JOURNAL OF PROPULSION AND POWER
Vol. 16, No. 1, January–February 2000

Ideal Gas Thermodynamic Properties of Propellants and Explosive Compounds

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The detailed ideal gas thermodynamic properties of 29 nitro and nitrate compounds are calculated together with two of their radicals. Most of these compounds are high explosives: TNT, RDX, HMX, PETN, NPN, and NG, whereas others serve as propellants or specialty fuels such as nitromethane. The thermodynamic properties were calculated from fundamental molecular data. The molecular data were gathered from the literature or calculated for this purpose. The enthalpy of formation of 1-nitro-pentane is estimated to be -39.3 ± 0.5 kcal/mole, and that of 1-nitro-hexane is -44.3 ± 0.7 kcal/mole.

Nomenclature

A, B, C = spectroscopic rotational constants of a molecule, cm^{-1}
C_p = heat content function, cal/mole K
H_T^0 = absolute enthalpy, kcal/mole
IA, IB, IC = moments of inertia of a molecule, g $cm^2 \times 10^{-39}$
Ia, Ib, Ic = moments of inertia of a molecule, g $cm^2 \times 10^{-39}$
Ir = internal moment of rotation, g $cm^2 \times 10^{-39}$
$Ired$ = reduced internal moment of rotation, g $cm^2 \times 10^{-39}$
n = stoichiometric factor
S_T = entropy, cal/mole K
$V_{(R)}$ = internal rotation barrier, kcal/mole
$\Delta H_f(T)$ = enthalpy of formation at temperature T, kcal/mole
ν = fundamental vibration in a molecule, cm^{-1}
σ = SYMNO, external symmetry of a molecule

Introduction

THE detailed thermodynamic data of most propellants and explosive compounds are not known or are unpublished in the open literature. The thermodynamic and thermochemical properties are involved in most computational aspects of these compounds, including the enthalpy of reaction, the adiabatic flame temperature obtained during combustion, the temperature and pressure obtained during (gaseous) detonation, estimation of reaction rates, safety estimations, etc.

This is an attempt to publish the thermodynamics of a list of nitro and nitrate compounds, some of them known as explosives, and others as propellants or specialty fuels. The data published are shown to be accurate enough for engineering purposes. The fundamental molecular data such as vibrations, moments of inertia, internal rotation barriers, and heats of formation were taken from existing sources (The NIST Webbook[1] for the experimental IR spectrum and the experimental heats of formation, Melius' BAC/MP4/MP2 collections[2] and the open literature for ab initio calculations), or were calculated using MOPAC 6 semi-empirical methods.[3] In all cases, the calculated data were supplemented where possible with experimental data. Checking group additivity methods was done where possible using the NIST 94 (Ref. 4) thermodynamic program and database, and Ritter and Bozzelli's Therm program.[5]

In the past, ab initio methods were known to be far more accurate than semi-empirical ones, but lately the difference has narrowed, and the semi-empirical methods of today are almost as good as the ab initio ones regarding the optimization of a molecule's structure and the estimation of its vibrations. However, the estimation of the heats of formation by semi-empirical methods are still unacceptable.

The list of compounds covered in this work are nitro-methane CH_3NO_2, CD_3NO_2, CHD_2NO_2, CH_2DNO_2; nitro-methyl radical $^*CH_2NO_2$; di-nitro-methane $CH_2(NO_2)_2$; tri-nitro-methane (TNF) $CH(NO_2)_3$; tetra-nitro-methane $C(NO_2)_4$; methyl-nitrate CH_3ONO_2; methyl-nitrate radical $^*CH_2ONO_2$; nitro-ethylene $CH_2{=}CHNO_2$; di-nitro-ethylene $O_2NHC{=}CHNO_2$; nitro-ethane $C_2H_5NO_2$; ethyl-nitrate $C_2H_5ONO_2$; nitro-propene-2$CH_3CH{=}CHNO_2$; nitro-cyclo-propane $C_3H_5NO_2$; nitroglycerin $C_3H_5(ONO_2)_3$; nitro-azetidine-Cy $(CH_2)_3N{-}NO_2$; 1, 3, 3-tri-nitro-azetidine $C_3H_4N(NO_2)_3$; hexogen 1, 3, 5-trinitro-triazine $C_3H_6(N{-}NO_2)_3$ (RDX); nitro-propane $C_3H_7NO_2$; propyl-nitrate $C_3H_7ONO_2$ (NPN); octogen (HMX) cyclotetramethylene tetranitramine $C_4H_8(N{-}NO_2)_4$; nitro-butane $C_4H_9NO_2$; penta-erythrytol-tetra-nitrate $C_5H_8(ONO_2)_4$ (PETN); n-nitro-pentane $C_5H_{11}NO_2$; nitro-benzene $C_6H_5NO_2$; tri-nitro-benzene $C_6H_3(NO_2)_3$; and tri-nitro-toluene $CH_3C_6H_2(NO_2)_3$ (TNT). The structure of these compounds is given in Fig. 1.

A large amount of data was retrieved in this study from the Melius database.[2] This is a database of molecular fundamentals and thermodynamic values calculated automatically with the Gaussian program for internal purposes at Sandia corporation. This database was made partially available to the public over the Internet.[2] There are no explanations, and it is believed that many of the species have never been inspected. The calculations were made partially with the Gaussian 86 BAC/MP4 method at the $\frac{6}{3}$-1G* level and with the Gaussian 94 BAC/MP4 method at the G2 level.

The fundamental vibrations, the bond lengths, and the moments of inertia of all the molecules were calculated using MOPAC 6 (Ref. 3) semi-empirical methods PM3, PM3/UHF, AM1, and AM1/UHF. The results have been compared with existing experimental or ab initio calculations. Gaussian 94 (Ref. 6) ab initio calculations were gathered from the literature where available, and so were IR spectra and other experimental data. For simple molecules, a program by Brinkmann and Burcat[7] was used to calculate moments of inertia and internal moments of rotation. In each case the enthalpies of formation were treated separately as reported next. In Table 1 all of the values for the enthalpy of formation, known and found for the species in this article are listed.

Finally, recommendations are made and polynomial representation of the thermodynamic properties are calculated.

Thermodynamic Calculations

The thermodynamic properties were calculated with the McBride and Gordon[8] thermodynamic program, version PAC97, using the molecular fundamentals, vibrations, moments of inertia, and internal rotation data. Where needed, the calculated molecular fundamentals were supplemented with internal rotation information. If this information is missing, then internal rotation data from other nitro compounds are used. This information is presented in Table 2.

Received 26 June 1998; revision received 24 November 1998; accepted for publication 24 November 1998.

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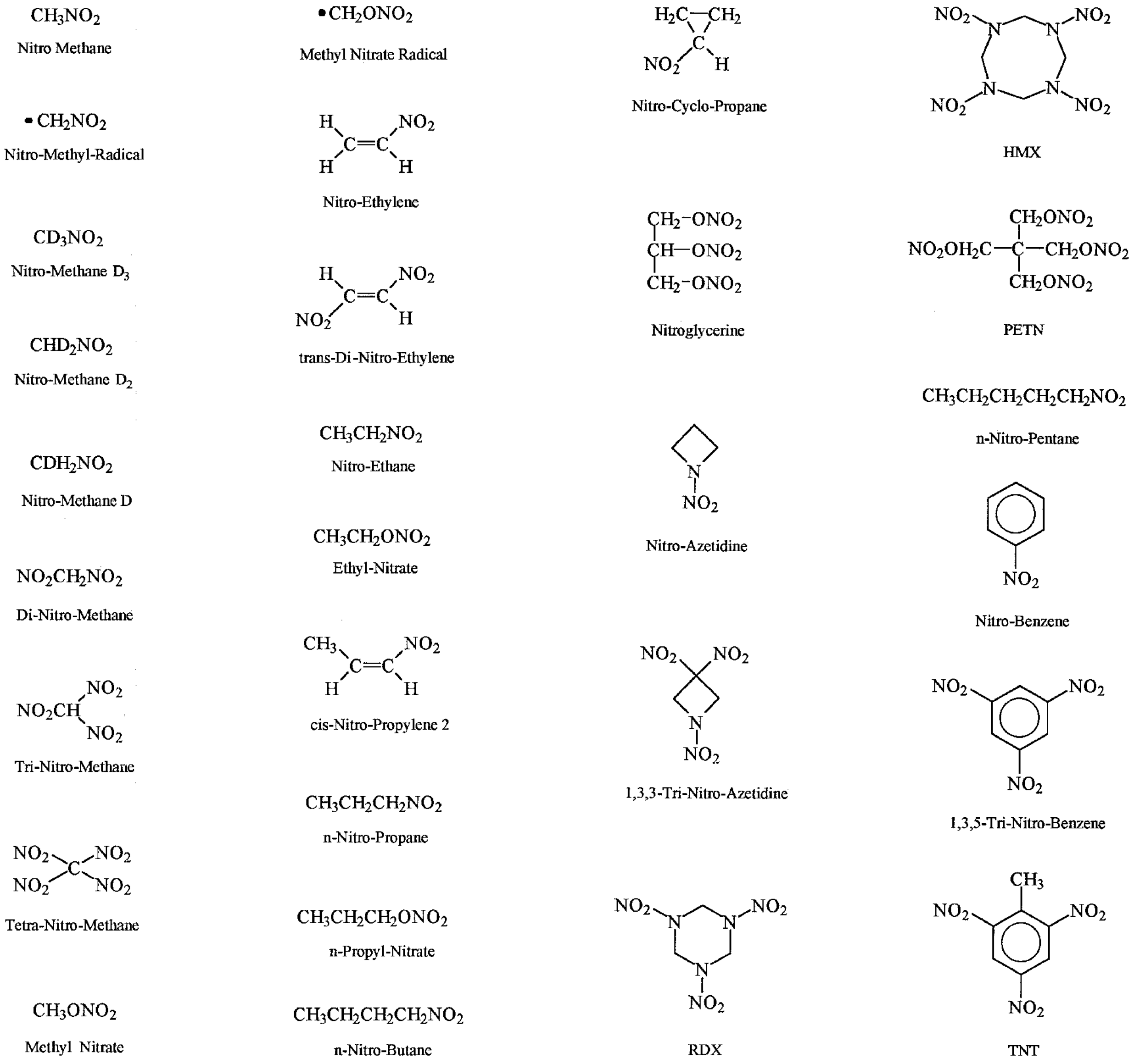

Fig. 1 Configuration formulas of all nitro and nitrate compounds.

The calculated thermodynamic properties were polynomialized and are represented in a polynomial form, ready for use in computerized applications. The format used is known as the OLD-NASA polynomial format,[8] and consists of two sets of polynomial coefficients for each species. The first set of seven coefficients represents the properties above 1000 K, and the second from 200 to 1000 K. Both polynomials give the same value at 1000 K for the properties. The 15th (last) coefficient records the value of $\Delta H_f(298)/R$.

