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Prediction of the Principal Performance Parameters of Explosives over a Wide Range of Initial Densities

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New correlations are introduced for extension of Kamlet and coworkers in determining detonation velocity and the adiabatic exponent to hold loading density of explosives less than 1 g/cm^3 as well as greater than 1 g/cm^3. The empirical equations of Kamlet and coworkers show large per cent deviation for loading density less than 1 g/cm^3; meanwhile the new correlations can be applied for CHNO explosives without any shortcoming in a wide range of loading density.

Key Words: Prediction, Performance parameters, Explosives.

INTRODUCTION

The prediction of the detonation characterization of high explosives and their performance stimulates the development of thermodynamic methods to calculate the detonation parameters. The performance of new energetic materials should be evaluated prior to their actual synthesis. This situation reduces the costs associated with synthesis, test and evaluation of the materials. The detonation parameters such as velocity, pressure and energy have been regarded as the principal measures of the performance of detonating explosives for many years.

With the advent of high speed, several sophisticated numerical codes were developed to predict detonation properties of high explosives[1, 2]. For example, CHEETAH is an equilibrium thermodynamical code used to estimate detonation parameters of high explosives[3]. Different equations of state (*i.e.*, BKWC, BKWS, JCZS, etc.) for the product species are used along with the computer code[3]. Some empirical formulas can also be used for quick calculations of detonation pressure and velocity[4–11] with about the same reliability as one might attach to the more complex computer output. Kamlet and coworkers[4–11, 12] investigated the inter-relationships between detonation parameters in an effort to analyze and understand the formidable appearance of the data of many computations for many CHNO explosives. They found empirical formulas that can be used for quick calculations of detonation velocity and pressure as well as the adiabatic exponent,

i.e., the pressure-volume slope in the adiabatic expansion of detonation gases, of CHNO explosives at loading density greater than 1 g/cm^3.

Since the existence of the large deviations in Kamlet's detonation velocity and the adiabatic exponent for loading density less than 1 g/cm^3, there are shortcomings in the equations for predicting of detonation performance of explosives over a wide range of loading densities. The purpose of this work is to provide a simple procedure for extension of Kamlet's correlations so that the general form of the empirical equations remains intact. The present work shows that the new adiabatic exponent correlation is a relatively insensitive element composition and only a function of loading density.

Thermochemical Estimation of Performance

For comparison with steady-state calculations, detonation velocities are measured at various charge diameters and extrapolated to an infinite diameter. In contrast to detonation velocity, which can typically be measured to within a few per cent, the detonation pressure is not a well-resolved measurement. Due to the existence of non-equilibrium effects in reaction zone, detonation pressures determined by various indirect methods span a range of 10–20%[13].

Kamlet and coworkers[4-11] found that the estimates of detonation pressure and velocity are possible using the following empirical expressions:

$$P\ (\text{kbar}) = 1.56\ (NM^{1/2}Q^{1/2})\ \rho_0^2 \tag{1}$$

$$D\ (\text{km s}^{-1}) = 1.01\ (N^{1/2}M^{1/4}Q^{1/4})(1 + 1.3\rho_0) \tag{2}$$

where N is the number of moles of gaseous products of detonation per gram of explosive, M is the average molecular weight of the gaseous products and Q is the heat of detonation per gram of explosive. They suggested the following overall stoichiometry for an explosive having the general formula $C_aH_bN_cO_d$:

$$C_aH_bN_cO_d \xrightarrow{d \le \frac{b-2a}{2}} \frac{b}{2}H_2O + \frac{c}{2}N_2 + \left(\frac{d}{2} - \frac{b}{4}\right)CO_2 + \left(a - \frac{d}{2} + \frac{b}{4}\right)C \tag{3a}$$

$$C_aH_bN_cO_d \xrightarrow{d \succ \frac{b-2a}{2}} \frac{b}{2}H_2O + \frac{c}{2}N_2 + aCO_2 + \left(\frac{d}{2} - \frac{b}{4} - a\right)O_2 \tag{3b}$$

where eq. (3b) applies for over oxidized CHNO explosives such as NG. We can readily obtain N and Q for under oxidized and over oxidized explosives.

The heat of detonation can be determined from the heats of formation of reactants and products of detonation through the relation:

$$Q \cong \frac{[\Delta H_f\ (\text{detonation products}) - \Delta H_f\ (\text{explosive})]}{\text{formula weight of explosive}} \tag{4}$$

The equilibrium composition of the product gases of eqn. (3) can be used for evaluating the heat of formation of detonation products. If the heat of formation

of the explosive is known, then using the standard heats of formation for gas-phase water and carbon dioxide and eqn. (4) will lead to the prediction of the heat of detonation of an explosive.

