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Approximate techniques for the calculation of heats of explosion using thermochemical computer codes

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Abstract

Procedures are outlined for calculating the heats of explosion (HEX) of neat energetic materials or propellant/explosive formulations using thermochemical computer codes. The "exact" method and three approximate techniques are described; the approximate techniques either eliminate the need to sum the internal energies of the predicted products, or eliminate the need to specify a freeze-out temperature. The various techniques are illustrated for HMX and a nitrocellulose/nitroglycerine (NC/NG) mixture.

INTRODUCTION

The heat of explosion (HEX) is usually defined as the difference between the energies of formation of a material and the energies of formation of the explosion products [1]. Experimentally, HEX is measured as the heat released when a material is ignited and burned in a bomb calorimeter in an inert atmosphere. The measurement is made after the products have cooled to near room temperature by noting the temperature rise of the calorimeter water jacket; HEX is calculated from this temperature rise using the effective heat capacity of the calorimeter body and water jacket. The experimentally determined HEX values include contributions due to cooling of the combustion products from the flame temperature T_{fl} to room temperature T_r, and phase changes such as water condensation. These contributions are not generally available for use in gun and rocket propulsion; however, HEX is much easier to measure than impetus or specific impulse, and therefore is a convenient way of ranking the energy content of different formulations. Note that *heat of explosion* is a misnomer for two reasons: (i) Many people consider the term "heat" to imply constant-pressure enthalpy H; an equally valid definition of this term is constant-volume internal energy U. Because a bomb calorimeter is a constant-volume device,

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the latter usage of the term will be used in this paper. (ii) The sample usually undergoes combustion rather than explosion. In addition, the energetic materials community reports HEX values as positive numbers, even though exothermic energy release should be negative according to thermodynamic convention. Strictly speaking then, HEX is defined in this paper as the absolute value of the total energy released during constant-volume combustion of a material in an inert atmosphere.

Measured HEX values depend somewhat on conditions; in particular, HEX generally increases with increasing loading density, or with bomb pre-pressurization. To some extent, this is predicted thermodynamically, but there are other potential contributions: at lower loading densities or pre-pressurization levels, mixing with the cold gas initially present in the bomb calorimeter may quench some of the chemistry before it attains thermodynamic equilibrium, and/or mixing with the cold gas may raise the freeze-out temperature T_{fo} of the cooling combustion products. T_{fo} is the temperature during cooling at which the ratios of the various combustion products become invariant [2], though phase changes may still occur.

It is increasingly of interest to be able to calculate HEX using a thermochemical code such as NASA-Lewis [3, 4]. This paper describes the "exact" method for calculating HEX with a thermodynamic code, as well as three approximate methods. Because the exact method requires the T_{fo}, which is rarely known, and because, in addition, it requires summing up the room temperature energies of the products using the mole fractions at T_{fo}, there is interest in approximate techniques which do not require knowledge of T_{fo}, and/or eliminate the need to make use of the composition of the combustion products. While illustrated here for the case of CHNO chemistry, these techniques may in fact be especially useful for chemistries involving other elements, where essentially nothing is known about T_{fo}.

HEX calculations are carried out on nitramines, cyclo-1,3,5-trimethylene-2,4,6-trinitramine (RDX) and cyclo-1,3,5,7-tetramethylene-2,4,6,8-tetranitramine (HMX), as well as on a mixture of nitroglycerine (NG) and nitrocellulose (NC) at 12.6% nitration level. Thermochemical calculations were carried out using CET89, a recent version of the NASA-Lewis code modified at the Army Research Laboratory (ARL) to run on a personal computer. This code uses a free energy minimization technique to calculate equilibrium species mole fractions, flame temperature, and thermodynamic properties; an ideal gas equation of state is used to calculate temperatures and pressures. All calculations were run on Intel 80386- and 80486-based PCs operating under MS-DOS. The procedures outlined in the following sections would be similar using other codes. The code used should support calculations at assigned (or constant) energy and volume, and at assigned temperature and volume; if the code does not support an assigned temperature and volume calculation, an assigned temperature and pressure calcula-

TABLE 1

Selected values for materials used in this study

Material	C	H	N	O	M in g mol^{-1}	ΔH_f° in kJ mol^{-1}
HMX	4	8	8	8	296.16	74.98
RDX	3	6	6	6	222.12	61.46
NC, 12.6% N	6	7.550	2.450	9.901	272.40	−707.93
NG	3	5	3	9	227.09	−370.70

tion may be substituted by esimating the pressure at T_{fo}. In all cases, the goal is to calculate or esimate

$$\mathrm{HEX} = \Delta U_{r,298} = |U_{\mathrm{prod}} - U_{\mathrm{react}}|/\mathrm{J\ g^{-1}} \tag{1}$$

where ΔU_r is the change in energy at constant volume for the calorimetric reaction, and U_{prod} and U_{react} are the internal energies of the products and reactants, respectively, at room temperature ($T_r = 25°\mathrm{C}$, 298.15 K). Analogous procedures could be used (using enthalpies instead of energies) for a constant pressure process. Table 1 lists values for the atomic make-up, molar mass, and enthalpy of formation for the materials being studied.

