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# EXTENSION OF THE JCZ PRODUCT SPECIES DATABASE

CONF-980803--

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A database has been created for use with the Jacobs-Cowperthwaite-Zwisler-3 equation-of-state (JCZ3-EOS) to determine thermochemical equilibrium states for energetic materials. The JCZ3-EOS uses the exponential 6 intermolecular potential function to describe interactions between molecules. Product species are characterized by $r^*$, the radius of the minimum pair potential energy, and $\varepsilon/k$, the well depth energy normalized by Boltzmann's constant. These parameters constitute the JCZS (S for Sandia) database describing 750 gases listed in the JANNAF tables and were obtained by using literature values of the Lennard-Jones potential, a corresponding states theory, pure liquid shock Hugoniot data, and fit values to an empirical EOS. Detonation velocities predicted with the JCZS database for a wide variety of explosives are in good agreement with data. Improved predictions of low density explosives is attributed to a better description of molecular interactions at intermediate pressures.

## INTRODUCTION

Determination of product species and associated equations-of-state (EOS) for energetic materials with complex elemental compositions remains a major unsolved problem. A simple EOS model is needed to predict thermochemical behavior of product species for conditions ranging from high pressure detonation states to low pressure ideal conditions. Such an EOS model should be based on physical arguments, rather than excessive curve fittings to a limited set of specific conditions. One such model, the Jacobs-Cowperthwaite-Zwisler-3 EOS[1] (JCZ3-EOS), uses exponential 6 (EXP 6) intermolecular potentials to describe the P-V-T relationship of the gaseous product species resulting from detonation of energetic materials.

The primary disadvantage of using the JCZ3-EOS for equilibrium calculations of energetic materials is that only 20 species have known JCZ3 molecular potential force constants.[3] Realistic thermochemical equilibrium calculations require an EOS with a large species database to encompass all possible product species in a detonation event. In this work, a new database for use with the JCZ3-EOS has been developed. This new database will be referred to as the JCZS (where the S refers to Sandia) EOS database. A methodology has been established to increase the size of the JCZS database to approximately 750 gas species. Among these species are all the gases in the JANNAF[2] database. For each species, force constants are obtained to parameterize an EXP 6 potential function. One technique of obtaining these constants relates Lennard-Jones (LJ) potential function parameters to the EXP 6 potential function parameters. Another technique uses a corresponding states (CS) theory to obtain the unknown molecular potential force constants. This method was used by Ross and Ree[4] for simple molecules. The remaining constants are obtained in the present work from a series of correlation and estimation techniques that are presented later. In addition to these techniques, a few important species constants were obtained by matching liquid shock Hugoniot data.

Hugoniot calculations with the JCZS-EOS are shown to reasonably replicate Hugoniot data for various molecules. Various detonation and cylinder expansion calculations using the JCZS-EOS also compare favorably to experimental data. The JCZS-EOS is shown to predict high pressure states from 500 kbar to expansion states near atmospheric pressure.

## JCZ3-EOS BACKGROUND

The JCZ3-EOS uses an equation based on P-V-T relationships similar to the Mie-Grüneisen EOS:[5]

$$P = \frac{G(V,T,\varphi)nRT}{V} + P_o(V,\varphi) \qquad (1)$$

where $P$, $n$, $R$, $T$, and $V$ represent the pressure, number of moles, universal gas constant, and volume, respectively. The form of the Grüneisen function, $G$, and the volume dependent internal pressure function, $P_o$, is documented (e.g., Ref. 1). Both $P_0$ and $G$ are composed of the EXP 6 potential function:

$$\varphi = \varepsilon\left(\frac{6}{\eta-6}\right)\exp\left[\eta\left(1-\frac{r}{r^*}\right)\right] - \varepsilon\left(\frac{\eta}{\eta-6}\right)\left(\frac{r^*}{r}\right)^6 \qquad (2)$$

where $\varepsilon$ is the well depth for the pair potential and $r^*$ is the radius of the minimum pair potential energy. The potential function is composed of a repulsive term which dominates at small values of $r$ and an attractive term which dominates at large values of $r$. The molecular force parameters $\varepsilon$, $\eta$, and $r^*$ are required for each product species. The force constant, $\varepsilon$, is often given as $\varepsilon/k$, where $k$ is Boltzmann's constant. The explicit dependence of the Grüneisen function, $G$, and the internal pressure function, $P_o$, on the potential function, $\varphi$, is not obvious and the interested reader is referred to Ref. 1 for more information. Hobbs and Baer[6] have shown that the

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* Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-ACO4-94AL85000.

investigators using $\eta = 13$ give the best agreement between measured and predicted liquid shock Hugoniots than investigators using other values of $\eta$. In the present study, $\eta$ is assumed to be 13 for all molecules, leaving $r^*$ and $\varepsilon/k$ to be determined for each molecule.

