

Ideal Gas Thermodynamic Properties of CH_3 , CD_3 , CD_4 , C_2D_2 , C_2D_4 , C_2D_6 , C_2H_6 , $\text{CH}_3\text{N}_2\text{CH}_3$, and $\text{CD}_3\text{N}_2\text{CD}_3$

Cite as: Journal of Physical and Chemical Reference Data **11**, 83 (1982); <https://doi.org/10.1063/1.555656>
Published Online: 15 October 2009

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Ideal Gas Thermodynamic Properties of CH₃, CD₃, CD₄, C₂D₂, C₂D₄, C₂D₆, C₂H₆, CH₃N₂CH₃, and CD₃N₂CD₃

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Ideal gas thermodynamic properties, C_p° , S° , $(G^\circ - H^\circ_{298})/T$, $H^\circ_T - H^\circ_{298}$, ΔH°_f , ΔG°_f and $\log K_p$ of formation for CH₃, CD₃, CD₄, C₂D₂, C₂D₄, C₂D₆, C₂H₆, CH₃N₂CH₃ and CD₃N₂CD₃ in the temperature range 0 – 3000 K and at 1 atmosphere have been calculated by statistical thermodynamic methods employing spectroscopic and other molecular constants. The rigid rotor-harmonic oscillator model has been used. Estimated uncertainties in the thermodynamic properties due to uncertainties in the molecular properties and estimates of the effects of vibrational anharmonicities are also reported for each compound at three temperatures.

Key words: Acetylenes; azomethanes; critically evaluated data; diazine dimethyls; enthalpy of formation; entropy; ethane; ethylene; Gibbs energy of formation; ideal gas thermodynamic properties; internal rotation; methane; methyl radical.

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1. Introduction

Deuterated compounds have been used in studies of hydrocarbon reactions in our laboratory [1]¹ and elsewhere [2,3], but there has been no compilation of thermodynamic properties for most of these compounds. The substances which we have included in this paper are ones of broad interest for which molecular data are available for calculating accurate thermodynamic properties. CH₃ has been included since recent data warrant an updating of the JANAF [4] table, while C₂H₆ is included because the current best table [5] goes up to only 1500 K, while extensive studies on ethane are now being reported above that temperature. On the other hand, we did not include the ethyl radical and some other important species since there are still considerable areas of uncertainty in establishing their properties.

Like deuterated hydrocarbons, azomethane, H₃C—N=N—CH₃, has been a subject of interest for gas kineticists for over fifty years. The decomposition was originally thought to be a true unimolecular process and the reaction pioneered experimental verification of developing theories [6]. Although it is now recognized that the decomposition is a complex chain reaction [7], there is still considerable interest in the molecule as a clean supplier of methyl radicals in both photochemical [8] and thermal [9] systems. In the course of a shock tube investigation of the decomposition of azomethane/deuterated hydrocarbon mixtures by two of us (R&S), it was discovered that there were no tables of thermodynamic properties for azomethane or azomethane-d₆ in the literature. As ordinarily prepared and under normal conditions, azomethane exists only in the trans form [10], and this paper deals exclusively with that configuration.

We have used the standard methods of statistical thermodynamics [5,11,12] along with recent spectroscopic and other molecular constants, using the rigid rotor-harmonic oscillator (RRHO) approximation. Since anharmonicity constants are

available only for methane and acetylene, it was thought best to use the RRHO method for all the molecules, since in thermochemical calculations some cancellation of error will occur if a uniform basis is used throughout. We have, however, made estimates of the anharmonicity contributions using a simplified method, and list these estimates in the tables.

Hindered internal rotation contributions were obtained by interpolation from the tables of Pitzer and Brewer [11]. Our computer program was checked using the data of Chao, Wilhoit, and Zwolinski [5] on ethane from 298 to 1500 K, and the ethylene data of the JANAF tables from 298 to 3000 K. Our data have been reported in the JANAF format, but rounded off to two decimal places.

2. Sources of Data

The vibrational frequencies of the deuterated hydrocarbons, CD₄, C₂D₂, C₂D₄, C₂D₆, and also azomethane and azomethane-d₆ were critically reviewed by Shimanouchi in 1972 [13] and 1977 [14]. In addition, a number of papers on molecular properties have appeared since then.

The principal moments of inertia were calculated using standard equations [11] for those molecules for which directly measured rotational constants are reported in the literature. These are the most precise values. Moments of inertia were also calculated from structural data obtained by other methods, following the general procedure of Knox [15]. Deuterated hydrocarbons were assumed to have the same molecular dimensions as the corresponding normal hydrocarbons. Vibrational frequencies of 4405 and 3119 cm⁻¹ for H₂ and D₂ molecules [15] were used in calculations of heats of formation of deuterated compounds. The spectroscopic data, the principal moments of inertia and other molecular constants of the hydrocarbons are listed in table 1. Moments of inertia calculated from structural data (table 2) are close to those obtained from rotational constants.

