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EQUILIBRIUM CALCULATIONS OF FIREWORK MIXTURES

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ABSTRACT

Thermochemical equilibrium calculations have been used to calculate detonation conditions for typical firework components including three report charges, two display charges, and black powder which is used as a fuse or launch charge. Calculations were performed with a modified version of the TIGER code¹ which allows calculations with 900 gaseous and 600 condensed product species at high pressure.² The detonation calculations presented in this paper are thought to be the first report on the theoretical study of firework detonation. Measured velocities for two report charges are available and compare favorably to predicted detonation velocities. However, the measured velocities may not be true detonation velocities. Fast deflagration rather than an ideal detonation occurs when reactants contain significant amounts of slow reacting constituents such as aluminum or titanium. Despite such uncertainties in reacting pyrotechnics, the detonation calculations do show the complex nature of condensed phase formation at elevated pressures and give an upper bound for measured velocities.

INTRODUCTION

Determination of product species, equations-of-state (EOS), and thermochemical properties of energetic materials remains a major unsolved problem. The thermochemical properties of pyrotechnics are difficult to calculate at high pressures due to complex compositions which produce various condensed-phases. For example, the JANNAF tables³ contain 33 gas-phase species and 24 condensed-phase species composed of Al, Cl, K, O, or Ti, typical components in a report charge. In this work, the BKWS-EOS is used to calculate detonation properties of pyrotechnics typically used in firework mixtures.

An equation-of-state extensively utilized to calculate detonation properties is the Becker-Kistiakowsky-Wilson equation-of-state (BKW-EOS). Mader⁴ gives the historical background and molecular covolumes for the BKW-EOS. A form of the EOS used in the present study is attributed to Cowan and Fickett:⁵

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

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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 , representing excluded volume, are discussed subsequently. The parameters α , β , κ , and θ are empirical constants. The quantity θ was added to the equation to prevent P from approaching infinity as T approaches zero.⁴ Typically, the parameters α , β , κ , θ , and k_i are adjusted to fit measured detonation properties. Three different parameterizations of the BKW-EOS are in use: BKWC,⁶ BKWR,⁷ and BKWS.² The C, R, and S represent CHEETAH reparameterization, Finger et. al.⁷ Reparameterization, and Sandia reparameterization, respectively.

1. BKWR-EOS

Parameters optimized in the BKWR-EOS included three BKW constants (β , κ , and θ) and 10 covolumes. The constants were calibrated using 10 measured detonation velocities (D), 10 measured detonation pressures (P), and 4 measured detonation temperatures (T). The BKWR-EOS produces adequate detonation velocities and pressures. However, the predicted detonation temperatures are about a thousand degrees too low and the energies of detonation are uniformly about 10% too high.⁸ To correct for these deficiencies, BKWR energies are corrected by normalizing with 1.62 g/cc PETN as a standard. The BKWR-EOS (13 gas and 1 condensed species) is only applicable to energetic materials consisting of C, H, N, O, and F.

2. BKWS-EOS

Parameters optimized in the BKWS-EOS only include the three BKW constants (β , κ , and θ). Unlike the BKWR-EOS and BKWC-EOS, covolumes used in the BKWS-EOS were assumed to be invariant and based on the molecular structure of the product species. Covolumes were obtained using measured van der Waal radii, bond lengths, and bond angles. The three BKW constants were calibrated using a density weighted cost function comprised of 103, 64, and 14 D , P , and T measurements, respectively. The BKWS-EOS predicts higher detonation temperatures leading to lower detonation energies allowing calculated energies of detonation to be used without correction. Since covolumes are not used as adjustable constants, the BKWS-EOS can be applied to a large number of product species. Currently the BKWS library considers approximately 900 gaseous products and 600 condensed reaction products found in the JANNAF tables³ and can be used for pyrotechnic mixtures.

A thermal-elastic equation-of-state¹ was used for condensed reaction products. However, thermal expansion and compressibility data were not available for all 600 condensed species. In the present study, most condensed phase species were assumed to be incompressible, although temperature and pressure dependent compressibility can be easily added when such information becomes available. Condensed Al , AlN , Al_2O_3 , Al_4C_3 , C and H_2O were included as compressible species.

