

## Prediction of heat of formation and related parameters of high energy materials

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### Abstract

Heat of formation is one of the most important parameters in the performance prediction of explosive and propellant formulations and their individual ingredients. This paper reports the development of user-friendly computer code for the prediction of heat of formation based on two approaches. In first methodology, the logic of Benson's Group additivity method and in the second method, the logic of Pedley method was used for predicting the heats of formation of high energy materials (HEMs). The predicted heats of formation by Benson method for various classes of high energy materials gave deviation in the range of 2–10%, whereas nearly 10–15% deviation was observed using Pedley methodology in comparison to experimental values. The linear regression coefficient values ( $R^2$ ) of 0.9947 and 0.9637 are obtained for heat of formation values predicted by this code using methodologies I and II, respectively. The newly developed code LOTUSES (version 1.3) has been validated by calculating the heats of formation of standard explosives such as TNT, pentaerythritol tetranitrate (PETN), RDX, HMX, etc., To the best of our knowledge, no such code is reported in literature which can predict heats of formation values integrated with performance parameters of HEMs belonging to all categories of organic compounds viz. aliphatic, aromatic and heterocyclic materials. The code can also be used to obtain parameters such as velocity of detonation, C–J pressure, volume of explosion products, power index, temperature of explosion and oxygen balance of HEMs. The code has been developed in Visual Basic having enhanced Windows environment. This software namely LOTUSES 1.3 is an updated version of the earlier ones namely LOTUSES 1.1 and 1.2 which do not cater for the calculation of heat of formation and temperature of explosion of HEMs. LOTUSES 1.3 is, therefore, a totally integrated software for computing most of the vital parameters of HEMs requiring mainly the molecular structural information of an explosive under consideration.

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### 1. Introduction

Intensive research and development work is on in many schools all over the globe to develop new high energy materials (HEMs) to meet the futuristic needs for defence, space and civil applications. In the last decade, Information Technology has undergone a revolution in the dissemination of scientific information through World Wide Web network. Scientists and technologists dealing with HEMs are making efforts to explore the knowledge and expertise available in the area of Information Technology for theoretical modelling and simulation work to achieve faster growth. Of particular importance in design-

ing new explosives, is the ability to predict the performance of such new compounds before the laborious and expensive task of synthesizing them is undertaken [1,2]. The search of energetic materials is best carried out presently using thermodynamics and molecular engineering approaches, which help in designing promising HEMs. In the recent past, theoretical calculations to predict detonation behaviour of explosives have evinced great interest [3–5]. Theoretical screening 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 [6–8].

One of the well-known codes currently used for predicting explosive performance parameters of any unknown or known HEM is Becker–Kistiakowsky–Wilson (BKW) CODE. The input parameters for BKW code are molecular formula,

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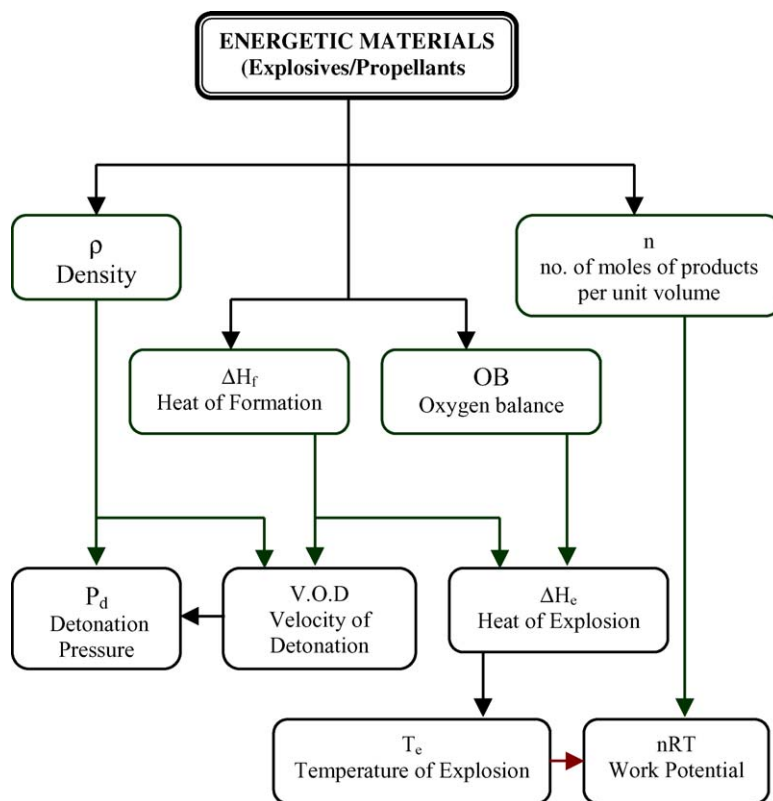


Fig. 1. Network of HEM parameters.

molecular weight, density and heat of formation. Another important widely used code for the performance prediction of ballistic parameters of rocket propellants is NASA-CEC-71. This code also utilizes molecular formula, density and heat of formation as important input parameters. The code REAL which predicts the ballistic performance parameters also requires heat of formation as an important input parameter. Authors have recently developed [1–4] a code named Linear Output Thermodynamic User-friendly Software for Energetic Systems (LOTUSES) which can simultaneously predict a wide range of properties and parameters of HEMs such as molecular weight, oxygen balance, velocity of detonation, C–J pressure, density, heat of explosion, relative strength of an explosive in comparison to 2,4,6-trinitro toluene (TNT) as well as the possible explosive decomposition products after explosion, volume of explosion products and air blast effects. The earlier versions [1,2] of LOTUSES code (version 1.1 and 1.2) also require heat of formation as an input parameter. Therefore, it can be realised that heat of formation is a vital parameter for the performance prediction of explosives and propellants [9–11]. The interdependence of these parameters in the field of HEMs is shown in Fig. 1 (network of HEM parameters) from which it can be observed that heat of formation of HEMs is one of the most vital characteristics determining their ultimate performance.

Rice et al computes the heats of formation at condensed phase by computing the B3LYP (Becke's three parameter hybrid, correlation are those due to Lee, Yang and Parr), 6-31G\* basic set and molecular energies [12]. Politzer et al. have established a correlation between the electrostatic potential of a molecule and

its condensed-phase heat of formation from heats of sublimation and vaporization [13,14]. Both the Rice et al. and Politzer et al. methods for computing heat of formation are based on density functional scheme, which involves too many complex input parameters.

In view of the above observations an attempt was made to develop a computer code which can predict heat of formation at gaseous phase, based on two different methodologies with very few input parameters and also to predict the possible explosion temperature. In the first methodology, the logic of Benson [15,16] is used and in the second methodology the approach of Pedley and co-workers [17,18] method are considered in the present work. The code developed based on the above approaches has been successfully integrated with the existing LOTUSES code (viz. versions 1.1 and 1.2) to make it more versatile and user-friendly in the explosive performance prediction of known HEMs as well as those of futuristic importance. Hence, the new methodology of predicting heat of formation from elemental composition and functional groups incorporated in LOTUSES 1.3 will be of immense value for the scientists, academicians and technologists working in the field of HEMs for designing high performance candidate molecules.