¹Figures in brackets indicate literature references.

Table 1. Spectroscopic and Other Molecular Constants of Hydrocarbons.

Property	CH ₃	CD ₃	CD ₄	C ₂ D ₂	C ₂ D ₄	C ₂ D ₆	C ₂ H ₆
1. Relative molecular mass (molecular weight)	15.035	18.053	20.067	28.050	32.078	36.106	30.070
2. Symmetry number dimensionless	6	6	12	2	4	6	6
3. Rotational constants ground state, cm ⁻¹							
A ₀			2.6326		2.4250	1.3416	2.6710
B ₀			2.6326	0.8478	0.7363	0.4597	0.6631
C ₀			2.6326		0.5635	0.4597	0.6631
4. Principal moments of inertia							
I _A , 10 ⁻⁴⁰ g cm ²	2.923	5.839	10.632		11.543	20.864	10.479
I _B , 10 ⁻⁴⁰ g cm ²	2.923	5.839		33.013	38.015	60.885	42.210
I _C , 10 ⁻⁴⁰ g cm ²	5.845	11.679			49.673	60.885	42.210
I _A I _B I _C , 10 ⁻¹¹⁷ g ³ cm ⁶	0.0499	0.3983	1.202		21.796	77.342	18.671
5. Vibrational frequencies, cm ⁻¹ (degeneracies)	3044(1) 607(1) 3162(2) 1396(2)	2153(1) 461(1) 2381(2) 1026(2)	2109(1) 1092(2) 2260(3) 998(3)	2705(1) 1765(1) 2439(1) 511(2) 538(2)	2262(1) 1518(1) 985(1) 726(1) 2315(1) 1000(1) 720(1) 780(1) 2342(1) 595(1) 2201(1) 1078(1)	2083(1) 1155(1) 843(1) 208 ^a (1) 2087(1) 1077(1) 2226(2) 1041(2) 970(2) 2235(2) 1081(2) 594(2)	2954(1) 1388(1) 995(1) 289 ^a (1) 2896(1) 1379(1) 2969(2) 1468(2) 1190(2) 2985(2) 1469(2) 822(2)
6. Reduced moment of inertia, I _r , 10 ⁻⁴⁰ g cm ²						5.308	2.6266
7. Internal rotation barrier height, V ₀ , cal mol ⁻¹						2800	2900
8. Enthalpy of formation ΔH _f ⁰ , kcal mol ⁻¹ , at 0 K, 298 K	35.92 35.10	33.896 33.143	-19.214 -21.091	52.864 52.903	11.003 9.124	-22.174 -25.663	-16.31 -20.041
9. Relative enthalpy H ₂₉₈ ⁰ - H ₀ ⁰ , kcal mol ⁻¹	2.476	2.569	2.471	2.591	2.721	3.157	2.841

^aTorsional vibrations treated as hindered internal rotors.

Table 2. Principal Moments of Inertia of Hydrocarbons, Calculated from Structural Data.

Property	CD ₄	C ₂ D ₂	C ₂ D ₄	C ₂ D ₆	C ₂ H ₆
1. Structural Parameters					
r(C-D), 10 ⁻⁸ cm	1.091	1.056	1.086	1.095	1.095
r(C-C), 10 ⁻⁸ cm		1.204	1.337	1.534	1.534
∠ DCD, degree	109.28		117.22	107.8	107.8
∠ DCC, degree			121.19	109.45	109.45
2. Principal moments of inertia					
I _A , 10 ⁻⁴⁰ g cm ²	10.689		11.446	20.940	10.481
I _B , 10 ⁻⁴⁰ g cm ²		32.838	38.089	60.982	42.249
I _C , 10 ⁻⁴⁰ g cm ²			49.536	60.982	42.249
3. I _A I _B I _C , 10 ⁻¹¹⁷ g ³ cm ⁶	1.222		21.597	77.871	18.708

2.1. Spectroscopic Data

Methyl and Methyl-d₃ Radicals

The vibrational frequencies and degeneracies of gaseous CH₃ and CD₃ radicals were those of Tan et al. [16]. Matrix isolation studies in inert gases by Snelson [17] and a more recent study by Jacox [18] are consistent with the values of Tan et al. [16] for gaseous radicals after accounting for matrix shifts. The infrared inactive band, ν_1 , was taken from ref. [16]. Since directly measured rotational constants are not available in the literature, principal moments of inertia were calculated for CH₃ and CD₃ from their structural data; $r(\text{C}-\text{H}) = 1.079 \pm 0.005 \text{ \AA}$ and $\angle \text{HCH} = 120^\circ$.

