Prediction of Detonation Velocities of Non-metal Nitrated Explosives by Simple Method

MOHAMMAD HOSSEIN KESHAVARZ

Department of Chemistry, Malek-ashtar University of Technology
Shahin-shahr P.O. Box 83145/115, Islamic Republic of Iran
Tel: (98)-0312-522-5071;   Fax: (98)-0312-522-5068
E-mail: mhkir@yahoo.com   mhkeshavarz@mut-es.ac.ir

A simple method is introduced for determining detonation veloci-
ties of non-metal nitrated explosives, which have significantly non-
ideal behavior. The number of moles of different atoms in 100 g of
pure or mixture and condensed phase heat of formation of explosives
are sufficient for reliable simply prediction of detonation velocity as
compared to complicated computer codes. Detonation velocities for
non-metal nitrated explosives with the general formula $C_aH_bN_cO_d$ are
predicted by the equation:

$$D \text{ (km/s)} = \left(\frac{-3.748}{\rho_0} \right) - 13.438a + 13.033b - 28.632c$$

$$+ 24.704d + 0.7265\Delta H_f$$

where ρ_0 is loading density and ΔH_f is crystalline heat of formation.
This procedure for non-metal nitrated explosives, which have non-
ideal behaviour, shows good agreement with experimental values.

**Key Words: Explosives, Detonation velocities, Non-metal ni-
trated.**

INTRODUCTION

Ammonium nitrate based explosives have been widely used as industrial
explosives or energetic compositions such as ANFO. They show non-ideal
behaviour and their detonation velocities do not easily reach theoretically
predicted values. Since ammonium nitrate as one of the major components of the
most nitrated based explosives has large values for the minimum diameter and
relatively small values for the critical diameter, it will never reach the ideal
behaviour for the most practical conditions as predicted by hydrodynamic theory[1].
The relatively low decomposition rate of ammonium nitrate causes a wide
reaction zone in combination with latent heat losses and refraction waves, which
extinguish the decomposition reaction[2]; this effect can be used to explain its
non-ideal behaviour. As another point of view, since assuming either complete
reaction or no reaction of the ammonium nitrate with rest of the reaction products
exhibits difference in observed and calculated performance, the ammonium based

explosives can be classified as non-ideal explosives. The experimentally observed detonation velocity may be reproduced by a computer code such as BKW[3], if some percentage of ammonium nitrate is assumed to decompose and the rest is intact. For example, the measured detonation velocity can be reproduced by BKW computer code if 50 and 19% of ammonium nitrate decompose in amatex and amatol, respectively[3]. Because more ammonium nitrate decomposition occurs at higher temperatures, various decomposition temperatures can be assumed for the cause of different amounts of ammonium nitrate decomposition.

Significantly different detonation properties can be expected for non-ideal explosives than predicted by equilibrium, one-dimensional and steady state calculations. The amount of reacted explosive may be a function of the reaction zone length and physical separation of the fuel and oxidizer in non-ideal explosive may result in extended chemical reaction zones. To predict detonation properties of non-ideal explosives *via* a computer code, partial equilibrium as a simple approximation can be used rather than complex reacting mechanism. By specifying the amount of initial ammonium nitrate, that is assumed to react, partial equilibrium is invoked by a computer code.

There is a continuing need in the case of ideal and non-ideal explosives for simple reliable prediction of detonation performance rather than complicated computer codes. It is the purpose of this investigation to obtain a simple correlation for predicting detonation velocity of nonmetal nitrated based explosives. In this paper, the influence of the heat of formation, chemical composition and initial densities of nitrated explosives in their detonation velocities are of particular importance. The calculated detonation velocity will compare with measured values for some nitrated explosives and the predictions of the BKWS-EOS using full and 50% interaction of ammonium nitrate with detonation products for some well-known ammonium nitrate based explosives.

Detonation velocities of non-metal nitrated explosives

Detonation velocity and detonation pressure are two important performance parameters for measuring the effectiveness of different explosives, which can be calculated by some computer codes such as BKW[3] and RUBY[4] and latter's offspring TIGER[5], CHEQ[6] and CHEETAH[7]. The equation of state (EOS) of detonation products are usually needed for the calculations of performance so that the BKW-EOS is used extensively to calculate detonation properties[3] and BKWS-EOS[8] is one of different parameterizations of the BKW-EOS. A non-ideal explosive can have Chapman-Jouguet detonation pressure and velocity significantly different from those expected from a computer code such as BKW for equilibrium and steady state calculations[3].

Some empirical methods have been introduced for the determination of the Chapman-Jouguet (C-J) detonation pressure of ideal pure or mixture of different classes of explosives[9–14]. Some of these correlations[9–11] have been recently

introduced that use the calculated combustion temperature based on computed heat of formation by PM3 procedure or experimental crystalline heat of formation. One of the most important detonation parameters is detonation velocity that can be measured directly with a high accuracy to within a few per cent at various charge diameters and extrapolated to an "infinite diameter".