## 2. Prediction of HEMs parameters

### 2.1. Heat of formation

Heat of formation of a HEM is required to calculate various parameters such as velocity of detonation of explosives [19–22],

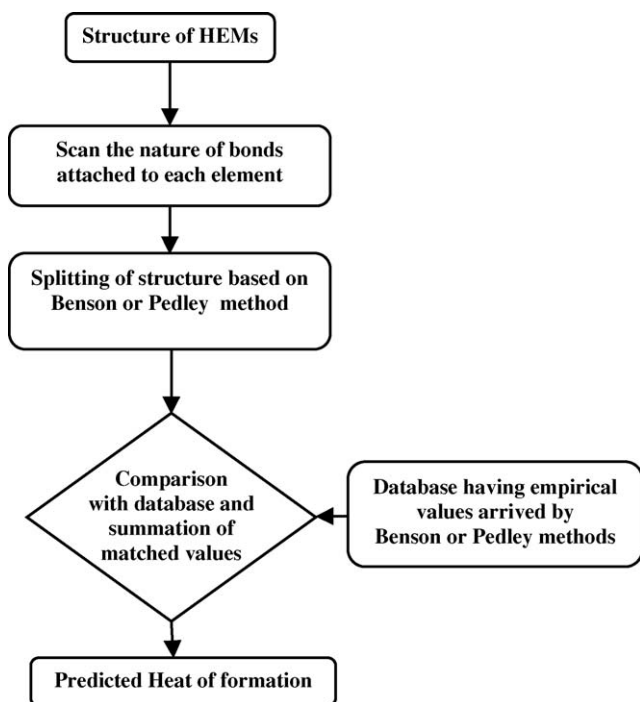


Fig. 2. Schematic depiction in the prediction of heat of formation.

specific impulse (Isp) of rocket propellants, impetus of gun propellants, heat of explosion, explosive power and power index, temperature of explosion, explosion products distribution [23], etc., of HEMs. In this work, we developed a computer code LOTUSES 1.3 to evaluate the heat of formation at gaseous phase for various HEMs using two different methods. The algorithm behind the computer programming in the prediction of heat of formation is shown in Fig. 2 as a flow chart.

### 2.1.1. Method I: Benson's Group additivity method

In the method of group additivity [15,16], groups of atoms within the molecule are assigned enthalpy values. The effects of interaction between various groups within the molecule and other factors are taken into account by the use of structural family corrections (for example, correction for benzene ring to account for resonance energy), but in general they are relatively small. The method involves a kind of shorthand, or notation, for describing the groups and is easily mastered.

First, a core atom is designated followed by a dash, which in turn is followed by a number of other atoms or subgroups in parentheses. The latter are the atoms or subgroups attached to the core atom. For instance, C-(C)<sub>2</sub>(H)<sub>2</sub> means a carbon atom core attached by single bonds to two other carbon atoms and two hydrogen atoms. Likewise, C-(C)(H)<sub>3</sub> would be a carbon atom core attached to another carbon atom and three hydrogen atoms. Carbon atoms that are double bonded are designated as C<sub>d</sub> and are attached to two other atoms or sub-groups. Aromatic carbon atoms, i.e., those present in a benzene ring are designated as C<sub>B</sub> and are also considered to be attached to only one other atom or sub-group [16]. A correction to the extent of about 25 kcal/mol is usually incorporated to account for the heat of sublimation ( $\lambda_s$ ) of solid explosive while calculating its heat of formation

[15,16]. It is agreed that the actual/experimental values of heat of sublimation will vary from compound to compound but this variation does not cause significant deviation in the computation of  $\Delta H_f$  based on Benson's Group additivity method. Moreover, this assumption is necessary in the case of yet-to-be synthesised candidate explosive molecules for which experimental heat of sublimation values are not available.

As an example of this, let us estimate the standard heat of formation of PETN (Fig. 3) as follows:

The groups and their values [15] as per Benson's method are:

$$1 \text{ each C-(C)}_4 = 1 (+0.50)$$

$$4 \text{ each C-(C)(O)(H)}_2 = 4 (-8.1)$$

$$4 \text{ each O-(C)(NO}_2) = 4 (-19.4)$$

(the values given in the parentheses are the assigned heat of formation for each entity)

$$\Delta H_f (\text{PETN, g}) = 0.5 + 4 (-8.1) + 4 (-19.4) = -109.5 \text{ kcal/mol}$$

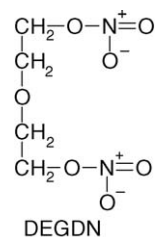
Subtracting the assumed value of the heat of sublimation:

$$\Delta H_f (\text{PETN, s}) = \Delta H_f (\text{PETN, g}) - \lambda_s$$

$$= -109.5 - 25.0 = -134.5 \text{ kcal/mol}$$

### 2.1.2. Method II: Pedley method for the prediction of heat of formation

Cox and Pilcher have reported a methodology to predict the enthalpy of formation of organic compounds by considering the molecular structure [17]. However, this method fails to predict enthalpy of formation of compounds having conjugation and steric interactions between non-bonded atoms. Pedley et al. of University of Sussex continued the work of Cox and Pilcher's method and devised an improved model to predict the enthalpy of formation. In the method of Pedley et al. [18] the molecular structure of the compound is split into its substructural units (functional groups) and each unit is given a specific notation indicating the functional groups to which it is attached. Each such unit is assigned a value for heat of formation. All these values of heat of formation corresponding to these substructural units present in the molecule are added to get the heat of formation of the compound. In the present work, the code and enthalpies of the constituent components (functional groups) were assigned in accordance with Pedley et al. method. The Pedley et al. method has been illustrated for the calculation of heat of formation of diethylene glycol dinitrate (DEGDN).



$$\Delta H_f^\circ = 4 \times h \{2 \text{ O}_2\} + h \{2 \text{ O}_2 (2 \text{ 2})\} + 2 \times h \{2 \text{ O}_2 (2 \text{ Nt})\}$$

(The first term refers to the four methylene groups having similar environment, i.e., each connected to a methylene group and -O- group. The second term refers to the central oxygen atom bridging two methylene groups. The third term refers to both the oxygen atoms each of which forms a bridge between -CH<sub>2</sub>- and -NO<sub>2</sub> groups.)

$$= 4 \times (-27.3 \pm 0.2) + (-114.9 \pm 0.0) + 2 \times (-79.4 \pm 0.5)$$

$$= -382.9 \pm 0.43 \text{ kJ/mol}$$

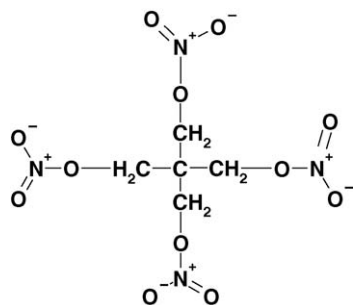


Fig. 3. Structure of PETN.

## 2.2. Explosion temperature

When an explosive detonates the reaction is extremely fast and initially the gases do not have time to expand to any great extent. The heat liberated by the explosion will raise the temperature of the gases, which will in turn cause them to expand and work on the surroundings to give a ‘lift and heave effect’. The quantity of heat generated by the products can be used to calculate the temperature of explosion [23].

