Articles

Two New Correlations for Predicting Detonating Power of CHNO Explosives

M. H. Keshavarz[*] and M. Oftadeh

*Department of Chemistry, Malek-ashtar University of Technology, Shahin-shahr P.O. Box 83145/115,
Islamic Republic of Iran*

For CHNO explosives, two new correlations of the form $P_{CJ} = 8.7(\alpha T_c)^{1/2}\rho_0^2 - 5$ and $P_{CJ} = 9.5(\alpha T_c')^{1/2}\rho_0^2 - 9$ have been demonstrated, which relate detonation pressure. P_{CJ}, combustion temperature of the explosive in gas phase. T_c, combustion temperature of the explosive in crystalline state. T_c': and the number of moles of gaseous products per unit weight of explosive. α, at initial density of the explosive. ρ_0. Experimental and semi-empirical PM3 procedures were used for the computation of T_c. Detonation pressures derived in this manner have a simple form without need to use computer code.

Key Words : C-J Pressure. Loading density, CHNO explosives

Introduction

Detonation performance of an explosive is measured by detonation pressure, velocity and energy. The Chapman-Jouguet (C-J) pressure has been regarded as the principal parameter for determining detonating power of explosives. Prediction of detonation pressure of various explosives at various initial (loading) densities by this simple procedure poses an important problem. Condensed explosives usually have loading density in the range 0.2-2 g/cm³. The performance of gas explosives is well established by the ideal gas equation of state (EOS). but performance of condensed matter can no longer be treated adequately by ideal gas EOS. The development of EOS requires shock description and detonation performance of the condensed matter. These include empirical and semi-empirical equations of state. analytical representation of the thermodynamic properties of dense fluids. and variational methods for computing the thermodynamic properties of a multicomponent multiphase mixture. The calculation of C-J pressures is usually performed with EOS and a computer code, such as TIGER.[1] which combines the Rankine-Hugoniot conservation equation, the C-J condition. the laws of chemical equilibrium, the density and the heat of formation of the explosive. To determine the shock and detonation performance of condensed matter, a detailed knowledge of the EOS of detonation products is required. Some EOSs used to describe the explosive performance are reviewed by Abdulazeem.[2] Among EOSs the Becker-Kistiakosky-Wilson (BKW-EOS) is the most widely used.[3,4] Kamlet and coworkers[5-7] introduced one empirical method for estimating the detonation pressure of an organic CHNO explosive at initial densities above 1.0 g/cc. Kamlet's

method requires the explosive composition and loading density as well as an estimate of the heat of formation as input parameters.

In the present study. we present two new correlations for predicting the C-J pressure of a CHNO explosive from calculated parameters at various loading densities. The interrelationships between detonation pressure. combustion temperature, density and the number of moles of estimated detonation products are investigated. In particular. we show that the approximate combustion temperature for a CHNO explosive in gas or solid phase together with an estimate of the number of moles of gaseous products and density can be linearly tied to detonation pressure.

Estimation of Combustion Temperature and Detonation Products

As a detonation wave traverses an explosive. the density and temperature rise. which can lead to the initiation of a chemical reaction. Due to the complex interaction between the shock wave and the chemical reaction of the explosion, the chemical bonds of the molecules of the explosive can be broken by the energy of the shock wave. The hot gases and solid residues left behind continue to exert pressure. Detonation products generally contain a large number of molecular species. The concentrations of these species change with temperature and pressure. At the same initial density for an oxygen-rich explosive. we can expect the major gaseous products to be CO, CO_2, H_2O, N_2 and H_2. To find a correlation for the detonation pressure as a function of the number of moles of detonation products, it was necessary to know the amounts and characteristics of the products. Detonation products are a complex mixture that may consist of more than one mixture in more than one phase. Furthermore, their concentrations can change with

[*]To whom correspondence should be addressed. Phone: +98-312-522-5071, Fax: +98-312-522-5068

pressure and temperature. Thus, at the first step, we assumed that the products are limited to CO, CO_2, H_2O, N_2 and H_2. For an oxygen lean explosive such as TNT, solid carbon is also one of the detonation products. This approximation simplified our procedure, because it is not necessary to know the precise composition of detonation products.

