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Studies on Empirical Approaches for Estimation of Detonation Velocity of High Explosives

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Abstract: Despite many computer based codes like CHEETAH, TIGER, RUBY, BKW, etc. the velocity of detonation (VOD) for explosive molecules and explosive mixtures (formulations) is estimated by several empirical formulations. This article discusses various approaches for the estimation of the velocity of detonation by empirical mathematical equations. The formulation proposed by Kamlet in 1968 is the oldest one and it is confirmed to be more reliable by many subsequent researchers. The method proposed by Rothstein (1978), Xiong (1985), Stein (1990), Keshavarz (2006) are discussed and compared for conventional explosive molecules like RDX, HMX, TNT, PETN, and HNS. The values of the velocity of detonation for these molecules are found to be very close to each other. Further comparison of empirical mathematical formulations was carried out for four other explosive molecules of relatively recent origin (CL-20, FOX-7, TATB and NTO). These molecules were selected as they were unknown at the time of the proposed formulations except that by Keshavarz (2006). For CL-20, the velocity of detonation by different methods is 9345.1 m/s (Kamlet), 9378.8 m/s (Rothstein), 9116.0 m/s (Xiong), 9383.7 m/s (Stein) and 9887.9 m/s (Keshavarz) respectively. The method proposed by Keshavarz gives a higher value of the velocity of detonation than the others. For FOX-7, the values are 8636.6 m/s (Kamlet), 8733.3 m/s (Rothstein), 8766.1 m/s (Xiong), 8645.0 m/s (Stein) and 8245.3 m/s (Keshavarz) respectively. In this case the Keshavarz approach gives a lower value of the velocity of detonation. For these molecules, the results by the Xiong method is very close to that obtained by the Kamlet method. Deviation, as well as dispersion of the calculated values by other methods, is on the high side.

Keywords : explosives, detonation, velocity of detonation (VOD), empirical, density, heat of formation

Introduction

Velocity of detonation is one of the salient performance parameters for high explosive molecules and formulations. A quick estimate of this parameter helps in selecting, tailoring and understanding the behavior of explosives in terms of blast overpressure, fragmentation, penetration and other expected end-effects. In addition to this, new explosive molecules can be identified from the myriads of possible combinations of elements as target futuristic molecules, if handy, ready-to-use, accurate, quick and reliable methods for the estimation of the velocity of detonation are established. For calculation of the velocity of detonation of explosives, many computer codes have been developed and used. RUBY, TIGER, CHEETAH, and BKW [1-4] are computer codes which have been developed for such applications. The computer codes are based on sound theoretical strategies and they consider a variety of input parameters. They have been made very user-friendly in the course of time. Although these codes are extensively used, tedious preparation of the input file, the requirement of a computer, cost of the codes and other requirements give empirical correlations an upper edge over existing codes. Above all, ease of hand calculation makes these empirical correlations versatile, relegating computer codes to secondary status. The empirical relations for the performance prediction of explosive parameters of explosives are developed to evolve an easier method for such predictions for existing molecules and compositions, as well as for futuristic formulations. The empirical approaches are based on statistical analysis of the behavior of existing explosives and all of them use certain physical and chemical parameters as input. Most of the formulations use the molecular formula of the explosive along with the density, heat of formation, etc. for prediction of the velocity of detonation. This paper discusses the approaches and compares their values for certain selected explosives.

Empirical Approaches

Since most of the explosive formulations and molecules contain carbon, hydrogen, nitrogen and oxygen (CHNO), many empirical predictions are based on these four elements. One of the famous and most popular approaches was proposed by Kamlet et al. [5]. It uses the molecular formula, density and heat of formation of the explosive and calculates the detonation parameters by empirical results. The method depends on calculation of three parameters – (i) moles of gaseous products of explosion per gram of explosive or N, (ii)