The following molar standard thermochemical functions can be obtained from the polynomial coefficients:

$$C^0_p/R = a_1 + a_2T + a_3T^2 + a_4T^3 + a_5T^4 \tag{1}$$

$$\frac{H^0_T}{RT} = a_1 + \frac{a_2T}{2} + \frac{a_3T^2}{3} + \frac{a_4T^3}{4} + \frac{a_5T^4}{5} + \frac{a_6}{T} \tag{2}$$

$$\frac{S^0_T}{R} = a_1 \ell n T + a_2T + \frac{a_3T^2}{2} + \frac{a_4T^3}{3} + \frac{a_5T^4}{4} + a_7 \tag{3}$$

$$\frac{G^0_T}{RT} = \frac{H^0_T}{RT} - \frac{S^0_T}{R} = a_1(1 - \ell n T) - \frac{a_2T}{2} - \frac{a_3T^2}{6} - \frac{a_4T^3}{12} - \frac{a_5T^4}{20} + \frac{a_6}{T} - a_7 \tag{4}$$

The H^0_T function is the so-called engineering "absolute enthalpy," defined as

$$H^0_T = \Delta_f H^0_{298} + \int_{298}^{T} \cdot \mathrm{d}T C^0_p(T) = \Delta_f H^0_{298} + (H_T - H_{298}) \tag{5}$$

so that H^0_T/RT values calculated from the polynomials can be used directly to compute standard enthalpies of reaction. Similarly, the G^0_T/RT function can be used directly to compute equilibrium constants of formation from reference elements, in terms of concentration through

$$K_c = (R'T)^{-\Delta n} \exp\left[\Delta a_1(\ell n T - 1) + \frac{\Delta a_2T}{2} + \frac{\Delta a_3T^2}{6} + \frac{\Delta a_4T^3}{12} + \frac{\Delta a_5T^4}{20} - \frac{\Delta a_6}{T} + \Delta a_7\right] \tag{6}$$

The mole number change and the coefficient changes are defined by $\Delta n = \Sigma n_j$ and $\Delta a_i = \Sigma n_j a_{ij}$, where the summations are over all reactant and product species j with the stoichiometric coefficients n_j taken to be positive for products and negative for reactants, and R' denotes the gas constant in units appropriate to pressure in bar and volume as used to measure concentrations, e.g., 83,1451 when concentrations are expressed as mole/cm^3. The terms a_i in Eq. (6) are the same as in Eqs. (1–4).

Table 1 Listed values of the enthalpy of formation at 298 K for nitro species in kcal/mole

Name	PM3	PM3/UHF	AMI	AM1/UHF	Melius	Pedley	NIST 94[a]	Experimental, NIST 97
Nitro-methane CH_3NO_2	-15.9^b	——	-9.9^b	——	−16.85 ± 2.1	−17.9	(−15.1)	−19.3 ± 0.3
$^*CH_2NO_2$	21.83	——	——	——	36.44	——	——	——
CD_3NO_2	——	——	——	——	——	——	——	−14.768
CD_2HNO_2	——	——	——	——	——	——	——	−13.795
CDH_2NO_2	——	——	——	——	——	——	——	−12.555
Dinitro-methane $CH_2(NO_2)_2$	−11.91	−11.91	$74.41, 2.9^b$	2.91	−11.87 ± 4.2	——	——	−14.7 ± 0.3
Trinitro-methane $CH(NO_2)_3$	$165.75, -4.7^b$	165.65	25.0^b	——	——	——	−0.2	-3.2^b
Tetra-nitro-methane $C(NO_2)_4$	$189.57, 6.4^b$	189.57	224.39	224.39	——	——	——	19.69
Methyl-nitrate CH_3ONO_2	-32.4^b	——	-31.3^b	——	−26.12 ± 3.55	−29 ± 1	−29.6	−29.16 ± 0.3
$^*CH_2ONO_2$	——	——	——	——	23.65	——	——	——
Nitro-ethylene $H_2C{=}CHNO_2$	7.17	7.17	15.95	15.95	7.94	——	13.4	——
Di-nitro-ethylene $C_2H_2(NO_2)_2$	−26.42	−26.42	−19.42	−19.50	85.12 ± 5.22	——	14.2	——
Nitro-ethane $C_2H_5NO_2$	-20.9^b	——	-16.9^b	——	−24.8 ± 1.2	−24.4	−24.6	-23.5^b
Ethyl-nitrate $C_2H_5ONO_2$	−38.03	−38.03	−38.11	−38.11	−34.50	——	——	−37.04 ± 0.7
Nitro-propene $CH_3CH{=}CHNO_2$	——	——	——	——	2.39 ± 2.12	——	5.5	——
Nitro-cy-propane $C_3H_5NO_2$	——	——	——	——	——	——	4.2, (6.42)	——
Nitroglycerine	$17.96, -76.6^b$	17.96	$18.92, -71.2^b$	18.92	——	——	−81.5	$-66.70 \pm 0.65, -92.5^b$
Nitroazetidine $C_3H_6N{-}NO_2$	——	——	——	——	27.28 ± 5.1	——	——	——
Trinitroazetidine	——	——	——	——	——	——	——	30.7
RDX hexogen	141.65	——	198.31	——	——	——	——	45.89
Nitro-propane	−26.21	−26.21	-23.8^b	−23.58	——	−29.7	−29.5	-30.0^b
Propyl-nitrate	−42.68	−42.68	−44.38	−44.38	——	−41.60	−42.60	——
HMX octogen	93.37	——	175.0	174.4	——	——	24.1	44.9 ± 6
Nitrobutane	−32.1	——	−30.4	−29.6	——	−34.4	−34.4	-34.4^b
PETN	-98.2^b	——	-95.3^b	——	−89.89	——	——	-92.5^b
n-nitro-pentane	−36.9	−36.9	−35.5	−35.5	——	——	−39.3	−39.3 ± 0.5
Nitro-benzene	14.5^b	——	25.3^b	——	14.18 ± 2.6	——	——	16.38 ± 0.16
Tri-nitro-benzene	189.65	94.64	——	136.8, 4	——	14.9	——	——
Tri-nitro-toluene	3.3^b	89.73	41.3^b	——	——	——	——	$5.76 \pm 1, 12.9^b$

[a] Values in parenthesis were evaluated with the program "Therm."[5]

[b] Data reported by Stewart[18] as part of the optimization of the MOPAC AM1 and PM3 methods.

Table 2 Internal rotation values for different nitro compounds

Compound	$I_r(CH_3)\times 10^{40}$ g, cm^2	$I_r(NO_2)\times 10^{40}$ g, cm^2	$V(2)NO_2$,[a] kcal/mole	$V(3)CH_3$,[a] kcal/mole	$V(2)NO_2$,[b] kcal/mole	$I_r(CX_3)\times 10^{40}$ g, cm^2	$I_r(NO_2)^c \times 10^{40}$ g, cm^2
CH_3NO_2	5.1666	59.60	——	9.1	0.0	5.187	59.316
$^*CH_2NO_2$	——	——	——	——	——	3.46	59.32
CD_3NO_2	——	——	——	——	——	10.36	——
CHD_2NO_2	——	——	——	——	——	8.64	——
CDH_2NO_2	——	——	——	——	——	6.91	——
$C_2H_3NO_2$	——	59.710	5.04	——	4.8	——	——
$C_2H_5NO_2$	5.1666	59.548	0.08	3.50	——	——	——
$CH_3CH{=}CHNO_2$	5.1536	59.606	1.50	8.8	——	——	——
N-nitro-azetidine	——	——	——	——	4.6	——	——
$C_6H_5NO_2$	——	59.350	3.11	——	2.8–3.3	——	——
CH_3ONO_2	5.280	17.4	2.32	9.1	——	——	——
$(CH_3)_2HNO_2$	——	——	——	——	>9	——	——

[a] Values taken from Melius, private communication. [b] Values taken from Habibollahzadeh.[30] [c] Values calculated using Brinkmann and Burcat's program.[7]

Individual Substances

Nitro-Methane CH_3NO_2

Nitro-methane is the simplest organic nitro compound, and has been investigated both experimentally[9] and by calculations.[10] The MOPAC calculations resulted in transition/inversion states as seen from the vibrational results of PM3 (one imaginary vibration).[11] Therefore, the calculated heats of formation are not listed. The IR spectrum[1] was adopted for the thermodynamic calculations, although McKean and Watt[9] published an assigned experimental spectrum. The actual difference in the calculated thermodynamic data (C_p, S, etc.) was less than 0.3 cal/mole K when using the McKean and Watt and the IR spectra.[1] Thus, the IR spectra[1] was preferred for the sake of compatibility with the other species (nitro-methyl-radical, deuterated-nitromethane, nitro-ethane, nitro-propane, nitro-butane, and nitro-benzene). The Melius[2] vibrations compare[11] very well with those of Bock et al.,[10] of McKean and Watt,[9] and the IR spectrum.[1] However Melius lists spin = 1 (when it should be zero), and $S^2 = 0.30$, which suggests spin contamination. Both are most likely wrong. The moments of inertia calculated with Brinkman and Burcat's[7] program are almost the same as the PM3 calculations, with Melius'[2] values showing a slightly tighter configuration. For nitro-methane, Politzer and Lane[47] show that the older Gaussian bond calculations are only 2% higher than the experimental value. The enthalpy of formation chosen for nitro-methane, $\Delta H_{298} = -19.3$ kcal/mole by Knobel et al.,[12] was taken from the NIST 1997 (Ref. 1) recommendation. It is half a kcal/mole higher than the latest Melius MP4/G2 1997 prediction[2] and 1.5 kcal higher than the older predictions.[14, 15]

Nitro-Methyl Radical $^*CH_2NO_2$

The experimental and calculated vibrational spectrum of this radical was published by McKee,[13] and it was calculated by Melius.[2] The PM3/UHF calculation resulted in a transition state, thus no S^2 value was found. The PM3 calculation, however, was successful. The experimental values[13] were adopted and the two missing vibrations were taken from the Gaussian 6-31G* calculation of McKee.[13] The PM3 moments of inertia were chosen and the reduced moments of inertia were calculated with the Brinkmann and Burcat program.[7] The vibrations of Melius agree[11] very well with the experimental data of McKee[13] and the PM3 calculations. The moments of inertia of Brinkmann and Burcat are in good agreement with the PM3 calculations, whereas Melius' values are a little bit lower. The S^2 value of Melius[2] is 0.773, almost like the theoretical value. The enthalpy of formation $\Delta H_{298} = 36.44 \pm 2.82$ kcal/mole was calculated by Melius.[2] No other value is available.