ASSIGNMENT OF THE THERMODYNAMIC QUANTITIES *H* AND *U*

The thermodynamic quantities H and U are the enthalpy and internal energy state functions for a given species. These quantities are related by the equation

$$H = U + PV \tag{2}$$

where P is pressure and V is volume. Equation (2) can be modified to handle either gaseous or condensed species as follows. For gaseous species, the ideal gas equation of state

$$PV = nRT \tag{3}$$

may be combined with eqn. (2) to give the following equation relating H and U

$$H = U + nRT \quad \text{(gases)} \tag{4}$$

where R is the gas constant, T is temperature, and n is the number of moles of gas involved. At room temperature, RT is equal to 2.48 kJ mol^{-1}. In the case of condensed (liquid or solid) species, the PV product of eqn. (2) is sufficiently small that the following approximation may be made

$$H \approx U \quad \text{(liquids, solids)} \tag{5}$$

Equations (4) and (5) allow the assignment of internal energy in terms of the corresponding enthalpy.

Enthalpies are assigned *in the code* by arbitrarily assuming $H^{\ominus}_{298.15} = (\Delta H^{\ominus}_{\mathrm{f}})_{298.15}$, where $(\Delta H^{\ominus}_{\mathrm{f}})_{298.15}$ is the standard heat of formation (relative to the reference elements at 298.15 K and 0.1 MPa pressure) of the species of interest. Equation (5) then becomes

$$U \approx H^{\ominus}_{298.15} = (\Delta H^{\ominus}_{\mathrm{f}})_{298.15} \tag{6}$$

for liquids and solids, and eqn. (4) becomes

$$U = H^{\ominus}_{298.15} - nRT = (\Delta H^{\ominus}_{\mathrm{f}})_{298.15} - nRT \tag{7}$$

for gases. Because most energetic materials of interest exist in condensed phases, eqn. (6) is generally sufficient to assign the reactant energy U on the assigned thermodynamic scale. If gaseous product energies need to be assigned, e.g., see the exact calculation, below, then eqn. (7) should be used.

A distinction needs to be made between the assigned quantity U and the energy of formation ΔU_{f}. In eqns. (6) and (7), U can be thought of as the internal energy of the product of a formation reaction (for the chemical species of interest) on the assigned energy scale; in other words, U represents an "absolute" energy on the scale defined by setting $H^{\ominus}_{298.15} = (\Delta H^{\ominus}_{\mathrm{f}})_{298.15}$. U differs from the energy of formation ΔU_{f} in that ΔU_{f} is defined as the difference between the U value for the formation species and the U values of the elemental constituents in their standard states. The use of the U values for the reactants and products in eqn. (1) to calculate HEX is equivalent to the use of the corresponding ΔU_{f} values, because the U contributions (to ΔU_{f}) from the elemental constituents would cancel out from the product and reactant internal energy terms. Often enthalpies of formation are more readily available than energies of formation: this formalism for internal energy was chosen to simplify the calculations involved by using eqns. (6) and (7).

HEX VERSUS HEAT OF COMBUSTION

The energy of combustion is measured experimentally using a bomb calorimeter filled with an excess of oxygen. For a CHNO species, the combustion products would be liquid H_2O and gaseous CO_2 and N_2, according to the equation [5]

$$\mathrm{C}_a\mathrm{H}_b\mathrm{O}_c\mathrm{N}_d + \left(a + \frac{b}{4} - \frac{c}{2}\right)\mathrm{O_2(g)} \rightarrow a\mathrm{CO_2(g)} + \frac{b}{2}\mathrm{H_2O(l)} + \frac{d}{2}\mathrm{N_2(g)} \tag{8}$$

The measured energy of combustion ΔU_{c} can be converted to the enthalpy of combustion ΔH_{c} using the equation

$$\Delta H_{\mathrm{c}} = \Delta U_{\mathrm{c}} + \Delta n_{\mathrm{g}} RT \tag{9}$$

where Δn_{g} is the change in the number of moles of gas for the reaction and R is the gas constant; eqn. (9) follows directly from eqn. (4). When

$C_aH_bO_cN_d$ exists entirely in the solid or liquid state, Δn_g takes on the value of $(d/2 + c/2 - b/4)$. The enthalpy of combustion is typically used to calculate the enthalpy of formation for the compound being combusted.