grams per mole for the gaseous products of explosion or M and (iii) chemical energy of the detonation reaction or Q. The paper compares results from the RUBY code and close matching is reported for many existing molecules and formulations. For RDX ($C_3H_6N_6O_6$) at a density of 1.712 g/cm^3, the velocity of detonation is calculated as 8.512 mm/μs (as against 8.437 mm/μs by the RUBY computer code). For HMX ($C_4H_8N_8O_8$) at a density of 1.903 g/cm^3, the velocity of detonation is calculated as 9.157 mm/μs (as against 9.238 mm/μs by the RUBY computer code). The method is versatile and can be used for explosive formulations also by using the equivalent molecular formula and density. For RDX/TNT – 77/23, the value of N = 0.0318, M = 27.50, Q = 1436, from which the detonation velocity can be calculated. Velocity of detonation = $1.01 \times \sqrt{\phi} \times (1 + 1.3\rho)$, where $\phi = N \sqrt{MQ} = 6.319$. At a density of 1.743 g/cm^3, the velocity of detonation is calculated as 8.292 mm/μs. This is a very simple formula and the number of input parameters is also low. This can be used for molecules as well as combination of molecules. The dependence of velocity of detonation on density can be estimated by the formulation. However, this is valid for explosives containing C-H-N-O elements only. The effect of confinement is also not simulated in the formulation. The formulation by Kamlet et al. has been investigated by several later researchers for its accuracy. Hardesty et al. [6] confirmed the use of Kamlet's equation for new formulations also using detonation pressure data. Zhou et al. [7] established the additive nature of the Kamlet parameter 'ϕ' for mixtures of explosive molecules. Keshavarz et al. [8] suggested the use of more gaseous products in Kamlet's formulation for better accuracy and showed, with selected explosives, that calculation of the chemical energy of detonation can be improved further. Later, Keshavarz [9] modified the relation to include fluorine and chlorine in the formulation. The proposed relation for the velocity of detonation is $D = 1.404 \times N^{½} (MQ)^{1/4}\rho - 1.97$. The scheme for conventional explosives assumes the use of oxygen in formation of carbon monoxide, water and then carbon dioxide in sequence. Politzer et al. [10] confirmed the products of explosion for explosive molecules by the simple approach of utilization of oxygen. Oxygen goes into the formation of water taking hydrogen atoms before forming carbon dioxide. This was confirmed by calculation from BKW codes for many popular explosives. Use of solid state enthalphies of formation in place of gas phase enthalphies of formation for explosion products is another finding to reduce errors in the Kamlet formulation. Despite all modifications and criticism, the method proposed by Kamlet is still considered more reliable than any contemporary or new method for prediction of the velocity of explosive detonation.

L.R. Rothstein [11] has generalized the empirical approach for prediction

of detonation velocity by calculation of a factor 'F', which is dependent on chemical bonds in the molecules, excess oxygen, nitro groups etc. The velocity of detonation bears a linear relation with this parameter and the velocity of detonation = (F – 0.26)/0.55. This correlation is independent of the heat of formation. For RDX at a density of 1.83 g/cm^3, the value of F = 5.18 and the velocity of detonation is calculated as 8.95 mm/μs. For HMX at a density of 1.90 g/cm^3, the value of F = 5.24 and the velocity of detonation is calculated as 9.05 mm/μs. The formulation is not suitable for explosive mixtures (formulations). However, this algorithm is used for making a software called LOTUSES [12-13].

Another formulation, although not very popular amongst researchers was developed by Xiong et al. [14]. According to this formulation the velocity of detonation = 67.6 $\sqrt{Q}$ + 243.2 × w × ρ. Here Q and ρ have the same meaning as given by Kamlet et al. The potential energy is denoted by 'w' by the authors and it is calculated after assessing the products of explosion using their co-volumes. Five conditions of explosive molecules and formulations are enumerated depending on oxygen availability from oxygen-rich to seriously deficient molecules. For RDX, at a density of 1.8 g/cm^3, the velocity of detonation is estimated by the method as 8744 m/s (as against 8754 m/s as a reported value). For HMX, the detonation velocity at a density of 1.90 g/cm^3 is calculated in the paper to be 9086 m/s (as against a reported value of 9100 m/s). For RDX/TNT – 78/22, the velocity of detonation at a density of 1.755 g/cm^3 is calculated to be 8348 m/s (against a reported value of 8306 m/s). The value is comparable to that given by Kamlet et al. for RDX/TNT – 77/23.