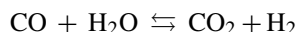
### 2.2.1. Conventional method

Let us compare the conventional method of calculating the explosion temperature ( $T_v$ ) of an explosive with the method adopted in LOTUSES 1.3.  $T_v$  is defined as the maximum temperature to which the explosion products are raised under adiabatic conditions. In the conventional method,

- one has to know the value of heat of explosion ( $\Delta H_e$ ) of the explosive to compute  $T_v$ .
- it is assumed that all the explosion products are raised from the initial or ambient temperature of the explosive ( $T_a$ ) to  $T_v$  using the heat of explosion ( $\Delta H_e$ ) formed during the explosion under adiabatic conditions.
- it is assumed that the entire  $\Delta H_e$  is used to raise the temperature of the products without doing any work of expansion which follows only as the next step. As the explosion is assumed to take place under adiabatic and isochoric (constant volume) conditions,  $T_v$  is also referred to as Adiabatic Isochoric Flame Temperature, the subscript ‘v’ in  $T_v$  denoting the constant volume conditions.
- the products are assumed to be in non-equilibrium condition and only the major or predominant products are considered for calculation of  $T_v$ . For example, in the explosion of RDX denoted below,



the products considered are only CO, H<sub>2</sub>O and N<sub>2</sub> and possible equilibrium states such as



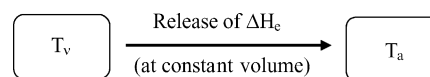
are neglected.

Table 1  
Molar internal energies of products  $C_v(T - T_a)$ ;  $T_a = 25^\circ\text{C} \sim 300\text{K}$

Temperature (K)	Molar internal energies of explosion products (kcal/mol)			
	N <sub>2</sub>	H <sub>2</sub> O	CO	CO <sub>2</sub>
2500	13.15	18.43	13.33	24.34
3000	16.57	23.81	16.78	30.81
3500	20.05	29.37	20.27	37.43
4000	23.79	35.03	23.79	44.13
4500	27.08	40.76	27.33	50.88
5000	30.62	46.54	30.88	57.67

- the ideal gas behaviour is assumed for all gases considering the high temperature ranges involved in explosion process.

Let us assume that during an explosive reaction,  $n_1$ ,  $n_2$  and  $n_3$  moles of CO, H<sub>2</sub>O<sub>(v)</sub> and CO<sub>2</sub> are produced, respectively, and the explosion temperature is  $T_v$ . After the heat of explosion ( $\Delta H_e$ ) is released, the gases cool to ambient temperature  $T_a$ . This can be represented as:



Conversely, we can imagine that the above gases are heated from  $T_a$  to  $T_v$  using the heat,  $\Delta H_e$ . The amount of heat needed to heat each gas is obtained by multiplying the number of moles of the gas produced, its molar heat capacity and the rise in temperature. If  $(C_v)_{\text{CO}}$ ,  $(C_v)_{\text{H}_2\text{O}}$  and  $(C_v)_{\text{CO}_2}$  are the molar heat capacities of CO, H<sub>2</sub>O and CO<sub>2</sub>, respectively, it can be written,

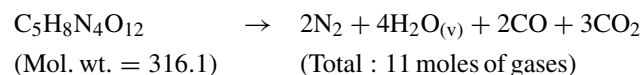
$$\Delta H_e = n_1(C_v)_{\text{CO}}[T_v - T_a] + n_2(C_v)_{\text{H}_2\text{O}}[T_v - T_a] + n_3(C_v)_{\text{CO}_2}[T_v - T_a]$$

i.e.,  $\Delta H_e = \sum C_v(T_v - T_a)$  where  $\sum C_v$  is the summation of the respective number of moles of the products multiplied by the corresponding values of  $C_v$ . This above equation can be rearranged as Eq. (1):

$$T_v = \frac{\Delta H_e}{\sum C_v} + T_a \quad (1)$$

As  $T_a$  and  $\sum C_v$  are constants, it is seen from the above equation that  $T_v$  linearly increases with  $\Delta H_e$ . For calculation of  $T_v$ , one needs to know the molar internal energies of the explosion products. These values are available [23] and some of them are given in Table 1.

The best way to calculate  $T_v$  is to plot the ‘‘calculated heat of explosion’’ against various temperatures, using Table 1. From the linear plot, we can find out the value of  $T_v$ , knowing the experimental value of  $\Delta H_e$ . For example, let us calculate the  $T_v$  of PETN, a well known explosive whose  $\Delta H_e$  is known to be 1510 cal/g PETN,  $\text{C}(\text{CH}_2\text{ONO}_2)_4$ , or  $\text{C}_5\text{H}_8\text{N}_4\text{O}_{12}$  undergoes the following explosive reaction:



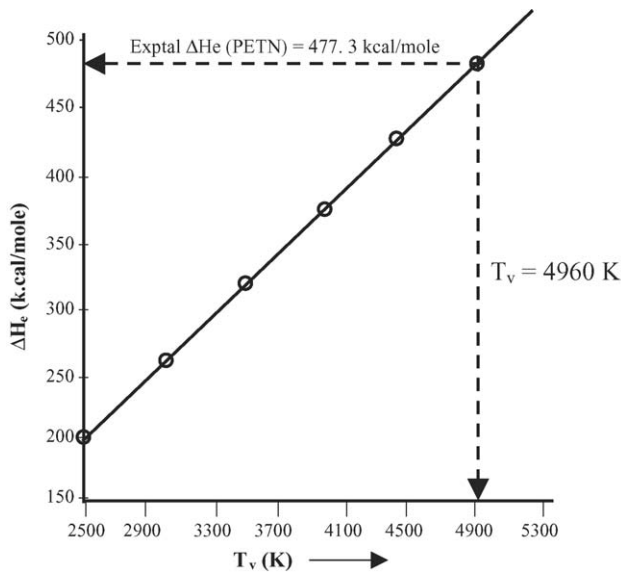


Fig. 4. Plot of calculated  $\Delta H_e$  against different  $T_v$  values for PETN.

We need the heat of explosion value in the unit of kcal/mol:

$$\Delta H_e = 1510 \text{ cal/g} = \frac{1510}{1000} \times 316.1 = 477.3 \text{ kcal/mol}$$

The minimum and maximum values of explosion temperature of explosives are about 2500 and 5000 K, respectively. We do not know the actual explosion temperature of PETN, though we are certain that it should be somewhere between 2500 and 5000 K. Using Table 1, we can calculate the expected  $\Delta H_e$  values of PETN had its explosion temperature been 2500 or 3000 or 3500 or 4000 or 4500 or 5000 K.

For example, at 2500 K (or had the explosion temperature been 2500 K), the expected value of  $\Delta H_e$  for the products, viz.  $2\text{N}_2 + 4\text{H}_2\text{O} + 2\text{CO} + 3\text{CO}_2$  would be

$$\begin{aligned} \Delta H_{e(2500)} &= 2(13.15) + 4(18.43) + 2(13.33) \\ &+ 3(24.34) \text{ kcal/mol} = 199.70 \text{ kcal/mol} \end{aligned}$$

Similar calculation yields  $\Delta H_e$  values of 254.37, 310.41, 367.67, 424.50 and 482.17 kcal/mol at 3000, 3500, 4000, 4500 and 5000 K, respectively. A plot of  $\Delta H_e$  against assumed  $T_v$  (Fig. 4) yields a straight line.