Deuterated Nitro-Methane CD_3NO_2

The vibrational spectrum was calculated by Bock et al.,[10] using ab initio methods at HF/631G* levels and compared with experimental data. MOPAC calculations for PM3 and PM3/UHF have resulted in transition state species only. Nevertheless, these data agree very well[11] with Bock et al.'s[10] experimental and calculated results. The experimental spectral results[10] were adopted. The moments of inertia were calculated using the Brinkmann and Burcat program.[7] These values are slightly smaller than the PM3 and PM3/UHF calculations. The enthalpy of formation was calculated from the value of the nondeuterated molecule according to the following equations:

$$\Delta_f H_0(\text{deuterated comp}) = \Delta_f H_0(\text{parent compound}) - \Delta E_{\text{comp}} + \Delta E_{\text{elements}}$$

where

$$\Delta E_{\text{comp}} = \Big[\sum v_I(\text{parent compound}) - \sum v_I(\text{deuterated comp})\Big] \times \frac{2.859121}{2}\text{cal/mole}$$

$$\Delta E_{\text{elements}} = n\Big(\sum v_{iH_2} - \sum v_{iD2}\Big) = n \times 1.8 \text{ kcal/mole}$$

where n is the number of hydrogen molecules H_2, that were deuterated. $\Delta H_f(0)$ of CH_3NO_2 is -15.915 kcal/mole, and the calculated $\Delta H_f(0)$ of CD_3NO_2 is -11.573 kcal/mole and $\Delta H_{298} = -14.768$ kcal/mole.

Di-Deuterated Nitro-Methane CHD_2NO_2

The experimental spectrum was published by McKean and Watt.[9] As with all deuterated and nondeuterated methane molecules, the MOPAC PM3 and PM3/UHF calculations showed transition states. The vibrations agree well with the experimental spectrum.[11] The heat of formation was calculated from the CH_3NO_2 value, using the equations described for the previous species. $\Delta H_{298} = -16.971$ kcal/mole. For the thermodynamic calculations, the experimental values were adopted together with the moments of inertia calculated using the Brinkmann and Burcat program.[7] As with CD_3NO_2 Birkmann's program give a slightly tighter configuration than the PM3 transition state.[11]

Mono-Deuterated Nitro-Methane CH_2DNO_2

The experimental vibrational spectrum was measured by Engelke et al.[16] As with all deuterated and nondeuterated methane molecules, the MOPAC PM3 and PM3/UHF calculations showed a transition state, and as with the other deuterated nitromethanes, the vibrations of those transition states agree almost exactly with the experimental vibrations.[16] The heat of formation was calculated as described in the former deuterated species. $\Delta H_{298} = -15.686$ kcal/mole. For the thermodynamic calculations, the experimental values were adopted together with the moments of inertia calculated using the Brinkmann and Burcat program.[7] As with the former deuterated molecules, Brinkmann and Burcat's moments of inertia are slightly smaller than the PM3 calculations.

Di-Nitro-Methane $CH_2(NO_2)_2$

Di-nitro-methane is rarely mentioned in the literature. Melius[2] calculates only transition states for this molecule. For the thermodynamic compilation, the PM3 calculations were chosen. The vibrations were not scaled because comparison of PM3 values of nitro-methane showed that this was unnecessary, if the vibrations are compared with the experimental (IR) values.[11] $S^2 = 0.0$, thus no spin contamination was found. For the internal moments of inertia as well as energy barriers, Melius' values from nitro-ethane[2] were taken. The experimental enthalpy of formation recommended by NIST 97 (Ref. 1), $\Delta H_{298} = -14.7$ kcal/mole by Knobel et al.,[12] was taken.

Tri-Nitro-Methane (TNF) $CH(NO_2)_3$

This propellant is mentioned in the literature where measured heats of formation in the liquid and solid form are presented.[1] Benson[17] gives an estimate of its gaseous heat of formation. The MOPAC calculations for AM1 and AM1/UHF have failed, resulting in transition states. The PM3 and PM3/UHF were successful with heats of formation very far from Benson's estimate. The other values are very close together. $S^2 = 0.0$, which shows no spin contamination. For the thermodynamic calculations, the PM3 vibrations were chosen because this species served Stewart[18] to calibrate the PM3 system. The heat of formation found experimentally by Carpenter,[19] $\Delta H_{298} = -3.2$ kcal/mole, was chosen. The internal rotation values were taken from Melius[2] or were estimated.

Tetra-Nitro-Methane $C(NO_2)_4$

Tetra-nitro-methane served as one of 28 nitro compounds used by Stewart[18] to calibrate the PM3 method for the heat of formation of nitro compounds. Our calculations with AM1 and AM1/UHF resulted in transition states only. The values of the calculated heats of formation for PM1 are very far apart from those of Stewart. The calculated PM3 and PM3 UHF vibrations and moments of inertia are identical and were chosen for the thermodynamic calculations. The NIST 97 experimental value[1] of Lebedev,[20] $\Delta H_{298} = 19.69$ kcal/mole, was adopted.

Methyl-Nitrate CH_3ONO_2

Experimental values are given by Brand and Cawthon,[21] and also by Czuchajowsky and Kucharski,[22] who calculated part of the vibrations. Additional BAC/MP4 calculations were made by Melius.[2] These agree well with Brand and Cawthon, but not so well with Czuchajowsky and Kucharski. The vibrations of Brand and Cawthon were adopted, and the Melius[2] moments of inertia were preferred because this configuration is tighter than that of Dixon and Wilson.[23] Melius reports $S^2 = 0.0$, i.e., no spin contamination. The NIST 97 (Ref. 1) recommended enthalpy of formation from Ray and Ogg,[24] which is very close to that of Pedley and Rylance,[25] $\Delta H_{298} = -29.0$ kcal/mole, was used.

Methyl-Nitrate Radical $^*CH_2ONO_2$

This radical was calculated by Melius[2] and adopted as is, $\Delta H_{298} = 23.65 \pm 4.91$ kcal/mole.

Nitro-Ethylene H_2=CHNO$_2$ $C_2H_3NO_2$

The only source for this species is that of Melius BAC/MP4/6-31G** calculations.[2] The MOPAC calculations are in very good agreement with those of Melius. However, the MOPAC calculation show $S^2 = 0.0$, whereas Melius lists spin = 1 (erroneous, it should be zero) and considerable spin contamination ($S^2 = 0.385$). Disregarding that as an error, the Melius values including the heat of formation were adopted, $\Delta H_{298} = 7.95 \pm 2.06$ kcal/mole.

trans-Di-Nitro-Ethylene O_2NHC=CHNO$_2$ $C_2H_2(NO_2)_2$

No molecular fundamental calculations were found for this species. Using MP4/G2, Melius[2] calculates transition states only. Of the three possible configurations, only the trans (the most abundant one), was calculated. The PM3 calculations were adopted. It showed no spin contamination ($S^2 = 0$). The NIST 94 (Ref. 4) estimate was used for the enthalpy of formation, $\Delta H_{298} = 14.2$ kcal/mole. This program is not sensitive enough to differentiate between the three isomers.

Nitro-Ethane $C_2H_5NO_2$

The thermodynamic properties of nitro-ethane was published by Stull et al.[14] BAC/MP4 calculations were performed by Melius,[2] again with an erroneous spin = 1 and some spin contamination $S^2 = 0.284$. The heat of formation was recalculated with the MP4/G2 method in 1997. The IR vibrational spectrum[1] was adopted and supplemented with the missing vibrations from Melius' calculations. The heat of formation of Melius[2] was adopted, $\Delta H_{298} = -24.80$ kcal/mole.

Ethyl-Nitrate $C_2H_5ONO_2$

Ethyl-nitrate was estimated by Stull et al.[14] and calculated by Melius.[2] The MOPAC calculations gave results very close to those of Melius.[2] Both calculations show $S^2 = 0.0$. The Melius[2] data were adopted for the thermodynamic calculations. For the enthalpy of formation, the NIST 97 (Ref. 1) recommendations[26] were chosen, $\Delta H_{298} = -37.04$ kcal/mole.

cis-1-Methyl-2-Nitro-Ethylene CH_3CH=CHNO$_2$ $C_3H_5NO_2$

This compound was calculated by Melius.[2] It gives an erroneous spin = 1 value, and a spin contamination of $S^2 = 0.346$. Nevertheless, these values were adopted for the thermodynamic calculations, $\Delta H_{298} = 2.39 \pm 2.12$ kcal/mole.

Nitro-Cyclo-Propane $C_3H_5NO_2$

Holtzclaw et al.[27] have published the vibrations and internal rotation barrier for nitro-cyclo-propane. Mochel et al.[28] published the moments of inertia: external and internal. The heat of formation was estimated using NIST 94 (Ref. 4), $\Delta H_{298} = 6.42$ kcal/mole.

Nitroglycerin $C_3H_5(ONO_2)_3$

Nitroglycerin is one of the oldest known explosives. It has a TNT equivalent value of 1.23. No information on molecular data was found in the literature for nitroglycerin, except the heat of formation.[1,29] In our case, the MOPAC restricted Hartree-Fock (RHF) and unrestricted Hartree-Fock (UHF) calculations gave the same results, as predicted by the theory, and the differences between PM3 and AM1 calculations are minimal. The $S^2 = 0.0$. The PM3 results of the vibrations and moments of inertia were chosen for the thermodynamic calculations, and the enthalpy of formation recommended by NIST 97 (Refs. 1 and 29), $\Delta H_{298} = -66.7 \pm 0.65$ kcal/mole.

n-Nitro-Azetidine (Cyclo-Trimethylene-Nitramine) C_3H_6N -NO_2

This compound was calculated by Melius.[2] No other source is available. The internal rotation calculated for this molecule is erroneous, but the other value are free of spin contamination. The internal moment of inertia was taken from values of other molecules as reported in Table 2. The rotation barrier value was taken from Habibollahzadeh et al.[30] $\Delta H_{298} = 27.28 \pm 5.1$ kcal/mole.

1, 3, 3-Trinitro-Azetidine $C_3H_4N(NO_2)_3$

This compound was investigated, measured, and calculated by Yu et al.[31] Their assignment and calculation is adopted, except for an internal rotation of the NO_2 group connected to the N ring atom. They seem not to have included internal rotations of the nitro groups. The two nitro groups on carbon atom 3 were not considered as rotors and the vibration assignment of Yu et al. was adopted. The heat of formation was taken from Politzer et al.,[32] $\Delta H_{298} = 30.7$ kcal/mole.