HEX is measured in a similar manner as the heat of combustion except that the calorimeter is filled with an inert gas instead of oxygen. A simple calculation for estimating the enthalpy of explosion ΔH_e can be derived if one assumes that the only observed combustion species are CO, CO_2, $H_2O(l)$, and N_2. This assumption excludes any consideration of O_2, H_2, or any fragmented species in the combustion products; the exclusion of H_2 is not unreasonable because the water–gas equilibrium freeze-out temperature would typically be in the 1500–1800 K range [6–9], resulting in equlibrium constants which are unfavorable to the production of H_2 [1, 2]. The explosion reaction is then approximated as

$$C_aH_bO_cN_d \rightarrow \left(c - a - \frac{b}{2}\right)CO_2(g) + \left(-c + 2a + \frac{b}{2}\right)CO(g) + \frac{b}{2}H_2O(l) + \frac{d}{2}N_2(g) \tag{10}$$

The enthalpy of combustion ΔH_c for eqn. (8) can be expressed as

$$\Delta H_c = a\Delta H_f[CO_2(g)] + \frac{b}{2}\Delta H_f[H_2O(l)] - \Delta H_f[C_aH_bO_cN_d] \tag{11}$$

In a similar fashion, the enthalpy of explosion ΔH_e for eqn. (10) can be expressed as

$$\Delta H_e = \left(c - a - \frac{b}{2}\right)\Delta H_f[CO_2(g)] + \left(-c + 2a - \frac{b}{2}\right)\Delta H_f[CO(g)] + \frac{b}{2}\Delta H_f[H_2O(l)] - \Delta H_f[C_aH_bO_cN_d] \tag{12}$$

Taking the difference between eqn. (11) and (12), the following equation is obtained (solving for ΔH_e)

$$\Delta H_e = \Delta H_c + (\Delta H_f[CO(g)] - \Delta H_f[CO_2(g)])\left(2a + \frac{b}{2} - c\right) \tag{13}$$

By making the approximation HEX $\approx -\Delta H_e$, eqn. (13) can be written (on a per gram basis) as

$$\text{HEX} \approx \frac{(-\Delta H_c) - 283.0(2a + 0.5b - c)}{M} \tag{14}$$

where ΔH_c is the enthalpy of combustion of the material in kJ mol^{-1}, M is the molar mass of the compound in g mol^{-1}, and the calculated HEX is in kJ g^{-1}. This particular approximation can be justified by the fact that the reactions in eqns. (8) and (10) would be expected to produce similar

TABLE 2

HEX values for selected energetic materials calculated using eqn. (14)

Material	$-\Delta H_c$ in kJ mol^{-1}	HEX in J g^{-1}		
		Eqn. (14)	Literature	Ref.
HMX	2792	5606	5674	10
RDX	2100	5630	5732	11
NC, 12.6% N	2732	3928	4071	12
NG	1524	7336	6150	12

amounts of products in the gas phase; the $\Delta n_g RT$ terms in eqn. (9) would roughly cancel out if the corresponding energies were used in place of the enthalpies in eqn. (13). Typically, it is easier to find values for enthalpies of formation than for enthalpies of combustion. Where the enthalpy of combustion cannot be found for a given species, it may be calculated using eqn. (11). Table 2 lists HEX values calculated using eqn. (14) as well as the literature values of HEX for HMX, RDX, NC, and NG. The enthalpy of combustion values listed in Table 2 were calculated using eqn. (11) and are only listed for use in eqn. (14). It should be noted that eqn. (14) only applies in the case of pure compounds where the heat of combustion can be expressed on a molar basis. In the case of a multi-component formulation, eqn. (14) could be used to generate *partial* HEX for each ingredient which could then be combined on a weight basis to estimate HEX for the formulation as a whole.