As the experimentally determined value for  $\Delta H_e$  is 477.3 kcal/mol, it can be read out from the plot that the actual value for  $T_v$  is about 4960 K.

### 2.2.2. LOTUSES 1.3

The main advantages of LOTUSES 1.3 over the conventional method in calculation of explosion temperature are the following.

- (a) There is no need to know the experimental values of  $\Delta H_e$  of an explosive to compute  $T_v$ . Since  $\Delta H_f$  values of explosives are computed by Benson's or Pedley's method based on their molecular structural information in the code,  $\Delta H_e$  for an explosive is automatically calculated by LOTUSES

1.3 using the basic principle that heat of explosion is the difference between heat of formation of products and that of the explosive as given in Eq. (2).

$$\Delta H_e = \sum_{\text{(Product)}} \Delta H_f - \sum_{\text{(Explosive)}} \Delta H_f \quad (2)$$

The values of  $\Delta H_f$  of products such as  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{N}_2$  are well known and they are stored inbuilt in the LOTUSES 1.3. This advantage assumes significance when one considers a candidate molecule of an explosive which is yet to be synthesized and hence its  $\Delta H_e$  value is not known. This will greatly help a HEM chemist to screen such candidate molecules in one go using LOTUSES 1.3 to decide whether it is worth pursuing its synthesis considering its computed energetics.

- (b) LOTUSES 1.3 carries out the iterative method of calculating  $\Delta H_e$  for different values of  $T_e$  at the intervals of 100 K using inbuilt stored values of  $C_v$  for the products in the temperatures range of 2000–5000 K. This is compared with  $\Delta H_e$  value obtained as described in (a) above to find out the value of  $T_v$ . Thus the manual process of plotting  $\Delta H_e$  against different values of  $T_v$  is avoided.

### 2.3. Oxygen balance (OB)

“Oxygen balance” is a parameter that tells us whether the oxygen atoms present in the molecule of an explosive are sufficient or insufficient for complete oxidation of the fuel elements like carbon and hydrogen [24]. The percentage excess or deficit of oxygen present in a compound required for its complete oxidation to  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , etc. is known as the oxygen balance (OB) of that compound. If the compound has less amount of oxygen in its molecule than required for complete oxidation, it is said to have a negative OB and vice-versa. For a “CHNO” explosive with formula  $\text{C}_x\text{H}_y\text{N}_w\text{O}_z$ , the OB% can be found out by a general formula as given in Eq. (3):

$$\text{OB}\% = \frac{100 \times \text{Mol. wt. of oxygen}}{\text{Mol. wt. of the compound}} \left( z - 2x - \frac{y}{2} \right) \quad (3)$$

Oxygen balance is one of the important parameters of high energy materials. The ideal OB requirement of an explosive compound is zero. The code developed by the authors automatically calculates the OB of an explosive using its molecular formula.

## 3. Result and discussion

### 3.1. Heat of formation

The validity of the Benson method was tested for 41 compounds containing HEMs as well as other materials used in the field of explosives and propellants. This list includes well known explosives and propellant ingredients including those which are used as plasticizers, stabilizers, etc. The said list excludes inorganic materials and deals only with organic CHNO type materials. Table 2 compares the heat of formation data predicted

Table 2

Comparison of  $\Delta H_f$  of HEMs and related compounds predicted by Benson method using LOTUSES and reported values

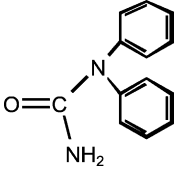
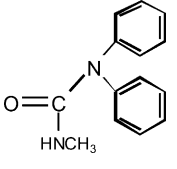
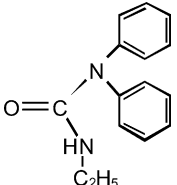
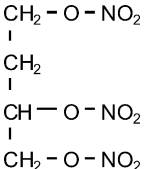
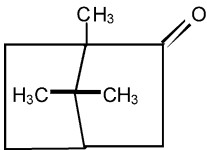
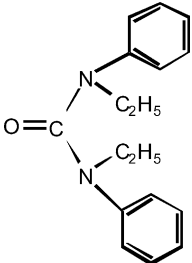
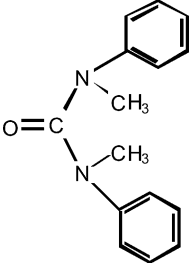
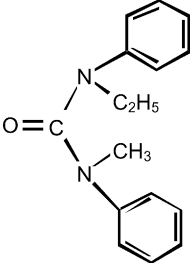
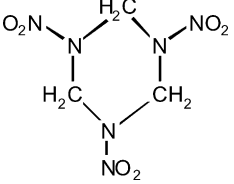
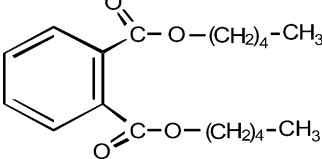
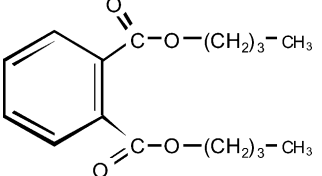
Sl no.	Name of HEM	Structure	Molecular formula	Oxygen balance	Heat of formation (kcal/mol)			Heat of explosion (kJ/kg)	$T_e$ (K)
					LOTUSES	Reported	Error (%)		
1	Akardite-I (diphenylurea)		$C_{13}H_{12}N_2O$	-233.67	-26.4	-26.7	1.12	6.32	<2000
2	Akardite-II (methyl diphenylurea)		$C_{14}H_{14}N_2O$	-240.40	-25.98	-25.5	-1.88	13.69	<2000
3	Akardite-III (ethyl diphenylurea)		$C_{15}H_{16}N_2O$	-246.35	-32.58	-33.5	2.74	-102.01	<2000
4	Butanetriol trinitrate, BTTN		$C_4H_7N_3O_9$	-16.58	-105.06	-104.7	-0.34	5381.10	4500
5	Camphor		$C_{10}H_{16}O$	-283.76	-78.98	-78.1	-1.12	-1436.25	<2000
6	Centralite I (diethyl diphenyl urea)		$C_{17}H_{20}N_2O$	-256.36	-26.36	-25.1	-5.02	5.62	<2000

Table 2 (Continued)

Sl no.	Name of HEM	Structure	Molecular formula	Oxygen balance	Heat of formation (kcal/mol)			Heat of explosion (kJ/kg)	$T_c$ (K)
					LOTUSES	Reported	Error (%)		
7	Centralite II (dimethyl diphenyl urea)		$C_{15}H_{16}N_2O$	-246.34	-13.16	-14.6	9.86	236.10	<2000
8	Centralite III (ethyle methyl urea)		$C_{16}H_{18}N_2O$	-251.63	-19.76	-18.4	-7.39	114.50	<2000
9	Cyclonite (RDX)		$C_3H_6N_6O_6$	-21.60	14	14.4	2.77	5041.58	4500
10	Diamyl phthalate		$C_{18}H_{26}O_4$	-234.98	-220.43	-220.9	0.21	-1550.49	<2000
11	Dibutyl phthalate		$C_{16}H_{22}O_4$	-224.17	-210.53	-211.2	0.31	-1557.95	<2000