1, 3, 5-Trinitro-Triazine (RDX) C_3H_6(N-NO_2)$_3$

This compound known as high explosive was calculated by Wu and Fried.[45] Its TNT equivalent value is 1.19. The MOPAC-PM3/UHF, and AM1/UHF calculations failed. For the thermodynamic calculations the Gaussian 94/DFT B-PW91 values of Wu and Fried were adopted, including the moments of inertia. The vibrations were scaled by 0.90, although the rough values were similar or smaller than the PM3 vibration results. It is assumed that the PM3 values are not correct because the optimal molecule is slightly distorted. The internal moment of inertia for NO_2 was taken from Melius,[2] and the rotation barrier from Habibollahzadeh et al.'s calculations[30] for nitropiperidine. The heat of formation of Pepekin et al.,[33] $\Delta H_{298} = 45.89$ kcal/mole, was recommended by NIST 97 (Ref. 1).

N-Nitro-Propane $CH_3CH_2CH_2NO_2$ $C_3H_7NO_2$

Stull et al.[14] calculated the thermodynamics of *n*-nitro-propane. The IR of this species is presented in the NIST WebBook.[1] The MOPAC RHF and UHF calculations of the PM3 method gave almost exact values as predicted by the theory, $S^2 = 0.0$. The AM1 calculations failed, but AM1/UHF was successful. For the thermodynamic calculations, the IR spectrum was adopted and supplemented with the missing vibrations from PM3. The enthalpy of formation of Pedley and Rylance[25] was accepted, $\Delta H_{298} = -29.7 \pm 0.1$ kcal/mole.

n-Propyl Nitrate (NPN) $C_3H_7ONO_2$

This is a well known explosive. The thermodynamic data of this species were estimated by Stull et al.[14] The MOPAC calculations were successfull and free of spin contamination. For this calculation, the PM3 vibrations were adopted and the moments of inertia were taken from AM1 because it showed a tighter molecular configuration. Stull's estimate[14] for the enthalpy of formation was adopted, $\Delta H_{298} = -41.6$ kcal/mole.

Octogen, Octahydro-1, 3, 5, 7-tetranitro-1, 3, 5, 7-tetrazocine; Cyclotetramethylene Tetranitramine (HMX) C_4H_8(N-NO_2)

Octogen is considered the most powerful explosive material available today. Its TNT equivalent ratio is 1.50. No thermodynamic or molecular data were found in the literature. This is the first attempt to calculate its molecular properties. The MOPAC calculations resulted in distorted molecular configurations, therefore the confidence in these results is very low. The PM3/UHF calculation failed to give any nontransitional state, while the others gave values quite different from each other. The AM1/UHF calculation is preferred because it has the lowest distortion, although a considerable spin contamination $S^2 = 0.339$. The enthalpy of formation was estimated using the solid enthalpy of formation recommendation of NIST 97 (Ref. 1), 17.9 (Ref. 34) kcal/mole and the difference between the solid heat of formation and the gas heat of formation of other explosives. Thus, the value estimated is $\Delta H_{298} = 44.9 \pm 6$; kcal/mole, in itself, a very doubtful value. This species has the lowest reliability of all the groups.

Nitro Butane $C_4H_9NO_2$

The species was mentioned in the literature by Stull et al.,[14] Stewart,[18] and by Cox and Pilcher.[35] The MOPAC PM3 and PM3/UHF have failed by giving transition states, however, the values found for the RHF and UHF transition states were identical. For the thermodynamic calculation, the IR vibrations were adopted and supplemented with the missing vibrations from the AM1 successful calculation. No spin contamination was found $S^2 = 0.0$. The internal rotation moments of inertia and barriers were taken from Chao et al.[36] The enthalpy of formation recommended by Stull et al., Pedley et al.,[15] and NIST 94 (Ref. 4,) $\Delta H_{298} = -34.4$ kcal/mole, was included.

PETN Penta Erythritol Tetra Nitrate $C_5H_8N_4O_{12}$ [$C(CH_2ONO_2)_4$]

No experimental value of the molecular fundamental properties is known for this explosive material. Its TNT equivalent value is 1.27. This was calculated by Melius[2] and is free of spin contamination. The moments of internal rotation and the rotation barrier were taken from Melius'[2] methyl-nitrate. The enthalpy of formation was taken from Cox and Pilcher,[35] $\Delta H_{298} = -92.5$ kcal/mole.

N-Nitro-Pentane $C_5H_{11}NO_2$

This species is not mentioned in the literature. It is calculated here for the first time using the MOPAC program. For the thermodynamic calculations, the PM3 results were chosen. The internal moments of inertia and the rotation barriers were taken from Chao et al.[36] The enthalpy of formation was estimated graphically. $\Delta H_{298} = 39.3 \pm 0.5$ kcal/mole (see the Discussion section).

Nitro-Benzene $C_6H_5NO_2$

Nitro-benzene was calculated by Stull et al.,[14] Stewart,[18] and Melius.[2] Melius lists a wrong spin = 1 and $S^2 = 0.423$. For the thermodynamic calculations, the IR spectrum[1] was used and supplemented with Melius' values.[2] Melius[2] gives values for the internal moment of inertia of the nitro group, and the rotation barrier is taken from Habibollahzadeh.[30] Recently, Politzer et al.[37] calculated the C–NO_2 bond as 1.465, compared with 1.459, calculated by Melius.[2] The enthalpy of formation was taken from Pedley et al.,[15] $\Delta H_{298} = 16.38 \pm 0.16$ kcal/mole.

Trinitro-Benzene $C_6H_3(NO_2)_3$

This species was not mentioned in the literature. The MOPAC/AM1 calculation failed because it optimized a transition state. The calculations of PM3, PM3/UHF, and AM1/UHF disagree with each other, although the S^2 values found in both PM3/UHF and AM1/UHF are very small (they should be zero). For the thermodynamic calculations, the PM3 values were taken and the enthalpy of formation was taken from Pedley et al.,[15] $\Delta H_{298} = 14.9$ kcal/mole.

Tri-Nitro-Toluene TNT $CH_3C_6H_2(NO_2)_3$

There are no experimental thermodynamic or other data on this basic explosive in the literature. The MOPAC calculations of AM1 and AM1/UHF have failed, and the PM3 calculation showed a transition state. Only the PM3/UHF was successful with no spin contamination. Because there are no reported IR spectra of TNT, the IR spectra[1] of toluene, 2-nitro-toluene, 4-nitro-toluene, and 2, 4-dinitro-toluene was analyzed and combined, and the missing vibrations were added using the successfully calculated MOPAC PM3/UHF (Fig. 2, vibrations in parenthesis). The internal moments of inertia for NO_2 and CH_3 were taken from Melius,[2] and the $V(2)$ value for the rotation barrier of NO_2 in the para position from nitrobenzene.[2] The $V(2)$ values for the two NO_2 groups adjacent to CH_3 have been estimated to be approximately twice the free (para) NO_2 value. The enthalpy of formation was taken from Lenchitz et al.,[38] following the NIST 97[1] recommendation, $\Delta H_{298} = 5.76 \pm 1$. Other estimates were proposed by Stewart,[39] $\Delta H_{298} = 3.3$ kcal/mole, and Cox and Pilcher,[35] proposed 12.9 kcal/mole.

The thermodynamic data of all 29 species are presented in Table 3 in the Benson[17] format, i.e., ΔH_{298}, S_{298}, and C_p as a function of temperature. In Fig. 2, a more favorable representation for engineering purposes is given in the OLD–NASA polynomial format[8] for direct use in computer programs.

The chosen molecular data for each species are listed as a header to the polynomial of the compound as devised by Burcat and McBride.[40]

Discussion

Fundamental Vibrations

Melius[41] explains that the BAC/MP4 method scales automatically all of the ab initio calculated vibrations by 12%. But because not all of the vibrations differ from the experimental ones, by the same percentage it has been found[42] that Melius' calculated vibrations[41] are 1–3% too low if less than 1000 cm^{-1}, 1–3% too high between

Table 3 Thermodynamic data for 29 propellants and explosive compounds[a]

Compounds	$\Delta_f H_{298}$	S_{298}	C_p 300	C_p 500	C_p 800	C_p 1000	C_p 1500	C_p 2000	C_p 2500	C_p 3500	C_p 4500
Nitro-methane CH_3NO_2	−80.75	282.86	55.77	80.80	107.22	118.48	134.43	141.91	145.85	149.59	151.22
$^*CH_2NO_2$	152.47	288.22	59.08	79.35	97.10	104.30	114.83	120.05	122.92	125.66	126.89
CD_3NO_2	−61.79	291.67	63.45	90.76	116.17	126.20	139.43	145.20	148.13	150.84	151.99
CD_2HNO_2	−57.72	289.26	61.07	87.37	112.81	123.15	137.31	143.76	147.12	150.27	151.64
CDH_2NO_2	−52.53	286.94	59.23	84.47	109.67	120.20	135.18	142.29	146.08	149.69	151.28
Dinitro-methane $CH_2(NO_2)_2$	−61.51	358.10	86.71	119.60	149.93	162.12	178.26	184.89	187.87	190.11	190.80
TNF trinitro-methane $CH(NO_2)_3$	−13.39	435.57	134.59	175.70	206.55	217.17	229.37	233.30	234.51	234.74	234.39
Tetra-nitro-methane $C(NO_2)_4$	82.38	503.72	176.73	224.52	257.00	267.15	277.44	279.76	279.82	278.64	277.54
Methyl-nitrate CH_3ONO_2	−122.01	305.79	76.88	104.42	131.68	142.93	157.90	164.01	166.78	168.94	169.68
$^*CH_2ONO_2$	98.95	312.17	77.05	100.55	120.95	128.89	138.97	142.76	144.30	145.30	145.54
Nitro-ethylene $H_2C{=}CHNO_2$	33.28	300.50	74.01	104.91	132.42	143.24	158.28	165.17	168.65	171.73	172.95
Di-nitro-ethylene $C_2H_2(NO_2)_2$	59.41	359.19	110.91	147.93	179.00	190.46	205.02	210.87	213.47	215.38	215.94
Nitro-ethane $C_2H_5NO_2$	−103.78	320.51	79.38	115.88	153.00	169.12	192.67	203.84	209.63	214.93	217.12
Ethyl-nitrate $C_2H_5ONO_2$	−154.98	928.86	95.54	138.17	179.70	196.99	220.93	231.47	236.63	241.11	242.87
Nitro-propene $CH_3CH{=}CHNO_2$	9.99	330.00	94.01	135.60	177.33	194.95	219.54	230.50	235.94	240.72	242.62
Nitro-cyclo-propane $C_3H_5NO_2$	17.57	317.04	91.01	139.92	181.79	198.28	221.73	232.83	238.62	243.95	246.17
NG nitroglycerine	−279.07	545.87	235.12	312.94	379.51	405.10	437.06	448.88	453.65	456.72	457.43
Nitroazetidine $C_3H_6N{-}NO_2$	114.12	328.95	101.21	157.44	212.41	235.26	267.35	281.62	288.52	294.32	296.50
1, 3, 3-trinitroazetidine	128.45	357.32	135.97	226.63	302.91	330.98	366.96	381.82	388.76	394.42	396.50
RDX hexogen	192.00	482.44	231.26	326.08	402.08	430.47	467.68	482.28	487.65	489.28	488.14
Nitro-propane	−124.27	350.05	104.61	155.36	205.01	226.25	256.72	270.79	277.92	284.18	286.46
NPN propyl-nitrate	−174.05	362.60	123.79	177.46	229.91	252.13	283.34	297.17	303.85	309.28	311.07
HMX octogen	187.86	568.83	276.66	391.74	501.71	546.99	609.69	636.18	647.26	653.32	653.54
Nitrobutane	−143.93	369.87	155.74	179.60	245.66	274.65	316.94	336.37	345.91	353.66	356.04
PETN pentaerythrytoltetranitrate	−387.02	614.71	296.08	422.02	537.11	580.92	635.20	655.75	664.39	670.52	672.33
n-nitro-pentane	−164.43	390.91	137.89	217.35	296.69	331.02	381.21	404.57	416.25	426.09	429.38
Nitro-benzene	68.53	348.80	121.06	183.86	239.83	261.91	291.82	305.21	311.98	318.08	320.59
2, 4, 6-tri-nitro-benzene	62.34	485.34	206.45	276.13	333.65	355.47	383.75	395.36	400.69	404.84	406.22
TNT 2, 4, 6-tri-nitro-toluene	24.10	501.32	215.23	288.95	361.50	392.49	435.49	454.37	436.56	471.37	474.35

