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Computer code to predict the heat of explosion of high energy materials

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ABSTRACT

The computational approach to the thermochemical changes involved in the process of explosion of a high energy materials (HEMs) vis-à-vis its molecular structure aids a HEMs chemist/engineers to predict the important thermodynamic parameters such as heat of explosion of the HEMs. Such a computer-aided design will be useful in predicting the performance of a given HEM as well as in conceiving futuristic high energy molecules that have significant potential in the field of explosives and propellants. The software code viz., LOTUSES developed by authors predicts various characteristics of HEMs such as explosion products including balanced explosion reactions, density of HEMs, velocity of detonation, CJ pressure, etc. The new computational approach described in this paper allows the prediction of heat of explosion (ΔH_e) without any experimental data for different HEMs, which are comparable with experimental results reported in literature. The new algorithm which does not require any complex input parameter is incorporated in LOTUSES (version 1.5) and the results are presented in this paper. The linear regression analysis of all data point yields the correlation coefficient $R^2 = 0.9721$ with a linear equation $y = 0.9262x + 101.45$. The correlation coefficient value 0.9721 reveals that the computed values are in good agreement with experimental values and useful for rapid hazard assessment of energetic materials.

1. Introduction

One of the most important thermodynamic parameters that determine the performance of explosives and propellants [1], which are broadly classified as high energy materials (HEMs) is their heat of explosion (ΔH_e). Heat of explosion (ΔH_e) is the quantity of heat released (illustrated in Fig. 1) when a HEM undergoes detonation as an explosive (e.g., RDX, HMX, TNT, etc.,) or deflagration (burning) as a propellant (e.g., a rocket propellant). Both these processes of detonation and deflagration occur even in the absence of external oxygen or air, because of the fact that the molecule of a HEM carries its own oxygen. ΔH_e is a quick and reliable criterion to evaluate the performance potential of a HEM [2]. For example, the higher the ΔH_e (usually expressed in cal/g or kJ/kg) of a rocket propellant the higher will be its "specific impulse", an index of propelling power of a rocket using this propellant. In recent past, theoretical calculations to predict detonation behaviour of explosives have evinced great interest [3–7]. Theoretical computation of notional materials allows for identification of promising candidates for additional study and elimination of poor candidates from further consideration, and thus, reducing costs associated with synthesis, and evaluation of the materials. This capability of computer-aided design leads to better designs and shorter design cycles.

For the existing computer codes such as BKW code, TIGER code, VLW code, etc., the user has to give molecular weight, density, heat of formation and many complex thermodynamic parameters as input parameter. Also these software's requires huge constants such as coefficients of EOS - α β, θ, κ; coefficients for Entropy fit - A, B, C, D, F, Enthalpy integration constant - IC, Heat of formation (Elements at 0K to Species at 0K) co-volume, etc. Also the number of coefficients different when different type of EOS is used. It is also observed that for the same EOS like BKW EOS, coefficients of EOS - α β, θ, κ; has been adjusted to different extent by different researchers. Apartment from the huge input constants, the user has to input some guess values for P, V, T to start the iteration as well as initial guess of the concentrations of the products. Some time the iteration won't converge due to improper/wrong initial guess values.

HEMs researchers all over the world are in the constant pursuit of conceiving and synthesizing a large number of compounds, the molecules of which are expected to have high ΔH_e values. Such a synthesis involves a lot of procedural challenges apart from high cost and hazards [8]. Thermochemical/hydrodynamic computer codes such as BKW (Charles L. Madder, first in 1956 for IBM

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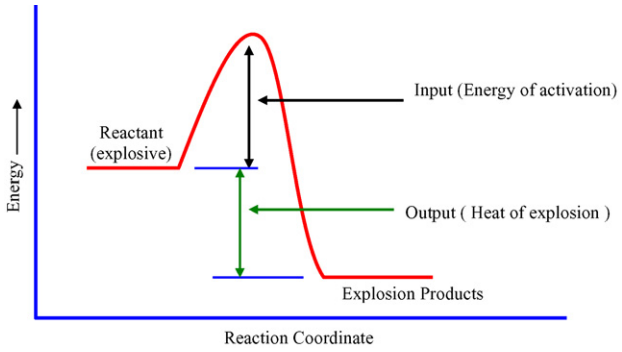

Fig. 1. Energy profile of an explosion reaction.