The detonation pressure is related to the specific impulse produced by the compound used as a propellant. (Check the following sentence for accuracy.) [There is a linear relationship between the detonation pressure of an explosive and the density squared times the specific impulse.[8]] The energy released by a detonation reaction, which occurs in a very short time, is completely transferred to the products, which leads to a rise in the temperature of gaseous products. The performance of an energetic material depends strongly on its temperature in the combustion reaction. To find the combustion products temperature, we assume that the heat of combustion of the explosive is used entirely to heat the gaseous products and it is constant over the temperature range between the initial and final combustion temperature.

We can write an expression for the combustion temperature that satisfies the above requirements as follows[9]:

$$T_c = T_i - \frac{\sum v_j \Delta H_{f,j}}{C_p(T)} \qquad (1)$$

where $\Delta H_{f,j}$ is the molar heats of formation of the explosive and gaseous products. $C_p(T)$ is the total heat capacity of the detonation products, which can be obtained from JANAF thermochemical data[10] at or near the combustion temperature. T_i and T_c are the initial (e.g. 298.15 K) and the combustion temperatures, respectively, and v_j is the stoichiometric coefficients in the decomposition reaction (v_j is positive for the products and negative for the explosive).

Correlation Determination

Theoretical stoichiometric decomposition reactions for some well-known CHNO explosives and other necessary calculated parameters in order to obtain the correlations are given in Table 1. In this study, the relations between C-J

detonation pressure, T_c, initial density and α are investigated. α is a parameter that provides a rough estimate of the number of gaseous products available per unit weight of explosive. We expected that the formation of light gaseous detonation products at high positive heat of formation of explosive increases the C-J detonation pressure. In Table 1, the stoichiometric decomposition reactions are written assuming all nitrogen atoms are converted to N_2 whereas oxygen atoms preferentially form H_2O and otherwise CO and CO_2. The remaining problem is how to use α and T_c as two parameters that can influence detonation pressure to predict the detonation pressure of an explosive. For simplicity and to exclude the crystal effects the heat of formation of the explosive in the gas phase was calculated from the semi-empirical PM3 procedure.[11] In this calculation, the experimental heats of formation of the detonation products are used. At a specified initial density, the relationship between the mentioned parameters is investigated through plotting the experimental C-J detonation pressure of different CHNO explosives versus various combinations of α and T_c. After the P_{CJ} of different CHNO explosives versus $(\alpha T_c)^{1/2}\rho_0^2$ was plotted (see Figure 1), the following linear relationship was obtained (correlation coefficient = 0.990):

$$P_{CJ} = 8.7(\alpha T_c)^{1/2}\rho_0^2 - 5 \qquad (2)$$

From Figure 1, one can conclude that P_{CJ} of a CHNO explosive is predictable at various loading densities by a simple procedure.

As shown in Figure 2, if in our calculations, the experimental heat of formation of solid state explosives is used, a similarly linear equation can be found as follows (correlation coefficient = 0.992):

$$P_{CJ}' = 9.5(\alpha T_c')^{1/2}\rho_0^2 - 9 \qquad (3)$$

where T_c' is the combustion temperature of the explosive in crystalline state. The standard heat of formation of the unreacted explosives and their combustion temperatures are given in Table 1. The experimental data to obtain Eqs. (2) and (3) are listed in Table 2.

Correlations (2) and (3) have similar behavior in predicting detonation pressure. As shown, there is no need to know the heat of formation of the explosive in crystalline form in

Table 1. Parameters Used in Calculations

Explosive[a]	Reaction Products	Gas phase ΔH_f(kcal/mol)[b]	T_c (K)	Solid phase ΔH_f(kcal/mol)[c]	T_c' (K)	α[d]
DATB	$6CO+2.5N_2+2.5H_2$	-6.665	1962	-29.2	1747	0.0453
HMX	$4CO+4N_2+4H_2O$	146.9	4077	17.9	3164	0.0405
TETRYL	$7CO+2.5N_2+1.5H_2+H_2O$	68.75	3126	4.67	2592	0.0418
NG	$3CO_2+1.5N_2+2.5H_2O+0.25O_2$	-74.68	4254	-90.8	4076	0.0319
NM	$CO+0.5N_2+0.5H_2+H_2O$	-16.04	2553	-27.0	2232	0.0492
PETN	$3CO_2+2CO+2N_2+4H_2O$	31.52	3808	-128.7	3542	0.0348
RDX	$3CO+3N_2+3H_2O$	74.48	3750	14.7	3176	0.0405