[a] Data in KJ/mole for the enthalpy of formation and J/mole-K for the entropy and heat content.

CH3NO2 Nitro-Methane STATWT =1 SYNMO = 1 IA = 6.45024 IB = 8.24944
IC = 14.181 I(red)=0.47695 V(2) = 0.0 kcal/mole ROSYM =2 ν = 598,639,666,
928,1083,1157,1380,1400,1440,1481,1561,2484,2767,2962. REF = 1

ΔH_f (298)= -19.3 kcal/mole REF=12

```
NITRO-METHANE       T04/98C  1.H  3.N  1.O  2.G   200.000  6000.000  B  61.04036 1
 6.73034759E+00 1.09601272E-02-4.05357875E-06 6.67102246E-10-4.04686823E-14    2
-1.29143475E+04-9.08147607E+00 3.54053638E+00 1.86559899E-03 4.44946580E-05    3
-5.87057133E-08 2.30684496E-11-1.11385976E+04 1.17870780E+01-9.71208165E+03    4
```

*CH2NO2 Nitro Methylene Radical SYMNO = 1 STATWT = 2 IA = 6.34509
IB = 6.7566103 IC = 13.1017 IRED=0.3267 V(2)= 0.08 kcal/mole ROSYM = 2
ν = (457,555),693,719,986,1095,1297,1419,1461,3055,3200 REF=13

ΔH_f (298)= 36.44 kcal/mole REF=2

```
NITRO-METHYL RAD  T04/98C  1.H  2.N  1.O  2.G   200.000  6000.000  B  60.03242 1
 7.67214886E+00 7.04674142E-03-2.55301211E-06 4.14646979E-10-2.49316782E-14    2
 1.52307521E+04-1.22510821E+01 2.46754293E+00 1.56130407E-02 4.71686464E-06    3
-2.05123642E-08 1.02705094E-11 1.69015807E+04 1.59016345E+01 1.83372153E+04    4
```

CD3NO2 Nitro-Methane D3 STATWT=1 SYMNO=1 IA = 6.96802 IB = 10.01365 IC = 15.945
I(red) =0.882277 V(2) = 0.16 kcal/mole ν = 435,542,631,885,942,1038,1046,
1075,1404,1548,898,2147,2283,2317 REF = 10

ΔH_f (298)= -14.768 kcal/mole REF = This Study

```
NITRO-METHANE D3  T04/98C  1.D  3.N  1.O  2.G   200.000  6000.000  B  64.05885 1
 8.82522749E+00 9.35166733E-03-3.53835387E-06 5.90989861E-10-3.62227245E-14    2
-1.13067808E+04-1.97818737E+01 2.37203218E+00 1.42408389E-02 2.16286890E-05    3
-4.09339693E-08 1.78857173E-11-8.89033378E+03 1.66836953E+01-7.43151250E+03    4
```

CD2HNO2 Nitro-Methane D2 STATWT = 1 SUMNO = 1 IA = 6.76188 IB = 9.55869
IC = 15.2841 I(red) = 0.754032 V(2) = 0.125 kcal/mole ν = 443,577,643,896,
923,977,1060,1285,1285,1405,1554,2187,2313,3000 REF=9

ΔH_f (298)= -13.795 kcal/mole REF = This Study

```
NITRO-METHANE D2  T04/98C  1.H  1.D  2.O  2.G   200.000  6000.000  B  63.05268 1
 8.08961148E+00 9.83765066E-03-3.67240992E-06 6.08123340E-10-3.70523025E-14    2
-1.05585014E+04-1.58799705E+01 2.86575841E+00 9.70884039E-03 2.98575468E-05    3
-4.74818909E-08 1.98756686E-11-8.40693607E+03 1.46207846E+01-6.94164250E+03    4
```

CDH2NO2 Nitro-Methane D STATWT = 1 SYMNO = 1 IA = 6.60202 IB = 8.90396
IC = 14.75046 I(red) = 0.619102 ROSYM = 2 V(2) = 0.104 kcal/mole
ν = 463,579,651,893,957,1099,1254,1304,1338,1480,1557,2221,2997,3082. REF = 16

ΔH_f (298)= -12.555 kcal/mole REF = This Study

```
NITRO-METHANE D   T04/98C  1.H  2.D  1.O  2.G   200.000  6000.000  B  62.04652 1
 7.42983565E+00 1.02242244E-02-3.76339564E-06 6.17531100E-10-3.73902847E-14    2
-9.68557204E+03-1.23529524E+01 3.23582229E+00 6.54117396E-03 3.47848512E-05    3
-5.08832580E-08 2.07922157E-11-7.79017302E+03 1.29867207E+01-6.31809439E+03    4
```

CH2(NO2)2 Di Nitro Methane STATWT = 1 SYMNO = 2 IA = 13.497367 IB = 49.930024
IC = 50.708 (Ir(NO2) = 5.96 ROSYM = 2 V(2) = 0.08 kcal/mole) × 2
ν = 2962,2875,1959,1951,1602,1555,1358,1275,1063,971,915,895,746,638,585,568,

430,412,194. REF = This Study ΔH_f (298)= -14.7 kcal/mole REF=12

```
DI-NITRO-METHANE  T10/98C  1.H  2.N  2.O  4.G   200.000  6000.000  B 106.03796 1
 1.14912019E+01 1.18834901E-02-4.59405883E-06 7.73301202E-10-4.75226143E-14    2
-1.22791660E+04-2.79393135E+01 2.13762234E+00 3.16667350E-02-1.09883048E-05    3
-1.02396987E-08 6.93005788E-12-9.32805967E+03 2.20134081E+01-7.39728499E+03    4
```

CH(NO2)3 Tri-Nitro Methane STATWT = 1 SYMNO = 3 IA = 50.830948 IB = 68.4055572
IC = 99.2098743 (Ir(NO_2)= 5.96 ROSYM = 2 V(2) = 0.1 kcal/mole) × 3
ν = 2749,1962,1572,1261,1232,1167,1135,1064,993,884,724,708,670,619,563,490,
449,421,368,347,335,210,170,157. REF = This Study.

ΔH_f (298)=-3.2 kcal/mole REF= 19

```
TRI-NITRO METHAN  T04/98C  1.H  1.O  6.N  3.G   200.000  6000.000  B 151.03556 1
 1.96645029E+01 9.80273423E-03-3.99278141E-06 6.90498702E-10-4.31223139E-14    2
-9.12328532E+03-6.52887368E+01 1.66436817E+00 6.81055678E-02-7.81450689E-05    3
 4.46832013E-08-1.01862362E-11-4.52669105E+03 2.56966436E+01-1.61029333E+03    4
```

Fig. 2 OLD-NASA polynomials of the thermodynamic data.

C(NO2)4 Tetra-Nitro-Metane SYMNO = 4 Ia = 81.178919 Ib = 109.0935512
Ic = 119.96637 (Ir(NO_2) = 5.96 ROSYM = 2 V(2)= 0.2 kcal/mole) × 4
ν = 1985,1565,1213,1192(2),1146,1129,1015,791,701,687,672,646,640,594,562,
491,481,408,378,357,354,344,333,206,191,183,146,138. REF = This Study.

ΔH_f(298)=19.69 kcal/mole REF = 20

```
TETRA-NITRO-METH  T10/98C  1.O  8.N  4.   0.G   200.000  6000.000  B 196.03316 1
 2.63028700E+01 9.03437992E-03-3.84962536E-06 6.80136488E-10-4.29929370E-14    2
 2.32054355E+02-9.52181326E+01 1.50837189E+00 9.93550200E-02-1.38531389E-04    3
 9.75231469E-08-2.77303820E-11 6.08687871E+03 2.77172777E+01 9.90833615E+03    4
```

CH3ONO2 Methyl-Nitrate SYMNO = 1 STATWT = 1 IA = 6.67244 IB = 17.20275
IC = 23.3497 Ir (NO2) = 5.96 ROSYM = 2 V(2) = 9.1 kcal/mole
Ir (CH3) = 0.53436 ROSYM = 3 V(3) = 2.32 kcal/mole ν=3008,2940,2907,1672,
1468,1435,1434,1287,1176,1136,1017,854,759,657,578,340. REF = 21

ΔH_f(298)=-29.0 kcal/mole REF = 24

```
METHYL-NITRATE    T05/98C  1.H  3.N  1.O  3.G   200.000  6000.000  B  77.03976 1
 9.77845489E+00 1.10069541E-02-4.25928645E-06 7.18198185E-10-4.42041793E-14    2
-1.88804487E+04-2.39163197E+01 3.91363583E+00 1.52137945E-02 1.73479131E-05    3
-3.37074473E-08 1.44322204E-11-1.66103232E+04 9.44208392E+00-1.46737980E+04    4
```

*CH2ONO2 METHYL-NITRATE-RADICAL STATWT = 2 SYMNO = 1 IA = 6.5230882
IB = 16.246015 IC = 22.69382 Ir(NO_2) = 5.96 ROSYM = 2 V(2) = 9.1 kcal/mole
Ir(CH_2) = 0.345711 ROSYM = 2 V(2) = 2.3 kcal/mole ν = 3142,3009,1727,1412,
1306,1165,1120,921,766,718,683,608,364.