An increase in density, pressure and internal energy is observed during the passage of a shock wave through the material. Since these quantities are not directly in shock experiments, they can be evaluated by the shock wave velocity D and the material or particle velocity U_P. The mass, momentum and energy conservation laws are used to define the relationship between velocities and the change in thermodynamic properties which are given as follows[14, 15]:

$$\frac{V_1}{V_0} = \frac{D - U_P}{D} \tag{5}$$

$$P_1 - P_0 = \frac{DU_P}{V_0} \tag{6}$$

$$E_1 - E_0 = \frac{1}{2}(P_1 + P_0)(V_0 - V_1) \tag{7}$$

where E, P and V are the internal energy, pressure and volume. Subscripts 0 and 1 refer to the initial and final states, respectively. Eqn. (7) represents the locus of all possible compression states attainable for a given initial state and is known as Hugoniot curve. By elimination of U_P from eqns. (5) and (6) one obtains the Rayleigh line equation, which defines a line in the P-V curve:

$$\frac{P_1 - P_0}{V_0 - V_1} = \rho_0^2 D^2 \tag{8}$$

where ρ_0 is the initial density.

The Chapman-Jouguet (CJ) hypothesis corresponds to steady-state detonation which determines uniquely the CJ point in the intersection of the Rayleigh line with the detonation Hugoniot curve. The CJ condition for a steady-state detonation chooses from all possible solutions the one that propagates with lowest velocity. The adiabatic exponent Γ_{CJ} is one of the important factors in evaluating detonation performance. It defines the initial pressure-volume slope in the isentropic expansion of detonation products for the CJ state or

$$\Gamma_{CJ} = \left(\frac{\partial \ln P}{\partial V}\right)_S \tag{9}$$

The subscript S indicates constant entropy.

An isentrope is also tangent to both the Rayleigh line and the product Hugoniot at the CJ point so that the negative logarithmic slope of the isentrope at the CJ point is given by

$$\Gamma_{CJ} = \frac{1 - P_0/P_1}{V_0/V_1 - 1} \tag{10}$$

Conservation laws relate ρ_{CJ} and Γ_{CJ} with ρ_0 in dense fluids where detonation product mixtures are obtained at high pressure:

$$\frac{\rho_{CJ}}{\rho_0} = \frac{\Gamma_{CJ} + 1}{\Gamma_{CJ}} \tag{11}$$

The adiabatic exponent can also be used as one of the most sensitive tests of various equation of state (EOS) models. Since Γ_{CJ} is a second-order derivative of free energy, it is extremely sensitive to slight deviation from the true equation of state of detonation products. Kamlet and Short[12] introduced a procedure for estimating Γ_{CJ} as a criterion for choice among conflicting experimental measurements of detonation properties of a number of CHNO explosives and for estimating detonation pressures from measured detonation velocities whose compositions, structures or heats of formation are not known. One of the well-known useful hydrodynamic relationships between P_{CJ} and D_{CJ} can be expressed as follows:

$$P_{CJ} = \frac{\rho_0 D_{CJ}^2}{\Gamma_{CJ} + 1} \tag{12}$$

By the use of eqns. (1) and (2) for P_{CJ} and D_{CJ} in to eq. (12), Kamlet and Short[12] obtained the following equation:

$$\Gamma_{CJ} = \frac{0.665}{\rho_0} + 0.702 + 1.107\rho_0 \tag{13}$$

They called this equation as "Rule for Gamma". The equation is valid only for CHNO explosive with loading density above 1 g/cm^3. It suggests that Γ_{CJ} is independent of chemical composition and is a monotonically increasing function of loading density.

Extension of Kamlet-Hurwitz and Kamlet-Short correlations for a wide range of loading densities

Kamlet and Hurwitz[7], in the derivation of eq. (1), tried to find the best values of X, Y and α in an equation of the following form:

$$D_{CJ} = (X + Y\rho_0)(NM^{1/2}Q^{1/2})^{\alpha} \tag{14}$$

They selected $\alpha = 0.50$ for convenience in calculation from different values obtained for pairs of explosives at identical loading density. They also involved separate graphical treatments of TNT data and of RDX-HMX data to obtain slopes and intercepts in plotting detonation velocity *vs.* loading density for finding the values of X and Y. This form of fitting shows large deviation as compared to reported values of CHNO explosives at $\rho_0 < 1$ g/cm^3. This is shown for some well-known explosives in Table-1.