## LENNARD-JONES POTENTIAL PARAMETERS

The force constants for the EXP 6 function are directly related to the force constants for the LJ potential function. The potential well depth, $\varepsilon/k$, is the same for both the LJ and EXP 6 potential function. The EXP 6 characteristic radius, $r$, can be obtained from the LJ characteristic radius, $\sigma$, as follows:[3,7] $r^* = \sigma \cdot 2^{1/6}$. About 200 of the 750 species listed in the JANNAF tables have LJ parameters. McGee et al.[3] give the references for the LJ parameters used in the present study.

## CORRESPONDING STATES ESTIMATES

The corresponding states assumption, as originally proposed by van der Waals,[8] is that the behavior of all substances is the same at the same reduced temperature ($T/T_c$), pressure ($P/P_c$), and volume ($V/V_c$). Pitzer[9] derived van der Waals' corresponding states principle by assuming 1) classical statistics, 2) spherically symmetric nonpolar molecules, 3) similar molecular vibrations for both liquid and gaseous states, and 4) conformal molecules. The conformal assumption implies that the functionality of the intermolecular potential is the same, although the force constants vary from molecule-to-molecule. Ross and Ree[10] used the corresponding states assumption to determine force constants for simple molecules as follows:

$$r^* = r^*_{ar} \,(V_c/V_{c,ar})^{1/3};\ \varepsilon/k = \varepsilon_{ar}/k \,(T_c/T_{c,ar}) \qquad (3)$$

where $V_c$ and $T_c$ are critical volume and critical temperature, respectively. The subscript *ar* refers to argon as the corresponding molecule. The values of $r^*_{ar}$, $\varepsilon_{ar}/k$, $V_{c,ar}$ and $T_{c,ar}$ used in the present study are 3.85 Å and 122 K, 74.9 cm³/mol, and 150.8 K, respectively.

Wilding and Rowley[11] obtained better predictions of thermophysical properties for nonspherical and polar molecules by performing Taylor series expansion's about simple fluids with respect to geometry and polarity. Hobbs and Baer[6] used these techniques with some success to determine EXP 6 force parameters for nonspherical and/or polar molecules. In this study, Eq. (3) is used to determine force parameters when critical properties are available.

Unfortunately, not all chemical species have critical properties. Critical properties of unstable species are rare, and do not exist for free radical species. For heavy metals and many ionic compounds, reported values are typically calculated with questionable accuracy. About 150 of the 750 gas species listed in the JANNAF tables have both the critical temperature and critical volume. Of these 150 species, 93 also have LJ parameters. Thus, approximately 250 of the 750 JANNAF species can be obtained using either the corresponding states (CS) technique or can be estimated with known LJ constants.[3]

## MOLECULAR VOLUME CORRELATION

The EXP 6 parameters for the remaining 500 gas species in the JANNAF tables were obtained by correlating the approach radius, as determined from the CS theory described in the preceding section, to molecular volume. Hobbs and Baer[12,13] determined atomic coordinates for the 750 JANNAF gas species in order to determine BKW covolumes. These atomic coordinates have been used to calculate molecular volume. Molecular volume is calculated by representing molecules as a collection of atoms with atomic radius equal to van der Waals radius. When atoms overlap in a molecule, the volume is only represented once.

Figure 1 shows a strong correlation between the cubed root of the molecular volume and the radius of the minimum pair potential energy, $r^*$, for 93 species calculated with critical volumes. Most of the species that deviate farthest from the linear correlation in Figure 1.A are monatomic and are plotted as open symbols. The monatomic species were eliminated from the least squares fit to obtain an improved correlation. The linear correlation using the polyatomic species in Figure 1.A can be used to estimate r* from molecular volumes:

$$r^* = 1.19\,(\mathit{Molecular\ Volume})^{1/3} + 0.68 \qquad (4)$$

The corrected LJ characteristic diameters, $\sigma{\cdot}2^{1/6}$, are also adequately correlated to molecular volume as shown in Figure 1.B. Again, most of the scatter in Figure 1.B is attributed to monatomic species.

