PREDICTION OF DETONATION CHARACTERISTICS OF CONDENSED EXPLOSIVES

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Abstract

To date, the only completely non-empirical method of predicting detonation parameters is that developed by Paterson and based on the virial equation of state. This method is more appealing now than in the past because of improved techniques for the estimation of virial coefficients, and because of interest in new explosive materials which cannot be expected to adhere to correlations based on familiar CHON explosives.

In the present work, the virial technique is updated and expanded to include explosives based on B,C, H, O, N and F. Predicted detonation pressures in CHON explosives agree with experimental values with an accuracy comparable to that exhibited by the Cook and Kistiakowsky-Wilson-Brinkley methods. A closed-form equation for detonation pressure is presented. The detonation parameters of several systems based on boron and fluorine are also predicted.

By applying suitable approximations to the solution for detonation pressure, an equation is derived which relates this parameter to the structure of the detonating molecule and the stoichiometry of the decomposition reaction. The detonation pressure rises nearly linearly with heat of explosion and very rapidly as the average number of atoms per product molecule decreases.

Introduction

A knowledge of the properties of stable detonations in explosive materials is necessary to an appreciation of the safety hazards encountered in handling these substances. The characteristics of detonations in conventional explosives have been deduced to a large extent from detonation velocity measurements, but such an approach cannot be applied to many compounds or mixtures which have been produced in small quantities, are impure, or indeed, may be hypothetical. When enough of a material of interest has been made to permit a shock sensitivity test, the final velocity of the acceptor shock can be compared with the predicted Chapman-Jouguet velocity to ascertain whether, in fact, a high-order detonation has been produced sympathetically. A scheme for predicting detonation characteristics might also be useful for predicting detonability and brisance, and for computing exothermicity and virial coefficients from experimental detonation measurements.

The prediction of Chapman-Jouguet (C-J) properties is made difficult by the lack of a simple equation of state for the hot, highly-compressed product gases. Those most commonly used have been the Abel and Kistiakowsky-Wilson (K-W) equations of state:

Abel: $P(V-\alpha)=NRT$ (1a)

Kistiakowsky-Wilson: $PV/NRT = 1 + x\exp(\beta x)$ (1b)

where P = pressure
V = specific volume
α = Abelian covolume
N = number of gaseous moles
R = gas constant
T = temperature
$x = \frac{Kk'}{V(T+\theta)^a}$
k' = KW covolume
and θ, a, β and K are empirically-determined constants.

When the Abel equation of state is used, the covolume is assumed to be a constant empirical property of the explosive or a generalized function of specific volume. Cook[1] found that a single curve of covolume versus C-J specific volume could be drawn through experimental points for two picrates, lead azide, mercury fulminate and a series of CHON explosives. The K-W equation has formed the basis of a computer code, RUBY[2], developed at the Lawrence Radiation Laboratory, which has been used widely to predict detonation parameters in CHON explosive systems. Here, the virial equation of state will be used.

Analysis

1. Mathematical Formulation in the Absence of Condensed Products

The general virial equation of state of a gas is

$$PV/NRT = 1 + b_o/V + a_2\,(b_2/V)^2 + a_3\,(b_3/V)^3 + \ldots \quad (2)$$

where b_i = virial coefficients
a_i = constants

Several particular virial equations have been proposed, differing only in minor aspects. They all predict nearly identical gas properties in the range of interest here. The simplest form, that due to Majumdar[3], was used

$$PV/NRT = 1 + b_o/V + .833\,(b_o/V)^2 + .287\,(b_o/V)^3 \equiv 1 + f\,(b_o/V) \quad (3a)$$

where b_o = high-temperature second virial coefficient.

In application to the problem at hand, Equation (3a) becomes

$$P_1V_1/nR'T_1 = 1 + f\,(b_o/V_1) = 1 + f \quad (3b)$$

where $\wedge_1$ = C-J condition
n = mols product gas/g
R' = 82.1 atm-cc/°K-mol
$b_o = \sum_{\substack{\text{all}\\ \text{gaseous}\\ \text{products}}} n_i b_{oi}$, cc/g product gas mix
b_{oi} = virial coefficient of the i-th gaseous product, cc/mol
n_i = mols of the i-th gaseous products/g product mix

It is assumed below that only gaseous products are formed by detonation; the analysis applicable when condensed species are formed will be discussed later.