-704, STRETCH BKW in 1961 for IBM 7030, using Fortran IV BKW in 1967) [9–12], RUBY (Levine and Sharples in 1962) [13], PANDA (Gerald I. Kerley in 1981) [14] and JCZS [15] have been reported in literature for the prediction of various thermodynamic as well as detonation parameters. But these codes involve too many complex input parameters. It is therefore useful to develop a computational approach to predict the ΔH_e without any complex input parameters and without any experimental data as input parameters. In the present work, the computational approach combines Stines and Kramer method [16] to compute heats of formation of HEMs and Kistiakowsky–Wilson (K–W) rule for predicting possible explosion products [17]. The results obtained by this computational approach are comparable with experimental results reported in literature.

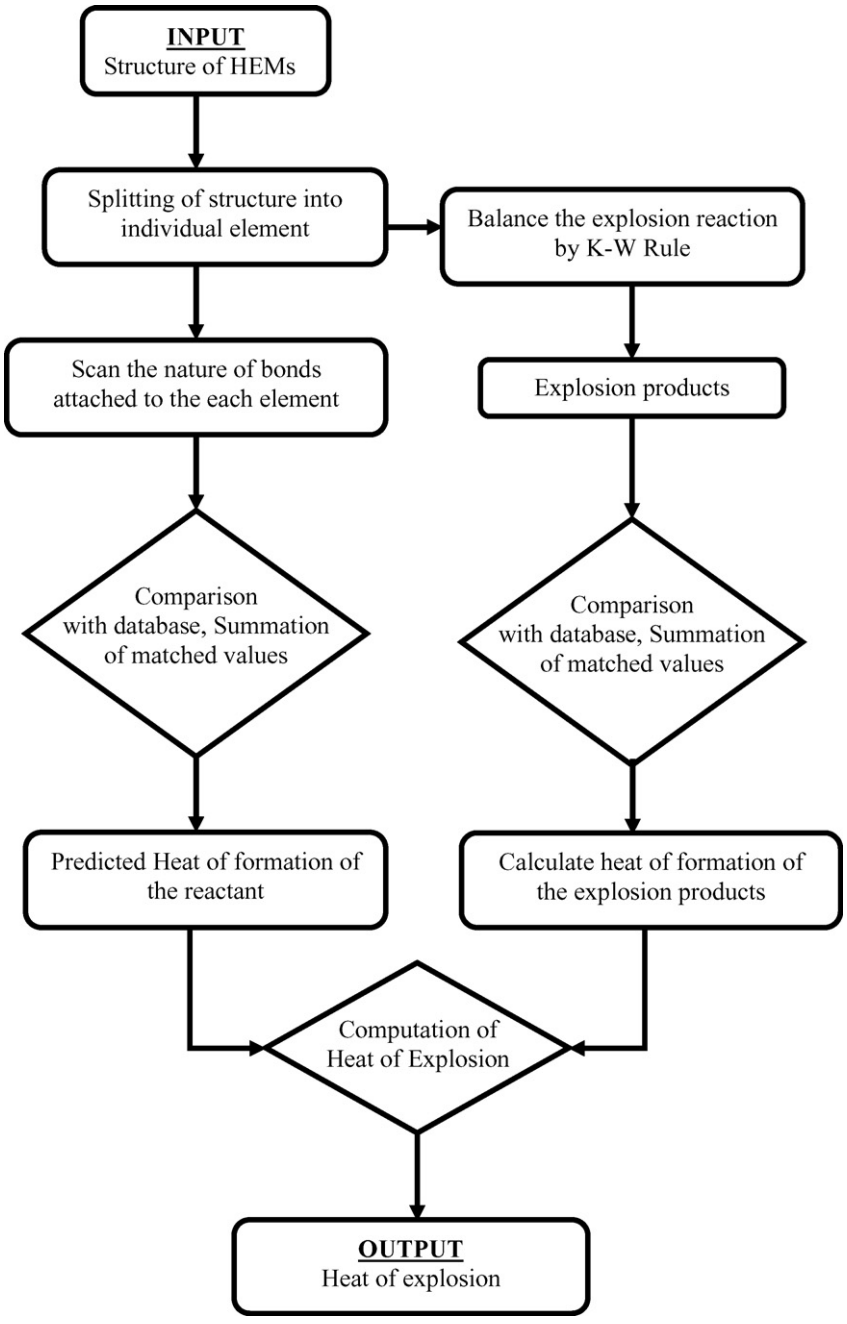

Fig. 2. Logic for computation of heat of explosion by LOTUSES.