A similar correlation for $\varepsilon/k$ with molecular volume was unsuccessfully sought. Electron density calculated from the molecular volume did not correlate to the

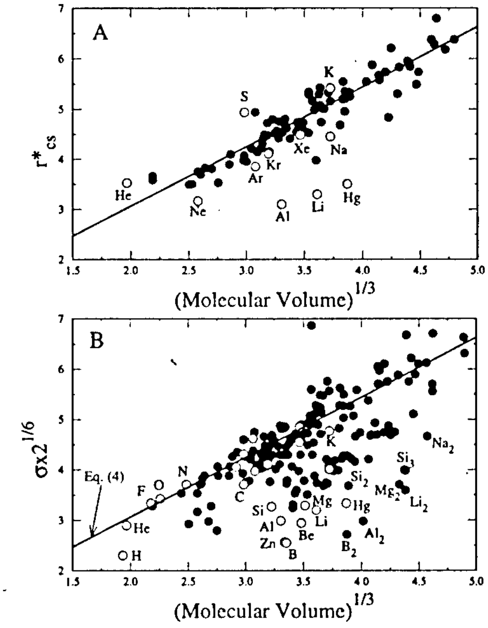

FIGURE 1. CORRELATION BETWEEN MOLECULAR VOLUME AND A) $r^*_{CS}$ FOR 95 SPECIES AND B) $\sigma{\cdot}2^{1/6}$ FOR 195 SPECIES. THE LINEAR CORRELATION IN A IS LABELED EQ. (4) IN B.

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potential well depth determined with the CS theory or with the literature LJ values. An alternative method for determining $\varepsilon/k$ was developed. This method involves choosing $r^*$ based on Eq. (4) and determining $\varepsilon/k$ by matching high pressure, pure species isentropes calculated with the BKWS-EOS, which is described subsequently.

## BKW DATABASES

The Becker-Kistiakowsky-Wilson equation-of-state (BKW-EOS) is used extensively to calculate detonation properties:

$$\frac{PV}{RT} = 1 + Xe^{\beta X} \text{ with } X = \frac{\kappa \sum n_i k_i}{V(T+\theta)^{\alpha}} \qquad (5)$$

where P, V, R, T, and $n_i$ represent pressure, molar gas volume, gas constant, absolute temperature, and mole fraction of the $i^{th}$ gaseous component, respectively. The summation extends over all components of the gaseous mixture. The covolume factors, $k_i$, represent excluded volume. The parameters $\alpha$, $\beta$, $\kappa$, and $\theta$ are empirical constants. Typically, the parameters $\alpha$, $\beta$, $\kappa$, and $\theta$ are *adjusted to fit measured detonation properties.*

Two different parameterizations of the BKW-EOS are in use: BKWC[14] and BKWS[13]. The C and S represent CHEETAH[14] parameterization and Sandia parameterization, respectively. In the BKWS parameterization, only $\beta$, $\kappa$, $\theta$ were optimized to match detonation properties, with covolumes based on physical arguments. In the BKWC parameterization, 31 parameters, including gas covolumes, $k_i$, were optimized to match detonation properties.

With the large number of adjustable parameters, the BKWC-EOS database was used to improve the prediction of detonation velocity and pressure over the BKWS by about 2% for energetic materials composed of C, H, N, and O. However, improvement in detonation property prediction may not be justified when experimental variability (5-10%) is considered. Also, the BKWC optimization was not constrained to consider measured properties such as H and O van der Waal radii. The BKWC optimized covolume of $H_2$ is larger than the covolume of $H_2O$, which is physically impossible.

The BKWC database is composed of only 23 gaseous products and 2 condensed products, while the BKWS database is composed of 750 gaseous products and 400 condensed reaction products. The BKWS database is used in the present study to obtain the remaining 500 $\varepsilon/k$ values where critical properties or LJ data are unavailable.

## BKWS-EOS ESTIMATES OF $\varepsilon/k$

Because the BKWS database provides acceptable results for high pressure detonation states and the ideal gas law provides accurate results for low pressure states, $\varepsilon/k$ can be estimated by matching isentropes at high pressure and low pressure states using the calculated $r^*$ from molecular volume data. In this study, the standard temperature and pressure (298 K and 1 atm) isentrope was chosen for fitting $\varepsilon/k$. Figure 2 shows the 298 K and 3,000 K isentrope for formyl fluoride. Parameters for the JCZS-EOS were chosen to be $r^* = 4.50$ Å and $\varepsilon/k = 150$ K using Eq. (4) for $r^*$ and fitting $\varepsilon/k$ to match the high pressure 298 K isentrope. Agreement between the JCZS and BKWS predictions at high pressure for both isentropes indicates that fitting the 298 K isentrope is sufficient to match isentropes at significantly different conditions.

