	1.1
B <sub>2</sub> O <sub>3</sub>	28.30		3.44e-06	5.0
B <sub>4</sub> C	21.92		6.30e-07	4.5
BaO	26.81		1.45e-06	4.0
BH <sub>3</sub> O <sub>3</sub>	43.09		2.50e-05	5.3
BN	11.03		6.00e-06	6.0
CaO	16.94		9.00e-07	4.0
Cu	7.12		7.43e-07	5.0
Fe	7.11		7.28e-07	4.7
Fe <sub>2</sub> O <sub>3</sub>	30.48		9.00e-07	5.0
Fe <sub>3</sub> O <sub>4</sub>	44.70		5.77e-07	2.0
FeO	12.60		7.11e-07	5.0
H <sub>2</sub> O	18.02	2.00e-04	4.64e-05	7.0
K	45.46		3.10e-05	3.6
K <sub>2</sub> O	40.60		1.75e-06	4.0
KO <sub>2</sub>	33.22		1.29e-06	4.0
Li <sub>2</sub> O	14.81		2.01e-06	4.0
LiCl	20.50		3.16e-06	4.6
LiF	9.84		1.45e-06	4.4
Mg	13.97		2.88e-06	4.0
MgH <sub>2</sub> O <sub>2</sub>	24.71		1.87e-07	4.7
MgO	11.26		7.10e-07	5.0
Mn	7.63		2.73e-06	3.8
MnO	13.31		6.71e-07	3.6
MnO <sub>2</sub>	17.30		5.00e-07	3.5
Mo	9.41		3.76e-07	3.9
MoO <sub>2</sub>	19.77		6.26e-07	5.0
MoO <sub>3</sub>	30.68		7.47e-06	4.0
Na(s)	23.70		1.57e-05	4.0
Na(l)	24.80		1.90e-05	4.0
NaCl	27.00		3.64e-6	4.3
Na <sub>2</sub> O	25.88		9.35e-07	6.0
Ni	6.59		5.42e-07	4.8
NiO	11.20		5.40e-07	3.9
NM	53.54		2.24e-05	4.5
NQ	58.80		6.43e-06	6.9
O <sub>10</sub> P <sub>4</sub>	118.78		1.70e-06	4.0
P	17.02		1.73e-06	4.0
Pb(s)	18.25		2.17e-06	4.9
Pb(l)	19.44		2.80e-06	4.9
PbO <sub>2</sub>	25.51		4.32e-07	4.0
S	15.49		1.96e-06	4.0
SiC	12.46		4.80e-07	3.2
SiO <sub>2</sub> (s)	22.68		3.75e-06	3.8
SiO <sub>2</sub> (l)	23.80		5.00e-06	4.2
Sn	16.31		1.85e-06	5.8
SnO <sub>2</sub>	21.55		8.00e-07	4.0
Ta	10.90		5.17e-07	3.5
Ta <sub>2</sub> O <sub>5</sub>	53.89		4.94e-07	4.0
TaC	13.69		5.50e-07	6.7
Ti	10.64		9.32e-07	3.0
Ti <sub>2</sub> O <sub>3</sub>	31.25		1.38e-06	4.0
TiB <sub>2</sub>	15.50		3.50e-07	3.0
TiC	12.15		4.00e-07	4.5
TiO	12.96		1.29e-06	4.0
TiO <sub>2</sub>	18.75		1.00e-06	4.0
W	9.55		3.22e-07	3.9
WO <sub>2</sub>	17.82		3.35e-07	5.0
Zn	9.16		1.55e-06	5.2
ZnO	14.52		7.23e-07	4.0
Zr	14.05		1.41e-06	4.0
ZrB <sub>2</sub>	18.29		4.80e-07	3.5
ZrO <sub>2</sub>	22.00		9.50e-07	5.5



## APPLICATION TO DETONATION

We now consider how the equation of state described above predicts the detonation behavior of condensed explosives. The overdriven shock Hugoniot of an explosive is an appropriate equation of state test. The overdriven Hugoniot tests the EOS across a broad range of thermodynamic states. The Hugoniot of PETN is shown in Figure 10. We have calculated the Hugoniot with the EXP6 model presented here and also with the JCZS [28] product library. JCZS calculations were performed without liquid water, since the temperatures reached in these simulations were far above the liquid region.



**FIGURE 10: THE SHOCK HUGONIOT OF PETN AS CALCULATED WITH EXP6 (SOLID LINE) AND THE JCZS LIBRARY (DOTTED LINE) VS. EXPERIMENT (ERROR BARS).**

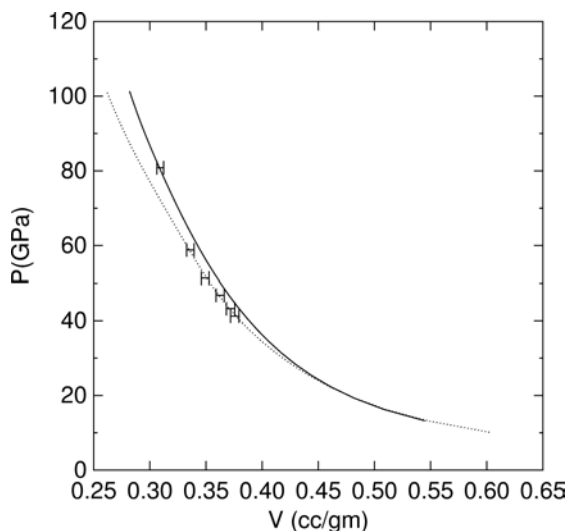
.In Figure 11 we calculate the shock Hugoniot of HMX/TATB (49% HMX, 47% TATB, 4% Estane) to experiment. Good agreement is seen with both product libraries.

We have applied the equation of state to numerous formulations containing the elements C, H, N, and O. We find that the EXP6 equation of state library improves significantly on previous BKW libraries. Its average error in the detonation velocity is

somewhat higher than that of JCZS. EXP6, however, is not fit to any detonation data, whereas many adjustable parameters in JCZS were fit to detonation data.

## CONCLUSION

In the present paper we have derived a numerically efficient and accurate equation of library state for a high pressure exp-6 fluid. The equation of state was based on HMSA integral equation theory, with a correction based on extensive Monte Carlo simulations. We have also shown that our new equation of state can be used to accurately model the properties of molecular fluids and detonation products. The accuracy of the equation of state of polar fluids is significantly enhanced by using a multi-species or cluster representation of the fluid.



**FIGURE 11. THE SHOCK HUGONIOT OF HMX/TATB AS CALCULATED WITH EXP6 (SOLID LINE) AND THE JCZS LIBRARY (DOTTED LINE) VS. EXPERIMENT (ERROR BARS).**

Our ability to model the behavior of shocked fluorocarbons and chlorocarbons helps to unify data that was previously apparently unrelated; the behavior of this class of materials under shocks over 35 GPa are now related to the properties of a small set of simple decomposition products.

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