3. BKWC-EOS

The success of the BKWS-EOS prompted Fried et al.⁶ to reoptimize the BKW parameters, including covolumes, freeze-out temperature, and condensed phase compressibility constants using a smaller product species database (23 gaseous products and 2 condensed products) determined from major species predicted using the BKWS-EOS. Parameters optimized in the BKWC-EOS include four BKW constants (a , β , κ , and θ), the freezing temperature used in cylinder expansion (T_f), three parameters in the condensed-phase carbon EOS (V_o , a , and b), and 23 covolumes. The 31 BKW constants were calibrated using an estimated error weighted cost function comprised of 32, 30, and 132 D , P , and expansion energies, respectively. With the large number of adjustable parameters, the BKWC-EOS was used to improve the prediction of detonation velocity and pressure over BKWS by about 1% for energetic materials composed of C, H, N, and O. However, improvement in detonation property prediction is superfluous when experimental variability (5-10%) is considered. Also, the BKWC optimization was not constrained to consider measured properties such

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as H and O van der Waal radii. The optimized covolume of H_2 became larger than H_2O in the BKWC-EOS which is physically impossible. Furthermore, with only a small set of product species, the BKWC-EOS is not applicable to pyrotechnic mixtures. Thus the BKWS-EOS was used for the calculations in the current paper. Reactant formation enthalpy and BKW covolume values can be found in Refs. 9 and 10, respectively.

REPORT CHARGES

1. $Ti/Al/KClO_4$ (15/15/70 Weight Percent)

Predicted and experimental detonation velocities are shown to be in reasonable agreement in Fig. 1 for the report charge $Ti/Al/KClO_4$ (15/15/70 mass percent). The effect of condensed-phase chemistry is pronounced at low densities. For example, detonation pressure, temperature, gas-phase and condense-phase yields for the $Ti/Al/KClO_4$ system are also shown in Fig. 1. The abrupt change in detonation properties at low density is caused by the formation of liquid potassium chloride which subsequently reduces the gas yield.

2. $Al/KClO_4$ (20/80 Weight Percent)

Predicted detonation properties including yields are shown in Fig. 2 for a report charge consisting of $Al/KClO_4$ (20/80 by weight). Hatanaka et al.¹² measured velocities around 1800-1900 m/s for this mixture as shown in Fig. 3 using a 3.57 cm diameter 20 cm long tube. Details on the experiment can be found in Ref. 12. The lines in Fig. 3 are drawn through the data points and are not predictions. A steady velocity was not obtained for the two initial densities as shown in Fig. 3.A. The 50 g booster may have overdriven the system although such conclusions are unsupported since no sound speed measurements have been determined for the report charge. Diffusion limited reactions with extended reaction zones make detonation velocity measurements difficult. In fact, high metal loading may result in fast deflagration rather than detonation for most pyrotechnics. A fast deflagration may be thought of as a nonideal detonation or nonequilibrium detonation. Despite uncertainties in detonation of pyrotechnic materials, the equilibrium calculations give a bounding value for detonation velocities and give insight into probable high pressure product compositions.

3. $Al/KClO_4/S$ (21.4/71.4/7.1 Weight Percent)

The effects of adding a burn modifier, sulfur, to the previously calculated report charge are shown in Fig. 4 for a 21.4/71.4/7.1 by weight mixture of $Al/KClO_4/S$. Experimental velocities (~ 2000 m/s) as shown in Fig. 3.B are in agreement with predicted detonation velocities (~ 2000 m/s). Primarily, the sulfur reacts with the excess oxygen to form SO and SO_2 which causes the temperature to increase slightly leading to increased detonation pressure and velocity.

Fig. 1. Predicted detonation A) velocity with measurements, pressure, and temperature, B) product yield for a mixture of $Ti/Al/KClO_4$ (15/15/70 by weight). The yield is given in g-moles per kilogram of reactant ($Ti/Al/KClO_4$).

Fig. 2. Predicted detonation A) velocity, pressure, and temperature and B) gas yields and condensed yields for a mixture of Al/KClO₄ (20/80 by weight). The yield is given in g-moles per kilogram of reactant (Al/KClO₄).

Fig. 3. Measured velocities¹² obtained in a 3.57 cm diameter 20 cm long tube containing a mixture of A) 20/80 weight percent Al/KClO₄ and B) 21.4/71.4/7.1 weight percent Al/KClO₄/S.