ΔH_f(298) = 23.65 kcal/mole REF = 2

```
Methyl Nitrate R  T05/98C  1.H  2.O  3.N  1.G   200.000  6000.000  B  76.03182 1
 1.03913885E+01 7.66103917E-03-3.02728077E-06 5.16124915E-10-3.19767406E-14    2
 7.78486241E+03-2.54151556E+01 2.98654023E+00 2.47990510E-02-1.17175684E-05    3
-5.36820166E-09 4.80947389E-12 1.00202588E+04 1.36939353E+01 1.19010741E+04    4
```

C2H3NO2 Nitroethylene STATWT =1 IA = 6.77795 IB = 17.4725 IC = 24.2505
Ir = 5.96 ROSYM = 2 V(2) = 5.04 kcal/mole ν= 3103,3094,3013,1699,1628,
1479,1378,1264,1066,1026,966,904,828,654,544,536,323.

ΔH_f(298) = 7.955 kcal/mole REF = 2

```
NITROETHYLENE     T11/97C  2.H  3.N  1.O  2.G   200.000  6000.000  B  73.05136 1
 1.00660026E+01 1.04932532E-02-3.92096997E-06 6.47758885E-10-3.93529661E-14    2
-3.10704319E+02-2.61804452E+01 2.75930739E+00 1.70703761E-02 2.37349272E-05    3
-4.77968933E-08 2.14789743E-11 2.29629458E+03 1.46559809E+01 4.00308858E+03    4
```

C2H2(NO2)2 Di-Nitroethylene-trans SYMNO = 2 STATWT = 1 IA = 15.0866142
IB = 70.306506 IC = 83.23265 (Ir(NO_2)= 5.96 ROSYM = 2
V(2) = 5.04 kcal/mole) × 2 ν= 3329,3033,2035,1906,1794,1620,1527,1439,1167,
1081,996,943,771,698,676,630,512, 474,418,353,291,140 REF = This Study

ΔH_f(298) = 14.2 kcal/mole REF = 4

```
DI-NITROETHYLENE  T05/98C  2.H  2.N  2.O  4.G   200.000  6000.000  B 118.04896 1
 1.56460865E+01 1.07958253E-02-4.19362099E-06 7.07938872E-10-4.35902999E-14    2
 9.19140603E+02-5.15469476E+01 2.71427290E+00 4.42404733E-02-3.07593033E-05    3
 3.50616078E-09 3.21103574E-12 4.63337698E+03 1.58746522E+01 7.14567665E+03    4
```

C2H5NO2 Nitro-Ethane STATWT = 1 IA = 7.4804 IB = 19.8289 IC = 26.2826
Ir(NO2) = 5.97 ROSYM = 2 V(2) = 0.08 kcal/mole Ir(CH3) = 0.51666 ROSYM = 3
V(3) = 3.5 kcal/mole ν= 3003,(2961),2956,(2929),2754,1582,1561,(1465),1460,
(1447),1400,1386,1252,1141,1117,996,881,774,(639,591,501,286).

ΔH_f(298)=-24.8 kcal/mole REF = 2

```
NITROETHANE       T04/98C  2.H  5.N  1.O  2.G   200.000  6000.000  B  75.06724 1
 9.21849299E+00 1.62001532E-02-5.98159944E-06 9.81277173E-10-5.93455530E-14    2
-1.68676292E+04-2.07232926E+01 3.37137598E+00 1.37914267E-02 3.84687528E-05    3
-6.02380553E-08 2.49654782E-11-1.43330647E+04 1.40009494E+01-1.24822894E+04    4
```

Fig. 2 OLD-NASA polynomials of the thermodynamic data (continued).

C2H5ONO2 Ethyl Nitrate STATWT = 1 IA = 9.9190168 IB = 32.356995 IC = 36.4527
Ir(NO2) = 5.96 ROSYM =2 V(2) = 9.1 kcal/mole Ir(CH3) = 0.5166 ROSYM = 3
V(3) = 3.5 kcal/mole ν= 3003,2959,2946,2933,2877,1703,1481,1468,1455,1427,
1403,1355,1296,1172,1086,1066,968,878,815,790,692,589,396,342,207. REF = 2

ΔH_f (298) = -37.04 kcal/mole REF = 26

```
ETHYL-NITRATE     T05/98C  2.H  5.N  1.O  3.G   200.000   6000.000  B  91.06664 1
 1.21360953E+01 1.70091385E-02-6.43739515E-06 1.07219880E-09-6.54950920E-14    2
-2.41902070E+04-3.71640527E+01 3.75721604E+00 1.93623098E-02 3.87534117E-05    3
-6.64089530E-08 2.82505579E-11-2.08444383E+04 1.11813240E+01-1.86391453E+04    4
```

C3H5NO2 Nitro-Propylene STATWT = 1 IA = 9.5524 IB = 30.9429 IC = 39.9889
Ir(NO$_2$) = 5.96 ROSYM = 2 V(2) = 1.5 kcal/mole Ir(CH$_3$)= 0.5166 ROSYM = 3
V(3) = 8.8 kcal/mole ν = 3091,3001,2954,2954,2888,1696,1629,1477,1457,1448,
1400,1354,1228,1081,1072,971,955,887,831,762.655,575,382,362,223.

ΔH_f (298) = 2.387 kcal/mole REF = 2

```
NITROPROPYLENE C  T11/97C  3.H  5.N  1.O  2.G   200.000   6000.000  B  87.07824 1
 1.16044034E+01 1.73925254E-02-6.55603780E-06 1.08945442E-09-6.64543040E-14    2
-4.17082639E+03-3.40158247E+01 3.65175571E+00 2.01896036E-02 3.27504513E-05    3
-5.72328212E-08 2.41049017E-11-9.72583112E+02 1.18667163E+01 1.20117818E+03    4
```

C3H5NO2 Nitro-Cyclo-Propane STATWT = 1 SYMNO =2 IA = 10.5515 IB = 28.5698
IC = 32.4822 Ir(NO$_2$) = 5.96 ROSYM = 2 V(2) = 4.7 kcal/mole ν = 3103,3095,
3019(2),2934,1571,1443,1407,1373,1325,1202,1118,1110,1075,1042,936,921,880,854,
828,770,645,483,309,289,730. REF = 27,28

ΔH_f(298)= 4.2 kcal/mole REF = 4

```
NITRO-CYCLO-PROP  T05/98C  3.H  5.N  1.O  2.G   200.000   6000.000  B  87.07824 1
 1.28562217E+01 1.60380202E-02-5.91815923E-06 9.70786323E-10-5.87171694E-14    2
-3.71800893E+03-4.27122315E+01 2.06472972E+00 2.06839369E-02 5.54644460E-05    3
-9.75050004E-08 4.31800396E-11 2.60851586E+02 1.85111076E+01 2.11351000E+03    4
```

C3H5N3O9 NG Nitroglycerine STATWT = 1 SYMNO = 2 IA = 113.023087
IB = 216.411718 IC = 260.003555 (Ir(NO2) = 5.96 ROSYM = 2
V(2) = 9.1 kcal/mole) × 3 ν = 3024,3014,2953,2941,2831,2142,3132,1537,1522,
1363,1359,1329,1318,1303,1231,1209,1160,1151,1145,1118,1093,1085,971,928,915,798,
701,676,654,639,627,622,582,478,470,463,409,379,348,317,312,276, 264,232,188,173,
97.7,62,60,54.1,44.4 REF = This Study

ΔH_f(298) =-66.7 kcal/mole REF = 29

```
NITROGLICERINE    T05/98C  3.H  5.N  3.O  9.G   200.000   6000.000  B 227.08752 1
 3.24464077E+01 2.44149769E-02-9.67605267E-06 1.65298018E-09-1.02555476E-13    2
-4.65896112E+04-1.31431034E+02 5.70797625E+00 9.52017978E-02-7.18228583E-05    3
 1.66304815E-08 3.01835927E-12-3.88975467E+04 7.78535957E+00-3.35645516E+04    4
```

C3H6N2O2 n-Nitro-Azetidine SYMNO = 2 STATWT = 1 IA = 17.7086 IB = 36.1404
IC = 47.502 Ir(NO2) = 5.96 ROSYM =2 V(2)=12.5 kcal/mole ν =2982,2973,
2964,2925,2914,2911,1641,1507,1481,1464,1431,1318,1284,1263,1214,1188,1182,1148,
1131,1113,946,902,900,827,822,806,722,593,475,247,241.7,136.7

ΔH_f(298) = 27.28 kcal/mole REF = 2

```
N-NITRO-AZETIDIN  T11/97C  3.H  6.N  2.O  2.G   200.000   6000.000  B 102.09292 1
 1.28386051E+01 2.27540814E-02-8.59766661E-06 1.42856214E-09-8.70663456E-14    2
 7.35548462E+03-4.36199680E+01 4.36363512E+00 7.73075634E-03 9.68585080E-05    3
-1.36307741E-07 5.56913572E-11 1.14684500E+04 9.18578377E+00 1.37257378E+04    4
```

C3H4N4O6 1,3,3-Tri-Nitro-Azetidine SYMNO = 2 STATWT = 1 IA = 60.59091
IB = 147.3316 IC = 169.6545 Ir(NO2) = 5.96 ROSYM =2 V(2)=12.5 kcal/mole
ν = 3036,3021,2973,2900,1589(2),1538,1510,1428,1403,1380,1365,1340,1325,1280,
1216,1200,1183,1172,1113,1085,1057(2),906,865(2),843(2),816,761(2),712,662(2),
626(3),601,564(3),480(2),162. REF = 31

ΔH_f(298)= 30.7 kcal/mole REF = 32

```
1,3,3 TRI-NITRO-  T05/98C  3.H  4.N  4.O  6.G   200.000   6000.000  B 192.08812 1
 2.22004023E+01 2.61448557E-02-1.00734632E-05 1.69575778E-09-1.04302158E-13    2
 4.95227016E+03-9.72924159E+01-3.22895573E+00 6.02068540E-02 4.89990294E-05    3
-1.24714696E-07 5.86010192E-11 1.35213474E+04 4.22296092E+01 1.54487516E+04    4
```

Fig. 2 OLD-NASA polynomials of the thermodynamic data (continued).

