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Estimation of the thermodynamic properties of nitroguanidine, hexahydro-1,3,5-trinitro-1,3,5-triazine and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine in the gas phase

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Abstract

Thermodynamic properties of nitroguanidine, hexahydro-1,3,5-trinitro-1,3,5-triazine and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine in the gas phase have been estimated using additivity techniques and statistical calculations. Ideal gas thermodynamic properties of urea, guanidine, methanimine, 2-propanimine, nitramide, *N*-methyl-*N*-nitromethanamine and 1,3,5-triazine required for these estimations were calculated by rigid-rotor harmonic-oscillator approximation using the molecular constants available from the literature. Estimations obtained by the difference method in addition to statistical calculations give satisfactory values of thermodynamic properties.

INTRODUCTION

Nitroguanidine (NG) and hexahydro-1,3,5-trinitro-1,3,5-triazine (commonly referred to as RDX) are important explosives and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) is a monopropellant material. There is some information about the structure [1–14] and vibrational spectra [9, 10, 15, 16] of these molecules but these data are insufficient for reliable statistical calculations of thermodynamic properties. The data on the enthalpy of formation are known for RDX and HMX [17, 18]. To estimate the thermodynamic properties of the title compounds the simple difference method [19] combined with statistical thermodynamic calculations has been used in this work.

NITROGUANIDINE

The nitrimine structure has been established for NG ($(NH_2)_2C{=}N{-}NO_2$) by X-ray [1], neutron diffraction [3], spectroscopic [15] and theoretical

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investigations [2, 4–6]. No complete vibrational assignment for NG is available and therefore its thermodynamic functions cannot be calculated by the statistical thermodynamic method.

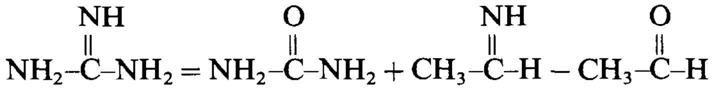
There are no experimental or theoretical data on the enthalpy of formation of gaseous NG.

In this work thermodynamic properties of NG were estimated based upon the thermodynamic properties of guanidine and using a difference method which was very helpful for estimation of gas phase thermodynamic properties of organic compounds [19].

Guanidine

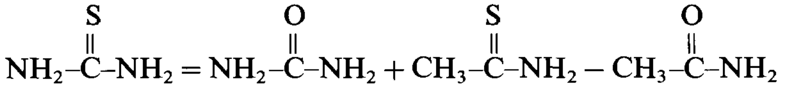
There are no experimental data on the enthalpy of formation of guanidine but this value was estimated by a bond energy scheme [20]: $\Delta_f H^\ominus$ (guanidine (g) 298.15 K) = 31.8 kJ mol^{-1}.

To estimate the enthalpy of formation of guanidine we considered the following equation including molecules with known values of $\Delta_f H^\ominus$



$$\begin{array}{lllll} & NH_2{-}\overset{\overset{NH}{\|}}{C}{-}NH_2 = & NH_2{-}\overset{\overset{O}{\|}}{C}{-}NH_2 & + CH_3{-}\overset{\overset{NH}{\|}}{C}{-}H & - CH_3{-}\overset{\overset{O}{\|}}{C}{-}H \\ \Delta_f H^\ominus & -14.9 & \leftarrow -235.5 & +54.5 & -(-166.1) \\ & & [21] & [22] & [23] \end{array} \qquad (1)$$

The bond energy scheme [20] predicts the value of $\Delta_f H^\ominus$ (298.15) for the $(NH_2)_2C{=}S$ molecule to be −15.1 kJ mol^{-1}, while the experimental value is 22.9 ± 1.6 kJ mol^{-1} [24]. The value estimated for this molecule using eqn. (2)



$$\begin{array}{lllll} & NH_2{-}\overset{\overset{S}{\|}}{C}{-}NH_2 = & NH_2{-}\overset{\overset{O}{\|}}{C}{-}NH_2 & + CH_3{-}\overset{\overset{S}{\|}}{C}{-}NH_2 & - CH_3{-}\overset{\overset{O}{\|}}{C}{-}NH_2 \\ \Delta_f H^\ominus & 15.5 & \leftarrow -235.5 & +12.7 & -(-238.3) \\ & & [21] & [23] & [23] \end{array} \qquad (2)$$

(15.5 kJ mol^{-1}) is in better agreement with experiment than the value estimated by the bond energy scheme.

Based upon these results we prefer the difference method estimation (eqn. (1)) to the bond energy scheme and our recommended value is $\Delta_f H^\ominus$(guanidine (g) 298.15 K) = −15 ± 10 kJ mol^{-1}.

To estimate the entropy and heat capacity values for guanidine we considered two difference equations and carried out the statistical calculation using estimated molecular constants of guanidine (Table 1).