COMPUTATIONAL METHODS USING THERMOCHEMICAL CODES

Exact calculation of HEX

The following equation is based on the definition of HEX presented in eqn. (1)

$$\mathrm{HEX} = \left| \frac{\sum_{j=1}^{m} X_j U_j}{\sum_{j=1}^{m} X_j M_j} - \frac{\sum_{i=1}^{n} X_i U_i}{\sum_{i=1}^{n} X_i M_i} \right| \quad \text{in J g}^{-1} \qquad (15)$$

where the m product mole fractions (X_j) in the first summation are those computed at the freeze-out temperature T_{fo}; the room temperature internal energies U_j are for the expected state following cooling to T_r, e.g., $H_2O(1)$, and division by the product molar masses M_j gives HEX units of energy per unit weight, e.g., J g^{-1}. For gaseous products, the U_j values are related to the enthalpies of formation by eqn. (7); the internal energies for use in the first term of eqn. (15) are, therefore, obtained by subtracting RT

(2.48 kJ mol^{-1}) from the room temperature enthalpies of formation in the JANAF thermochemical tables [13]. The second term in eqn. (15) is simply the internal energy (J g^{-1}) of the propellant or energetic material, obtained by summing U_i for the n ingredients. For the usual case of a solid or liquid material, eqn. (6) applies, so the enthalpies of formation can be used. Most thermochemical codes permit ingredient weight fractions to be input rather than mole fractions; most codes output the total energy of the formulation, providing the second term in eqn. (15) directly.

The exact procedure for calculating HEX using a thermochemical code has been previously described [14] and will now be summarized. If the code supports an assigned temperature and volume mode, as does the NASA-Lewis code, a volume (or loading density, ρ) and T should be specified, where an assumed T_{fo} is used for T, and the code run to produce the minimum energy (equilibrium) combustion product composition. For a CHNO formulation, the only significant products are usually CO, CO_2, H_2, $H_2O(g, l)$, N_2, CH_4, NH_3, and C(gr), where the methane, ammonia, and graphite result from oxygen deficiency in the energetic material or formulation. The predicted mole fractions at T_{fo} are then used, together with the molar masses and room-temperature internal energies, to perform the summation in the first term of eqn. (15). In the original implementation [14], this was done by taking the product mole fractions at T_{fo} from the thermochemical code output, and inputting them into a small program running on a programmable calculator. More recently, we have done the summation by down-loading the thermochemical code output into a spreadsheet. Yet another procedure, for some thermochemical codes, is to enter the gas composition returned from the assigned temperature and volume calculation as input to an assigned energy and volume calculation, which is then run at $T_r = 298.15$ K; when specifying the composition, any gaseous H_2O should be condensed to liquid for the room-temperature calculation. The final composition returned from the assigned energy and volume calculation is ignored, only making use of the output U for the mixture; because the calculation is run specifying constant U, the calculation is essentially a lazy way of summing up the internal energy of the input (T_{fo}) composition at room temperature. Of course, the ideal procedure would be to modify the thermochemical code to calculate a HEX automatically for one or more specified freeze-out temperatures.

Table 3 shows calculated HEX for HMX and for a 60/40 mixture (by weight) of nitrocellulose (12.6% N)/nitrogylcerine (NC/NG) using the exact procedure. The variation of HEX with loading density ρ is readily apparent in the data of Table 3, and is due to increased formation of C(gr), CH_4, and NH_3 with decreasing freeze-out temperature.

It a code does not support an assigned temperature and volume (or ρ) mode, the problem then becomes one of estimating the pressure at T_{fo}, i.e., the freeze-out pressure P_{fo}, so that an assigned temperature and pressure

TABLE 3

HEX ($J\ g^{-1}$), exact calculation

$\rho/g\ cm^{-3}$	HMX [a], T_{fo}/K				NC/NG [b], T_{fo}/K			
	900	1100	1300	1500	900	1100	1300	1500
0.01	6293	5782	5674	5674	5891	5402	5347	5347
0.05	6443	6046	5740	5678	6054	5611	5372	5351
0.10	6481	6146	5828	5694	6096	5711	5418	5356
0.20	6510	6238	5937	5736	6125	5820	5502	5368
0.50	6535	6347	6084	5849	6150	5945	5636	5427

[a] HMX: $U \approx \Delta H_f^\circ = +74.98\ kJ\ mol^{-1} = +253.2\ J\ g^{-1}$. [b] NC (12.6%N): $U \approx \Delta H_f^\circ = -707.93\ kJ\ mol^{-1} = -2598\ J\ g^{-1}$. NG: $U \approx \Delta H_f^\circ = -370.70\ kJ\ mol^{-1} = -1633\ J\ g^{-1}$. For 60% NC + 40% NG: $U = -2212\ J\ g^{-1}$.