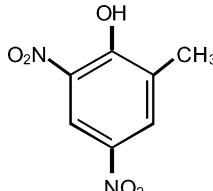
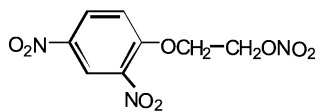
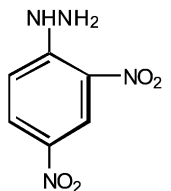
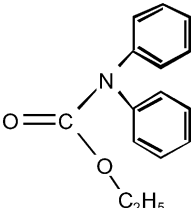
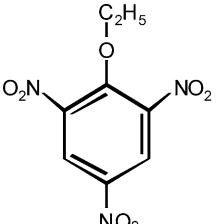
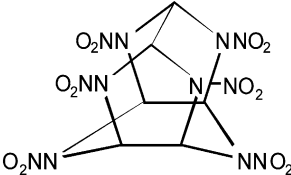
12	Diethyleneglycol dinitrate	$\begin{array}{c} \text{CH}_2 - \text{O} - \text{NO}_2 \\   \\ \text{CH}_2 \\   \\ \text{O} \\   \\ \text{CH}_2 \\   \\ \text{CH}_2 - \text{O} - \text{NO}_2 \end{array}$	$\text{C}_4\text{H}_8\text{N}_2\text{O}_7$	-40.78	-96.2	-94.37	-1.99	3929.39	3200
13	Dinitro orthocresol		$\text{C}_7\text{H}_6\text{N}_2\text{O}_5$	-96.89	-61.57	-61.46	-0.17	1521.06	<2000
14	Dinitrodimethylamide (DNDMOA)	$\begin{array}{c} \text{NO}_2 \\   \\ \text{O}=\text{C}-\text{N}-\text{CH}_3 \\   \\ \text{O}=\text{C}-\text{N}-\text{CH}_3 \\   \\ \text{NO}_2 \end{array}$	$\text{C}_4\text{H}_8\text{N}_4\text{O}_6$	-38.81	-69.15	-72.7	4.88	3113.79	2900
15	Dinitrodioxy ethylamide dinitrate (NENO)	$\begin{array}{c} \text{NO}_2 \\   \\ \text{O}=\text{C}-\text{N}-\text{CH}_2-\text{CH}_2\text{ONO}_2 \\   \\ \text{O}=\text{C}-\text{N}-\text{CH}_2-\text{CH}_2\text{ONO}_2 \\   \\ \text{NO}_2 \end{array}$	$\text{C}_6\text{H}_8\text{N}_6\text{O}_{12}$	-17.96	-141.19	-134.5	-4.97	4525.58	3900
16	Dinitrophenoxy ethyl nitrate		$\text{C}_8\text{H}_7\text{N}_3\text{O}_8$	-67.35	-63.2	-66.4	4.81	2306.11	2300
17	Dinitrophenyl hydrazine		$\text{C}_6\text{H}_6\text{N}_4\text{O}_4$	-88.81	18.09	16.08	-12.5	2638.80	2700



Table 2 (Continued)

Sl no.	Name of HEM	Structure	Molecular formula	Oxygen balance	Heat of formation (kcal/mol)			Heat of explosion (kJ/kg)	$T_c$ (K)
					LOTUSES	Reported	Error (%)		
18	Dioxyethylnitramine dinitrate, DINA	$\begin{array}{c} \text{CH}_2 - \text{CH}_2 - \text{O} - \text{NO}_2 \\   \\ \text{N} - \text{NO}_2 \\   \\ \text{CH}_2 - \text{CH}_2 - \text{O} - \text{NO}_2 \end{array}$	$\text{C}_4\text{H}_8\text{N}_4\text{O}_8$	-26.65	-88.99	-87.1	-2.17	4342.40	3600
19	Dipentaerythrotol hexanitrate, DPEHN	$\begin{array}{c} \text{CH}_2\text{ONO}_2 \quad \text{CH}_2\text{ONO}_2 \\   \quad \quad   \\ \text{O}_2\text{NOCH}_2 - \text{C} - \text{CH}_2 - \text{O} - \text{CH}_2 - \text{C} - \text{CH}_2\text{ONO}_2 \\   \quad \quad   \\ \text{CH}_2\text{ONO}_2 \quad \text{CH}_2\text{ONO}_2 \end{array}$	$\text{C}_{10}\text{H}_{16}\text{N}_6\text{O}_{19}$	-27.46	-205.2	-220	6.72	4725.03	3900
20	Diphenyl urethane		$\text{C}_{15}\text{H}_{15}\text{NO}_2$	-235.39	-55.48	-61.8	10.22	-35.34	<2000
21	Ethritol trinitrate (TMPTN)	$\begin{array}{c} \text{CH}_2\text{ONO}_2 \\   \\ \text{C}_2\text{H}_5 - \text{C} - \text{CH}_2\text{ONO}_2 \\   \\ \text{CH}_2\text{ONO}_2 \end{array}$	$\text{C}_6\text{H}_{11}\text{N}_3\text{O}_9$	-50.52	-122.02	-114.6	-6.44	3292.29	2800
22	Ethyl picrate		$\text{C}_8\text{H}_7\text{N}_3\text{O}_7$	-77.76	-43.58	-48	9.20	2334.06	2400
23	Hexanitro hexaaza isowurtzitane (CL20)		$\text{C}_6\text{H}_6\text{N}_{12}\text{O}_{12}$	-10.95	83	88.91	6.64	5910.00	>5000

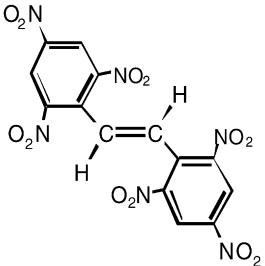
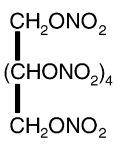
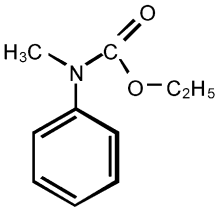
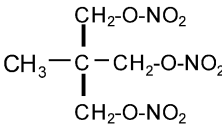
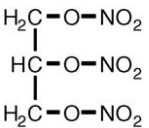
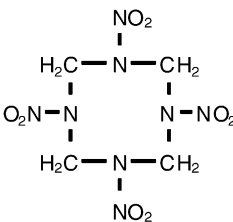
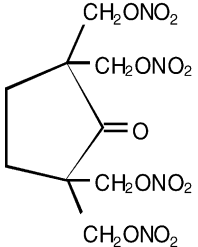
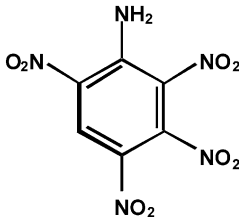
24	Hexanitrostilbene (HNS)		$C_{14}H_6N_6O_{12}$	-67.51	13.71	13.8	0.65	3106.99	3300
25	Mannitol hexanitrate (MHN)		$C_6H_8N_6O_{18}$	7.07	-160.47	-161.5	0.63	5880.72	>5000
26	Methyl phenyl urethane		$C_{10}H_{13}O_2N$	-218.72	-92.13	-91.8	-0.35	-903.18	<2000
27	Metriol trinitrate (MTN)		$C_5H_9N_3O_9$	-34.48	-117.07	-113.8	-2.87	4064.68	3400
28	Nitroglycerine (NG)		$C_3H_5N_3O_9$	3.52	-120.23	-118.9	-1.11	5117.78	4500
29	Octogen, HMX		$C_4H_8N_8O_8$	-21.60	27	28.68	5.85	5159.29	4500