No thermodynamic properties are available from the literature for $(NH_2)_2C{=}O$ (The thermodynamic properties of $(NH_2)_2C{=}O$ were calculated using an incorrect vibrational assignment [25] (see also ref. 26).),

TABLE 1

Estimations of the enthalpy of formation (kJ mol^{-1}), entropy and heat capacity (J K^{-1} mol^{-1}) for guanidine in the ideal gas state

		$NH_2\text{-}\overset{\overset{\Large NH}{\|}}{C}\text{-}NH_2 = NH_2\text{-}\overset{\overset{\Large O}{\|}}{C}\text{-}NH_2 + H_2C{=}NH - H_2C{=}O$	$NH_2\text{-}\overset{\overset{\Large NH}{\|}}{C}\text{-}NH_2 = NH_2\text{-}\overset{\overset{\Large O}{\|}}{C}\text{-}NH_2 + CH_3\text{-}\overset{\overset{\Large NH}{\|}}{C}\text{-}CH_3 - CH_3\text{-}\overset{\overset{\Large O}{\|}}{C}\text{-}CH_3$	$NH_2\text{-}\overset{\overset{\Large NH}{\|}}{C}\text{-}NH_2$ Statistical calculation, this work	$NH_2\text{-}\overset{\overset{\Large NH}{\|}}{C}\text{-}NH_2$ Recommended values
$\Delta_f H^\circ$(298.15 K)		−21.8	–		−15 ± 10[a]
S°(298.15 K)		291.40	292.65	290.12	291.4 ± 2.5
$C_p^\circ(T)$	298.15	81.78	79.58	80.49	80.62 ± 2.0
	300	82.13	79.95	80.81	80.96
	400	99.36	97.95	96.90	98.07
	500	113.25	112.15	110.54	111.98
	600	124.36	123.52	121.87	123.25
	800	141.07	140.70	139.47	140.41
	1000	153.53	153.50	152.70	153.24
	1200	163.31	163.47	162.96	163.25
	1400	171.05	171.28	170.98	171.10
	1500	174.29	174.55	174.31	174.38

[a] See text.

$H_2C{=}NH$ and $(CH_3)_2C{=}NH$ molecules which appear in the equations in Table 1, and their values were calculated in this work using known molecular constants (see Appendix). The thermodynamic properties for $H_2C{=}O$ and $(CH_3)_2C{=}O$ were taken from the literature [27, 28].

In order to carry out a statistical calculation of thermodynamic properties for guanidine, the structural parameters and vibrational frequencies of this molecule were estimated by comparison with parent compounds ($(NH_2)_2C{=}O$, $(CH_3)_2C{=}NH$) and using the results of an ab initio calculation of the geometry of guanidine [4] and spectroscopic data for NG [15, 29] (C_s symmetry, $\sigma = 1$; product of three principal moments of inertia $I_A I_B I_C = 1010 \times 10^{-117}\ g^3\,cm^6$; vibrational frequencies ν_i: 3450, 3400(3), 3260, 1670, 1640, 1611, 1450, 1300, 1284, 1000(2), 800(2), 600, 550, 400(2), 230(2)).

As can be seen from Table 1, $S^{\circ}(298.15\ K)$ and $C_p^{\circ}(T)$ values estimated by different methods are in good agreement and the recommended values of the thermodynamic properties for guanidine (which are the mean of these estimations) may be considered as reliable enough.

Nitroguanidine

Thermodynamic properties for two isomers of NG were calculated by the difference method using two equations (Table 2) inserting values for guanidine from Table 1 and values for $CH_3{-}NH{-}CH_3$, $H_2N{-}NH_2$, $CH_3{-}NH{-}NH_2$ and $CH_3{-}NH_2$ from the literature [23, 30-33]. Thermodynamic properties for $(CH_3)_2N{-}NO_2$ and $H_2N{-}NO_2$ molecules are calculated in this work (see Appendix).

It follows from Table 2 that the thermodynamic properties for the two isomers of NG are almost the same. As the recommended values we consider the thermodynamic properties for nitrimine isomer.

HEXAHYDRO-1,3,5-TRINITRO-1,3,5-TRIAZINE

The infrared and Raman spectra of RDX have been investigated in the vapor phase, in solutions and in the solid phases [9, 10, 16] and the vibrational assignments have been made on the basis of a normal coordinate analysis [9]. The complete vibrational assignment for RDX [9] is based upon the vibrational spectra of RDX in solutions and in the solid phase. We could calculate thermodynamic functions of gaseous RDX by a statistical mechanical method using vibrational assignment [9] and assuming that the vibrational frequencies in the different phases are similar. However, this assumption is often inaccurate in the low-frequency region. Owing to this, as well as to the lack of information about barrier to internal rotation for NO_2 groups, it is impossible to carry out a reliable statistical calculation. For that reason estimations by the difference method were made for RDX

TABLE 2

Estimations of the enthalpy of formation (kJ mol^{-1}), entropy and heat capacity (J K^{-1} mol^{-1}) for nitroguanidine in the ideal gas state

		$NH_2-\overset{\overset{N-NO_2}{\|}}{C}-NH_2 = NH_2-\overset{\overset{NH}{\|}}{C}-NH_2$ $+ CH_3-\overset{\overset{NO_2}{\|}}{N}-CH_3 - CH_3-NH-CH_3$	$NH_2-\overset{\overset{NH}{\|}}{C}-NH-NO_2 = NH_2-\overset{\overset{NH}{\|}}{C}-NH-NH_2 + H_2N-NO_2 - H_2N-NH_2$ $\uparrow$ $NH_2-\overset{\overset{NH}{\|}}{C}-NH_2 + CH_3-NH-NH_2 - CH_3-NH_2$	$NH_2-\overset{\overset{N-NO_2}{\|}}{C}-NH_2$ Recommended values
$\Delta_f H^\circ$(298.15 K)		−1.2	4.4	−1 ± 20
S°(298.15 K)		352.1	352.5	352 ± 5
$C_p^\circ(T)$	298.15	114.92	111.95	114.92 ± 4
	300	115.37	112.19	115.37
	400	137.68	138.43	137.68
	500	155.19	157.33	155.19
	600	169.13	171.93	169.13
	800	189.53	192.04	189.53
	1000	203.21	206.54	203.21
	1200	214.57	217.09	214.57
	1400	222.75	225.55	222.75
	1500	226.18	228.21	226.18

together with statistical calculations. To estimate the thermodynamic properties of RDX by the difference method it is necessary to know the thermodynamic properties of hexahydro-1,3,5-triazine and these values are estimated in this work.