Methane-d₄

The vibrational frequencies of methane-d₄ have been investigated extensively by analysis of infrared and Raman spectra [19-22]. Frequencies ν_2 , ν_3 and ν_4 observed by various workers are very close to one another, within the experimental error of less than 1 cm^{-1} , and not much different from the values recommended by Shimanouchi [13]. The vibrational frequencies used in our calculations were taken from the more recent works of Brodersen, Gray, and Robiette [20] and Kreiner and Robiette [22]. Brodersen et al. [20] obtained a precise value of B_0 for CD₄ from the ν_3 Raman band of CD₄, which was used in our calculations.

Acetylene-d₂

The fundamental vibrations, ν_1 , ν_2 , and ν_4 for acetylene and acetylene-d₂ were taken from the high resolution Raman

spectroscopic studies of Fast and Welsh [23]. The measurement of ν_2 by Ghersesti et al. [24] was in close agreement with those of Fast and Welsh [23]. While the bending fundamental vibration ν_5 , obtained from the absorption spectrum of C₂D₂ by Huhanatti et al. [25] was taken, the stretching frequency, ν_3 , was taken from the work of Smit et al. [26]. The ground state rotational constant for acetylene-d₂ was obtained from both infrared [24,25] and Raman [23] spectral studies. The Raman values of B_0 show good agreement with infrared values within the error limits. It was pointed out by Fast and Welsh [23] that the infrared values are somewhat more accurate than the Raman values; the infrared value [25] was therefore used in our calculations.

Ethylene-d₄

Recently acquired spectroscopic data on ethylene and ethylene-d₄ have been summarized by Duncan and Hamilton [27] and these values were used for calculating thermodynamic properties of C₂D₄. The rotational constants were taken from the work of Duncan, Wright, and Leberghe [28].

Ethane and Ethane-d₆

The absorption frequencies of C₂H₆ and C₂D₆ have been obtained by Spoliti et al. [29] in inert gas matrices and compared with those of the gas phase. The more recent values appear to be those recommended by Shimanouchi [13] and therefore were used in our calculations, but the perpendicular band, ν_7 , of C₂H₆ was that of Cole et al. [30]. The most recent experimental rotational constants of C₂H₆, summarized by Duncan, McKean, and Bruce [31] were used for calculating the moments of inertia of these molecules.

Azomethane and Azomethane-d₆

A recent infrared investigation by Durig, Pate, and Harris [32] has been critically reviewed by Shimanouchi [14]. However, a more recent study on vibrational spectra of gaseous trans-azomethane and transazomethane-d₆ was reported by Craig, Ackermann, and MacPhail [33] and vibrational frequencies were taken from this study. These are listed in table 3.

The moments of inertia for these molecules were calculated from their structural parameters. Two recent electron diffraction studies of azomethane [34,35] have been reported. Bond lengths and angles were taken from the work of Almenningen et al. [34] and agreed quite well with other studies. Table 3 lists all relevant structural parameters, which were assumed to be the same for azomethane-d₆.

Arbitrary coordinates passing through the center of mass of the molecules were selected and the moments and products of inertia were calculated. The molecule has a plane of symmetry so that two principal axes lie in this CNNC skeletal plane. A program was written which varied the angle α between the N-N bond and one of these axes, the other two being defined as mutually perpendicular, until the products of inertia were all zero.

The principal axis of smallest moment of inertia was found to lie in the CNNC plane and passes through the mid-point of the N-N bond at an angle $\alpha = 46.30^\circ$ and through the N-C bonds very close to the C atoms. In these calculations it was assumed that the C-N bond coincided with the axis of rotation of the methyl groups. The principal moments of inertia calculated (I_A, I_B, I_C) are given in table 3.

Table 3. Spectroscopic and Other Molecular Constants for Azomethane and Azomethane-d₆.

Property	Azomethane	Azomethane-d ₆
Molecular Weight	58.083	64.120
Point Group	C _{2h}	C _{2h}
Symmetry number	2	2
Structural parameters		
r(C-N), 10 ⁻⁸ cm	1.482	1.482
r(N=N), 10 ⁻⁸ cm	1.247	1.247
r(C-H), 10 ⁻⁸ cm	1.105	1.105
∠ CNN, degree	112.3	112.3
∠ NCH, degree	107.5	107.5
Principal moments of inertia		
I _A , 10 ⁻⁴⁰ g cm ²	20.63	31.47
I _B , 10 ⁻⁴⁰ g cm ²	190.82	242.15
I _C , 10 ⁻⁴⁰ g cm ²	200.29	251.33
Reduced moment of inertia		
I _r , 10 ⁻⁴⁰ g cm ²	4.25	7.65
Vibrational frequencies, cm ⁻¹	2989, 2926, 1563, 1437, 1381, 1179, 919, 591, 2977, 1416, 1027, 214 ^a , 2981, 1440, 1111, 312, 222 ^a , 2988, 2925, 1447, 1384, 1112, 1008, 353	2234, 2127, 1569, 1122, 1044, 1034, 761, 523, 2225, 1027, 803, 191 ^a , 2239, 1049, 896, 261, 166 ^a , 2240, 1115, 1112, 1051, 921, 900, 304
Internal rotation barrier height, V _o , cal mol ⁻¹	1700	1700
Enthalpy of formation ΔH _f ^o (290.15K), kcal/mol	35.54	28.50
Relative enthalpy H ₂₉₈ ^o - H ₀ ^o , kcal mol ⁻¹	3.945	4.341

^a Torsional vibrations treated as hindered internal rotors.