Table 2 (Continued)

Sl no.	Name of HEM	Structure	Molecular formula	Oxygen balance	Heat of formation (kcal/mol)			Heat of explosion (kJ/kg)	$T_e$ (K)
					LOTUSES	Reported	Error (%)		
30	Pentaerythritol tetrahydrate (PETN)	$\begin{array}{c} \text{CH}_2\text{-O-NO}_2 \\   \\ \text{O}_2\text{N-O-CH}_2\text{-C-CH}_2\text{-O-NO}_2 \\   \\ \text{CH}_2\text{-O-NO}_2 \end{array}$	$\text{C}_5\text{H}_8\text{N}_4\text{O}_{12}$	-10.12	-134.5	-130.1	-3.38	5725.39	5000
31	Pentaerythritol trinitrate (PETRIN)	$\begin{array}{c} \text{CH}_2\text{-O-NO}_2 \\   \\ \text{HO-CH}_2\text{-C-CH}_2\text{-O-NO}_2 \\   \\ \text{CH}_2\text{-O-NO}_2 \end{array}$	$\text{C}_5\text{H}_9\text{N}_3\text{O}_{10}$	-26.55	-153	-134	-14.18	4310.33	3500
32	Propylene glycol dinitrate	$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH-O-NO}_2 \\   \\ \text{CH}_2\text{-O-NO}_2 \end{array}$	$\text{C}_3\text{H}_6\text{N}_2\text{O}_6$	-28.89	-82.69	-83.1	0.49	4306.96	3500
33	Tetramethylolcyclopentanone tetranitrate		$\text{C}_9\text{H}_{12}\text{N}_4\text{O}_{13}$	-45.80	-175.29	-161.6	-8.47	3229.11	2900
34	Tetranitroaniline		$\text{C}_6\text{H}_3\text{N}_5\text{O}_8$	-32.21	-11.7	-13.3	12.03	4194.96	4500

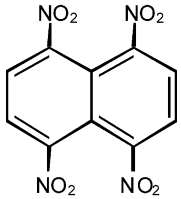
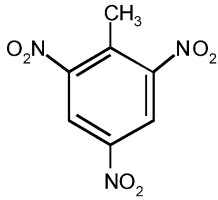
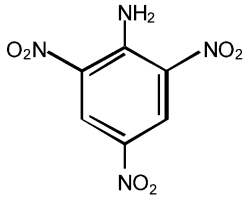
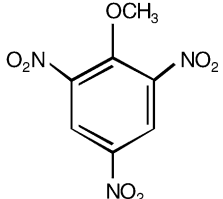
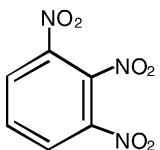
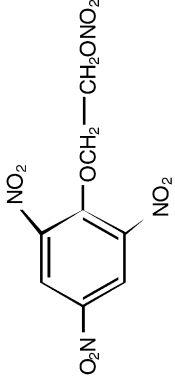
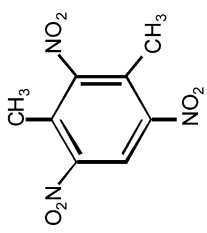
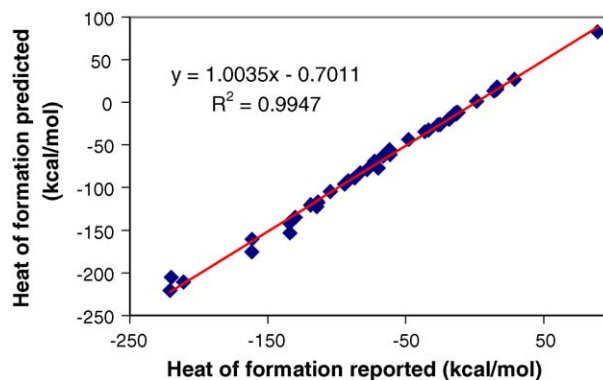
35	Tetranitronaphthalene (TNN)		$C_{10}H_4N_4O_8$	-72.68	15.15	15.84	4.35	3107.86	3400
36	Trinitotoluene (TNT)		$C_7H_5N_3O_6$	-73.96	-11.98	-12.1	0.99	2732.48	2800
37	Trinitroaniline (TNA)		$C_6H_4N_4O_6$	-56.10	-13.9	-13.7	-1.46	2685.40	2700
38	Trinitroanisole		$C_7H_5N_3O_7$	-62.51	-34.6	-36.3	4.68	2623.24	2600
39	Trinitrobenzene		$C_6H_3N_3O_6$	-56.30	1.39	1.3	-6.92	3174.81	3200

Table 2 (Continued)

Sl no.	Name of HEM	Structure	Molecular formula	Oxygen balance	Heat of formation (kcal/mol)		Heat of explosion (kJ/kg)	$T_c$ (K)
					LOTUSES	Reported		
40	Trinitrophenoxethyl nitrate		$C_8H_6N_4O_{10}$	-45.25	-77.2	-70	3316.94	3200
41	Trinitroxylyene (TNX)		$C_8H_7N_3O_6$	-89.56	-19.73	-19	2439.11	2500

Fig. 5. Experimental vs. predicted  $\Delta H_f$  derived by Benson's method.

by Benson's method using LOTUSES 1.3 with the reported values. A linear straight line having correlation coefficient ( $R^2$ ) 0.9947 with straight line equation of  $y = 1.0035x - 0.7011$  was obtained on plotting (Fig. 5) the heat of formation reported in literature [25,26] along the  $x$ -axis and predicted heat of formation by Benson method using our computer code (LOTUSES 1.3) along the  $y$ -axis. The heat of formation predicted using Pedley's method is tabulated in Table 3. A linear straight line having correlation coefficient ( $R^2$ ) 0.9637 with straight line equation of  $y = 0.9111x + 2.8709$  was obtained on plotting (Fig. 6) the heat of formation reported in literature [22,23] along the  $x$ -axis and predicted heat of formation by Pedley's method using our computer code (LOTUSES 1.3) along the  $y$ -axis. The error percentage (deviation of heat of formation predicted from that reported in literature) obtained in methods I and II are depicted as bar diagram in Figs. 7 and 8, respectively, for comparison of reliability of prediction. It is clear from Figs. 5–8, that heat of formation values predicted by Benson's method have better agreement with those reported in literature as compared to Pedley's method. This is probably due to the fact that Benson's method takes into account each bond attached to a particular core atom whereas in Pedley's method, only the substructural environment around a core atom is considered. For example in the case of DEGDN (Section 2.1.2) each methylene group is shown to be attached to an oxygen atom and another methylene group whereas if one

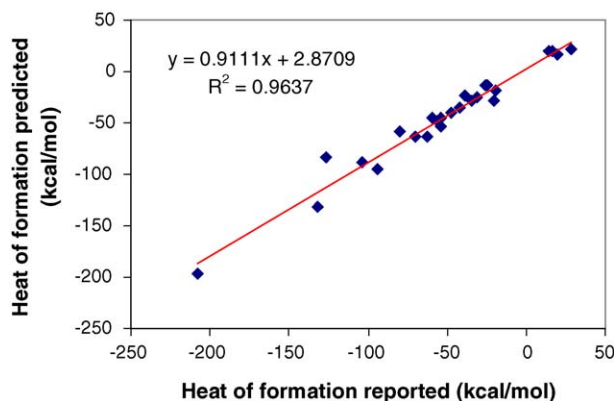
Fig. 6. Experimental vs. predicted  $\Delta H_f$  derived by Pedley's method.