Stine [15] approached the calculation of detonation velocity by a much simpler method. He has used statistical curve fitting for selected explosives to find the coefficients. The developed formulation is able to predict detonation velocity for a variety of explosives. The final relation, which is used to calculate detonation velocity in km/s = 3.69 + ρ (-13.85 C + 3.95 H + 37.74 N + 68.11 O + 0.6917 H_f)/MW. This formulation is valid for C-H-N-O explosives. For the first time direct use of heat of formation in kcal/mol is seen. In earlier formulations (by Kamlet and Xiong), chemical energy of detonation in cal/mol is used. For RDX (ρ = 1.806 g/cm^3) and HMX (ρ = 1.905 g/cm^3), the velocity of detonation is reported to be 8.70 km/s and 9.03 km/s respectively. The developed formulation is not explored for explosive formulations, where more than one explosive molecule is present. However, the equation can be used for such applications.

In the recent past, Keshavarz et al. have suggested several methods for empirically estimating the velocity of detonation. Kamlet's method is improved so that deviation of prediction and experimental results can be narrowed for explosives at loading densities of lower than 1 g/cm^3 [16]. They claim that

Kamlet's method is not very reliable at densities lower than 1 g/cm^3. The velocity of detonation in km/s = $\sqrt{\phi} \times (0.779 + 1.442\rho) = N^{1/2} M^{1/4} Q^{1/4} \times (0.779 + 1.442\rho)$. For RDX ($\rho$ = 1.80 g/cm^3) and HMX (ρ = 1.89 g/cm^3), the velocity of detonation is reported to be 8.79 km/s and 9.12 km/s respectively. For non-metal nitrated explosives, another formulation was developed by Keshavarz [17]. The formulation and examples are explained by taking an explosive formulation; pure molecules were not discussed. The velocity of detonation in km/s = $(-3.748/\rho) - 13.438\,C + 13.033\,H - 28.632\,N + 24.07\,O + 0.7265\,H_f$. Here H_f is the crystalline heat of formation in kcal/mol. This formulation resembles to some extent Stine's formulation [15]. However, numerical values and the sign of coefficients, dependence on density and heat of formation are different. Yet another correlation was proposed by Keshavarz [18]. As per this approach the velocity of detonation in km/s = $1.90 + [-2.97\,C + 9.32\,H + 27.68\,N + 98.9\,O + 1.22\,H_f] \times (\rho/MW)$. For RDX ($\rho$ = 1.80 g/cm^3) and HMX (ρ = 1.89 g/cm^3), the velocity of detonation is reported to be 8.81 km/s and 9.12 km/s respectively. The dependence of velocity of detonation on the heat of formation was eliminated in another paper [19]. The final correlation for the velocity of detonation in km/s = $1.6439 + 3.5933\,\rho - 0.1326\,C - 0.0034\,H + 0.1206\,N + 0.0442\,O - 0.2768\,X$. Here, in place of the heat of formation, another term 'X' is introduced, which is the number of specific groups like $-NH_2$, $-NH_4$ or  in the explosive. For RDX (ρ = 1.80 g/cm^3) and HMX (ρ = 1.89 g/cm^3), the velocity of detonation is reported to be 8.68 km/s and 9.20 km/s respectively. The calculation is also possible for mixtures of explosives by this method and RDX/TNT – 77/23 at a density of 1.74 gives the velocity of detonation as 8.06 km/s by this formulation.

There are other approaches, where mathematical formulations for quick calculation of the velocity of detonation are developed, based on certain advanced instrumental outcomes and molecular modeling. These approaches lack quick estimation and simplified input parameters for the required predictions. Lemi Türker [20] has used a density function approach for the calculation of total energy of the explosive molecules (E). Using the number of NO_2 groups (N) present, a relation is developed by regression analysis for the prediction of the velocity of detonation (D in km/s). The relation is $D^2 = -393.6877 - 0.2454(NE/M) - 114.0793(E/M)$, where M is the molecular weight of the explosive. For RDX, the molecular weight (M) is 222, the total energy (E) is -897.265 (in Hartree units) and the number of NO_2 groups (N) is 3, the velocity of detonation is estimated as 8.326 km/s. Similarly, for HMX the molecular weight (M) is 296, the total energy (E) is -1196.354 (in Hartree units) and the number of NO_2 groups (N) is 4, the velocity of detonation is estimated as 8.45 km/s. Obviously these values

are well away from the values obtained by other researchers. This method is not described further here because calculation of the total energy in the specified unit is not available.