Not all values of $r^*$ predicted with Eq. (4) were adequate to match the BKWS isentropes. For such species, $r^*$ was slightly adjusted to match the BKWS isentrope.[3] For such cases, Eq. (4) was used as an initial estimate of $r^*$, and both $r^*$ and $\varepsilon/k$ were fit to the BKWS isentrope. The force parameters for these "specially fit" molecules are not unique, and various combinations of parameters will give an adequate match to the BKWS isentrope.

Caution must be used when using the JCZS-EOS for molecules with $\varepsilon/k$ estimated from BKWS predictions. The parameters for these molecules are only as good as the BKWS predictions. Because the BKWS-EOS was calibrated at high pressures with explosives composed primarily of C, H, N, O, F, and Cl, species with substantially different atomic compositions may be in error. One method to determine the accuracy of the BKWS and JCZS predictions would be to compare Hugoniot predictions to pure liquid shock Hugoniot data.

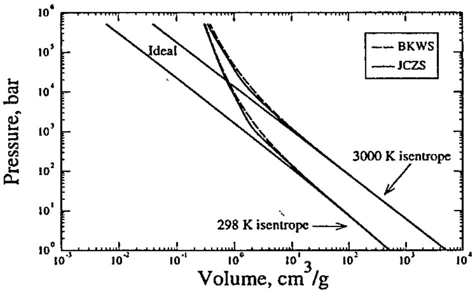

**FIGURE 2. 298 K AND 3000 K FORMYL FLUORIDE (CHFO) ISENTROPE PREDICTIONS USING THE IDEAL GAS EOS, BKWS-EOS, AND THE JCZS-EOS.**

## PURE LIQUID SHOCK HUGONIOT DATA

The accuracy of an EOS can be tested by comparing predictions to data of pure liquid shock Hugoniots. Figure 3 shows a comparison between liquid shock Hugoniot data and predicted liquid shock Hugoniot using the JCZS-EOS for water, hydrogen, carbon tetrachloride, trichloromethane, carbon dioxide, oxygen, argon, methanol, ammonia, and methane. BKWS and BKWC predictions are shown for water and hydrogen in Figure 4.A and 4.B. JCZS parameters are shaded in Table 1. The JCZS parameters can be used to predict liquid shock Hugoniot data reasonably well. The BKWC predictions for $H_2O$ and $H_2$ are inadequate.

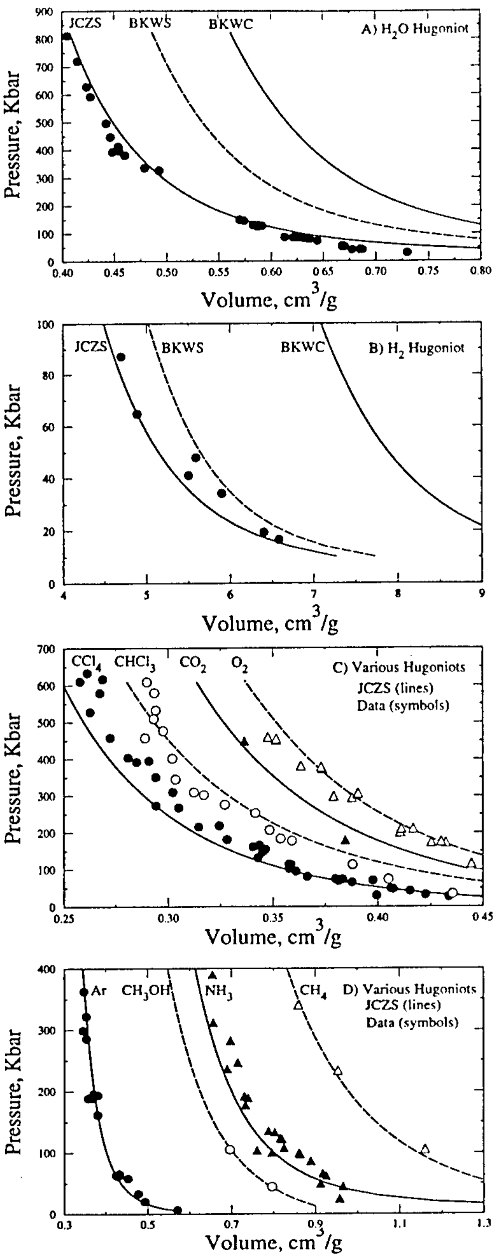

FIGURE 3 PREDICTED (LINES) AND MEASURED (SYMBOLS) HUGONIOTS FOR VARIOUS SPECIES. THE PREDICTIONS IN C AND D WERE MADE WITH THE JCZS DATABASE. SOURCES FOR THE DATA ARE GIVEN IN REFERENCE 3.