Table 3  
Comparison of  $\Delta H_f$  predicted by Pedley's method and reported

S. no.	Name	Empirical formula	Heat of formation (kcal/mol)		
			Reported	LOTUSES	Error (%)
1	Butanediol dinitrate	C <sub>4</sub> H <sub>8</sub> N <sub>2</sub> O <sub>6</sub>	-70	-63.862	8.76
2	Cyclonite (RDX)	C <sub>3</sub> H <sub>6</sub> N <sub>6</sub> O <sub>6</sub>	19.73	16.204	17.86
3	Diethyleneglycol dinitrate (DEGDN)	C <sub>4</sub> H <sub>8</sub> N <sub>2</sub> O <sub>7</sub>	-94.4	-94.431	-0.03
4	Dimethylhydrazine (DMH)	C <sub>2</sub> H <sub>8</sub> N <sub>2</sub>	14.63	20.076	-37.22
5	Dioxyethylnitramine dinitrate, DINA	C <sub>4</sub> H <sub>8</sub> N <sub>4</sub> O <sub>8</sub>	-55.6	-47.538	14.49
6	Dipentaerythrol hexanitrate, DPEHN	C <sub>10</sub> H <sub>16</sub> N <sub>6</sub> O <sub>19</sub>	-208	-196.677	5.44
7	Ethriol trinitrate (TMPTN)	C <sub>6</sub> H <sub>11</sub> N <sub>3</sub> O <sub>9</sub>	-104	-87.523	15.84
8	Ethylenedinitramine (EDNA)	C <sub>2</sub> H <sub>6</sub> N <sub>4</sub> O <sub>4</sub>	-20.5	-28.967	-41.30
9	Ethyl nitrate	C <sub>2</sub> H <sub>5</sub> NO <sub>3</sub>	-41.6	-35.372	14.96
10	Methyl nitrate	CH <sub>3</sub> NO <sub>3</sub>	-34.8	-27.701	20.40
11	Nitroethane	C <sub>2</sub> H <sub>5</sub> NO <sub>2</sub>	-30.8	-24.450	20.61
12	Nitroglycol (EGDN)	C <sub>2</sub> H <sub>4</sub> N <sub>2</sub> O <sub>6</sub>	-54.39	-53.919	0.86
13	Nitromethane	CH <sub>3</sub> NO <sub>2</sub>	-19.5	-17.734	9.055
14	Octogen, HMX	C <sub>4</sub> H <sub>8</sub> N <sub>8</sub> O <sub>8</sub>	28.6	21.606	24.45
15	Pentaerythritol trinitrate (PETN)	C <sub>5</sub> H <sub>9</sub> N <sub>3</sub> O <sub>10</sub>	-127	-82.983	34.65
16	Propylene glycol dinitrate	C <sub>3</sub> H <sub>6</sub> N <sub>2</sub> O <sub>6</sub>	-62.2	-62.596	-0.63
17	Propyl nitrate	C <sub>3</sub> H <sub>7</sub> NO <sub>3</sub>	-47.8	-40.487	15.29
18	Tetranitromethane (TNM)	CN <sub>4</sub> O <sub>8</sub>	16.55	19.598	-18.41
19	Triethyleneglycol dinitrate (TEGN)	C <sub>6</sub> H <sub>12</sub> N <sub>2</sub> O <sub>8</sub>	-132	-132.027	-0.02
20	Urea	CH <sub>4</sub> N <sub>2</sub> O	-79.63	-58.747	26.22
21	Isopropyl nitrate	C <sub>3</sub> H <sub>7</sub> NO <sub>3</sub>	-54.3	-45.650	15.92
22	Dinitromethane	CH <sub>2</sub> N <sub>2</sub> O <sub>4</sub>	-25.2	-14.077	44.13
23	Dinitrobutane	C <sub>4</sub> H <sub>8</sub> N <sub>2</sub> O <sub>4</sub>	-59.6	-44.168	25.89
24	1,1-Dinitropropane	C <sub>3</sub> H <sub>6</sub> N <sub>2</sub> O <sub>4</sub>	-39	-24.067	38.28
25	N-Nitrodiethylamine	C <sub>4</sub> H <sub>10</sub> N <sub>2</sub> O <sub>2</sub>	-25.33	-12.691	49.89

writes the Benson's code for the same molecule, each methylene group will be shown to be attached to (1) a carbon atom of the adjacent methylene group, (2) two hydrogen atoms, (3) an oxygen atom. This shows that Benson's method is more thorough than Pedley's method in accounting for the bonding environment of any subgroup in a molecule. Even in Benson's method, the deviation from reported values becomes significant in case of those molecules in which strong intra- and inter-molecular hydrogen bonding exists or those molecules which have a high

level of strain in the bonding, as such factors are not taken into account in Benson's method.

### 3.2. Temperature of explosion

Temperature of explosion is an important parameter for energetic materials and they are used to compute the work potential of HEMs. The predicted explosion temperature values of above referred 41 compounds are depicted in Table 2. The table also

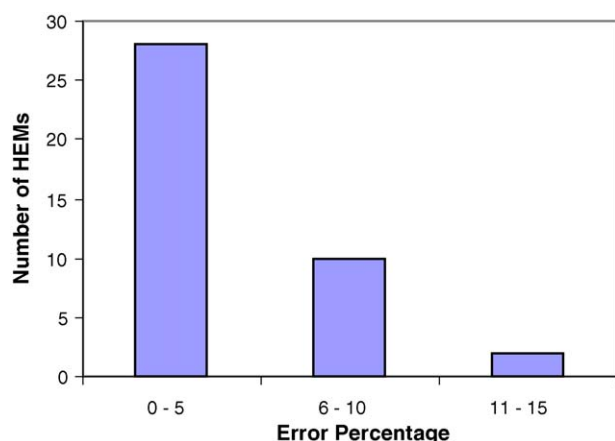


Fig. 7. Error percentage in Benson's method.

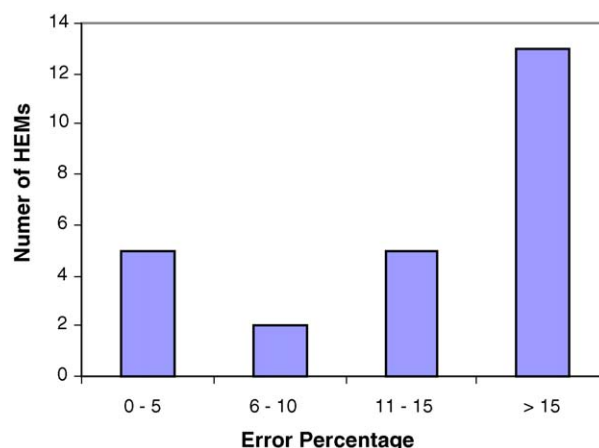


Fig. 8. Error percentage in Pedley's method.