2.2. Internal Rotation

Ethane and Ethane-d₆

Weiss and Leroi [36] were able to observe directly the torsional frequencies for C₂H₆ (289 cm⁻¹) and C₂D₆ (208 cm⁻¹) by using sample pressures of a few atmospheres. Two recent additional papers [37,38] exist which confirm these torsional frequencies.

Hirota, Saito, and Endo [39], based on the microwave spectrum of CH₃CHD₂, obtained a value of 2.90 ± 0.03 kcal mol⁻¹ for the barrier to internal rotation in ethane gas.² This value is very close to the value of 2.928 ± 0.025 kcal mol⁻¹ obtained by Nicolas and Barthelat [40]. Microwave results on a few molecules with internal rotation of a methyl group indicate that the CH₃ barrier is always larger than the CD₃ barrier by 1%–4%. In fact, Kirtman et al. [41] recently estimated the decrease in barrier in going from C₂H₆ to C₂D₆ to be 0.102 kcal mol⁻¹. Therefore, the barrier in C₂D₆ was calculated to be 2.80 ± 0.03 kcal mol⁻¹.

The reduced moment of inertia for the CH₃ rotor was observed by Hirota et al. [39], who obtained a value of $I_r = 2.6266 \pm 0.0023 \times 10^{-40}$ g cm² which is close to the methyl group moment of inertia calculated by Shaw et al. [42]. The reduced moment of inertia for the CD₃ rotor was calculated from its structural parameters to be $5.038 \pm 0.021 \times 10^{-40}$ g cm².

The torsional frequencies, barrier to internal rotation and reduced moments of inertia used for calculating thermodynamic properties of C₂D₆ and C₂H₆ are listed in table 1.

Azomethane and Azomethane-d₆

The frequencies of the CH₃ and CD₃ torsional vibrations, ν_{12} (b_g) and ν_{17} (a_u), treated as hindered internal rotors, were taken from ref. [33] and are listed in table 3.

No measured value for the height of the barrier for internal rotation is available in the literature for the trans compound. The difficulty arises from the fact that the trans form does not have a dipole moment, so its microwave spectrum cannot be studied. However, Durig et al. [32] calculated a value of 2.69 kcal mol⁻¹ for the solid compound and suggested that it should be somewhat smaller in the gas phase. For example, for propylene the gas phase barrier (1.98 kcal mol⁻¹) was found to be smaller than that in the solid phase (2.7 kcal mol⁻¹) [32]. A microwave study by Stevens, Curl, and Engel [43] revealed a barrier of 1.32 kcal mol⁻¹ for the gaseous cis form, a value which is in reasonable agreement with the calculated barrier of 1.13 kcal mol⁻¹ by Flood, Pulay, and Boggs [44]. It was pointed out by Sarachaman [45] in his paper on cis-2-butene that trans barriers tend to be greater than cis ones. From the above discussion it can be concluded that V_0 for gaseous trans-azomethane is probably greater than 1.32 and less than 2.69 kcal mol⁻¹.

Pratt [46] calculated the barrier for the trans compound using the structural parameters listed in table 3 and obtained

1.64–1.69 kcal mol⁻¹ for V_0 by using three different basis sets. Although the absolute accuracy of these calculations is not very high, Pratt noted that barriers so calculated are found to be reasonable where comparison with good experimental values can be made. From the data on the cis isomer and other related molecules we consider the value of Pratt, 1.7 kcal mol⁻¹, to be a reasonable estimate, and therefore have used it in our calculations. The uncertainty is estimated to be 0.4 kcal mol⁻¹. The barrier was assumed to be the same for trans-azomethane-d₆.

Reduced moments of inertia, I_r , for internal rotation were calculated from the moment of inertia of the methyl group about the CN axis, the principal moments of inertia of the molecule and the direction cosines of the C–N bond with the three principal axes, using the formulae of Pitzer and Gwinn [47], and are presented in table 3.

A computer program was written to calculate $1/Q_f$ and V_0/RT values for C₂H₆, C₂D₆, CH₃N₂CH₃ and CD₃N₂CD₃ by obtaining contributions at each temperature by interpolation from the tables of Pitzer and Brewer [11]. Crowder and Riley [48] adapted a similar procedure previously for obtaining restricted internal rotation contributions.