Hexahydro-1,3,5-triazine

There are no spectroscopic data required for statistical calculation and thermodynamic properties for hexahydro-1,3,5-triazine were estimated using five approaches based on the difference method and Benson group additivity scheme (Table 3).

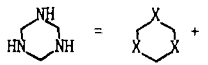
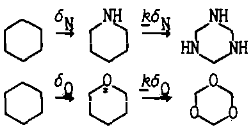
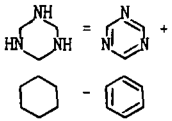
Hexahydro-1,3,5-trinitro-1,3,5-triazine

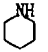
Thermodynamic properties for the RDX molecule were estimated by the difference method using five sets of values of thermodynamic properties for hexahydro-1,3,5-triazine (Table 4, columns A–E) and by comparison of the thermodynamic properties of RDX and cyclohexane with those of suitable aliphatic analogs (Table 4, column F). Values of $S^{\ominus}(298.15\ \mathrm{K})$ and $C_p^{\ominus}(T)$ were also calculated by a statistical mechanical method (Table 4, columns G–I). The chair conformation of C_{3v} symmetry with the NO_2 groups in the axial positions was accepted for RDX [7, 8, 10]. Structural parameters were estimated by comparison with parameters of $(CH_3)_2N{-}NO_2$ [43] and hexahydro-1,3,5-triazine [44, 45] molecules. The vibrational assignment obtained from infrared and Raman spectra of RDX in solutions and solid phase [9] was used in this work. Internal rotation in the molecule was taken into account with torsional frequencies (Table 4, column G) or with a potential barrier of 2800 cm^{-1} (Table 4, column H). The barrier height was considered to be similar in value to that of the $(CH_3)_2N{-}NO_2$ molecule [46]. This value is close to the barrier height for RDX obtained by theoretical calculation (3500 cm^{-1}) [7]. Free rotation of NO_2 groups was also considered in this work (Table 4, column I). The following molecular constants of RDX were accepted in the calculations: $\sigma = 3$; $I_A I_B I_C = 5070780 \times 10^{-117}\ \mathrm{g}^3\ \mathrm{cm}^6$; ν_i, 3070(3), 2970(3), 1591, 1573, 1532, 1459, 1434, 1423, 1389, 1377, 1373, 1352, 1320, 1310, 1275, 1271, 1232(2), 1219, 1190, 1040, 1026, 1019, 996, 991, 947, 926, 915, 883, 853, 844, 783, 755, 738(2), 670, 602, 588, 486, 461, 410(2), 369, 345, 300, 223, 208, 145(3) (torsion), 110, 90, 70.

The value of $\Delta_f H^{\ominus}(\mathrm{RDX\ (g)}\ 298.15\ \mathrm{K}) = 191.6\ \mathrm{kJ\ mol^{-1}}$ recommended in Table 4 was calculated from experimental values of $\Delta_f H^{\ominus}(\mathrm{RDX\ (c)})$ and $\Delta_s H^{\ominus}$ and it is in good agreement with experimental data for other *N*-nitro- and *N*-nitrosamines [17]. This value coincides with value of 205.3 $\mathrm{kJ\ mol^{-1}}$ obtained from other experimental data [18] within the uncertainty of the recommended value.

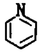
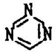
TABLE 3

Estimations of the enthalpy of formation (kJ mol^{-1}), entropy and heat capacity (J K^{-1} mol^{-1}) for hexahydro-1,3,5-triazine in the ideal gas state

		 3 [CH_3-NH-CH_3 − CH_3-X-CH_3] + 3δ [a] A	B		 + 3 δ	Benson group additivity method: 3 [N-(H)(C)$_2$] + 3 [C-(H)$_2$(N)$_2$] + 0.5 Ring corr [] [d]
		X = O	X = CH_2	C	D	E
$\Delta_f H^\circ$(298.15 K)		62.7	105.2	138.0	74.8	118.5
S°(298.15 K)		309.42	312.80	315.75	313.45	304.87
$C_p^\circ(T)$	298.15	100.39	105.25	105.23	104.05	–
	300	100.98	105.84	105.77	104.52	86.43
	400	140.44	144.68	144.19	141.19	126.52
	500	181.30	182.20	182.09	176.91	163.95
	600	218.93	215.37	215.77	208.84	195.28
	800	278.43	267.93	268.90	259.75	242.88
	1000	319.25	306.41	307.29	296.81	275.65

[a] δ was obtained from the equation  =  + CH_3-NH-CH_3 − CH_3-X-CH_3 + δ. Thermodynamic properties for these compounds, as well as for the  molecule are known from the literature [23, 28, 30, 34–37].