Table 1
Heat of formation of common explosion products

Formula	Name	Molecular weight (g/mol)	Heat of formation (ΔH_f) (kJ/mol)
CO	Carbon monoxide	28	−111.8
CO_2	Carbon dioxide	44	−393.5
H_2O	Water	18	−240.6
H_2	Hydrogen molecule	2	0
O_2	Oxygen molecule	12	0
N_2	Nitrogen molecule	14	0

2. Computational approach

Computational approach described in this paper involves a systematic procedure in which thermodynamic parameters are computed from its structural information. The advent of advanced computer system has dispelled one of the principal drawbacks of laborious time consuming mathematical calculations. Sufficient experimental data on estimating ΔH_f for HEMs in different phase states has been collected [18–20]. This set of data forms the basis for computing ΔH_e for various HEMs. Computation of ΔH_f and ΔH_e from the model described below is versatile, convenient and require structural information only.

In the present computational approach, the structural information of HEMs is given as input for the computation of the heat of formation of energetic reactants using Stine and Kramer method [16] extended to terminal groups such as –OH, –NH, $–NH_2$, C=O and hydrogen attached to aromatic and nonaromatic carbon [21]. To calculate the ΔH_e and other explosive performance parameters, a knowledge of the composition of the gaseous products of explosion is essential [19]. The software developed by the authors ensures that once the molecular structure of a HEM is known, it is converted in to coded structural information giving various types of bonding involved in the molecule thereby, predicting the following: (i) most probable products of explosion based on Kistiakowsky–Wilson hierarchy rules (ii) ΔH_f of the products (iii) ΔH_f of the energetic reactant and (iv) the resultant heat of explosion. The logic of above discussed is illustrated in Fig. 2. The heat of formation of most common explosion products are given in Table 1 Since the data shown in Table 1 is stored inbuilt in LOTUSES (version 1.5), it will compute the sum of heat of formation of explosion products (ΔH_f of the products). Once the ΔH_f of the energetic reactant and ΔH_f of the products are computed by LOTUSES (version 1.5), it will automatically compute the heat of explosion (ΔH_e) using the following well-known relation.

$$\Delta H_e = \sum \Delta H_f(\text{products}) - \sum \Delta H_f(\text{reactant})$$

3. About LOTUSES (version 1.5)

The software LOTUSES (version 1.5) is developed to run on windows operating system using modern modular and object-oriented techniques in Visual Basic 6.0. This installation package occupies about 50 MB of hard disk space in the computer and can be installed in Windows 98, 2000 as well as in Windows XP. In addition to thermodynamic parameters such as heat of explosion, heat of formation it also predicts performance parameters of HEMs such as velocity of detonation, CJ Pressure, density, relative strength, power index, etc. [21–25]. The output of the programme can be directly printed (attached to the standalone PC or LAN) as well as stored in various formats (.txt, .html, .doc, .xls, .pdf).

4. Results and discussions

Heat of explosion for various HEMs are computed by using above discussed logic (illustrated in Fig. 2) and the results are presented in Table 2 The ΔH_f of reactants were computed using Stine and Kramer method. The possible explosion products were predicted by K–W rule applicable to most of CHNO type HEMs and corresponding standard heat of formation were computed. The computational approach has been validated by comparing the predicted ΔH_e values with the experimentally determined results reported in the literature [20]. It does not include any heat generated by secondary reactions of the explosive or its products with air.

The predicted heats of explosion and corresponding experimental values for twenty HEMs are plotted in Fig. 3. The linear regression analysis of all data points in Fig. 3 yields the correlation coefficient $R^2 = 0.9721$ with a linear equation $y = 0.9262x + 101.45$. The correlation coefficient value 0.9721 reveals that the computed values are in good agreement with experimental values. Hence the algorithm included in the software code LOTUSES (version 1.5) for the computation of heat of explosion will be useful to design futuristic high energy molecules without any experimental data.