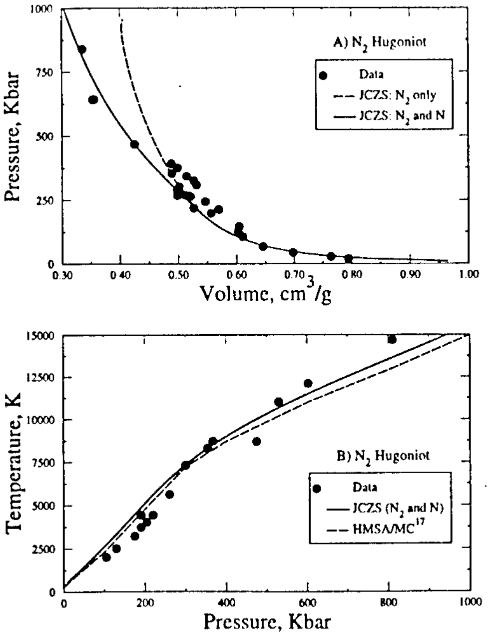

FIGURE 4. COMPARISON OF MEASURED (SYMBOLS) AND PREDICTED (LINES) A) PRESSURE AND B) TEMPERATURE ALONG THE LIQUID NITROGEN HUGONIOT. SOURCE OF DATA GIVEN IN REFERENCE 17.

Some caution must be used when using pure liquid shock Hugoniot data since the species may break into smaller fragments at elevated temperatures and pressures. Sheffield[15] suggests that if the Hugoniot deviates from the "universal" liquid Hugoniot,[16] then the species is likely breaking into smaller fragments. For example, Figure 4 shows the Hugoniot for liquid nitrogen with two predictions from the JCZS database by using $N_2$ as the sole reaction product and by using both N and $N_2$ as reaction products. The heat capacity for atomic N and $N_2$ were taken from Reference 17 and are thought to be good to 15,000 K. At approximately 300 Kbars and 7500 K, the $N_2$ breaks into N. Fried and Howard[17] used the hypernetted-mean spherical approximation with Monte Carlo simulations (HMSA-MC) to calculate the Hugoniot for $N_2$. The HMSA-MC pressure calculations were essentially identical to the JCZS predictions and are not shown in Figure 4. However, the HMSA-MC prediction of temperature along the Hugoniot is shown in Figure 4.B and are slightly different than the JCZS predictions.

## DAKOTA OPTIMIZATION

The JCZS parameters, for the major species shown in Table 1, were slightly adjusted using constrained optimization to obtain optimal agreement with detonation velocity measurements. The source of the initial $r^*$ values were either from the LJ values (lj), isentrope fit values (fit), or the corresponding states values (cs) and is labeled in the superscript of $r^*$ in Table 1. During the fitting process, $r^*$ was found to be more sensitive than $\varepsilon/k$ when fitting BKWS isentropes. The $\varepsilon/k$ values were left as the original lj, fit, or cs values.

CHEETAH,[14] a C version of the FORTRAN equilibrium code TIGER,[18] was chosen as the analysis code to solve the CJ detonation problem for the 32 explosives used to parameterize the BKWC database.[14] An objective function was minimized using DAKOTA[19] (Design Analysis Kit for OpTimizAtion). The objective function was the root mean square error (*rms*) between calculated ($D_{i,c}$) and measured ($D_{i,c}$) detonation velocities:

$$rms = \sqrt{\frac{1}{N}\sum_{i=1}^{N}\left(\frac{D_{i,m}-D_{i,c}}{D_{i,m}}\right)^2} \qquad (6)$$