Comparison/Discussion of Approaches

The empirical formulations developed for the calculation of the velocity of detonation take into consideration molecular formula, especially the number of atoms of carbon, hydrogen, nitrogen and oxygen. Density and heat of formation form an integral part of the input parameters in all of them except Keshavarz [19], where the heat of formation is removed from the input parameters for the prediction of the velocity of detonation. Most of the developed approaches are restricted to CHNO-explosives. However, Rothstein [11], and Keshavarz [8, 9] have also included other elements like fluorine and chlorine in the empirical formulation. The approach proposed by Xiong [14] can also include aluminum. One of the papers by Keshavarz [17] gives coefficients valid for low density and for a molecular weight of 100. The developed formulation is used for the prediction of conventional high explosive molecules at normal densities, but the predictions do not stabilize. Therefore, another paper by Keshavarz [19] is considered for the comparison of results.

Each of the approaches referred to predicts the velocity of detonation of popular explosives like RDX, HMX at different densities and values of the heat of formation and other parameters also vary from paper to paper. To rationalize the results, the density and heat of formation of RDX is taken as 1.816 g/cm^3 and 16 kcal/mol respectively (from ICT database [21]). The values of the velocity of detonation using empirical approaches by Kamlet [5], Rothstein [11], Xiong [14], Stein [15] and Keshavarz [19] are 8842.7 m/s, 8937.8 m/s, 8803.8 m/s, 8825.4 m/s and 8741.7 m/s respectively. The values are very close to each other. The relative deviation for the given methods assuming Kamlet's output as the correct one is +1.07% (Rothstein), -0.44% (Xiong), -0.195% (Stein) and -1.14% (Keshavarz) respectively. The correlation by Stein gives a better resemblance to Kamlet's result for RDX at standard crystal density and heat of formation. However, the value calculated using the Rothstein method is slightly on the high side. Similar calculations were carried out for other conventional explosives like TNT, PETN, HNS etc. at the highest density. The reported heat of formation from the thermo-chemical database [21] and the results are compiled in Table 1.

Table 1. Velocity of detonation (m/s) by empirical approaches

Molecules	Density (g/cm^3)	Kamlet [5]	Rothstein [11]	Xiong [14]	Stine [15]	Keshavarz [19]
RDX	1.816	8842.7	8937.9	8803.8	8825.4	8741.7
HMX	1.910	9146.5	9040.2	9118.6	9076.1	9270.3
TNT	1.654	7009.0	6663.1	7021.5	6846.6	7273.2
PETN	1.778	8708.1	7384.1	8598.0	8421.0	8358.4
HNS	1.745	7287.6	6693.3	7304.5	7124.9	7299.8
TETRYL	1.731	7774.8	7769.5	7774.8	7665.7	7879.5

It is clear from the Table 1 that the Kamlet formulation gives a very high estimate for PETN, which is not shown by any of the other existing empirical methods. In the paper by Kamlet [5], PETN is not reported in Table 1 of velocity of detonation. Keshavarz [18] has reported the value of the velocity of detonation for PETN as 8650 m/s at a density of 1.76 g/cm^3, whilst as per calculation carried out by the author, it is 8646.6 m/s at this density. The calculated value is for a density of 1.778 g/cm^3 as indicated in the thermochemical database [21]. For all other molecules, Kamlet's approach can be considered reliable and matching experimental observations. Of the given approaches, Xiong's formulation is very close to the velocity of detonation proposed by Kamlet.