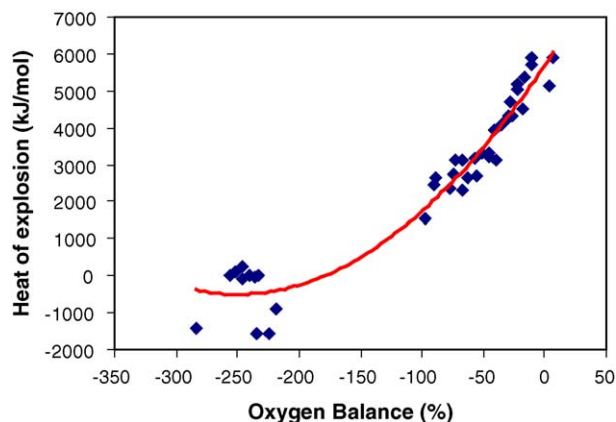


Fig. 9. The effect of oxygen balance on heat of explosion.

includes, apart from HEMs, related materials such as plasticizers, stabilizers, etc., which are used in the explosives and propellant formulations. The mean molar heat capacities of some gaseous products such as  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{H}_2\text{O}$ ,  $\text{H}_2$  and  $\text{N}_2$  at various temperatures in the range 2000–5000 K are stored in a backend database to LOTUSES. Hence, the LOTUSES 1.3 code predicts the temperature of explosion in the range between 2000 and 5000 K.

### 3.3. Oxygen balance

It is observed from Fig. 9, that the heat of explosion reaches a maximum for an oxygen balance of zero, since this corresponds to the stoichiometric oxidation of carbon to carbon dioxide and hydrogen to water. The oxygen balance can therefore be used to optimise the composition of the explosives or propellant formulations as per the requirement.

## 4. Conclusion

Our objective of this research was to evaluate the applicability and accuracy of calculation schemes for estimating heat of formation of high energy materials using Benson's as well as Pedley's method. From observations it is concluded, that heat of formation values predicted by Benson method have better agreement with figures reported in literature as compared to Pedley's method. Both the methodologies were incorporated with the computer software named LOTUSES 1.3 to evaluate heat of formation of HEMs. This software LOTUSES 1.3 gives reasonable agreement between computed and experimental heat of formation values. The code can also be used to obtain temperature of explosion and oxygen balance of HEMs. In addition to these, it can compute parameters such as VOD, C–J pressure, volume of explosion products, density, heat of explosion and power index as in earlier versions. The major advantage of LOTUSES 1.3 is its ability to screen candidate HEMs which are yet to be synthesized by predicting their performance parameters with the help of their molecular structural information. The fairly accurate knowledge of the heat of formation values and other parameters enable the

HEM technologist to formulate better performing explosives and propellants.

## Acknowledgements

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## References

- [1] H. Muthurajan, R. Sivabalan, N. Venkatesan, M.B. Talawar, S.N. Asthana, Computational approaches for performance prediction of high energy materials, in: Proceedings of 4th International High Energy Materials Conference, India, 2003, pp. 470–486.
- [2] H. Muthurajan, R. Sivabalan, M.B. Talawar, S.N. Asthana, Artificial Intelligence methodology for Thermodynamic Analysis of High Energetic Materials, in: Proceedings of 14th National Symposium on Thermal Analysis, India, 2004, pp. 225–228.
- [3] H. Muthurajan, R. Sivabalan, M.B. Talawar, S.N. Asthana, Development of novel computer code for prediction of heat of formation of high energetic materials, in: Proceeding of 7th International Seminar on "New Trends in research of Explosives" at Department of Theory and Technology of Explosives, University of Pardubice, Czech Republic, 20–24 April 2004, pp. 202–223.
- [4] H. Muthurajan, R. Sivabalan, M.B. Talawar, S.N. Asthana, J. Hazard. Mater. 112 (2004) 17.
- [5] Stanley F. Sarner, Propellant Chemistry, Reinhold Publishing Corporation, New York, 1966.
- [6] B.M. Rice, J. Hare, Thermochem. Acta 384 (2002) 377.
- [7] M.S. Miller, B.M. Rice, A.J. Kotlar, R.J. Cramer, Clean Products Processes 2 (2000) 37.
- [8] M.J. Kamlet, S.J. Jacobs, J. Chem. Phys. 48 (1968) 23.
- [9] J.R. Stine, J.F. Eramer, Estimation of heats of formation and the development of chemical databases useful for energetic materials, 26th JANNAF Combustion meeting, Jet Propulsion Laboratory, Pasadena, California, CPIA Publication, vol. II, 1989, pp. 53–56.
- [10] D.V. Sukhachev, T.S. Pivina, Propellants Explosives Pyrotechnics 19 (1994) 159.
- [11] S. Bourasseau, J. Energetic Mater. 8 (5) (1990) 416.
- [12] B.M. Rice, S.V. Pai, J. Hare, Combust. Flame 118 (1999) 445.
- [13] P. Politzer, J.S. Murray, J.M. Seminario, P. Lane, M.E. Grice, M.C. Concha, J. Mol. Struct. (Theochem.) 573 (2001) 1.
- [14] P. Politzer, P. Lane, M.C. Concha, in: P. Politzer, J.S. Murray (Eds.), Energetic Materials—Part 1, Elsevier, Amsterdam, 2003, pp. 247–277 (Chapter 9).
- [15] P.W. Cooper, Explosives Engineering, VCH Publishers Inc., New York, United States of America, 1996.
- [16] R.C. Reid, J.M. Prausnitz, T. Sherwood, The Properties of Gases and Liquids, third ed., McGraw-Hill, New York, 1977.
- [17] J.D. Cox, G. Pilcher, Thermochemistry of Organic and Organometallic Compounds, Academic Press, New York, 1970.
- [18] J.B. Pedley, R.D. Naylor, S.P. Kirlly, Thermochemical Data of Organic Compounds, second ed., Chapman and Hall Publication, New York, 1986.
- [19] P.W. Cooper, Introduction to detonation physics, in: J.A. Zukas, W.P. Walters (Eds.), Explosive Effects and Applications, Springer-Verlag, New York, United States of America, 1997, pp. 115–135 (Chapter 4).
- [20] J.R. Stine, J. Energetic Mater. 8 (1990) 41.
- [21] L.R. Rothstein, R. Petersen, Propellants Explosive 4 (1979) 56.
- [22] L.R. Rothstein, Propellants Explosive 6 (1981) 91.

- [23] J. Akhavan, *The Chemistry of Explosives*, The Royal Society of Chemistry, UK, 1998.
- [24] J.C. Oxley, *The chemistry of explosives*, in: J.A. Zukas, W.P. Walters (Eds.), *Explosive Effects and Applications*, Springer-Verlag, New York, United States of America, 1997 (Chapter 5).
- [25] *ICT Database of Thermochemical Values*, Version 3.0, Fraunhofer Institut Chemische Technologie, 2001.
- [26] R. Meyer, J. Kohler, A. Homburg, *Explosives*, fifth ed., Wiley-VCH Publications, Germany, 2002.