C3H6N6O6 RDX 1,3,5-Triazine STATWT = 1 SYMNO = 6 IA = 137.8906
IB = 137.8906 IC = 245.5315 (Ir(NO_2) = 5.97 ROSYM = 2 V(2)= 16.7 kcal/mole) × 3
ν = 2770,2767(2),2688,2684(2),1337,1332(2),1295(2),1280,1218(2),1207,1181,1180,
1104(2),1097,1081,1042,1027,1012(2),907(2),818,807,806,762,702(2),638,590,583,
581,554(2),528,501(2),320,307, 303,302,273,266(2),154,152,91.3,90.2,79.03

REF = 45 ΔH_f(298)= 45.89 kcal/mole REF = 33

```
RDX 135 Triazine  T 6/98C  3.H   6.N   6.O   6.G   200.000  6000.000  B 222.11748 1
 3.27884812E+01 2.84393334E-02-1.11821531E-05 1.88280824E-09-1.15260232E-13    2
 9.54327013E+03-1.42802148E+02 1.46580269E+00 1.05297168E-01-5.23365036E-05    3
-2.70780427E-08 2.44647856E-11 1.84793520E+04 2.07951964E+01 2.30921606E+04    4
```

C3H7NO2 1-Nitro-Propane STATWT = 1 IA = 13.094016 IB = 35.457574
IC = 37.3826884 Ir(NO2) = 5.96 ROSYM = 2 V(2) = 0.08 kcal/mole
Ir(CH3) = 0.51666 ROSYM =3 V(3) = 3.5 kcal/mole Ir(C2H5) = 2.104 ROSYM = 2
V(2)= 9.0 kcal/mole ν = (3187,3088,3080,3031),2981,2905,2280,(1907),1567,1447,
(1415,1403,1392),1377,1232,1225,(1155,1140,1134,1068,1052),885,796,727,619,601,
569,(474,417,268)*. In Parenthesis values added to IR bands. REF = 1

ΔH_f(298)= -29.7 kcal/mole REF = 25

```
NITRO-PROPANE  I  T05/98C  3.H   7.N   1.O   2.G   200.000  6000.000  B  89.09412 1
 1.27038541E+01 2.12000123E-02-7.88951874E-06 1.29872564E-09-7.87331819E-14    2
-2.09708557E+04-3.93362344E+01 2.45041896E+00 2.99807749E-02 2.82471382E-05    3
-6.00704031E-08 2.66264111E-11-1.71521009E+04 1.84229851E+01-1.49455350E+04    4
```

C3H7ONO2 NPN n-Propyl-Nitrate STATWT = 1 IA = 15.235443 IB = 51.655271
IC = 55.1180418 Ir(NO_2) = 5.96 ROSYM = 2 V(2) = 9.1 kcal/mole
Ir(CH_3) = 0.51666 ROSYM = 3 V(3) = 3.5 kcal/mole Ir(C_2H_5) = 3.027 ROSYM = 2
V(2) = 9.0 kcal/mole ν = 3182,3088,3077,3049,3027,2955,2948,2099,1537,1430,
1413,1403,1401,1359,1341,1300,1161,1155,1129,1108,1105,1025,941,917,815,641,609,
541,461,359,301,244,179. REF = This Study

ΔH_f(298) = -41.6 kcal/mole REF = 14

```
C3H7NO3 NPN       T05/98C  3.H   7.N   1.O   3.G   200.000  6000.000  B 105.09352 1
1.52256437E+01 2.22034122E-02-8.38746793E-06 1.39150880E-09-8.47131095E-14     2
-2.78718897E+04-5.27407711E+01 4.46362749E+00 2.95649058E-02 3.53085312E-05    3
-6.91816807E-08 3.01929999E-11-2.37681986E+04 8.34607830E+00-2.09338133E+04    4
```

C4H8N8O8 HMX Octogen SIGMA= 128. STATWT = 1. Ia = 166.71154 Ib = 333.65031
Ic = 355.174455 4 × (Ir(NO_2) = 5.96 V2 = 16.7 kcal/mole) ν=3110,3076,
3034,2992,2979,2977,2914,2912,2076,2062,2051,1968,1892,1747,1726,1706,1464,1412,
1406,1397,1385,1382,1367,1366,1356,1338,1312,1271,1258,1224,1179,1167,1141,1127,
1109,1071,1046,1021,1005,1004,990,963,819,776,758,736,714,696,676,662,638,625,
624,608,544,494,471,434,358,348,338,312,256,218,143,130,122,108,97.1,80.3,74.6,
64.6,55.5,393. This Study

ΔH_f(298)= 44.9 kcal/mole REF = This study

```
C4H8N8O8 HMX      T 6/98C  4.H   8.N   8.O   8.G   200.000  6000.000  F 296.15664 1
 3.44746335E+01 4.64515729E-02-1.79061365E-05 2.98652447E-09-1.81854443E-13    2
 7.27250557E+03-1.48183270E+02 8.14013076E+00 8.33153720E-02 2.72627839E-05    3
-9.98161338E-08 4.69225870E-11 1.63985782E+04-3.22778664E+00 2.25944283E+04    4
```

C4H9NO2 1-Nitro-Butane STATWT = 1 IA = 17.914472 IB = 52.800976
IC = 57.4685911 Ir (NO2) = 5.96 ROSYM =2 V(2) = 0.08 kcal/mole
Ir(CH3)= 0.51666 ROSYM =3 V(3) = 3.5 kcal/mole Ir(C2H5) = 2.104 ROSYM =2
V(2) = 9.0 kcal/mole Ir(C3H7) = 2.22 ROSYM = 3 V(3) =13.64 kcal/mole
ν = (3157,3092,3083,3062,3060,3056),2970,2889,2760,2276,1568,1440,(1425,1408,
1405,1400,1394),1379,(1374,1346,1278,1241),1211,(1191,1160),1123,(1088,1054,
1033),900,860,752,712,611,(535,446,368,243). REF = 4 ΔH_f(298) = -34.4 kcal/
mole REF=4

```
NITRO-BUTANE      T05/98C  4.H   9.N   1.O   2.G   200.000  6000.000  B 103.12100 1
 1.27918861E+01 2.96302599E-02-1.10618131E-05 1.81914243E-09-1.10094356E-13    2
-2.40186756E+04-4.05022397E+01 4.50296897E+00 1.41859282E-02 9.14552906E-05    3
-1.29431188E-07 5.23563809E-11-1.98606730E+04 1.15748426E+01-1.73106533E+04    4
```

Fig. 2 OLD-NASA polynomials of the thermodynamic data (continued).

C5H8N4O12 PETN Tenta-Erytritol-Tetra-Nitrate STATWT =1 SYMNO = 4 IA = 172.42
IB = 461.12 IC = 462.62 (Ir(NO_2)= 5.96 ROSYM = 2 V(2) = 9.1 kcal/mole) X 4

ν = 3029,3028,3006,2999,2972,2971,2936,2929,1735,1730,1711,1710,1494,1485,1473,
1469,1445,1435,1424,1417,1390,1380,1363,1362,1334,1325,1288,1256,1199,1198,1128,
1098,1079,1072,1055,1022,988,974,969,962,923,918,865,810.3(2),807(2),773,764,
724,696,694,667,663,645,590,541,462,409,408,372,284,274,249,222,218,199,184,166,
139,114,112.5,75.4,67.8,65.1,60,57. REF = 2

ΔH_f (298) =-92.5 kcal/mole REF = 35

```
C5H8N4O12 Penta   T11/97C  5.H  8.N  4.O 12.G   200.000  6000.000    316.13828 1
 4.25040700E+01 4.10042694E-02-1.61689012E-05 2.75711794E-09-1.70941686E-13    2
-6.50322400E+04-1.89116403E+02 1.01352700E+01 7.43509172E-02 7.88937283E-05    3
-1.68084561E-07 7.46302599E-11-5.32741276E+04-8.15169085E+00-4.65475416E+04    4
```

C5H11NO2 1-Nitro-Pentane STATWT=1 SYMNO=2 IA=21.264770 IB = 85.889716
IC = 100.4047696 Ir (NO2) = 5.96 ROSYM =2 V(2) = 0.08 kcal/mole
Ir(CH3)= 0.51666 ROSYM =3 V(3) = 3.5 kcal/mole Ir(C2H5) = 2.104 ROSYM =2
V(2) = 9.0 kcal/mole Ir(C3H7) = 2.22 ROSYM = 2 V(2) =13.64 kcal/mole

ν = 3183,3088,3069,3034,3027,3024,2992,2955,2949,2947,2893,1901,1611,1474,1421,
1410,1403,1402,1398,1386,1367,1341,1300,1253,1173,1167,1153,1146,1129,1121,1081,
1039,1020,990,965,926,866,830,805,691,615, 480,470,394,315,295,214 REF = 1

ΔH_f(298) =-39.3 kcal/mole REF = This Study

```
NITRO-PENTANE      T06/98C  5.H 11.N  1.O  2.G   200.000  6000.000  B 117.14788 1
 1.59382106E+01 3.48884183E-02-1.29633850E-05 2.12755256E-09-1.28618354E-13    2
-2.80406921E+04-5.83080492E+01 4.00703926E+00 2.29727394E-02 1.04023119E-04    3
-1.55573589E-07 6.44328697E-11-2.26341947E+04 1.39586649E+01-1.97764150E+04    4
```

C6H5NO2 Nitro-Benzene SYMNO = 2 STATWT = 1 IA = 20.6002 IB = 63.9627
IC = 84.5628 Ir(NO_2)= 5.96 ROSYM = 2 V(2) = 2.8 kcal/mole ν = 3084,2935,
2888,2700,1966,1912,1797,1609,1541,1481,1353,1312,1245,1171,1103,1070,1020,
(1019,1004,999,977),928,(860),854,787,692,(674,665,599,510,436,409,388,254.49,
171.09) REF = 1 and 2 ΔH_f (298)=16.38 kcal/mole REF = 15

```
NITRO-BENZENE      T11/97C  6.H  5.N  1.O  2.G   200.000  6000.000  B 123.11124 1
 1.71572651E+01 2.10600071E-02-7.92285643E-06 1.31641516E-09-8.03337816E-14    2
 4.22627769E+02-6.59268666E+01 3.22564706E-01 4.78049433E-02 1.44052454E-05    3
-6.09010999E-08 2.98988437E-11 6.00070276E+03 2.56985144E+01 8.24268899E+03    4
```

C6H3(NO2)3 1,3,5-Tri-Nitro-Benzene SYMNO = 6 STATWT = 1 IA = 111.42859
IB = 172.18627 IC = 252.862147 Ir(NO2)=5.96 ROSYM = 2 V(2) = 3.11 kcal/mole

ν = 3071,3038,2993,1923,1913,1742,1720,1671,1594,1580,1431,1368,1321,1209,1183,
1121,1113,1018,1000,970,952,939,843,778,751,748,688,680,644,591,568,522,504,448,
393,350,335,323,294,256,251,147,129,87.5,66. REF = This Study

ΔH_f(298)=14.9 kcal/mole REF = 15

```
TRI-NITRO BENZEN  T 5/98C  6.H  3.N  3.O  6.G   200.000  6000.000  C 213.10644 1
2.87195273E+01 2.08056280E-02-8.03680268E-06 1.35348056E-09-8.32405765E-14    2
-3.92148064E+03-1.15710853E+02 2.18818193E+00 1.02515207E-01-1.05642628E-04    3
 5.50716150E-08-1.13737832E-11 3.11892525E+03 1.95711122E+01 7.49792832E+03    4
```