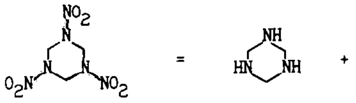
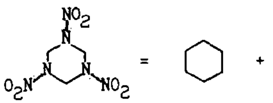
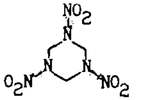
[b] The value of k in the first line was accepted the same as in the second line. Thermodynamic properties for all compounds were taken from the literature [23, 34–36].

[c] δ was obtained from the equation  =  +  −  + δ. Thermodynamic properties for these compounds are known from the literature [23, 34, 36, 38–40]; thermodynamic properties for the  molecule are calculated in this work (see Appendix).

[d] [C-(H)$_2$(N)$_2$] ≈ [C-(H)$_2$(C)(N)], see refs. 41 and 42.

TABLE 4

Estimations of the enthalpy of formation (kJ mol^{-1}), entropy and heat capacity (J K^{-1} mol^{-1}) for hexahydro-1,3,5-trinitro-1,3,5-triazine in the ideal gas state

		Difference method									
											
		$3\,[\mathrm{CH_3{-}\overset{NO_2}{\overset{\vert}{N}}{-}CH_3 - CH_3{-}NH{-}CH_3}]$ [a]				$3\,[\mathrm{CH_3{-}\overset{NO_2}{\overset{\vert}{N}}{-}CH_3 - CH_3{-}CH_2{-}CH_3}]$ [b]		Statistical calculations			Recommended values [e]
								ν_{tors} [c]	V_0 [d]	Free rotation	
		A	B	C	D	E	F	G	H	I	
$\Delta_f H^\circ$(298.15 K)		104.1	146.6	179.4	116.2	159.9	176.3				191.6 ± 15
S°(298.15 K)		491.5	494.9	497.8	495.5	486.9	476.7	445.5	464.0	497.1	484.5 ± 15
$C_p^\circ(T)$	298.15	203.29	208.15	208.13	206.95	188.70	196.45	194.76	196.78	183.27	194.67 ± 10
	300	204.21	209.07	209.00	207.75	189.66	197.28	195.78	197.80	184.28	195.60
	400	259.27	263.51	263.02	260.02	245.35	247.76	248.23	250.70	236.31	248.63
	500	310.93	311.83	311.72	306.54	293.58	291.58	292.39	295.61	280.26	294.55
	600	356.57	353.01	353.41	346.48	332.92	326.01	327.60	331.60	315.37	331.86
	800	425.79	415.29	416.26	407.11	390.24	373.44	377.61	382.32	365.27	385.51
	1000	469.16	456.32	457.20	446.72	425.56	398.93	410.21	414.33	397.82	418.77
	1200						412.41	432.48	435.18	420.06	442.3 [f]
	1400						417.79	448.23	449.24	435.80	458.1 [f]
	1500						424.15	454.40	454.55	441.96	463.9 [f]

[a] Thermodynamic properties given in columns A–E were calculated using different values of thermodynamic properties for hexahydro-1,3,5-triazine from Table 3. Thermodynamic properties for the $(\mathrm{CH_3})_2\mathrm{N{-}NO_2}$ molecule were taken from the Appendix and for $\mathrm{CH_3{-}NH{-}CH_3}$ from refs. 23, 30. [b] Thermodynamic properties for $\mathrm{CH_3{-}CH_2{-}CH_3}$ were taken from refs. 23, 37. [c] Torsion about the N–N bond was taken into account with three torsional frequencies $\nu_{\mathrm{tors}} = 145\ \mathrm{cm}^{-1}$ [9]. [d] The barrier height for N–N torsion ($V_0 = 2800\ \mathrm{cm}^{-1}$) was accepted to be the same as in the $(\mathrm{CH_3})_2\mathrm{N{-}NO_2}$ molecule. [e] See text. [f] Values interpolated on the basis of statistical calculations.

The values of $S^\ominus(298.15\,\mathrm{K})$ and $C_p^\ominus(T)$ recommended for RDX in Table 4 are the average of values given in columns C, E, F, H and I. The estimations by the difference method (C, E, F) were selected as giving the best agreement with recommended value of $\Delta_f H^\ominus$. Statistical calculations given in columns H and I (Table 4) are considered as more reliable.

While our calculations were being done, the papers on structure and vibrational frequencies of RDX obtained from electron diffraction [47] and ab initio [48] studies were published. Although the experimental and calculated structural parameters [47, 48] are somewhat different from those estimated by us, they should not substantially change the thermodynamic properties calculated by the statistical method. Most importantly, the calculated six lowest vibrational frequencies ($N-N$ torsions and out-of-plane bends at N atoms) [48] are considerably lower than these frequencies observed in the solid phase and solutions [9]. Therefore we carried out the statistical calculation (the same as in Table 4, column G) using the six lowest fundamentals from the ab initio study [48]. The calculated values of $S^\ominus(298.15\,\mathrm{K})$ and $C_p^\ominus(298.15\,\mathrm{K})$ coincide with those recommended in Table 4 for RDX within 1.5 and $1\,\mathrm{J\,K^{-1}\,mol^{-1}}$, respectively. This discrepancy in the $C_p^\ominus(1500\,\mathrm{K})$ value amounts to $10\,\mathrm{J\,K^{-1}\,mol^{-1}}$.