Paterson[4] has shown that

$$V_1 = \frac{k_1 V_o + \alpha_1}{k_1 + 1} \tag{4}$$

where α_1 = in undetonated state
and k_1 is defined by

$$k_1 = 1 + nR/C_{v1} - d\alpha/dV\big|_1 \tag{5}$$

where C_{v1} = heat capacity of product gases at the C-J point,

$$\text{cal/g} - {}^\circ\text{K} = \sum_{\substack{\text{all}\\ \text{products}}} n_i \mathcal{C}_{v1i}$$

R = 1.987 cal/mol - °K
$\mathcal{C}_v$ = molar heat capacity at constant volume

From Equations (1a) and (3a),

$$\alpha = \frac{V f}{1+f} \tag{6}$$

The heat capacity at constant volume of a virial gas is independent of pressure and, at low pressures,

$$\mathcal{C}^\circ_{pi} - \mathcal{C}^\circ_{vi} = R = \mathcal{C}^\circ_{pi} - \mathcal{C}_{v1i} \tag{7}$$

where $\overset{\circ}{V}$ = at zero pressure and C-J temperature.

Define γ_1 by

$$_1 = \mathcal{C}^\circ_p/\mathcal{C}^\circ_v = C^\circ_p/C^\circ_v \tag{8}$$

Multiplying Equation (7) by n_i and summing over all products; and using Equations (5) and (8),

$$k_1 = \gamma_1 - d\alpha/dV\big|_1 \tag{9}$$

Then, performing the required differentiation in Equation (9) with the aid of (6), and substituting the result and (6) into (4),

$$V_o(g-f) = V_1(g+1) \tag{10}$$

where

$$g = \gamma_1(1+f)^2 - V_1 df/dV\big|_1 - f^2$$

Equation (10) gives the C-J specific volume as a function of γ_1, b_o and V_o. When the heat of explosion and the mean heat capacity of the product gases between T_o and T_1 ($\bar{C}_v$) are known, the value of V_1 found from Equation (10) can be substituted into the Rankine-Hugoniot equation and (3b) to yield C-J pressure. The values of the remaining C-J variables are then easily determined with the aid of Equation (9).

The procedure indicated above involves cycling on both pressure and temperature if the product distribution is unknown; if, however, the products formed are stipulated, cycling on only temperature is required. As both γ_1 and $\bar{C}_v$ are weak functions of temperature, few iterations are needed.

Both γ_1 and $\bar{C}_v$ can be found from published thermochemical tables. V_o is known. Taylor[5] has tabulated the high temperature second virial coefficients of the most frequently observed products of detonation in CHON explosives, and the values of b_o for other species can be estimated or calculated from measured intermolecular force constants.

2. Corresponding Equations when Condensed Products are Formed

The results cited above are applicable only in the absence of condensed detonation products; however, explosives which produce solids can be treated if certain assumptions are made regarding the participation of the solid in the detonation process. It is assumed here that the solids produced are incompressible and in thermal and momentum equilibrium with the product gases. The first of these assumptions is not strictly true, but Cowan and Fickett[6] have shown that only a small error in predicted C-J properties is so introduced. Upon carrying out the earlier analysis in this case, Equation (10) is replaced by

$$V_o^{\dagger}(g^{\dagger}-f)=V_1(g^{\dagger}+1) \tag{11}$$

where $V_o^{\dagger} = \dfrac{V_o-\phi(1-m)}{m}$

$$g^{+} = \gamma_1^{+}(1+f)^2-V_1\, df/dV|_1 - f^2$$

V_1 = specific volume of the gas at the C-J plane
ϕ = specific volume of the condensed phase
m = weight fraction of detonation products which are gaseous
$\gamma_1^{+} = 1 + nR/C_{v1}$
n = mols gas per gram total products
C_v = heat capacity at constant volume of total products, cal/g-°K

Equation (11) reduces to Equation (10) when m = 1.

Applications

1. Comparison with Experiment.

In a fashion analagous to that applicable in the absence of condensed products, all the detonation parameters of an explosive can be calculated once Equation (11) is solved for V_1. A computer program has been written to predict the detonation parameters of any exothermic material or mixture, requiring as input the loading density and heat of formation of the explosive, and the stoichiometric coefficients of each of 29 possible products, including any solid.