2.3. Enthalpies of Formation

No experimental data are available on the heat of formation of CD₃, C₂D₂, CD₄, C₂D₄, and C₂D₆. Therefore the heats of formation were calculated from those of the normal compounds assuming that the difference at 0 K may be calculated from the zero-point vibrational energies. For example for CD₃,

$$\Delta H_{f0}^\circ(\text{CD}_3) = \Delta H_{f0}^\circ(\text{CH}_3) + [E_{v0}(\text{CD}_3) - E_{v0}(\text{CH}_3)] - 3/2[E_{v0}(\text{D}_2) - E_{v0}(\text{H}_2)]$$

where E_{v0} is the zero-point vibrational energy, a sum of 6 terms in the case of CD₃ and CH₃. From this value the heat of formation at 298.15 K may be calculated as

$$H_{f298}^\circ(\text{CD}_3) = \Delta H_{f0}^\circ(\text{CD}_3) + (H_{298}^\circ - H_0^\circ)(\text{CD}_3) - (H_{298}^\circ - H_0^\circ)(\text{C}) - 3/2(H_{298}^\circ - H_0^\circ)(\text{D}_2).$$

Calculated enthalpies, $H_{298}^\circ - H_0^\circ$, for CD₃ and other molecules were used, while values for C (graphite), H₂ (gas) and D₂ (gas) were taken from American Petroleum Institute tables [49]. In calculating the zero point vibrational energy difference torsional frequencies were included as they behave as vibrations at low temperatures.

Thermodynamic functions, $(H_T^\circ - H_{298}^\circ)$ and S° , of D₂ (gas) needed for calculating the heat of formation and Gibbs energy of formation at higher temperatures are available, but not at hundred-degree intervals, in the range 1600–3000 K [49]. Hence the needed quantities were read from smoothed curves, the values used being listed in table 4.

Recent values for heats of formation of CH₃ radical, methane and ethane were used in the calculations. Baghal-Vayjooee, Colussi, and Benson [50] reported a value of 35.1 ± 0.15 kcal mol⁻¹ for the heat of formation of methyl radical at room temperature. Pittman and Pilcher [51] obtained values of -17.80 ± 0.10 and -20.04 ± 0.07 kcal mol⁻¹ for the heats of formation of methane (gas) and ethane (gas) from measurements of heats of combustion by flame calorimetry. Another

²Thermodynamic quantities are expressed in kcal units to permit the tables in this paper to be used conveniently with other existing tables (1 cal = 4.184 J).

source for heat of formation of normal hydrocarbons is ref. [4]. The calculated heats of formation of CD_3 , CD_4 , C_2D_2 , C_2D_4 , and C_2D_6 are listed in table 1.

Various estimates of the heat of formation of azomethane are reviewed by Engel [52]. These have now been superseded by the direct measurement of Rossini and Montgomery [53] and their value, $\Delta H_f^\circ(298.15 \text{ K}) = 35.54 \pm 1.23 \text{ kcal mol}^{-1}$ has

been used here. The heat of formation of azomethane- d_6 was calculated from zero point energies following the same procedure described above for hydrocarbons. Heats of formation of $\text{CH}_3\text{N} = \text{NCH}_3$ and $\text{CD}_3\text{N} = \text{NCD}_3$ at various temperatures were calculated using thermodynamic data for H_2 , D_2 , and N_2 and C from ref. [49]. For $\text{CD}_3\text{N}_2\text{CD}_3$ we obtain $\Delta H_{f298}^\circ = 28.50 \pm 1.23 \text{ kcal mol}^{-1}$, as listed in table 3.

Table 4. Entropy and Enthalpy of Deuterium, D_2 , for the Ideal Gas State at 1600–3000 K.

Temp; K	Entropy S° $\text{cal deg}^{-1} \text{ mol}^{-1}$	Enthalpy $H^\circ_T - H^\circ_{298}$ ^a kcal mol^{-1}
1600	47.03	9.796
1700	47.53	10.627
1800	48.00	11.465
1900	48.45	12.310
2000	48.85	13.162
2100	49.28	14.021
2200	49.67	14.887
2300	50.05	15.760
2400	50.41	16.640
2500	50.79	17.528
2600	51.13	18.423
2700	51.49	19.325
2800	51.81	20.235
2900	52.15	21.153
3000	52.45	22.079

$$^a H^\circ_T - H^\circ_{298} = (H^\circ_T - H^\circ_0) - (H^\circ_{298} - H^\circ_0)$$

2.4. Estimates of Uncertainties

Uncertainties in the thermodynamic properties have been calculated using the standard approach, in which the uncertainty in the result is taken to be the square root of the sum of the squares of the contributions from the various sources. These include molecular dimensions or rotational constants, vibrational frequencies, rotational barriers, and heats of formation. For methyl radicals and azomethanes the molecular dimensions are known to about 0.5%, leading to uncertainties in the principal moments of inertia of 1%, while for the other molecules these uncertainties are smaller.