We believe that in the case of the RDX molecule estimations obtained by the statistical thermodynamic technique in addition to estimations by the difference method give satisfactory values of the thermodynamic properties.

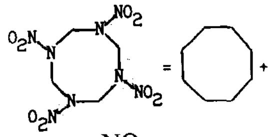
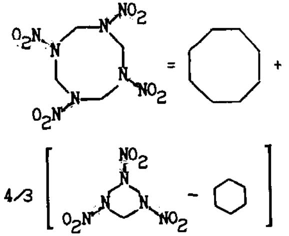
OCTAHYDRO-1,3,5,7-TETRANITRO-1,3,5,7-TETRAZOCINE

Domalski and Hearing [18] recommended the value of enthalpy of formation of gaseous HMX (Table 5) obtained from experimental sublimation data. No expeirmental or theoretical data on the entropy and heat capacity of HMX are available. Information known from structural and spectroscopic investigations [11-13, 49, 50] is insufficient for statistical calculation of thermodynamic functions.

The Benson group additivity approximation and difference method were used to estimate thermodynamic properties of HMX (Table 5). The recommended value of $\Delta_f H^\ominus$ is the mean of three estimations presented in Table 5. As well as for RDX, our value chosen for HMX is somewhat different from one cited by Domalski and Hearing [18], while these values coincide with one another within the uncertainty of the recommended value. We believe that, in terms of additivity rules, the values recommended in this work correlate well. The recommended values of entropy and heat capacities are based on the equation including the RMX molecule.

TABLE 5

Estimations of the enthalpy of formation (kJ mol^{-1}), entropy and heat capacity (J K^{-1} mol^{-1}) for octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine in the ideal gas state

		Experiment [18]	Estimations, this work			Recommended values
			Benson group additivity method	Difference method		
			4 [N–(H)(C)$_2$] + 4 [C–(H)$_2$(N)$_2$] + Ring corr [cyclooctane] + $4[\mathrm{CH_3{-}\overset{\displaystyle NO_2}{\overset{|}{N}}{-}CH_3} - \mathrm{CH_3{-}NH{-}CH_3}]$ [a,b]	 $4[\mathrm{CH_3{-}\overset{\displaystyle NO_2}{\overset{|}{N}}{-}CH_3} - \mathrm{CH_3{-}CH_2{-}CH_3}]$ [b]		
$\Delta_f H^\ominus$(298.15 K)		248.9	252.4	275.2	295.6	275 ± 30
$S^\ominus$(298.15 K)			611.9	598.2	608.7	608.7 ± 15
$C_p^\ominus(T)$	298.15			267.67	265.30	265.30 ± 20
	300		250.99	268.75	266.51	266.51
	400		324.96	334.32	335.48	335.48
	500		387.47	390.27	394.23	394.23
	600		437.16	433.48	441.28	441.28
	800		508.90	492.98	509.07	509.07
	1000		553.91	526.15	552.60	552.60
	1200			545.04	584.89	584.89
	1400			553.70	607.45	607.45
	1500			562.93	615.93	615.93

[a] [C–(H)$_2$(N)$_2$] ≈ [C–(H)$_2$(C)(N)], see refs. 41, 42. [b] Thermodynamic properties for $(CH_3)_2N{-}NO_2$ were taken from the Appendix and for $(CH_3)_2NH$, $CH_3CH_2CH_3$ and cyclooctane from refs. 23, 30, 36, 37. [c] Thermodynamic properties for hexahydro-1,3,5-trinitro-1,3,5-triazine are given in Table 4 and those for cyclohexane and cyclooctane in ref. 36.

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APPENDIX: THERMODYNAMIC PROPERTIES OF MOLECULES CALCULATED IN THIS WORK BY THE STATISTICAL MECHANICAL TECHNIQUE

Based on the selected values of molecular constants, the ideal gas thermodynamic functions at a pressure of 1 bar (heat capacity $C_p^\ominus$, entropy $S^\ominus$, Gibbs energy $-(G^\ominus - H_0^\ominus)/T$, and enthalpy $(H^\ominus - H_0^\ominus)$) were calculated by the standard statistical mechanical method using a rigid-rotor harmonic-oscillator approximation. The accepted enthalpy of formation $\Delta_f H^\ominus$(298.15 K), and the calculated thermodynamic functions have been used to calculate the enthalpies of formation $\Delta_f H^\ominus(T)$, the Gibbs energies of formation $\Delta_f G^\ominus(T)$, and the logarithm of the equilibrium constant of formation $\log K_f^\ominus$ by the usual thermodynamic formulae (subscript f denotes formation by the reaction kC(c, graphite) + $l H_2(g) + m O_2(g) + n N_2(g) = C_k H_{2l} O_{2m} N_{2n}(g)$).