Table 2
Comparison of experimental value and predicated by LOTUSES

S. no.	HEM's Name	Empirical formula	Heat of explosion (kJ/kg)		Error%
			Experimental	LOTUSES	
1	Bi-trinitroethyl nitramine (BTENA)	$C_5H_5N_8O_{14}$	4857	5321	−9.55
2	Bitrinitroethylurea (BTNEU)	$C_5H_6N_8O_{13}$	6542	6382	2.45
3	Butene triol trinitrate	$C_4H_7N_3O_9$	6153	5737	6.76
4	Cyclonite (RDX)	$C_3H_6N_6O_6$	5723	5087	11.11
5	Dinitronaphthalene	$C_{10}H_6N_2O_4$	2635	2506	4.9
6	Dioxyethylnitramine dinitrate (DINA)	$C_4H_8N_4O_8$	5384	5021	6.75
7	Dipentaerythritol hexanitrate (DIPEHN)	$C_{10}H_{16}N_6O_{19}$	5208	4814	7.57
8	Erythritol trinitrate	$C_6H_{11}N_3O_9$	4110	3725	9.36
9	Ethylene dinitramine (EDNA)	$C_2H_6N_4O_4$	5343	5179	3.06
10	Mannitolhexa nitrate (MHN)	$C_6H_8N_6O_{18}$	6380	5937	6.95
11	Methyl nitrate	CH_3NO_3	6869	6562	4.46
12	Metriol trinitrate	$C_5H_9N_3O_4$	4992	4532	9.21
13	Ethylene glycoldinitrate (EGDN)	$C_2H_4N_2O_6$	7390	6881	6.89
14	Nitroisobutylglycerol trinitrate	$C_4H_6N_4O_{11}$	7755	7244	6.59
15	Nitromethane	CH_3NO_2	4763	4718	0.94
16	Nitrourea	$CH_3N_3O_3$	3865	3645	5.69
17	Pentaerythritol trinitrate (PETRIN)	$C_5H_9N_3O_{10}$	5301	4704	11.27
18	Pentaerythritol tetranitrate (PETN)	$C_5H_8N_4O_{12}$	6404	6130	4.28
19	Tetranitromethane (TNM)	CN_4O_8	2259	2206	2.33
20	Tetryl	$C_7H_5N_5O_8$	4773	4527	5.16

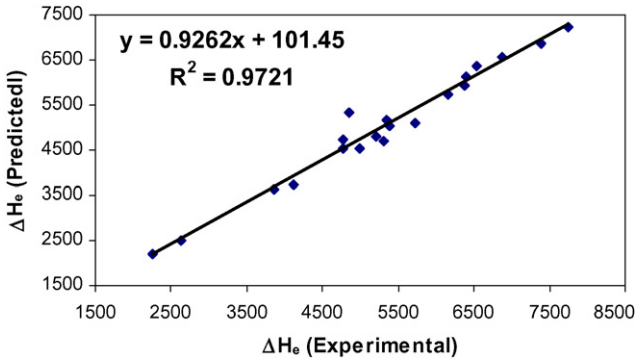

Fig. 3. Comparison of heat of explosion.

5. Conclusion

The computational approach described in this paper predicts ΔH_e values from the structural information of HEMs. The methodology combines the prediction of heat of formation (ΔH_f) of energetic reactants from its structural information using Stine and Kramer method and explosion products required for the estimation of heat of explosion, which is calculated by LOTUSES based on Kistiakowsky–Wilson hierarchy rules. Hence less input parameter (only structural information) is sufficient to compute the heat of explosion using LOTUSES (version 1.5). The variation between the computed and experimentally determined ΔH_e values was calculated and the regression coefficient value 0.9721 shows that predicted results are in good agreement with the experimental results reported in literature. The output of the LOTUSES (version 1.5) can be directly printed (attached to the standalone PC or LAN) as well as stored in various formats (.txt, .html, .doc, .xls, .pdf). The computational approach for this computation is simple, convenient and does not require any complex input parameters. This computer-aided design will leads to better designs and shorter design cycles as well as hazard assessment of energetic materials.

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