Table 1. Subset of parameters used in JCZS database*

| Gas | $r^*$ | $\varepsilon/k$ | Gas | $r^*$ | $\varepsilon/k$ |
|---|---|---|---|---|---|
| $CClF_3$ | $4.71^{lj}$ | 244 | CO | $3.88^{lj}$ | 98 |
| CClFO | $5.06^{fit}$ | 300 | $CO_2$ | $4.22^{lj}$ | 227 |
| $CCl_4$ | $5.98^{cs}$ | 631 | $C_2F_3N$ | $5.86^{cs}$ | 252 |
| $CF_2$ | $4.87^{lj}$ | 94.2 | $C_2F_4$ | $6.03^{cs}$ | 2.48 |
| $CF_2O$ | $5.59^{cs}$ | 240 | $C_2F_6$ | $7.36^{cs}$ | 237 |
| $CF_3$ | $5.65^{lj}$ | 121 | $C_2H_4$ | $4.50^{lj}$ | 281 |
| $CF_4$ | $6.40^{lj}$ | 134 | $C_2H_6$ | $4.01^{lj}$ | 252 |
| $CF_4O$ | $6.40^{fit}$ | 200 | $C_3O_2$ | $5.22^{cs}$ | 361 |
| CFO | $4.72^{fit}$ | 200 | ClH | $3.35^{cs}$ | 263 |
| $CHCl_3$ | $6.05^{lj}$ | 340 | FH | $3.70^{lj}$ | 330 |
| $CH_2ClF$ | $4.86^{lj}$ | 318 | H | $2.00^{lj}$ | 145 |
| $CH_2F_2$ | $4.36^{lj}$ | 318 | $H_2$ | $2.85^{lj}$ | 38 |
| $CH_2O$ | $4.40^{cs}$ | 330 | $H_2O$ | $3.06^{lj}$ | 356 |
| $CH_2O_2$ | $4.46^{fit}$ | 200 | $H_3N$ | $3.33^{lj}$ | 481 |
| $CH_3$ | $4.15^{lj}$ | 144 | HO | $3.29^{lj}$ | 80 |
| $CH_3F$ | $4.95^{cs}$ | 256 | N | $2.25^{fit}$ | 71 |
| $CH_3OH$ | $4.23^{lj}$ | 482 | $N_2$ | $4.00^{cs}$ | 102 |
| $CH_4$ | $4.23^{cs}$ | 154 | $N_2O$ | $5.18^{lj}$ | 232 |
| $CHF_3$ | $5.71^{cs}$ | 242 | NO | $4.15^{lj}$ | 117 |
| CHFO | $4.50^{fit}$ | 150 | $NO_2$ | $4.77^{cs}$ | 349 |
| CHNO | $4.80^{lj}$ | 232 | $O_2$ | $3.86^{cs}$ | 125 |
| CNO | $4.89^{lj}$ | 232 | Ar | $3.85^{cs}$ | 122 |

* Parameters used in Hugoniot calculations are shaded.

where the subscripts *i, m,* and *c* represent the $i^{th}$ explosive, measured, and calculated, respectively. *N* represents the number of detonation velocity measurements, 32.

Table 2 shows the overall percent RMS error for predicted detonation velocity and detonation pressure using the BKWS, BKWC, and two JCZS databases. The first JCZS database only considered the 44 species listed in Table 1 for the detonation calculations. The second JCZS predictions considered all 132 species in the JANNAF tables composed of species containing C, H, N, O, Cl, or F. Since the RMS percent errors for both JCZS databases are similar, the smaller JCZS data set is probably sufficient for energetic materials composed of C, H, N, O, Cl, or F.

Table 2 also shows the overall percent RMS error for predicted detonation velocities and detonation pressure of the explosives in Reference 14 excluding the nonideal explosives containing TATB (TATB, RX26, and LX17) and HNB. The nonideal explosives may not reach complete equilibrium and probably should not be considered in the RMS percent error calculation. Excluding nonideal explosives should make the RMS percent error smaller as shown in Table 2 for the JCZS databases. Note that the RMS percent error using the empirical BKWC database increases when nonideal explosives are excluded from the performance database.

## VALIDATION OF THE JCZS-EOS DATABASE

Detonation velocity measurements are probably good to within a few percent.[20] Detonation pressure measurements are probably good to within 20%.[21] Similar to detonation pressure measurements, detonation temperature measurements are probably good to within 20%. Detonation temperatures are measured by the brightness of the detonation front interacting with a detector. Void free systems such as liquid explosives or single crystal systems are believed to be more accurate. Measurements in porous systems include the effects of shocked air or perhaps low-density explosive material jetting into the voids rather than the brightness of the pure detonation products. Comparisons of measured detonation temperatures to calculated detonation temperatures should be done with caution.

Table 2. RMS percent errors - optimization

| EOS - # of gases | $D^*$, % | $D^{\dagger}$, % | $P^*$, % | $P^{\dagger}$, % |
|---|---|---|---|---|
| BKWS - 132 | 5.1 | 5.2 | 9.5 | 9.5 |
| BKWC - 22 | 2.3 | 2.5 | 8.2 | 8.2 |
| JCZS - 44 | 2.6 | 2.1 | 8.5 | 8.1 |
| JCZS - 132 | 2.6 | 2.2 | 8.3 | 8.0 |

*CHNOCLF explosives in Reference 14 (includes nonideal explosives).

†CHNOCLF explosives in Reference 14 excluding the nonideal explosives containing TATB and HNB.