$(NH_2)_2C{=}O$, *urea*

Ideal gas thermodynamic properties for urea are given in Table A1. The product of the principal moments of inertia, $I_A I_B I_C = 936.8 \times 10^{-117}$ g^3 cm^6, for the planar structure of C_{2v} symmetry ($\sigma = 2$) was calculated using the rotational constants determined from microwave investigation [51]. Vibrational frequencies are those observed from infrared spectra of urea isolated in an argon matrix [52, 53], ν_i: 3548, 3440, 1734, 1594, 1014, 1000, 410 (a_1), 600, 228 (a_2), 618, 542, 233 (b_1), 3448, 3440, 1594, 1394, 790, 578 (b_2). The calculated value of $S^\ominus(360\ K) = 298.6$ J K^{-1} mol^{-1} is in good agreement with the calorimetric value of 298.2 J K^{-1} mol^{-1} [26]. The enthalpy of formation was taken from ref. 21.

$H_2C{=}NH$, *methanimine*

Ideal gas thermodynamic properties for methanimine are given in Table A2. Molecular constants determined from microwave and infrared data [54, 55] were used in this work: planar C_s symmetry ($\sigma = 1$); $I_A I_B I_C = 2.96 \times 10^{-117}$ g^3 cm^6; ν_i: 3262.6, 3024.5, 2914.2, 1638.3, 1452.0, 1344.3, 1058.2, 1127.0, 1060.8. The value of $\Delta_f H^\ominus$ was determined from the kinetic investigation [56] (see also ref. 57).

$(CH_3)_2C{=}NH$, *2-propanimine*

Ideal gas thermodynamic properties for 2-propanimine are given in Table A3. The product of the principal moments of inertia, $I_A I_B I_C = 1459 \times 10^{-117}$ g^3 cm^6, for the structure of C_s symmetry ($\sigma = 1$) was calculated using structural parameters estimated from ab initio calculations [58, 59]. Vibrational frequencies (3262, 3013, 2985, 2957, 2938, 1665, 1425(2), 1400, 1393, 1332, 1104, 1070, 808, 752, 500, 398 (a′), 2970, 2961, 1449, 1445, 1108, 1018, 816, 426 (a″)) are those observed from infrared and Raman spectra and calculated by the ab initio method [58]. Free rotation of methyl groups was accepted [59] ($I_{red} = 0.498 \times 10^{-39}$ g cm^2). The value of $\Delta_f H^\ominus$ was estimated in this work by comparison of enthalpies of formation for $(CH_3)_2C{=}O$, $H_2C{=}NH$ and $H_2C{=}O$ molecules.

H_2NO_2, *nitramide*

Ideal gas thermodynamic properties for nitramide are given in Table A4. Molecular constants determined from microwave and infrared data [60, 61]

TABLE A1

Ideal gas thermodynamic properties for urea

T/K	C_p°/J K^{-1} mol^{-1}	S°/J K^{-1} mol^{-1}	$[-(G^\circ - H_0^\circ)/T]$/(J K^{-1} mol^{-1})	$H^\circ - H_0^\circ$/kJ mol^{-1}	$\Delta_f H^\circ$/kJ mol^{-1}	$\Delta_f G^\circ$/kJ mol^{-1}	log K_f°
0	0.000	0.000	0.000	0.000	−220.129	−220.129	∞
100	41.764	220.119	184.582	3.554	−226.988	−204.114	106.617
200	61.460	255.001	211.502	8.700	−231.924	−179.198	46.801
298.15	79.087	282.949	230.534	15.627	−235.500	−152.516	26.720
300	79.383	283.439	230.859	15.774	−235.559	−152.004	26.466
400	93.639	308.308	247.176	24.453	−238.131	−123.735	16.158
500	104.967	330.467	261.658	34.404	−239.828	−94.926	9.917
600	114.085	350.439	274.818	45.373	−240.838	−65.839	5.732
700	121.605	368.607	286.939	57.168	−241.338	−36.628	2.733
800	127.982	385.272	298.203	69.656	−241.437	−7.372	0.481
900	133.509	400.673	308.744	82.736	−241.213	21.876	−1.270
1000	138.364	414.996	318.661	96.335	−240.723	51.085	−2.668
1100	142.658	428.389	328.034	110.390	−240.009	80.232	−3.810
1200	146.466	440.968	336.926	124.850	−239.102	109.307	−4.758
1300	149.846	452.828	345.390	139.669	−238.036	138.296	−5.557
1400	152.848	464.045	353.469	154.807	−236.820	167.201	−6.238
1500	155.515	474.683	361.198	170.228	−235.490	196.014	−6.826

TABLE A2

Ideal gas thermodynamic properties for methanimine

T/K	C_p°/J K^{-1} mol^{-1}	S°/J K^{-1} mol^{-1}	$[-(G^\circ - H_0^\circ)/T]$/(J K^{-1} mol^{-1})	$H^\circ - H_0^\circ$/kJ mol^{-1}	$\Delta_f H^\circ$/kJ mol^{-1}	$\Delta_f G^\circ$/kJ mol^{-1}	log K_f°
0	0.000	0.000	0.000	0.000	112.914	112.914	∞
100	33.259	189.961	156.704	3.326	110.228	114.426	−59.769
200	33.980	213.116	179.768	6.670	107.748	119.563	−31.226
298.15	38.083	227.324	193.195	10.176	105.000	125.941	−22.064
300	38.192	227.560	193.406	10.246	104.947	126.070	−21.950
400	44.962	239.446	203.461	14.394	102.240	133.528	−17.437
500	52.024	250.245	211.752	19.246	99.906	141.627	−14.795
600	58.450	260.309	219.015	24.777	97.993	150.160	−13.072
700	64.095	269.753	225.596	30.910	96.449	158.979	−11.863
800	69.029	278.641	231.676	37.572	95.224	168.000	−10.969
900	73.343	287.027	237.365	44.695	94.269	177.157	−10.282
1000	77.115	294.954	242.731	52.223	93.541	186.408	−9.737
1100	80.411	302.462	247.823	60.103	93.003	195.722	−9.294
1200	83.289	309.585	252.676	68.291	92.627	205.079	−8.927
1300	85.802	316.353	257.316	76.748	92.382	214.458	−8.617
1400	87.998	322.794	261.765	85.441	92.258	223.855	−8.352
1500	89.920	328.932	266.039	94.339	92.226	233.256	−8.123