It can be proposed that the detonation performance of a non-metal nitrated high explosive can most appropriately be expressed as its elemental composition, loading density and heat content in condensed phase. It is clear that the heat of formation is a measure of energy content of an energetic material and usually enters into the calculation of performance of explosives. Some theoretical methods can be used to calculate heat of formation for some classes of explosives[15–18]. Though assumed decomposition products are usually necessary for calculation of detonation performance, it is possible to represent detonation velocity of non-ideal nonmetal nitrated explosive as a functions of its composition on the basis of an approach proposed earlier by some authors[9–21] for defining and evaluating in a fairly simple and straightforward manner detonation velocity of ideal explosives. Higher percentage of ammonium nitrate in the mixture with other high explosives such as TNT and RDX usually decreases detonation velocity. One can express detonation velocity of non-ideal nonmetal nitrated explosives as a function of basic parameters, namely the elemental composition, oxygen balance, heat of formation and initial density of mixture; various combinations of mentioned parameters are studied and optimized with experimental data. The results show that the following simple correlation on the basis of 100 g of pure or mixture can give a reliable prediction of detonation velocity of non-ideal nonmetal nitrated explosives with the general formula $C_aH_bN_cO_d$:

$$D \text{ (km/s)} = \left(\frac{-3.748}{\rho_0}\right) - 13.438a + 13.033b - 28.632c + 24.704d + 0.7265\Delta H_f$$

(1)

where ρ_0 is initial density in g/cm^3 and ΔH_f is condensed heat of formation in kcal/mol. The new correlation requires no prior knowledge of any measured, estimated or calculated physical, chemical or thermochemical properties of explosive and assumed detonation products other than heat of formation and loading density of explosive.

The heat of formation and other necessary data in using Eq. (1) are given in Table-1. Predicted detonation properties of well-known ammonium nitrate based explosives by new correlation and BKWS-EOS are compared with experimental values in Table-2 so that full and partial equilibria of ammonium nitrate are used for BKWS-EOS. It is assumed that in the case of partial equilibrium only 50% of ammonium nitrate interacts with combustion products. Detonation properties for explosives containing nitrate salts were predicted adequately by using new correlation.

TABLE-1
PARAMETERS USED IN CALCULATIONS

Explosive	Chemical formula (based on 100 g of compound)	Condensed phase ΔH_f (kcal/mol)
Ammonium nitrate	$H_5N_{2.5}O_{3.75}$	–109.25 (8)
Hydrazine nitrate	$H_{5.26}N_{3.16}O_{3.16}$	–62.14 (3)
21/79 Hydrazine/hydrazine nitrate	$H_{6.78}N_{3.81}O_{2.50}$	–41.09 (3)
70/30 Hydrazine/hydrazine nitrate	$H_{10.33}N_{5.32}O_{0.946}$	7.85 (3)
Amatex-20	$C_{1.73}H_{2.99}N_{2.14}O_{2.90}$	–22.74 (8)
Amatex-40	$C_{1.44}H_{3.48}N_{2.09}O_{3.12}$	–47.07 (8)
Amatol-80/20	$C_{0.616}H_{4.44}N_{2.26}O_{3.53}$	–88.72 (8)
Amatol-60/40	$C_{1.23}H_{3.88}N_{2.03}O_{3.31}$	–68.19 (8)
ANFO-6/94	$C_{0.43}H_{5.54}N_{2.35}O_{3.53}$	–105.25 (3)
75/25 HMX/hydrazine nitrate	$C_{1.01}H_{3.34}N_{2.81}O_{2.81}$	–10.99 (3)

TABLE-2
COMPARISON OF DETONATION VELOCITY OF THE NEW CORRELATION,
EQ. (1), AND BKWS-EOS[8] (USING FULL AND PARTIAL, 50%, INTERACTION OF
AMMONIUM NITRATE WITH DETONATION PRODUCTS) AND MEASURED VALUES

Name	ρ_0 (g/cc)	D_{exp} (km/s)	D_{new} (km/s)	% Dev new	$D_{BKWS-EOS}$ (km/s), full	% Dev BKWS-EOS full	$D_{BKWS-EOS}$ (km/s), partial	% Dev BKWS-EOS partial
Ammonium nitrate	0.7	1.5^8	1.50	–0.04	3.57	138	2.23	48.7
Hydrazine nitrate	1.626	8.691^3	8.69	0.00	—	—	—	—
21/79 Hydrazine/ hydrazine nitrate	1.4418	8.6^3	8.52	0.97	—	—	—	—
70/30 Hydrazine/ hydrazine nitrate	1.14	8.025^3	8.03	–0.02	—	—	—	—
Amatex-20	1.66	7.55^8	7.55	0.01	8.05	6.6	7.53	–0.3
Amatex-40	1.61	7.01^8	6.58	6.12	7.97	13.7	6.84	–2.4
Amatol-80/20	1.6	5.2^8	5.12	1.46	8.46	62.7	5.65	8.7
Amatol-60/40	1.6	5.76^3	5.76	0.00	8.05	39.8	6.24	8.3
ANFO-6/94	0.88	5.5^3	5.50	0.04	—	—	—	—
75/25 HMX/ hydrazine nitrate	1.86	9.1^3	8.86	2.58	—	—	—	—