In the present work, two explosive performance databases are used to evaluate the JCZS-EOS database: the LLNL performance database[14] (as used in Table 2) and the SNL performance database.[13] Explosives in the LLNL performance database consist of 32 detonation velocity measurements and 31 detonation pressure measurements. Since the LLNL database was used to optimize some of the *r** values in Table 1, a different set of explosives is needed to validate the JCZS-EOS database. Explosives in the SNL performance database consist of 111 detonation velocities, 67 detonation pressures, and 14 detonation temperature measurements for explosives which contain C, H, N, O, Cl, and F at various densities. The SNL performance database was used to validate the prediction of detonation velocity, pressure, and temperature. Additionally, the LLNL performance database was used to examine total energy of detonation and expansion energies since these parameters were not considered in the optimization procedure

Another method of evaluating the JCZS-EOS database is to compare measured detonation velocity of gases at high initial pressures to predictions. The detonation velocity of various gases at high initial pressures were measured by Bauer[22] and evaluated by Schmitt.[23]

## EXPLOSIVE PERFORMANCE

A comparison of JCZS predictions to measured detonation velocities and pressures are given in Figure 5 for the SNL performance database. Table 3 shows the overall percent RMS error in predicting detonation velocity, pressure, and temperature using the BKWS-EOS, BKWC-EOS, JCZS-small, and JCZS-large databases. The better agreement with data using the JCZS-EOS database is consistent with the results from the LLNL performance database given in Table 2. The overall percent RMS error in the predicted detonation temperatures is higher for the JCZS-EOS than the BKWC-EOS. However, the predicted RMS error is within the expected accuracy of the optical temperature

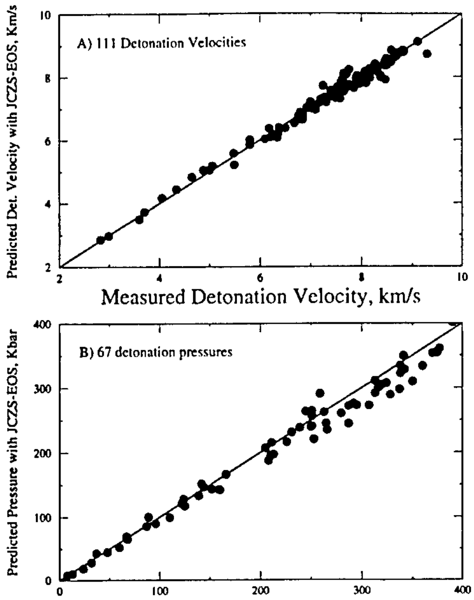

FIGURE 5. COMPARISON BETWEEN PREDICTED AND EXPERIMENTAL DETONATION A) VELOCITIES AND B) PRESSURES. SOURCE OF DATA IN REFERENCE 13.

Table 3. RMS percent errors - validation

| EOS-gases | D*,% | D$^\dagger$,% | P*,% | P$^\dagger$,% | T*,% |
|---|---|---|---|---|---|
| BKWS-132 | 5.1 | 5.1 | 10.5 | 10.5 | 4.2 |
| BKWC-22 | 3.0 | 3.1 | 7.6 | 7.6 | 4.6 |
| JCZS-44 | 2.3 | 2.0 | 8.3 | 8.2 | 9.0 |
| JCZS-132 | 2.3 | 2.0 | 8.2 | 8.1 | 8.7 |

*CHNOCLF explosives in Reference 13 (includes nonideal explosives).

$^\dagger$CHNOCLF explosives in Reference 13 excluding the nonideal explosives containing TATB and HNB.

measurements which may be as high as 20%. The JCZS predicted detonation temperatures are similar to measured detonation temperatures for homogeneous explosives. For example, the RMS error for the NM detonation temperature is 0.3% for the JCZS-EOS compared to 6.8% for the BKWC-EOS.

## EXPANSION STATES

Table 4 gives the percent RMS error for the total energy of detonation labeled as E and the expansion energies at relative volumes of 2.2, 4.1, and 6.5 labeled as $E_{2.2}$, $E_{4.1}$, and $E_{6.5}$. The JCZS prediction of the total energy of detonation is comparable to the BKWC predictions and better than the BKWS predictions. The expansion energies predicted with the JCZS-EOS were within 2% of the BKWC predictions which were calibrated to match the experimental measurements. A better comparison of the expansion energy would be to compare cylinder wall velocities as predicted with a shock physics code.

Table 4. RMS percent errors – validation*

| Database | E, % | $E_{2.2}$, % | $E_{4.1}$, % | $E_{6.5}$, % |
|---|---|---|---|---|
| BKWS | 8.0 | 10.8 | 9.1 | 7.4 |
| BKWC | 6.5 | 5.8 | 5.2 | 4.9 |
| JCZS | 6.5 | 8.0 | 6.9 | 7.0 |

*CHNOCLF explosives in Reference 14 excluding the nonideal explosives containing TATB and HNB.