TABLE A3

Ideal gas thermodynamic properties for 2-propanimine

T/K	C_p°/J K^{-1} mol^{-1}	S°/J K^{-1} mol^{-1}	$[-(G^\circ - H_0^\circ)/T]/(\mathrm{J\,K^{-1}\,mol^{-1}})$	$H^\circ - H_0^\circ$/kJ mol^{-1}	$\Delta_f H^\circ$/kJ mol^{-1}	$\Delta_f G^\circ$/kJ mol^{-1}	$\log K_f^\circ$
0	0.000	0.000	0.000	0.000	17.514	17.514	∞
100	43.513	244.894	203.007	4.189	9.570	28.609	−14.943
200	56.966	278.719	232.991	9.146	2.660	50.351	−13.150
298.15	75.512	304.805	252.420	15.618	−4.000	75.187	−13.172
300	75.889	305.273	252.745	15.758	−4.124	75.675	−13.176
400	96.369	329.920	268.982	24.375	−10.247	103.227	−13.480
500	115.263	353.498	283.545	34.976	−15.343	132.201	−13.811
600	131.626	375.997	297.094	47.342	−19.397	162.114	−14.113
700	145.648	397.368	309.906	61.223	−22.567	192.623	−14.374
800	157.720	417.624	322.116	76.407	−24.979	223.540	−14.595
900	168.166	436.819	333.804	92.713	−26.758	254.717	−14.783
1000	177.225	455.017	345.024	109.994	−28.000	286.063	−14.942
1100	185.087	472.286	355.815	128.118	−28.794	317.511	−15.077
1200	191.915	488.690	366.210	146.977	−29.202	349.018	−15.192
1300	197.849	504.292	376.237	166.472	−29.297	380.536	−15.290
1400	203.013	519.147	385.918	186.521	−29.103	412.058	−15.374
1500	207.517	533.311	395.276	207.052	−28.684	443.554	−15.446

TABLE A4

Ideal gas thermodynamic properties for nitramide

T/K	C_p°/J K^{-1} mol^{-1}	S°/J K^{-1} mol^{-1}	$[-(G^\circ - H_0^\circ)/T]$/(J K^{-1} mol^{-1})	$H^\circ - H_0^\circ$/kJ mol^{-1}	$\Delta_f H^\circ$/kJ mol^{-1}	$\Delta_f G^\circ$/kJ mol^{-1}	log K_f°
0	0.000	0.000	0.000	0.000	10.387	10.387	∞
100	34.629	222.008	188.534	3.347	4.933	26.116	−13.641
200	45.656	248.982	212.469	7.303	0.372	49.151	−12.837
298.15	58.677	269.666	227.976	12.430	−3.000	73.853	−12.939
300	58.910	270.030	228.235	12.539	−3.054	74.328	−12.942
400	70.504	288.616	241.048	19.027	−5.359	100.500	−13.124
500	79.950	305.402	252.268	26.567	−6.742	127.141	−13.282
600	87.467	320.669	252.415	34.952	−7.427	153.992	−13.406
700	93.479	334.620	271.748	44.010	−7.605	180.915	−13.500
800	98.377	347.433	280.419	53.611	−7.405	207.837	−13.570
900	102.446	359.262	288.531	63.658	−6.915	234.715	−13.622
1000	105.882	370.239	296.159	74.079	−6.199	261.528	−13.661
1100	108.816	380.472	303.364	84.818	−5.308	288.257	−13.688
1200	111.343	390.051	310.193	95.829	−4.274	314.901	−13.707
1300	113.530	399.052	316.686	107.075	−3.129	341.451	−13.720
1400	115.434	407.536	322.875	118.526	−1.889	367.912	−13.727
1500	117.096	415.558	328.789	130.154	−0.582	394.282	−13.730