Vibrational frequencies of CD_4 and C_2D_2 have been measured to within 0.1 cm^{-1} . Shimanouchi [13] has assigned ranges of uncertainty for the selected values of frequencies for each molecule, and we have used the maximum uncertainty he has recommended in our calculations.

Calculated total uncertainties in various thermodynamic functions obtained from uncertainties in various sources are listed for each compound at three temperatures, 298, 1500, and 3000 K, in the tables.

2.5. Estimates of Vibrational Anharmonicity Effects

To estimate the effects of anharmonicities in the absence of detailed information, we have used the approach which Duncan, McKean, and Mallinson [54] used for calculating harmonic frequencies from observed frequencies. They have assigned an anharmonicity constant to each fundamental vibration and then neglected cross terms. In the usual expression for vibrational

term values (omitting cross terms)

$$T = \sum_i \omega_i(v_i + 1/2) - \sum_i \omega_i x_i(v_i + 1/2)^2$$

they set $x_i = 0.02$ for C–H stretching, $x_i = 0.01$ for bending and $x_i = 0.075$ for C–C stretching. For isotopic molecules they used $x_i^D = x_i^H(v_i^D/v_i^H)$. We simplified a little more by using the same x_i for C–C stretching and bending. We then used simplified forms of the equations of Pennington and Kobe [55], including only those terms involving x_{ii} , to estimate the anharmonicity effects.

Since full first-order anharmonic calculations are available for C_2H_2 [4] and also for CH_4 and CD_4 [56] it was possible to test this method of estimation for these molecules. For the relatively stiff C_2H_2 , we obtained better agreement with the full calculations by reducing the x_i 's to 0.014 for C–H stretching and 0.005 for other frequencies. These x_i 's were used in estimating effects for C_2D_2 . The calculated results are shown in table 5. For CH_4 and CD_4 good agreement was found with x_i 's of 0.018 for C–H stretching and 0.009 for other frequencies. We used these values for all the other compounds except C_2D_4 , for which we used intermediate values of 0.016 and 0.007. These estimates are shown in the tables.

From these estimates it can be seen that the expected partial cancellation of errors does occur in some types of reaction. For example, for $\text{C}_2\text{D}_6 \rightarrow 2\text{CD}_3$ at 3000 K, the anharmonicities would change $\log K_p$ by approximately $2(0.05) - (0.16) = -0.06$, a factor of 0.87. Clearly, at high temperatures the effects of anharmonicities become larger than the uncertainties from other sources.

Table 5. Comparison of Harmonic and Anharmonic Oscillator Calculations for C₂H₂.

Property	T, K	Harmonic	Anharmonic	Difference	
				Actual	Estimated
C_p , cal mol ⁻¹ K ⁻¹	1500	17.93	18.29	0.36	0.40
	3000	19.91	20.82	0.91	0.90
S° , cal mol ⁻¹ K ⁻¹	1500	71.15	71.34	0.19	0.27
	3000	84.36	84.97	0.61	0.70
$H^\circ - H^\circ_{298}$, kcal mol ⁻¹	1500	18.36	18.54	0.18	0.26
	3000	47.11	48.26	1.15	1.23
$-(G^\circ - H^\circ_{298})$, kcal mol ⁻¹	1500	58.98	58.91	0.07	0.10
	3000	68.88	68.66	0.22	0.29
$\log K_p$	1500	-4.99	-4.98	0.01	0.02
	3000	-1.19	-1.14	0.05	0.06

3. Results

Methyl and Methyl-d₃ Radicals

Thermodynamic data for these radicals are presented in tables 6 and 7. Results for CH₃ are not very different from the JANAF [4] values, since their estimates of vibrational frequencies and heat of formation, although based on limited experimental data, were quite close to those measured more recently. Estimated uncertainties in each thermodynamic function for CH₃ and CD₃ are given in table 8.

Acetylene-d₂

These data are given in table 9; the corresponding uncertainties are listed in table 10. In comparing them with the JANAF data for C₂H₂, it should be noted that the JANAF table does include anharmonicity corrections which, naturally, are small at low temperatures but increase at higher temperatures. For other hydrocarbons, the JANAF tables use the RRHO approach.

Methane-d₄ and Ethylene-d₄

Thermodynamic properties are given in tables 11 and 13. These data are directly comparable with those of the JANAF tables for CH₄ and C₂H₄, and of Chao and Zwolinski [5] for ethylene, both of which also used the RRHO approach. Estimated uncertainties for CD₄ and C₂D₄ are listed in tables 12 and 14.

Ethane and Ethane-d₆

As these molecules exhibit internal rotation, the contributions to each thermodynamic functions arising from the internal rotation were calculated and then added to the corresponding contributions from other degrees of freedom to yield the final thermodynamic properties at each temperature, which are given in tables 15 and 16. The estimated uncertainties for these molecules are given in table 17.