In order to compare the various empirical approaches, four molecules of recent origin CL-20, FOX-7, TATB and NTO are considered. All of them are CHNO explosives and their properties are taken from the ICT Database of Thermochemical Values [18]. During the publication of all the considered empirical formulations, these molecules were not very popular and estimates for such molecules can be a confirmatory proof of accuracy of the formulations. Keshavarz's approach [19] is relatively new and the molecules were well known when those formulations were proposed. The applicability of these mathematical formulations to these four molecules has been investigated. The properties are reproduced in Table 2.

Table 2. Input parameters for selected explosives

Molecule	Formula	Density (g/cm^3)	Heat of Formation (kcal/mol)	Molecular weight
CL-20	$C_6H_6N_{12}O_{12}$	1.970	81.02	438.188
FOX-7	$C_2H_4N_4O_4$	1.885	-32.00	148.079
TATB	$C_6H_6N_6O_6$	1.937	-33.40	258.150
NTO	$C_2H_2N_4O_4$	1.930	-24.08	130.063

For the same density and heat of formation, calculations are made by each method, described in the paper. As per the method described by Kamlet [5], for CL-20, the value of the three parameters N, M and Q are 0.03079, 31.111 and 1544.95 cal/g respectively. This gives a detonation velocity of 9345.1 m/s. Similar calculations were repeated for the other molecules and the values are tabulated in Table 2. Calculations were repeated for the methods proposed by the other researchers and the velocity of detonation was calculated for each molecule. The results are tabulated in Table 3.

Table 3. Velocity of detonation (m/s) by empirical approaches

Molecules	Kamlet [5]	Rothstein [11]	Xiong [14]	Stine [15]	Keshavarz [19]
CL-20	9345.1	9378.8	9116.0	9383.7	9887.9
FOX-7	8602.9	8733.3	8766.1	8645.0	8245.3
TATB	7941.9	7859.5	8033.4	7835.3	7950.1
NTO	8636.6	8362.6	8659.2	8801.3	8957.4

Although the experimental values of many of these explosives are quoted in the literature, the density and heat of formation considered for such calculations are variable. Experimental results are deliberately not considered for comparison for this reason. However, if the superiority of the Kamlet method is confirmed by other researchers, the results by the Kamlet [5] method may be taken to be the accurate ones. Of the given methods, Xiong's [14] approach leads to values of the velocity of detonation very near to those from Kamlet's method. Stein's [15] approach over-predicts the velocity of detonation for CL-20, while the value for TATB is under-predicted. Clearly, the dispersion of values is higher by this method. Keshavarz's method [19] returns a value for FOX-7 to be very low and that for NTO is on the high side. This method lacks accuracy, if Kamlet's method is considered as standard. The Rothstein [11] approach gives a higher value for CL-20 and a lower value for NTO. Clearly, all methods fail to match the results from Kamlet's method except that of Xiong's.

If the complexity of the method is considered, the methods proposed by Kamlet and Xiong are calculation intensive. They need estimation of probable products of explosion and then further calculations for salient parameters are made. Compared to that, the methods proposed by Rothstein, Stein and Keshavarz give very easy correlations which can be employed using a hand calculator. The Keshavarz method is the simplest one, but deviations are higher. The method by Stein is the most accurate of these three methods. So, considering both complexity of calculation and accuracy, Stein's empirical approach gives the velocity of detonation of explosives very close to that predicted by Kamlet.

Conclusion

There is no doubt, that Kamlet's approach [5] is the oldest and the best one for prediction of the velocity of detonation of explosives. Other attempts have been made for the calculation of the velocity of detonation for selected explosives. Kamlet's formulation is discussed for its merits and demerits by researchers and is still considered as more accurate than the other methods. Rothstein's [11] method has limited application due to dependence on molecular structure and it cannot be used for explosive formulations with convenience. The methods proposed by Xiong [14] and Stine [15], although not very popular, are accurate for easy calculation. Keshavarz has made several attempts to modify the existing formulations and proposed a new method for certain specific cases. All of the developed formulations were used for the prediction of the velocity of detonation for CL-20, FOX-7, TATB and NTO. The results show a close match amongst the various formulations for the chosen explosive molecules. Amongst the proposed methods, Xiong's empirical method gives results very close to those from Kamlet's empirical approach for the 4 selected explosive molecules.

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