[a]See appendix A for glossary of compound names and chemical formulas. [b]Heat of formation calculated by PM3 procedure. [c]Standard heat of formation of unreacted explosive at 1 atm and 298 K. Values listed taken from Dobratz and Crawford [13]. [d]Number of gaseous products available per unit weight of explosive.
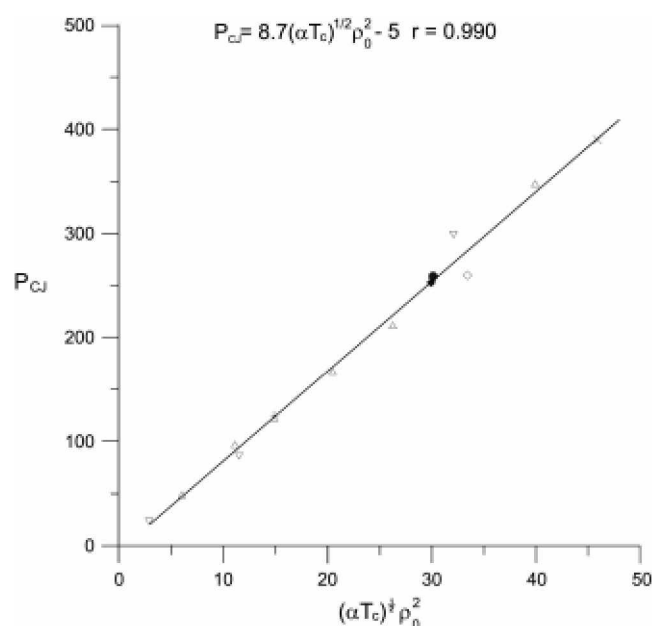
Figure 1. The experimental CJ Detonation Pressure (Table 2) versus $(\alpha T_c)^{1/2}\rho_0^2$, where heat of formation calculated by PM3 method is used to estimate the combustion temperature. The points are: ◆ NG; × HMX; ☐ TETRYL; ● DATB; ▽ PETN; △ RDX; + NM.
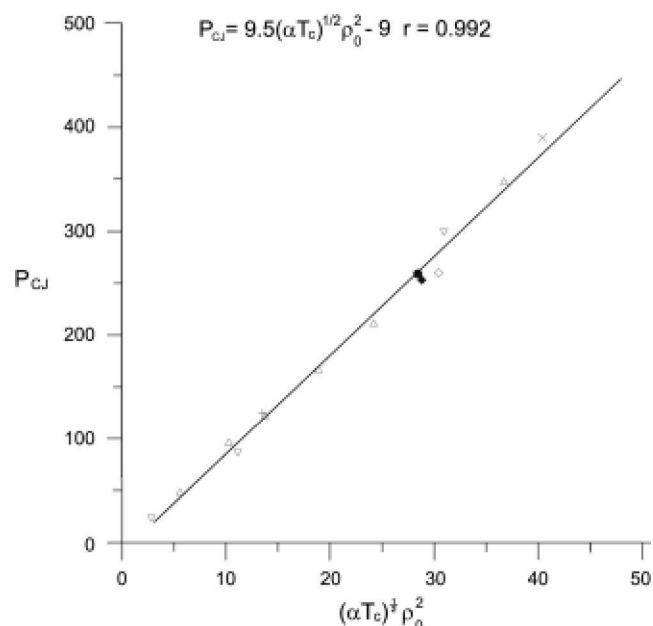
Figure 2. The experimental CJ Detonation Pressure (Table 2) versus $(\alpha T_c')^{1/2}\rho_0^2$, where experimental heat of formation is used to estimate the combustion temperature. The parameters and points are defined in fig. 1.

using Eq. (2). Detonation velocity of any unknown explosive can be readily determined from detonation pressure at any loading density.[12] Therefore, the correlations obtained in this work can be used to determine the performance of any CHNO explosive, regardless of whether the experimental heat of formations of explosives in the crystalline state is known or not.

Table 2. Experimental Chapman-Jouguet pressure at different initial densities used in Eqs. (2) and (3) for CHNO explosives

Explosive[a]	ρ_0 (g/cm³)	P_{CJ} (kbar)
DATB	1.788	259.0
HMX	1.90	393.0
TETRYL	1.71	260.0
NG	1.59	253.0
NM	1.135	125.0
PETN[b]	0.48	24.0
	0.99	87.0
	1.67	300.0
RDX[c]	0.70	47.8
	0.95	95.9
	1.10	121.6
	1.29	166.2
	1.46	210.8
	1.80	347.0

[a]Measured values of detonation pressure taken from Dobratz and Crawford [13] except were noted. [b]Ref. [14]. [c]Ref. [15].