calculation can then be carried out to find the composition at freeze-out. The P_{fo} can be estimated from [14]

$$P_{fo} = P_{fl}\left(\frac{T_{fo}}{T_{fl}}\right) \tag{16}$$

where T_{fl} and P_{fl} are the adiabatic flame temperature and pressure, i.e., the T and P before any cooling occurs. T_{fl} and P_{fl} are computed using an assigned energy and volume calculation. Equation (16) overestimates P_{fo} somewhat, because, in general, condensed species form at T_{fo}, and/or the average molar mass of the gases increase on cooling to T_{fo}. This leads to the resulting HEX being a little too high; for typical CHNO propellants the error is usually only 85 $J\ g^{-1}$ or less [14]. This error can be eliminated by using an iterative procedure in place of eqn. (16). This is done as follows. First, estimate P_{fo} from the ideal gas equation of state $P = \rho RT/M$ (for P in MPa and ρ in $g\ cm^{-3}$, $R = 8.314\ cm^3\ MPa\ mol^{-1}\ K^{-1}$) for the ρ and T_{fo} of interest, using a reasonable guess for the molar mass M. Run the thermodynamic code at assigned temperature and pressure using this P and T. The resulting retuned M is then used with the ideal gas equation of state to obtain an improved estimate of P_{fo}, this procedure being repeated until the computed ρ is within, say, 1% of the desired ρ. If the initial estimate of M is close, generally only two runs will be required; otherwise there should be sufficient to produce HEX values identical to those with a code having the assigned temperature and volume option.

The $C_V dT$ *approximate method*

The first approximate method we will describe preserves the concept of a freeze-out temperature, while eliminating the need to sum up room temperature internal energies for the product species in equilibrium at T_{fo}. Starting from eqn. (1), we have

$$\mathrm{HEX} = |U_{\mathrm{prod}} - U_{\mathrm{react}}| \approx |(U_{\mathrm{fo}} - C_{\mathrm{V}}\Delta T) - U_{\mathrm{react}}| \tag{17}$$

where C_{V} and U_{fo} are the specific heat and total internal energy of the product gases at T_{fo}, respectively, and $\Delta T = T_{\mathrm{fo}} - 298.15$. Here, we are essentially approximating the internal energy of the products after cooling to room temperature by subtracting $C_{\mathrm{V}}\Delta T$ from the internal energy output by the thermochemical code for the products at the freeze-out temperature: U_{fo} in eqn. (17) is calculated from an assigned temperature and volume calculation run at a specified ρ and by setting $T = T_{\mathrm{fo}}$. Because specific heat is actually a temperature-dependent quantity, an exact procedure would involve evaluation of $\int C_{\mathrm{V}}\mathrm{d}T$ rather than $C_{\mathrm{V}}\Delta T$. Also, this approximation does not include the energy of phase changes such as water condensation. For typical CHNO formulations, the net result of these approximations is that the HEX values are about 170 J g^{-1} lower than for the exact method, as shown in Table 4. For HMX and NC/NG over a range of loading densities, simply adding 170 J g^{-1} to the HEX from eqn. (17) gives values that are within a fraction of a percent of those from the exact method described above.

Depending on the thermochemical code, some caution is required in determining the appropriate C_{V} to use in eqn. (17). Many codes output only C_p, even for constant volume calculations. In this case, C_{V} can be estimated from

$$C_{\mathrm{V}} = C_p - \left(\frac{R}{M}\right) \tag{18}$$

where M is the average molar mass of the products. In the case of the NASA-Lewis code output, C_{V} can also be determined from

$$C_{\mathrm{V}} = \frac{-C_p}{\gamma_{\mathrm{s}}\left(\frac{\partial \ln V}{\partial \ln P}\right)_T} \tag{19}$$

where $(\partial \ln V/\partial \ln P)_T$ is the returned compressibility and γ_{s} is the isentropic gamma, which is generally within a few percent of $\gamma = C_p/C_{\mathrm{V}}$. With the NASA-Lewis code, there are, however, additional complications: the C_p and γ_{s} returned by the code are equilibrium rather than frozen values, in that they include contributions due to shifting chemical equilibria in the combustion products. For propellants and explosives, the equilibrium C_p may be considerably higher than the frozen C_p needed for the present calculation. The use of equilibrium rather than frozen properties will result in anomalously high HEX values. The safest way to preclude this potential problem when using the NASA-Lewis code is to request that transport values also be returned; this results in frozen specific heats being returned, resulting in

TABLE 4

$C_V \mathrm{d}T$ method approximate HEX (J g^{-1}) and percentage difference from "exact" calculation (Table 3)