Azomethane and Azomethane-d₆

The various thermodynamic property contributions from internal rotation were calculated and added twice to the corresponding contributions from other degrees of freedom to obtain the final thermodynamic functions. Pitzer and Gwinn [42] have derived an equation for calculating I' for molecules with several symmetric rotors, taking into account interactions between rotors. However, in the case of azomethane no interaction was observed from infrared vibrational studies [32]; therefore no interaction term was included in our final calculations. If there is an interaction that is too small to detect spectroscopically, the effects on the thermodynamic properties would be smaller than those introduced by other experimental uncertainties. Thermodynamic tables for trans-azomethane and trans-azomethane-d₆ are presented in tables 18 and 19. Uncertainties in the various thermodynamic functions, which apply to both substances, are given in table 20.

Table 6. Ideal Gas Thermodynamic Properties of Methyl (CH_3) Radical.

T, K	$\text{cal K}^{-1} \text{mol}^{-1}$			kcal mol^{-1}			
	C_P°	S°	$-(G^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	ΔH°_f	ΔG°_f	$\text{Log } K_p$
0	0.00	0.00	INF	-2.47	35.92	35.92	INF
100	7.97	37.18	53.99	-1.68	35.55	35.52	-77.62
200	8.46	42.82	47.14	-0.86	35.39	35.52	-38.82
298	9.18	46.33	46.33	-0.00	35.10	35.65	-26.15
300	9.19	46.39	46.33	0.02	35.09	35.65	-25.97
400	9.98	49.14	46.70	0.98	34.77	35.89	-19.61
500	10.76	51.45	47.42	2.01	34.44	36.21	-15.83
600	11.49	53.48	48.27	3.13	34.12	36.59	-13.33
700	12.19	55.30	49.14	4.31	33.83	37.03	-11.56
800	12.85	56.97	50.02	5.56	33.56	37.50	-10.24
900	13.48	58.52	50.88	6.88	33.32	38.01	-9.23
1000	14.06	59.98	51.72	8.26	33.12	38.54	-8.42
1100	14.60	61.34	52.53	9.69	32.94	39.09	-7.77
1200	15.09	62.63	53.32	11.18	32.79	39.66	-7.22
1300	15.53	63.86	54.08	12.71	32.65	40.23	-6.76
1400	15.92	65.02	54.82	14.28	32.54	40.82	-6.37
1500	16.28	66.13	55.54	15.89	32.44	41.42	-6.04
1600	16.59	67.19	56.24	17.53	32.34	42.02	-5.74
1700	16.87	68.21	56.91	19.21	32.26	42.63	-5.48
1800	17.12	69.18	57.57	20.91	32.19	43.24	-5.25
1900	17.34	70.11	58.20	22.63	32.12	43.84	-5.04
2000	17.54	71.01	58.82	24.37	32.06	44.48	-4.86
2100	17.72	71.87	59.42	26.14	32.00	45.10	-4.69
2200	17.88	72.70	60.01	27.92	31.94	45.72	-4.54
2300	18.02	73.49	60.57	29.71	31.88	46.35	-4.40
2400	18.15	74.26	61.13	31.52	31.82	46.98	-4.28
2500	18.27	75.01	61.67	33.34	31.77	47.61	-4.16
2600	18.38	75.72	62.20	35.17	31.71	48.25	-4.06
2700	18.47	76.42	62.71	37.02	31.65	48.89	-3.96
2800	18.56	77.09	63.21	38.87	31.59	49.52	-3.87
2900	18.64	77.75	63.70	40.73	31.53	50.17	-3.78
3000	18.71	78.38	64.18	42.60	31.47	50.81	-3.70

Table 7. Ideal Gas Thermodynamic Properties of Methyl- d_3 (CD_3) Radical.