C7H2(NO2)3 TNT Tri-Nitro-Toluene SYMNO = 2 STATWT = 1 IA = 158.50629
IB = 171.65362 IC = 314.929913 Ir(NO_2)para = 5.96 ROSYM = 2
V(2) = 3.11 kcal/mole (Ir(NO_2)meta = 5.96 ROSYM = 2 V(2) = 7 kcal/mole) X 2
Ir(CH_3) = 0.51666 ROSYM = 3 V(3) = 3.5 kcal/mole

ν =3080,3050,2989,2942,2875,2828,2747,2700,2450,1945,1915,1858,1817,1790,1716,
1656,1609,1554,1490,1430,1393,1345,1265,1204,1151,1103,1063,1023,942,908,854,
827,780,733,666,(651),600,(543),524,(497),457,(371,360,346,320,301,274,264,159,
150,144,106,70.) REF = This Study

ΔH_f (298)= 5.76 kcal/mole REF = 38

```
TRI-NITRO TOLUEN  T 5/98C  7.H  5.N  3.O  6.G   200.000  6000.000  D 227.13332 1
 2.62323485E+01 3.08249282E-02-1.16857989E-05 1.94730669E-09-1.18966543E-13    2
-8.21343086E+03-1.01706192E+02 4.99444797E+00 8.99017655E-02-7.93846083E-05    3
 4.28434430E-08-1.11552302E-11-1.96446053E+03 8.89961538E+00 2.89852800E+03    4
```

Fig. 2 OLD-NASA polynomials of the thermodynamic data (continued).

Table 4 Comparison of the thermodynamic data with the literature cal/mole K

Compound	T, K	Stull et al.[14]		Melius†		This study	
		C_p	S	C_p	S	C_p	S
CH_3NO_2	300	13.76	65.82	——	——	13.329	67.688
	1000	28.17	90.87	——	——	28.316	92.531
CH_3ONO_2	300	18.34	72.27	——	——	18.374	73.200
	1000	34.19	103.87	——	——	34.160	104.809
$CH_2=CHNO_2$	300	——	70.6[a]	17.648	70.581	17.688	71.931
	1000	——	——	34.272	102.179	34.236	103.537
$C_2H_5NO_2$	300	18.78	75.51	18.948	77.742	18.973	76.721
	1000	40.67	111.24	40.407	114.425	40.422	112.251
$C_2H_5ONO_2$	300	23.36	83.40	——	——	22.834	78.741
	1000	46.69	125.68	——	——	47.082	120.847
$CH_3CH=CHNO_2$	300	——	79.3[a]	22.868	80.373	22.469	79.012
	1000	——	——	46.688	122.310	46.594	120.453
$C_3H_6N{-}NO_2$	300	——	——	23.890	79.392	24.190	78.771
	1000	——	——	55.042	127.357	56.227	127.177
$C_3H_4N{-}(NO_3)_3$	300	——	——	32.498[b]	85.787[b]	32.498	85.601
	1000	——	——	78.835[b]	154.299[b]	79.106	154.487
$C_3H_7NO_2$	300	24.52	85.16	——	——	25.002	83.817
	1000	53.06	131.64	——	——	54.076	131.353
$C_3H_7ONO_2$	300	29.10	92.28	——	——	29.586	86.746
	1000	59.08	145.32	——	——	60.260	140.892
$C_4H_8N_8O_8$	300	69.57[c]	——	——	——	66.124	——
$C_4H_9NO_2$	300	29.99	94.47	——	——	27.663	88.573
	1000	65.39	151.57	——	——	65.642	144.188
$C_5H_{11}NO_2$	300	——	103.5[a]	——	——	——	93.632
$C_6H_5NO_2$	300	——	——	28.771	82.940	28.935	83.544
	1000	——	——	62.110	138.514	62.598	139.355
$C_7H_5(NO_2)_3$	300	58.90[c]	——	——	——	51.442	——

[a] Estimate from NIST 94 (Ref. 4). [b] Results from Yu et al.[31] [c] Experimental measurements averaged by Yin et al.[46]

1000 and 1500 cm^{-1}, and 1% too low around 3000 cm^{-1}, whereas the average difference is less than 1%. Judging from our compound vibrations, we can agree with this statement as our Gaussian 94 calculations show an error of being approximately 10% too high. The MOPAC calculations, and specifically, the PM3, show very good correlation with the IR spectrum[1] as well as with the Melius Gaussian BAC/MP4 data.[2] Because the thermodynamic data are not very sensitive to the exact value of the vibrations, the MOPAC and BAC/MP4 values of the vibrations were used as is, and only the Gaussian 94 data of RDX were scaled by 10%.

IR Spectrum

It is known that the IR spectra is a good indicator of the fundamental vibrations, but not necessarily a correct one. Looking at the assignment of vibrations in the literature, it is possible to see that some of the bands are not pure, but are the sum of two or more vibrations. Therefore, the use of the IR spectrum as is, can only approximate the real vibrational spectrum of the molecule. On the other hand, making a detailed assignment of the IR spectrum is beyond the scope of this research. Nevertheless, it can be shown that the IR spectra is very similar to the assigned spectrum and to the MOPAC or BAC/MP4 calculated vibrations.[11] Therefore, wherever available, the IR spectra [from NIST 97 (Ref. 1)] was used and supplemented with the missing vibrations from the calculations.

Enthalpies of Formation

It has been found in practice that while MOPAC and other ab initio programs give results regarding the fundamental vibrations of the molecules in close relation to each other, the predictions of the enthalpy of formation can differ up to a factor of 2. The mean absolute error of the AM1 method was reported to be 12 kcal/mole.[39,43] For 26 nitro-organic compounds and three organic nitrates, the optimized error was found to be 5.2 kcal/mole for the PM3 and 15.7 kcal/mole for the AM1 method.[18,39] Some authors[44] have tried methods to improve these results.

Melius[41] explains the way the BAC/MP4 method calculates and corrects the enthalpies of formation, but from Table 1 it can be seen that his results are on the average of 3 kcal/mole lower than the experimental values, although mostly within the assigned error value. It is found that Benson's group additivity method[17] is far more reliable than any other estimate. But even this method does not give a uniform answer because there are disputes among different groups of researchers regarding specific values of some of these groups. In this research, the NIST 94 (Ref. 4) program was used to evaluate all species possible, because none of them were incorporated into the program's database.

The enthalpy of formation of the first four homologous mononitro carbons and the first three nitrate compounds, were plotted in Fig. 3 as a function of the number of carbon atoms in the molecule. In both cases, a straight line is obtained that raises the question that these values are experimental or evaluated as a straight line by Stull.[14] In any case, if these values are correct, then the value of the gaseous enthalpy of formation of 1-nitro-pentane and 1-nitro hexane can be estimated. The value found for nitro-pentane is −39.3 ± 0.5 kcal/mole as compared to the value of the liquid enthalpy of formation of −51.5 ± 0.4 kcal/mole.[15] Continuing on the same slope, it is possible to estimate the gaseous enthalpy of formation of 1-nitro hexane as −44.3 ± 0.7 kcal/mole and the liquid enthalpy of formation as −57.8 ± 0.7 kcal/mole. The error levels are based on the percent confidence of the straight line which is better than 95%. Butyl nitrate cannot be estimated the same way, because the three points scatter from the straight line, causing the error of the estimate to be larger than ~5 kcal/mole.

Accuracy of Calculations

For most of the nitro compounds, the thermodynamic properties have not been measured experimentally, except for the very simple nitromethane and methyl-nitrate. In Table 4,[46] the present results are compared with other calculations of simple nitro and nitrate compounds previously made by Stull et al.,[14] by Melius,† and others. These prove that although the IR spectra were not fully assigned and analyzed spectroscopically, the results are very close to previous calculations. The main differences in the entropy, of the size up to 2 cal/mole K, is caused mainly by taking into account different internal rotations with different rotation barrier values,

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† Melius, C., private communication.

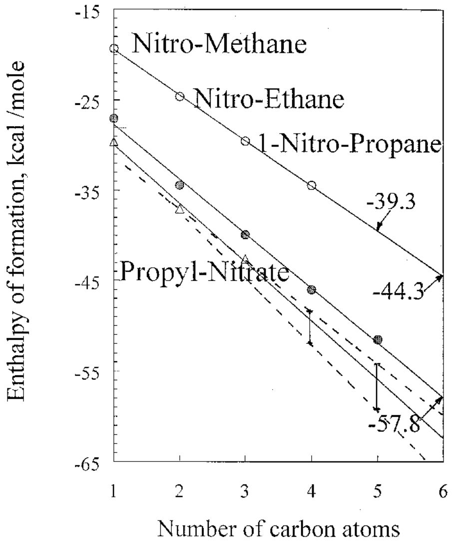

Fig. 3 Enthalpy of formation of the first four *n*-nitro carbons and the first three *n*-nitrate homologues as a function of the number of carbon atoms in the molecule: ○, gaseous enthalpies of formation; and ●, liquid enthalpies of formation. The 1-nitro-pentane and 1-nitro hexane values are estimated on this graph and their values are shown: - - -, error limits for the nitrate extrapolation.

rather than differences in the vibration values caused by improper assignment.

The method used by Burcat and McBride,[40] to classify the reliability of the polynomials of Fig. 2, was introduced. The category assigned to each species is shown by a letter appearing in column 68 of its first data record:

A denotes the most accurate calculations, and is reserved for results obtained with the direct summation method, for atoms and diatomic molecules, and for species for which anharmonicity corrections were included.

B denotes calculations done using the rigid rotor-harmonic oscillator (RRHO) approximation, including internal rotations, where present, and taking low-lying electronic excitations into account.

C includes species whose properties were calculated by the RRHO method using shortcuts, estimated vibrational frequencies, or cases where internal rotor contributions were estimated as a free rotor.

D and E categories include data estimated from group additivity methods. Such species were normally assigned to the E category, but if reliable supplementary information could be used, the D category was assigned.

The F category was reserved for rough approximations, with very large error limits.

As seen in Fig. 2, most of our species belong to class B, with the exception of tri-nitro-benzene, which is class C because the MOPAC calculations differ so much between themselves; TNT is class D because it is a combination of vibrations from other Toluene nitro compounds; and HMX is class F because the molecular data were obtained for distorted molecules, and there is also a great uncertainty regarding its gaseous heat of formation.

Conclusions

It has been shown that by using semiempirical calculations and IR experimental results it was possible to provide, with relative reliability, all of the molecular fundamental data needed to calculate the thermodynamic properties of the given group of propellants and explosives. It is believed that the data provided are presently the most accurate available.

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