ρ/(g cm^{-3})	T_{fo}/K			
	900	1100	1300	1500
HMX				
0.01	6075 (−3.46)	5611 (−2.96)	5510 (−2.89)	5527 (−2.59)
0.05	6205 (−3.69)	5883 (−2.70)	5577 (−2.84)	5535 (−2.52)
0.10	6238 (−3.75)	5996 (−2.44)	5674 (−2.64)	5552 (−2.49)
0.20	6259 (−3.86)	6088 (−2.40)	5791 (−2.46)	5807 (−2.24)
0.50	6280 (−3.90)	6188 (−2.51)	5954 (−2.14)	5724 (−2.14)
HMX + 170 J g^{-1}				
0.01	6245 (−0.76)	5781 (−0.02)	5680 (0.11)	5697 (0.41)
0.05	6375 (−1.06)	6053 (0.12)	5747 (0.12)	5705 (0.48)
0.10	6408 (−1.13)	6166 (0.33)	5844 (0.27)	5722 (0.49)
0.20	6429 (−1.24)	6258 (0.32)	5961 (0.40)	5977 (0.20)
0.50	6450 (−1.30)	6358 (0.17)	6124 (0.66)	5894 (0.77)
NC/NG				
0.01	5661 (−3.90)	5201 (−3.72)	5150 (−3.68)	5176 (−3.20)
0.05	5799 (−4.21)	5427 (−3.28)	5180 (−3.57)	5176 (−3.27)
0.10	5832 (−4.33)	5544 (−2.92)	5234 (−3.40)	5180 (−3.29)
0.20	5858 (−4.36)	5653 (−2.87)	5326 (−3.20)	5201 (−3.11)
0.50	5879 (−4.41)	5766 (−3.01)	5481 (−2.75)	5268 (−2.93)
NC/NG, + 170 J g^{-1}				
0.01	5831 (−1.02)	5371 (−0.57)	5320 (−0.50)	5346 (−0.02)
0.05	5969 (−1.40)	5597 (−0.25)	5350 (−0.41)	5346 (−0.09)
0.10	6002 (−1.54)	5714 (−0.05)	5404 (−0.26)	5350 (−0.11)
0.20	6028 (−1.58)	5823 (−0.05)	5496 (−0.11)	5371 (−0.06)
0.50	6049 (−1.64)	5936 (−0.15)	5651 (0.27)	5438 (−0.20)

HEX values similar to those determined using codes that output only frozen parameters. In this case, only eqn. (18) should be used to calculate a frozen C_p; under frozen conditions, eqn. (19) reduces to $C_V = C_p/\gamma$, where γ is not explicitly calculated by the code. Note, however, that for systems which produce condensed products, the returned transport properties (including C_p) are for the gas phase only; in addition, the M returned by the NASA-Lewis code (for use in eqn. (18)) is not a true average molar mass, but rather corresponds to a quantity defined by total mass (both gaseous and condensed) divided by the moles of gas only. When dealing with systems that produce significant amounts of condensed products, it is recommended to use either a code (other than NASA-Lewis) which returns true average molar masses or a different approximate method.

The room-temperature method

This is the first of two methods that not only do not require weighted summation of product internal energies (eqn. (15)), but, in addition, do not require freeze-out temperatures to be specified. Such approximate methods are particularly appropriate for chemistries or calorimetric conditions where there is little information about the freeze-out temperature(s).

In the room-temperature approximate method, it is assumed that there is no freeze-out of chemistry on cooling of the products to T_r. This is equivalent to saying that $T_{fo} = T_r = 298.15$ K. To do the calculation, an assigned temperature and volume (or density) calculation is carried out for the desired loading densities, specifying $T = 298.15$. From the returned U_{prod} for the combustion products at 198.15 K, U_{react} is subtracted (eqn. (1)) to give HEX. In using this method, we usually restricted the products to CO, CO_2, H_2, N_2, H_2O, and $H_2O(l)$, because otherwise at this low temperature unrealistically large amounts of C(gr), CH_4, NH_3, and other products are predicted. As shown in Table 5, it is then found that the computed HEX values are virtually independent of loading density for CHNO systems, with HEX = 5669 J g^{-1} for HMX and 5347 J g^{-1} for NC/NG. The HEX values are similar to those calculated in the exact method with a high, e.g., 1500 K,

TABLE 5

Summary of all methods for HEX in J g^{-1} at selected conditions

ρ/(g cm^{-3})	"Exact"		"$C_v dT + 170$"		"Room T" No. of species		"Inert diluent" No. of species		Eqn. (14) [b,d]	Lit. [c,d]
	900 K	1500 K	900 K	1500 K	6	All	6 + Ar	All		
HMX										
0.01	6293	5674	6245	5697	5665	6816	5669	6255	5606	5674
0.05	6443	5678	6375	5705	5669	6820	5669	6255	5606	5674
0.10	6481	5694	6408	5722	5669	6820	5669	6255	5606	5674
0.20	6510	5736	6429	5977	5669	6820	5669	6255	5606	5674
0.50	6535	5849	6450	5894	5669	6820	5669	6828 [a]	5606	5674
NC/NG										
0.01	5891	5347	5831	5346	5339	6368	5318	5845	5291	–
0.05	6054	5351	5969	5346	5343	6372	5318	5845	5291	–
0.10	6096	5356	6002	5350	5347	6376	5318	5845	5291	–
0.20	6125	5368	6028	5371	5347	6376	5318	5845	5291	–
0.50	6150	5427	6049	5438	5347	6376	5318	6355 [a]	5291	–