Fig. 4. Predicted detonation A) velocity, pressure, and temperature and B) gas yields and condensed yields for a mixture of Al/KClO₄/S (21.4/71.4/7.1 by weight). The yield is given in g-moles per kilogram of reactant (Al/KClO₄/S).

DISPLAY CHARGES

1. Ba(NO₃)₂/S/Al/KClO₃ (8/8/46/38 Weight Percent) Green Display

The detonation and expansion characteristics of a typical 1 g/cc green display composition consisting of 8/8/46/38 weight percent Ba(NO₃)₂/S/Al/KClO₃ are shown in Fig. 5.A and 5.B. The detonation velocity, pressure and temperature were calculated to be 460 m/s, 690 bar and 3500 K, respectively. The total gas yield and various condensed-phase product yields are also shown in Fig. 5.B. The gas phase consists of primarily of KCl, N₂, AlS, S, K₂, S₂, K, AlCl, and Al₂O. These calculations were performed assuming 57 possible gas-species and 27 possible condensed-phase species. The BaS solid yield increases during the expansion.

Fig. 5. Predicted detonation and expansion properties for $\text{Ba}(\text{NO}_3)_2/\text{S}/\text{Al}/\text{KClO}_3$ (8/8/46/38 weight percent) green display (shown in A and B), $\text{SrCO}_3/\text{S}/\text{KClO}_4$ (25/15/60 weight percent) red display (shown in C and D), and $\text{KNO}_3/\text{charcoal}/\text{S}$ (75/15/10 weight percent) black powder.

2. $\text{SrCO}_3/\text{S}/\text{KClO}_4$ (25/15/60 Weight Percent) Red Display

The detonation and expansion characteristics of a typical 1g/cc red display composition consisting of 25/15/60 weight percent $\text{SrCO}_3/\text{S}/\text{KClO}_4$ are shown in Fig. 5.C and 5.D. The detonation velocity, pressure and temperature were calculated to be 1570 m/s, 6800 bar, and 2280 K, respectively. The total gas yield and various condensed species are shown in Fig. 5.D. The gas phase consists primarily of O_2 , SO_2 , CO_2 , SO_3 , Cl_2 , Cl , ClO , K_2Cl_2 , and SrCl_2 . These calculations were performed assuming 52 possible gas-species and 18 possible condensed-phase species.

BLACK POWDER ($\text{KNO}_3/\text{CHARCOAL}/\text{S}$, 75/15/10 Weight Percent)

The detonation and expansion characteristics of 1g/cc black powder consisting of 75/15/10 weight percent $\text{KNO}_3/\text{charcoal}/\text{S}$ are shown in Fig. 5.E and 5.F. The charcoal was assumed to have the properties of graphite. The detonation velocity, pressure and temperature were calculated to be 2680 m/s, 18600 bar, and

2350 K, respectively. Dobratz¹³ reports the detonation velocity of black powder to be 1350 m/s for an initial density of 0.9-1.1g/cc. The large differences in charcoal compositions make comparison to experimental data difficult. Also, nonideal detonation behavior has been postulated² for explosives which contain nitrate salts. The total gas yield and various condensed species are shown in Fig. 5.F. These calculations were performed assuming 46 possible gas-species and 11 condensed-phase species.

SUMMARY AND CONCLUSIONS

Detonation calculations presented in this paper are thought to be the first report on the theoretical study of firework detonation for three report charges, two display charges, and black powder. The expansion characteristics of the display charges and black powder were also investigated. Predicted velocities for two report charges were in adequate agreement with measured velocities. However, these measured velocities may not represent ideal detonation velocities. Such conclusions can not be supported without further experimental verification. Furthermore, the calculated detonation states which assume complete equilibrium may not be valid for highly nonideal pyrotechnic mixtures. For example, the calculated detonation velocity for black powder is a factor of two larger than measured values. The discrepancy between calculated results and measured results may be attributed to unreacted metal. Measured pyrotechnic velocities may be fast deflagrations which are not represented adequately by equilibrium assumptions. Still, the detonation calculations do show the complex nature of condensed phase formation at elevated pressures and give an upper bound for measured velocities.

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