It is instructive to compare the present method of prediction with established techniques; the current study was initiated in an effort to obtain refined predictions of detonation pressure, so this parameter is used in the comparisons to follow. In Table I, results of the present analysis and that due to Cook are compared with experimental data on a number of high explosives. The two techniques predict the experimental detonation pressures with comparable accuracy. A similar comparison with the predictions of the RUBY code is included as Table II. When these predictive methods are applied to other classes of explosive compounds,

the virial coefficient approach, because of its more fundamental basis, is expected to predict detonation properties at least as accurately as the other approaches. The virial technique also offers the advantage of leading to explicit solutions for detonation parameters, as will be shown below.

Table I. Detonation Pressures Predicted from Generalized Covolumes (Cook) and from the Virial Equation of State

Compound	ρ_o, g/cc	Reference for product distribution	Detonation Pressure: Virial Equation	Cook	Experimental	Ref.
Nitroglycerin	1.6	5	217	247	253	b
TNT	1.0	5	60	67*	64	b
TNT	1.455	5	120	136*	165	b,c
RDX	1.20	a	133	136	141	a,b
RDX	1.40	a	181	181	213	b
RDX	1.59	a	242	223	287	b
RDX	1.755	a	305	276	366	b
Mean percent error			14	14**		

* Experimental results on TNT were used by Cook to generate the generalized plot of covolume versus C-J specific volume.

** Excluding TNT

a. M. A. Cook, "The Science of High Explosives", Reinhold, 1958.
b. A. N. Dremin et al, Eighth Symp. (Int'l.) on Combustion, Williams and Wilkins, 1960, p. 610.
c. W. B. Garn, J. Chem. Phys. 32, 653 (1960).

Table II. Detonation Pressures Predicted from the RUBY Code[2] and from the Virial Equation of State

Reference for product distributions: C. R. Mader, "Detonation Performance Calculations using the Kistiakowsky-Wilson Equation of State" Los Alamos Scientific Laboratory Report LA-2613, October 9, 1961.

Compound	ρ_o, g/cc	Detonation Pressure: Virial Equation	RUBY	Experimental	Ref.
NM	1.128	76	151	130	a
NM/TNM 1/.071 mol/mol	1.197	105	168	138	b
NM/TNM 1/.25 mol/mol	1.310	149	195	156	b
NM/TNM 1/.5 mol/mol	1.397	167	200	168	b
AN/TNM 1/1.25 mol/mol	1.380	196	191	156	b
EDB/TFDNE 1/7.5 mol/mol	1.467	189	185	206	c
Mean percent error		17	19		

Table II (Cont'd.)

NM = nitromethane
TNM = tetranitromethane
AN = acyrlonitrile
EDB = ethylderaborane
TFDNE = tetrafluorodinitroethane

a. W. C. Davis, Los Alamos Scientific Laboratory unpublished data
b. W. Garn, Los Alamos Scientific Laboratory unpublished data
c. W. Garn and C. L. Mader, Los Alamos Scientific Laboratory unpublished data

In gaseous detonations, $b_o << V_1$, and the virial equation reduces to the ideal equation of state. Therefore, the computer program described above can be used to determine the ratio between C-J pressure and initial pressure for gases sufficiently exothermic to justify the inequality $P_1 >> P_o$.

2. Detonations in High Energy Propellant Systems

A substantial amount of effort has been expended to determine and optimize high-impulse propellant systems. Many of these mixtures contain atoms different from those in solid secondary explosives. The computer program referred to above accepts product species containing fluorine and boron, and has been used to predict the detonation characteristics of several impulse-optimized bipropellants based on these elements. The results of the analysis are presented as Table III. Product distributions are from Dobbins[7], except where noted.

As none of the mixtures in Table III have been optimized as explosives, only qualitative conclusions can be drawn regarding this use of bipropellants. They exhibit the desirable high energy of perfectly or nearly balanced systems, but have too low a density and too high a volatility to be very promising.