Kamlet-Hurwitz correlation can be corrected in another form so that it can predict detonation velocity at various loading densities. This can be done as Fig. 1 through plotting $\frac{D_{CJ}(exp)}{N^{1/2}(MQ)^{1/4}}$ *vs.* loading density, where $D_{CJ}(exp)$ is the experimental detonation velocity. The following correlation is obtained:

$$D\ (km\ s^{-1}) = (N^{1/2}M^{1/4}Q^{1/4})(0.779 + 1.442\rho_0) \tag{15}$$

Comparisons of this equation and Kamlet-Hurwitz correlation with the measured values for some well-known CHNO explosives are given in Table-1. The large deviations in Kamlet-Hurwitz prediction are observed at initial density less than 1 g/cm^3, meanwhile this modification can determine D_{CJ} to within about a few per cent at any loading density. In Fig. 1, all CHNO explosives are reasonably close to the least square line and exhibit a R^2-correlation coefficient of 0.985.

TABLE-1
COMPARISON OF DETONATION VELOCITY OF THE NEW CORRELATION AND KAMLET-HURWITZ (K-H) WITH MEASURED VALUES[19]

Name	ρ_0 (g/cm^3)	D_{exp} (km/s)	$D_{K\text{-}H}$ (km/s)	D_{new} (km/s)	% dev (K-H)	% dev (new)
PETN	0.48	3.60	4.27	3.83	–18.72	–6.48
	0.88	5.06	5.64	5.34	–11.51	–5.46
	0.99	5.48	6.02	5.75	–9.83	–4.92
	1.23	6.37	6.84	6.65	–7.38	–4.42
	1.45	7.18	7.59	7.48	–5.75	–4.15
	1.60	7.75	8.11	8.04	–4.59	–3.76
	1.70	8.07	8.45	8.42	–4.68	–4.31
	1.76	8.27	8.65	8.64	–4.63	–4.51
RDX	0.56	4.05	4.55	4.13	–12.24	–2.03
	0.70	4.65	5.02	4.66	–8.06	–0.17
	0.95	5.80	5.88	5.60	–1.37	3.50
	1.10	6.18	6.39	6.16	–3.44	0.32
	1.20	6.77	6.73	6.54	0.52	3.46
	1.29	7.00	7.04	6.87	–0.60	1.80
	1.40	7.46	7.42	7.29	0.56	2.32
	1.46	7.60	7.62	7.51	–0.31	1.15
	1.60	8.13	8.10	8.04	0.34	1.13
	1.66	8.24	8.31	8.26	–0.82	–0.29
	1.72	8.46	8.51	8.49	–0.62	–0.34
	1.77	8.70	8.68	8.68	0.19	0.27
	1.80	8.75	8.79	8.79	–0.42	–0.45
HMX	0.75	4.88	5.19	4.84	–6.36	0.79
	1.00	5.80	6.04	5.78	–4.22	0.36
	1.20	6.85	6.73	6.53	1.78	4.68
	1.40	7.30	7.41	7.28	–1.53	0.27
	1.60	7.91	8.09	8.03	–2.33	–1.53
	1.89	9.11	9.09	9.12	0.27	–0.10
Tetryl	1.61	7.58	7.40	7.35	2.33	3.06
	1.68	7.50	7.62	7.59	–1.61	–1.16
	1.71	7.85	7.71	7.69	1.73	2.04
	1.73	7.72	7.78	7.76	–0.73	–0.49
DATB	1.78	7.60	7.54	7.54	0.76	0.76
NG	1.60	7.70	8.17	8.10	–6.10	–5.20
TATB	1.83	7.58	7.61	7.62	–0.40	–0.55
NM	1.13	6.28	6.38	6.16	–1.61	1.87

The following new correlation for adiabatic exponent can be obtained from eqns. (2), (12) and (15):