[a] $H_2O(l)$ appears at this and higher ρ. [b] From Table 2. Values for NC/NG are calculated by taking 60% HEX_{NC} + 40% HEX_{NG} calculated using eqn. (14). [c] No loading density was given for the literature value for HMX (Table 2). [d] It is not intended to imply that these values are independent of loading density.

rather than low, e.g., 900 K, T_{fo}. This results primarily from the exclusion of C(gr), CH_4, and NH_3, and, to a much smaller extent, from alteration of the water–gas equilibrium ($CO + H_2O \rightleftharpoons CO_2 + H_2$) due to formation of H_2O(l) at equilibrium. Allowing all species, the HEX increases to about 6820 J g^{-1} for HMX, and about 6376 J g^{-1} for NC/NG. As in the exact and $C_V dT$ approximate methods, a dummy assigned energy and volume calculation can be used, if desired, to calculate U_{react} from the energies of formation for the separate ingredients and an assigned temperature and pressure calculation can be used, with estimated P, to obtain the product U_{prod} if the code does not offer the assigned temperature and volume mode. For CHNO chemistry with CH_4, NH_3, and C(gr) excluded, the density-(pressure-) independence of the computed U_{prod} means that an accurate estimate of P is not necessary, so no iterations are required.

The inert diluent method

The other approximate method that avoids both the summation of eqn. (15) and the need to specify T_{fo} is the inert diluent method. In this method, a large excess of inert gas, e.g., argon, is added to the energetic material, and an assigned energy and volume (or density) calculation is run. The effect of the diluent is to provide a heat sink for the reaction exothermicity, resulting in computed adiabatic flame temperatures that are only a few degrees above room temperature. HEX is determined using the equation

$$\mathrm{HEX} = |U_{prod} - U_{react}| = N \int C_V \, dT \approx \frac{NC_p \Delta T}{\gamma} \qquad (20)$$

where ΔT is the computed temperature rise ($T_{fl} - T_{initial}$), N is the reciprocal of the weight fraction of propellant or explosive in the mixture, and C_p and γ are as previously defined. The small ΔT serves three purposes: (a) it allows condensables to condense, as in the calorimeter; (b) it reduces the error associated with assuming a constant specific heat; and (c) for the NASA-Lewis code, the low T_{fl} makes it less likely that the C_p will be too large due to equilibrium reaction effects, although in some cases phase equilibria could result in the equilibrium C_p being larger than the frozen ones. Unlike all the other methods described above, this method does not require the explicit subtraction of U_{react} from an approximation to U_{prod}, but instead evaluates HEX according to the right-hand side of eqn. (20). As for the room temperature method, it is necessary to exclude many species that would otherwise be predicted in unreasonable amounts, including CH_4, NH_3, and C(gr), and, as for the room-temperature method, this results in HEX values that are almost totally independent of loading density.

A convenient diluent is argon. Using 1 part formulation + 999 parts (by weight) of argon ($N = 1000$), the ΔT is typically 20–22 K. For sufficient accuracy, it is necessary to have the code output T_{fl} to ± 0.1, or preferably

±0.01 K. Less diluent, e.g., $N = 100$, can be used if the source code is not available to make this format modification. Using 999 parts of argon, and allowing only CO, CO_2, H_2, N_2, H_2O, and $H_2O(l)$ to form, eqn. (20) gives HEX values of 5669 J g^{-1} for HMX, and 5318 J g^{-1} for NC/NG. For HMX, as shown in Table 5, this value is identical to that using the room temperature method; for NC/NG, it is 29 J g^{-1} less. If all species are allowed, HEX values for HMX are about 586 J g^{-1} higher, and for NC/NG about 527 J g^{-1} higher, but unrealistically high amounts of graphite, e.g., 20–30 mol%, are predicted. With all species allowed and 999 parts argon, there is a sudden additional increase of 510 (NC/NG) to 573 (HMX) J g^{-1} in going from $\rho = 0.2$ to $\rho = 0.5$ g cm^3; this is due to the appearance of $H_2O(l)$ at this loading density. Of course, $H_2O(l)$ would appear at much lower loading densities if it were not for the argon diluent. This points out the value of running the code for extremely high loading densities, e.g., $\rho = 10$ or 100 g cm^{-3}; although these are unachievably high loading densities, they force the water to condense as it would in the absence of the inert diluent.