Conclusion

In the present study, , the relationship between combustion temperature and the number of moles of gaseous products per molecular weight of explosive has been shown to predict P_{CJ} for any CHNO explosive. In this simple method, there is no need to have accurate composition of detonation products. It is assumed that the gaseous products are limited to CO, CO_2, H_2O, N_2, and H_2. As shown in Table 1, it is preferred that a pair of oxygen atoms available can be used to form $CO+H_2O$ instead of CO_2+H_2. In particular, the experimental heat of formation of the explosive or the computed value using the PM3 procedure alone without the correction for crystal effects is used to calculate the combustion temperature to determine the detonation pressure.

The advantages of the new correlations are: 1) simply calculated input data, 2) estimation of the detonation properties of an explosive over a wide range of loading density 3) for the determination of the detonation performance the heat of formation in gas phase or solid state can be used 4) there is no need to know the accurate composition of detonation products.

Appendix A. Glossary of compound names

1. DATB: 1,3-diamino-2,4,6-trinitrobenzene ($C_6H_5N_5O_6$)
2. HMX: cyclotetramethylene tetranitramine ($C_4H_8N_8O_8$)
3. TETRYL: N-methyl-N-nitro-2,4,6-trinitroaniline ($C_7H_5N_5O_8$)
4. TNT: 2,4,6-trinitrotoluene ($C_7H_5N_3O_6$)
5. NG: nitroglycerine ($C_3H_5N_3O_9$)
6. NM: nitromethane (CH_3NO_2)
7. PETN: pentaerythritol tetranitramine ($C_5H_8N_4O_{12}$)
8. RDX: cyclomethylene trinitramine ($C_3H_6N_6O_6$)

References

1. Cowperthwaite, M.; Zwisler, W. H. In *TIGER Computer Program Documentation*; Stanford Research Institute: SRI publication number 1973; p 2106.
2. Abdualazeem, M. S. *High Temp. High Press.* **1998**, *30*, 387.
3. Mader, C. L. *Numerical Modeling of Explosives and Propellants*, 2nd Ed.; CRC Press: 1998; p 31.
4. Mader, C. In *Detonation Properties of Condensed Explosives Computed Using the Becker-Kistiakosky-Wilson Equation of State*; Los Alamos Scientific Laboratory Report LA-2900, New Mexico, 1963.
5. Kamlet, M. J.; Ablard, J. E. *J. Chem. Phys.* **1968**, *48*, 36.
6. Kamlet, M. J.; Dickinson, C. *J. Chem. Phys.* **1968**, *48*, 43.
7. Kamlet, M. J.; Jaccobs, S. J. *J. Chem. Phys.* **1968**, *48*, 23.
8. Gill, R.; Asaoka, L; Baroody, E. *J. Energ. Mater.* **1987**, *5*, 287.
9. Politzer, P.; Murray, J. S.; Grice, M. E.; Sjoberg, P. In *Chemistry of Energetic Materials*; Olah, G. A.; Squire, D. R., Eds; Academic Press Inc: 1991; p 77.
10. Stull, D. R.; Prohet, H. *JANAF Thermochemical Tables*, 2nd ed.; National Burea of Standard: NSRDS-NBS 37, Washington, 1971.
11. Stewart, J. J. P. *J. Comp. Chem.* **1989**, *10*, 221.
12. Keshavarz, M. H.; Oftadeh, M. In *Proceedings of the 28th International Pyrotechnics Seminar*, Australia, 2001; p 417.
13. Dobratz, B. M.; Crawford, P. C. *LLNL Explosives Handbook, Properties of Chemical Explosives and Explosives Simulants*, UCRL-52997 Change 2; Lawrence Livermore National Laboratory, University of California: 1985.
14. Horninig, H. C.; Lee, E. L.; Finger, M.; Kurrie, J. E. In *Proceedings of the Fifth Symposium (International) on Detonation*; Office of Naval Research: ACR-184, Washington, DC, 1970; p 422.
15. Kuznetsov, N. M.; Shevdov, K. K. *Combust. Explos. Shock Waves* **1966**, *2*(4), 52.