Conclusions

Ammonium nitrate is the cheapest source of oxygen available in the condensed form for commercial explosives such as amatol. This study had as its original purpose to develop a simple method for estimating detonation velocities of nonmetal nitrated high explosives that contain carbon, hydrogen, oxygen and nitrogen. The results of this work are remarkable because the important data for this method is only heat of formation that can be easily obtained from data of pure components[22]. As seen, the introduced simple hand calculated empirical correlation for determining detonation velocities show surprisingly very good agreement with experimental values at loading density which may be taken as appropriate validation tests of the new method for nonmetal nitrated $C_aH_bN_cO_d$ explosives.

To calculate the detonation properties of nitrated explosives as non-ideal explosives by a computer code, partial equilibrium rather than a complex reacting mechanism can be used to predict detonation properties of non-ideal explosives. In this case specifying the amount of initial nitrate, that is assumed to react, is needed for calculation. However, the present method is exceedingly simple and at the same time gives results that are comparable to predicted values by a complex computer code involving the equation of state of the products. There is also no need to know the initial reacting nitrate in the new method. Simple correlation complemented computer output is introduced for desk calculation detonation velocities of non-metal nitrated explosives through condensed phase heat of formation and atomic composition of pure or mixed explosives on the basis of 100 g of compound. Given the chemical formula of a real or hypothetical nonmetal nitrated high explosives with $C_aH_bN_cO_d$ composition, one can estimate detonation velocities of explosives to within about a few per cent.

In brief, a relatively accurate method of estimating detonation velocities of nonmetal nitrated explosives is introduced which is only based upon the atomic composition of either pure or mixed explosives and condensed phase heat of formation.

REFERENCES

1. A. Miyake, K. Takahara, T. Ogawa, Y. Ogata, Y. Wada and H. Arai, *J. Loss Prevent. Proc. Ind.,* **14,** 533 (2001).
2. M.A. Cook, The Science of High Explosives, Van Nostrand Reinhold (1958).
3. C. L. Mader, Numerical Modeling of Explosives and Propellants, CRC Press, 2nd Edn. (1998).
4. H.B. Levine and R.E. Sharples, Operator's Manual for RUBY, Lawrence Livermore Laboratory Report UCRL-6815, Livermore, CA (1962).

5. M. Cowperthwaite and W.H. Zwisler, TIGER Computer Program Documentation, Stanford Research Institute, SRI Publication No. 2106 (1973).
6. A.L. Nichols and F.H. Ree, CHEQ 2.0 User's Manual, UCRL-MA-106754, Lawrence Livermore National Laboratory, Livermore, CA (1990).
7. L.E. Fried, W.M. Howard and P.C. Souers, CHEETAH 2.0 User's Manual, Lawrence Livermore National Laboratory, Livermore, CA (1998).
8. M.L. Hobbs and M.R. Baer, Proceedings of the Tenth Symposium (International) on Detonation, Boston, MA (1993).
9. M.H. Keshavarz and M. Oftadeh, *High Temp.-High Press.*, **34**, 495 (2002).
10. ———— , *Bull. Korean Chem. Soc.*, **24**, 19 (2003).
11. ———— , *Indian J. Eng. Mater. Sci.*, **10**, 236 (2003).
12. M.H. Keshavarz and H.R. Pouretedal, *Thermochim. Acta*, **414**, 203 (2004).
13. M.H. Keshavarz and M. Oftadeh, *Theo. Pract. Energ. Mater.*, **5B**, 271 (2003).
14. M.H. Keshavarz, *Asian J. Chem.*, **17**, 663 (2005).
15. B.M. Rice and J. Hare, *Thermochim. Acta*, **384**, 377 (2002).
16. P. Politzer, J.S. Murray, M.E. Grice, M. Desalvo and E. Miler, *Mol. Phys.*, **91**, 923 (1997).
17. B.M. Rice, V.V. Pai and J. Hare, *Combust. Flame*, **118**, 445 (1999).
18. M.H. Keshavarz and M. Oftadeh, *High Temp.-High Press.*, **36**, 499 (2004).
19. R.L. Rothstein and R. Petersen, *Propellants and Explosives*, **4**, 56 (1979).
20. R.L. Rothstein , *Propellants and Explosives*, **6**, 91 (1981).
21. J.R. Stine, *J. Energetic Mater.*, **8**, 41 (1990).
22. B.M. Dobratz and P.C. Crawford, LLNL Explosives Handbook, Properties of Chemical Explosives and Explosive Simulants, UCRL-52997 Change 2, Lawrence Livermore National Laboratory, University of California (1985).

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LUGO, SPAIN

Contact:

Alberto Cepeda Saez

University of Santiago de Compostela

Campus of Lugo

Veterinary Faculty

E-27002 Lugo, Spain

Tel.: +34 (982) 25 45 92

Fax: +34 (982) 25 45 92

E-mail: cepeda@lugo.usc.es