With the inert diluent method, it is also possible to shift the ratios of predicted combustion products by using one of the combustion products as the (not exactly inert) diluent. For example, for HMX, using CO_2 as the diluent increases CO somewhat, lowering HEX by 29 J g^{-1} compared to argon, using CO as diluent ($N = 700$) suppresses all water formation (HEX unchanged), using H_2O as diluent ($N = 500$, $H_2O(l)$ not allowed) suppresses all CO (HEX increased 4 J g^{-1}), and using H_2 as diluent ($N = 50$ due to much lower C_p for H_2) causes more $H_2O(l)$ to form and increases CO/CO_2, causing HEX to decrease by 50 to 117 J g^{-1} depending on ρ. While these changes are small due to the low ΔU for the water–gas ($CO + H_2O \rightleftharpoons CO_2 + H_2$) reaction, for other chemistries, use of a combustion product as diluent may in some cases help force a better match between predicted products and those recovered from the calorimeter, producing a better match between experimental and theoretical HEX values.

SUMMARY

Three approximate methods to estimate HEX for energetic materials using a standard thermochemical code have been outlined. The results of these methods have been compared to those obtained using the exact method for calculating HEX at a given freeze-out temperature. One of these methods requires the use of a freeze-out temperature while the other two do not. The three approximate methods and the exact method are reviewed below.

The exact method is based on running an assigned temperature and volume calculation at an assumed freeze-out temperature. The calculated product composition (at T_{fo}) is used to calculate a room-temperature internal energy based on the room-temperature internal energies for the product species. Any gaseous water is converted to liquid water prior to calculating the internal energy of the combustion products. HEX is calculated by subtracting the internal energy of the uncombusted material from that of its combustion products.

The $C_V dT$ approximate method is also based on running an assigned temperature and volume calculation at an assumed freeze-out temperature. This method avoids the summation of combustion-product internal energies by subtracting the quantity $C_V \Delta T$ from the calculated internal energy at the freeze-out temperature to get the approximate internal energy of the combustion products at room temperature. As in the exact method, HEX is calculated by subtracting the internal energy of the uncombusted material from that of its combustion products. The ΔT is $T_{\mathrm{fo}} - 298.15$ K and the C_V is the constant volume heat capacity, either returned by the code or calculated as a derived quantity from other values returned by the code. One needs to be careful to choose a code that can handle condensed species if they are produced. For the CHNO chemistries considered in this report, the HEX values calculated were about 170 J g^{-1} lower than those using the exact method.

The room-temperature method requires no pre-assigned freeze-out temperature, and, like the $C_V dT$ approximate method, avoids the summation of combustion-product internal energies. As is the case with the exact method and the $C_V dT$ approximate method, this method is based on an assigned temperature and volume calculation, but unlike these other two methods, the calculation is run at 298.15 K. The combustion-product internal energy is calculated directly from the code, and HEX is determined by subtracting the internal energy of the uncombusted material from that of its combustion products. There is a need to restrict the permissible product species when using this method to prevent excess formation of C(gr), CH_4, NH_3, and similar combustion products in the code. The calculated HEX is virtually independent of loading density when this method is used.

The inert diluent method, like the room-temperature method, requires no assumed freeze-out temperature and also avoids the summation of combustion-product internal energies. In this method, a large excess of inert gas, e.g., argon, is added to the energetic material and an assigned energy and volume calculation is run. The effect of the diluent is to limit the temperature rise to a few tens of degrees. HEX is determined using a few quantities reported by the code without the need to subtract U_{react} from an approximation to U_{prod}. As with the room-temperature method, there is a need to omit species such as C(gr), CH_4, and NH_3, and the calculated HEX values are almost totally independent of loading density. Due to the small temperature rise, the code is required to output temperature to ± 0.1 K or ± 0.01 K. Water can be forced to condense out using large loading densities of 10 or 100 g cm^{-3}, but because HEX is relatively unaffected by loading density, this does not make a large difference.

Because two of the approximate techniques (room temperature and inert diluent) eliminate the need to specify a composition freeze-out temperature, these may be appropriate for situations where T_{f_0} is unknown, especially in cases which cannot be described by simple chemistry (such as metallized propellants or pyrotechnics). It is interesting to note that these two methods give similar values which seem to be quite independent of loading density if the number of product species allowed is kept small.

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