$$\Gamma_{CJ} = \frac{0.389}{\rho_0} + 0.442 + 1.335\rho_0 \quad (16)$$

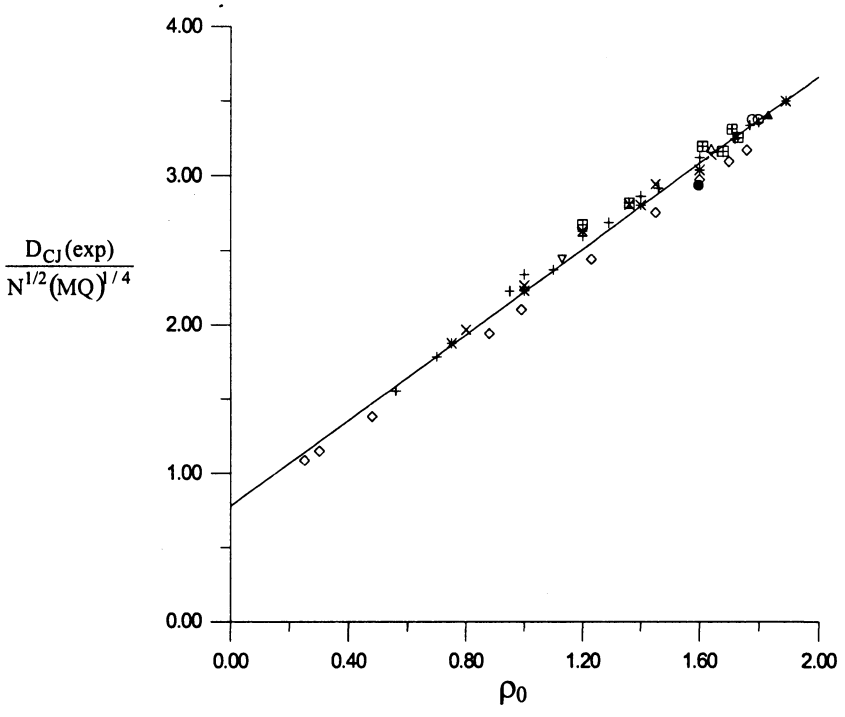

Fig. 1. The $\frac{D_{CJ}(exp)}{N^{1/2}(MQ)^{1/4}}$ *vs.* loading density. The points are: ◊ PETN; × TNT; ○ DATB; * HMX; + RDX; ⊞ Tetryl; ● NG; Δ TNM; ▲ TATB; ∇ NM

The validity of this relationship can be better demonstrated by using detonation pressure and velocity measurements and corresponding experimental Γ_{CJ} values derived from eqn. (13). These data at various loading densities are assembled in Table-2.

Conclusions

An extension of Kamlet-Hurwitz[7] and Kamlet-Short[12] has been developed that the performance determination of CHNO explosives can be hand-calculated at any loading density. The new correlations have the general form of Kamlet and coworkers. They are based on a simple scheme for decomposition of oxygen-rich and oxygen-lean explosives, by assuming the reaction products to consist of H_2O, N_2, CO_2 and either C (graphite) or O_2. The fundamental variable in the correlations is the heat of detonation of an explosive compound of composition CHNO, which can be approximated as the difference between heat of formation and that of the explosive formulation, divided by the formula weight of the

explosive. As indicated in Tables 1 and 2, the new equations can predict the detonation velocity and adiabatic exponent much better than that of Kamlet and coworkers at $\rho_0 < 1$ g/cm^3. Since the detonation velocity can be measured to within a few per cent, the new adiabatic correlation may be used for estimating detonation pressures from measured detonation velocities.

TABLE-2
PREDICTION OF ADIABATIC EXPONENT OF THE NEW CORRELATION AND KAMLET-SHORT (K-S) CORRESPONDING TO MEASURED VALUES OF DETONATION PRESSURE AND VELOCITY[19]

Name	ρ_0 (g/cm^3)	Γ_{CJ}(exp)	Γ_{CJ} (K-S)	Γ_{CJ} (new)
PETN	0.48	1.59	2.60	1.89
	0.88	2.31	2.42	2.06
	0.99	2.42	2.46	2.16
	1.23	2.59	2.60	2.40
	1.45	2.59	2.76	2.65
	1.60	2.61	2.88	2.82
RDX	0.56	1.87	2.49	1.88
	0.70	2.15	2.41	1.93
	0.95	2.33	2.44	2.12
	1.10	2.44	2.52	2.26
	1.20	2.62	2.58	2.37
	1.29	2.81	2.64	2.47
	1.40	2.66	2.72	2.56
	1.46	3.00	2.77	2.66
	1.60	3.02	2.88	2.82
	1.72	2.93	2.99	2.96
	1.77	2.96	3.03	3.02
	1.80	3.04	3.06	3.06
HMX	0.75	1.98	2.41	1.96
	1.00	2.06	2.46	2.17
	1.20	2.52	2.58	2.37
	1.40	2.55	2.72	2.59
	1.60	2.58	2.88	2.82
	1.89	3.02	3.14	3.17
Tetryl	1.61	3.09	2.89	2.83
	1.68	2.95	2.95	2.92
DATB	1.78	3.10	3.04	3.04
NG	1.60	2.75	2.88	2.82
TATB	1.83	3.04	3.09	3.10
NM	1.13	2.71	2.53	2.29

Furthermore, due to different reported values for detonation pressures, it can be used as a criterion for selecting detonation pressures of explosives.

A description of the shape of the detonation isentrope is required for wave-propagation computations. The adiabatic exponent is a parameter used to describe the detonation isentrope. However, it is also found that increasing of Γ_{CJ} with increasing ρ_0 obtained by eqn. (16) is consistent with the findings of Deforneaux[16], Johannson and Persson[17], Hardesty and Kennedy[18]. This work confirms the pervious one that Γ_{CJ} is independent of chemical composition and is strongly dependent on the explosive's loading density.

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