TABLE A5

Ideal gas thermodynamic properties for *N*-methyl-*N*-nitromethanamine

T/K	$C_p^\ominus$/J K^{-1} mol^{-1}	$S^\ominus$/J K^{-1} mol^{-1}	$[-(G^\ominus - H_0^\ominus)/T]$/(J K^{-1} mol^{-1})	$H^\ominus - H_0^\ominus$/kJ mol^{-1}	$\Delta_f H^\ominus$/kJ mol^{-1}	$\Delta_f G^\ominus$/kJ mol^{-1}	log $K_f^\ominus$
0	0.000	0.000	0.000	0.000	20.066	20.066	∞
100	55.550	245.310	203.510	4.180	9.322	48.510	−25.339
200	80.081	291.587	236.605	10.996	1.580	90.835	−23.723
298.15	103.337	327.886	260.829	19.993	−4.800	136.042	−23.834
300	103.780	328.526	261.244	20.184	−4.912	136.911	−23.838
400	127.012	361.611	282.259	31.741	−10.034	185.003	−24.159
500	147.519	392.204	301.214	45.495	−13.713	234.219	−24.468
600	164.750	420.681	318.787	61.136	−16.119	284.050	−24.728
700	179.105	447.185	335.260	78.348	−17.517	334.198	−24.938
800	191.121	471.900	350.812	96.871	−18.104	384.494	−25.105
900	201.224	495.012	365.569	116.499	−18.039	434.816	−25.236
1000	209.755	516.672	379.611	137.062	−17.450	485.104	−25.339
1100	216.979	537.017	393.010	158.407	−16.452	535.306	−25.419
1200	223.122	556.171	405.821	180.420	−15.118	585.406	−25.482
1300	228.363	574.245	418.087	203.005	−13.522	635.383	−25.530
1400	232.848	591.337	429.853	226.077	−11.699	685.239	−25.566
1500	236.701	607.534	441.155	249.569	−9.710	734.967	−25.593

TABLE A6

Ideal gas thermodynamic properties for 1,3,5-triazine

T/K	C_p°/J K^{-1} mol^{-1}	S°/J K^{-1} mol^{-1}	$[-(G^\circ - H_0^\circ)/T]$/(J K^{-1} mol^{-1})	$H^\circ - H_0^\circ$/kJ mol^{-1}	$\Delta_f H^\circ$/kJ mol^{-1}	$\Delta_f G^\circ$/kJ mol^{-1}	log K_f°
0	0.000	0.000	0.000	0.000	240.969	240.969	∞
100	36.415	219.060	185.175	3.389	235.321	252.779	−132.037
200	50.053	248.081	209.819	7.652	230.195	272.247	−71.103
298.15	69.817	271.599	226.326	13.498	225.600	293.891	−51.488
300	70.223	272.032	226.607	13.628	225.520	294.313	−51.244
400	91.825	295.225	240.871	21.742	221.787	317.840	−41.505
500	110.710	317.810	254.014	31.898	219.154	342.176	−35.746
600	126.022	339.400	266.462	43.763	217.473	366.956	−31.946
700	138.254	359.780	278.352	57.000	216.491	391.952	−29.247
800	148.098	378.907	289.739	71.335	216.026	417.057	−27.231
900	156.120	396.829	300.653	86.559	215.937	442.193	−25.664
1000	162.736	413.631	311.120	102.512	216.136	467.327	−24.410
1100	168.247	429.408	321.163	119.069	216.556	492.428	−23.383
1200	172.877	444.252	330.809	136.132	217.156	517.481	−22.525
1300	176.795	458.248	340.078	153.621	217.905	542.475	−21.797
1400	180.131	471.476	348.996	171.472	218.794	567.411	−21.170
1500	182.989	484.003	357.583	189.631	219.791	592.276	−20.625

were used for thermodynamic properties' calculation: planar C_s symmetry ($\sigma = 1$); $I_A I_B I_C = 637.10 \times 10^{-117}$ g^3 cm^6; ν_i: 3359, 1558, 1350, 951, 798, 693, 629 (a′), 3478, 1613, 1227, 485, 402 (a″). The $\Delta_f H^\ominus$ value was taken from ref. 62.

$(CH_3)_2N–NO_2$, N-methyl-N-nitromethanamine

Ideal gas thermodynamic properties for *N*-methyl-*N*-nitromethanamine are given in Table A5. The product of the principal moments of inertia, $I_A I_B I_C = 11752 \times 10^{-117}$ g^3 cm^6, for the structure of C_{2v} symmetry ($\sigma = 2$) was calculated using structural parameters determined from an electron diffraction investigation [43]. Vibrational frequencies (3033, 2948, 1462, 1441, 1304, 1248, 1023, 838, 626, 427 (a_1), 2993, 1456, 1144 (a_2), 3033, 2948, 1528, 1454, 1411, 1292, 1110, 619, 350 (b_1), 2993, 1450, 1050, 762, 225 (b_2)) are those observed from infrared and Raman spectra [63]. Internal rotation of nitro and methyl groups was accepted: $V_0(NO_2) = 2800$ cm^{-1}, $V_0(CH_3) = 1050$ cm^{-1} [46], $I_{red}(NO_2) = 3.94 \times 10^{-39}$ g cm^2, $I_{red}(CH_3) = 0.59 \times 10^{-39}$ g cm^2. The $\Delta_f H^\ominus$ value was taken from ref. 23.

$C_3H_3N_3$, 1,3,5-triazine

Ideal gas thermodynamic properties for 1,3,5-triazine are given in Table A6. The product of the principal moments of inertia, $I_A I_B I_C = 4478 \times 10^{-117}$ g^3 cm^6, for the planar structure of D_{3h} symmetry ($\sigma = 6$) was calculated using structural parameters determined by electron diffraction [64]. Vibrational frequencies (3042, 1132, 992 (a_1'), 1350, 1038 (a_2'), 925, 737 (a_2''), 3056, 1556, 1410, 1174, 675 (e′), 1031, 340 (e″)) recommended by Wiberg [65] on the basis of ab initio calculation were adopted in this work. The $\Delta_f H^\ominus$ value was taken from ref. 38.