## GAS DETONATIONS AT HIGH INITIAL PRESSURES

Figure 6 shows predicted (lines) and measured (symbols) detonation velocities of various gases at different elevated initial pressures The compositions of the gas mixtures are also shown in Figure 6. The BKWC database does not consider H and OH as reaction products and cannot adequately predict the detonation velocities for the hydrogen oxygen system as shown in Figure 6.A. The JCZS-EOS database adequately predicts the detonation velocity for all of the gas mixtures in Figure 6.

## SUMMARY AND CONCLUSIONS

The JCZ3 product species library has been expanded to include approximately 750 gas-phase products. The force constants for this library, $r^*$ and $\varepsilon/k$, have been obtained by using pure liquid shock Hugoniot data; by correcting the LJ characteristic approach radii to conform to the mathematical form of the EXP 6 potential function and using literature values for the potential well depth; by using corresponding states theory to calculate the EXP 6 force constants; and by using a semi-empirical formula based on the molecular volume to determine the approach radii and obtaining the potential well depth by matching isentropes with the BKWS-EOS. Some of the EXP 6 parameters were slightly adjusted to predict optimal detonation velocities using the optimization toolkit, DAKOTA.

Detonation simulations have been performed with the JCZS-EOS database and have displayed reasonable agreement with experimental results for detonation velocity, detonation pressure, and detonation temperature. Predicted detonation velocities with the JCZS-EOS are shown to be within 2% of measured values for many explosives. The predicted velocities with the BKWC-EOS for the same set of explosives were shown to be within 3%. The detonation pressure, temperature, and expansion states were all shown to be within 10% of reported values. The JCZS-EOS is shown to predict low density explosives with the same accuracy as high density explosives. The better agreement at these intermediate states is attributed to modeling molecular interactions which is not done in the semi-empirical BKW-EOS.

The JCZ3-EOS with the improved product species database has been shown to adequately predict detonation states, as well as expansion states, for various explosives. Better agreement between measured detonation performance and predicted detonation performance for gases at elevated initial pressures is attributed to a larger product species database with an adequate physical description of molecular interactions. Such predictions support the hypothesis that improved predictions of explosive performance can be realized by using a more fundamental EOS with an adequate number of product species, rather than merely increasing the number of fitting parameters used by empirical based equations-of-states.

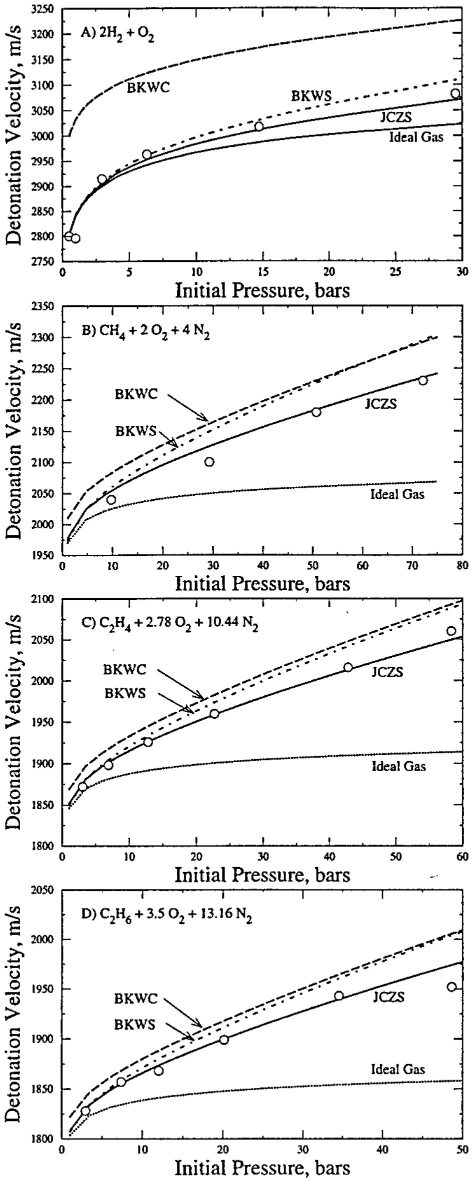

**FIGURE 6. PREDICTED (LINES) AND MEASURED[22] (SYMBOLS) DETONATION VELOCITIES FOR GAS MIXTURES AT ELEVATED INITIAL PRESSURES.**

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Report Number (14) SAND--97-1938C
CONF-980803--

Publ. Date (11) 1998
Sponsor Code (18) DOE/DP, XF
UC Category (19) UC-700, DOE/ER

ph