Table III. Predicted Detonation Characteristics of High-Energy Bipropellants

Oxidizer	Fuel	Percent oxidizer	Basis	Loading Density, g/cc	Detonation Properties: Temperature, °K	Velocity, mps	Pressure, kb
N_2O_4	N_2H_4	33	Mol*	1.222	5170	6710	131
N_2F_4	N_2H_4	50	Mol**	1.438	8280	8250	224
F_2	N_2H_4	55	Weight	1.230	6250	9990	248
F_2	B_5H_9	20	Weight	1.172	7520	6790	137
NF_3	B_5H_9	87	Weight	1.288	7160	6800	141
OF_2	UDMH	72	Weight	1.209	6940	8340	187

* Stoichiometric to H_2O and N_2
** Stoichiometric to HF and N_2. This mixture is ordinarily hypergolic

3. Approximate Solution for Detonation Pressure

The procedure outlined above yields fair predictions of the detonation characteristics of systems of interest. If, however, some further assumptions are made in the analysis, equations can be derived which still predict detonation parameters with fair accuracy, yet can be used to make more rapid estimates of C-J properties of interest. In addition, these equations can indicate to what degree various properties of a detonating explosive and its products affect the conditions behind a C-J detonation.

It can be shown that, if heat capacity is independent of temperature, the C-J properties can be determined when the values of only four parameters are specified; these variables are b_o, V_o^+, γ^+, and Q, the standard change, in calories, of internal energy accompanying the reaction. Dimensionless or reduced detonation parameters can be defined as functions of only b_o, V_o^+ and γ^+, viz:

$$P' \equiv \frac{P_1 m}{Q+C_v T_o} = \left[\frac{C_v V_1}{nR'(1+f)} - 0.0121\ (V_o^+ - V_1)\right]^{-1} \quad \text{atmosphere-g/cal} \tag{12}$$

V_1 is found from Equation (11). Cgs units are used except where indicated. The analysis to follow will be limited to the deviation of a simple method of predicting detonation pressure; similar approaches can be used to derive analogous equations for other detonation parameters.

A digital computer was used to prepare tables of reduced detonation parameters for a series of input values of V_o^+, b_o and γ_1^+. The range of independent variables covered was:

(1) γ_1^+: 1.01 to 1.30, in intervals of 0.01

(2) b_o: 0.6 to 1.4 cc/g, in intervals of 0.1 cc/g

(3) V_o^+: 0.5 to 1.0 cc/g, in intervals of 0.1 cc/g

Over the range of interest of these variables, plots of P' versus $\gamma^+ - 1$ are essentially linear and pass through the origin, with the degree of curvature rising as b_o and $\rho_o^+ = 1/V_o^+$ increase. However, even for the largest values of b_o and ρ_o^+, $P\,C_v/nR$ decreases only eleven percent between γ^+ values of 1.01 and 1.30. Therefore,

$$P' \doteq \frac{nR}{C_v}\ \mu(b_o, V_o^+) \tag{13}$$

where μ = slope of plot of P' versus $\gamma^+ - 1$.

Usually, $Q \gg C_v T_o$, so

$$P \sim \frac{QnR}{mC_v}\ \mu(b_o, V_o^+) = \frac{QR}{M_p C_v}\ \mu \tag{14}$$

where M_p = mean molecular weight of the gaseous products

Plots of $\mu(b_o, V_o^+)$ are given as Figure 1.

Equation (14) indicates some directions to be taken in tailoring molecules to produce high or low detonation pressures. It would appear to be rather difficult to effect large changes in the virial coefficient, although a study of this property might indicate which classes of compounds should detonate more or less strongly. The formation of solid detonation products is seen from Fig. 1 to reduce detonation pressure and the well-known effects of loading density and heat of detonation are confirmed. From a statistical mechanical interpretation of M_pC_v, a very important parameter determining detonation pressure is found to be the average number of atoms in the product gases. In the absence of condensed products, as this ratio is lowered from five to four to three to two, with no other changes, predicted detonation pressure rises from $P_1 \equiv P^*$ to $1.3P^*$ to $1.9P^*$ to $3.6P^*$! The effect of this parameter bears further study.

Conclusions

A method of predicting the Chapman-Jouguet detonation characteristics of a condensed explosive has been developed. The gaseous explosion products are assumed to obey the virial equation of state. The analysis involves no adjustable parameters and predicts detonation pressure as well as or better than solutions based on the Abel or Kistiakowsky-Wilson equations. The solution has been simplified to permit the explicit estimation of detonation pressure, which is seen to rise very rapidly as the average number of atoms per product molecule decrease.

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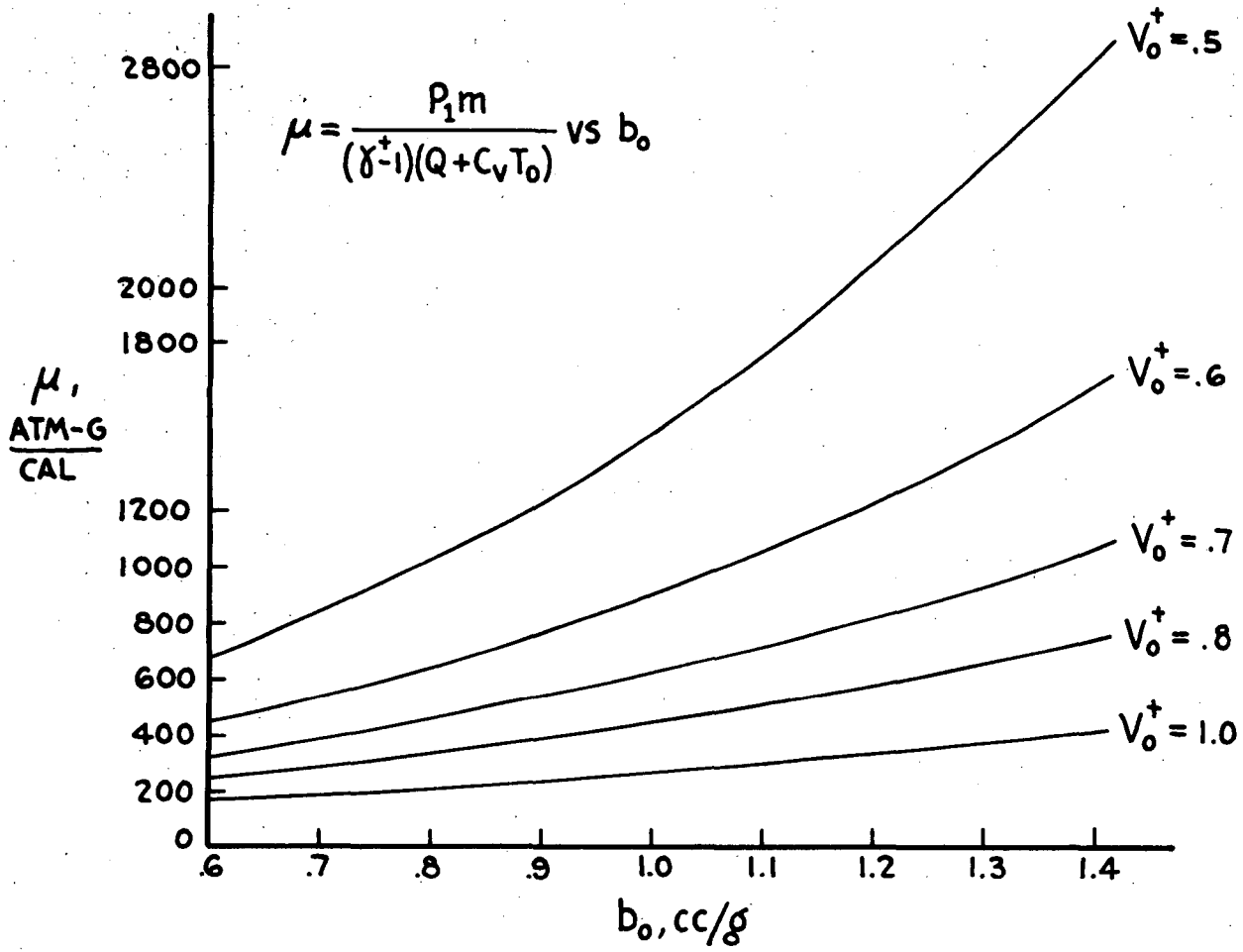
FIG. 1



REDUCED DETONATION PRESSURE vs. HIGH TEMPERATURE SECOND VIRIAL COEFFICIENT