T, K	$\text{cal K}^{-1} \text{mol}^{-1}$			kcal mol^{-1}			
	C_P°	S°	$-(G^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	ΔH°_f	ΔG°_f	$\text{Log } K_p$
0	0.00	0.00	INF	-2.57	33.90	33.90	INF
100	8.06	39.80	57.54	-1.77	33.69	33.77	-73.81
200	8.94	45.63	50.27	-0.93	33.40	33.97	-37.12
298	9.99	49.39	49.39	-0.00	33.14	34.30	-25.16
300	10.02	49.46	49.39	0.02	33.14	34.31	-25.00
400	11.07	52.49	49.80	1.07	32.90	34.74	-18.98
500	12.04	55.06	50.60	2.23	32.69	35.23	-15.40
600	12.94	57.34	51.54	3.48	32.50	35.75	-13.02
700	13.77	59.40	52.52	4.82	32.34	36.31	-11.34
800	14.52	61.28	53.49	6.23	32.21	36.88	-10.08
900	15.18	63.03	54.46	7.72	32.11	37.47	-9.10
1000	15.75	64.66	55.40	9.26	32.03	38.07	-8.32
1100	16.25	66.19	56.31	10.87	31.97	38.68	-7.68
1200	16.67	67.62	57.19	12.51	31.92	39.29	-7.16
1300	17.03	68.97	58.05	14.20	31.87	39.91	-6.71
1400	17.34	70.24	58.88	15.92	31.83	40.53	-6.33
1500	17.60	71.45	59.67	17.66	31.80	41.16	-6.00
1600	17.83	72.59	60.45	19.43	31.76	41.95	-5.73
1700	18.03	73.68	61.19	21.23	31.73	42.58	-5.47
1800	18.20	74.71	61.91	23.04	31.71	43.20	-5.24
1900	18.35	75.70	62.61	24.87	31.69	43.82	-5.04
2000	18.48	76.65	63.29	26.71	31.67	44.34	-4.85
2100	18.60	77.55	63.95	28.56	31.64	45.01	-4.68
2200	18.70	78.42	64.59	30.43	31.62	45.61	-4.53
2300	18.79	79.25	65.21	32.30	31.59	46.22	-4.39
2400	18.87	80.05	65.81	34.18	31.56	46.80	-4.26
2500	18.94	80.82	66.40	36.07	31.52	47.50	-4.15
2600	19.01	81.57	66.96	37.97	31.48	48.10	-4.04
2700	19.07	82.29	67.52	39.87	31.43	48.82	-3.95
2800	19.12	82.98	68.06	41.78	31.37	49.42	-3.86
2900	19.17	83.65	68.59	43.70	31.31	50.14	-3.78
3000	19.21	84.30	69.10	45.62	31.23	50.73	-3.70

Table 8. Estimated Uncertainties and Anharmonic Effects in Tabulated Thermodynamic Properties of CH₃ and CD₃.

Property	Uncertainty, (anharmonic effect) at		
	298 K	1500 K	3000 K
C_p° , cal K ⁻¹ mol ⁻¹	.01(.01)	.01(.36)	.01(.9)
S° , cal K ⁻¹ mol ⁻¹	.03(.00)	.04(.19)	.03(.6)
$-(G^\circ-H^\circ_{298})/T$ cal K ⁻¹ mol ⁻¹	.03(.00)	.04(.06)	.04(.23)
$H^\circ-H^\circ_{298}$, kcal mol ⁻¹	.15(.00)	.15(.20)	.02(1.1)
ΔH°_f , kcal mol ⁻¹	.00(.00)	.00(.20)	.15(1.1)
ΔG°_f , kcal mol ⁻¹	.15(.00)	.16(.09)	.19(.7)
$\log K_p$.11(.00)	.02(.01)	.01(.05)

Table 9. Ideal Gas Thermodynamic Properties of Acetylene-d₂ (C₂D₂).

T, K	cal K ⁻¹ mol ⁻¹			kcal mol ⁻¹			$\log K_p$
	C_p°	S°	$-(G^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH°_f	ΔG°_f	
0	0.00	0.00	INF	-2.59	52.86	52.86	INF
100	7.20	39.91	58.84	-1.89	52.88	51.62	-112.82
200	9.69	45.58	50.88	-1.06	52.85	50.39	-55.06
298	11.77	49.87	49.86	0.00	52.90	49.17	-36.06
300	11.80	49.95	49.86	0.02	52.91	49.15	-35.80
400	13.09	53.53	50.35	1.27	52.97	47.88	-26.16
500	14.01	56.55	51.29	2.63	52.98	46.61	-20.37
600	14.79	59.18	52.39	4.07	52.96	45.34	-16.51
700	15.48	61.51	53.53	5.59	52.92	44.07	-13.76
800	16.11	63.62	54.66	7.17	52.85	42.81	-11.69
900	16.66	65.55	55.77	8.90	52.78	41.55	-10.09
1000	17.15	67.33	56.83	10.50	52.71	40.31	-8.81
1100	17.57	68.98	57.86	12.23	52.64	39.07	-7.76
1200	17.94	70.53	58.86	14.01	52.57	37.95	-6.89
1300	18.25	71.98	59.81	15.82	52.50	36.62	-6.16
1400	18.53	73.34	60.73	17.66	52.42	35.40	-5.53
1500	18.76	74.63	61.61	19.52	52.35	34.20	-4.98
1600	18.97	75.84	62.46	21.41	52.27	33.10	-4.52
1700	19.15	77.00	63.29	23.31	52.20	31.90	-4.10
1800	19.30	78.10	64.08	25.24	52.12	30.69	-3.73
1900	19.44	79.15	64.84	27.17	52.05	29.49	-3.39
2000	19.56	80.15	65.58	29.12	51.98	28.23	-3.09
2100	19.67	81.10	66.30	31.08	51.91	27.07	-2.82
2200	19.76	82.02	66.99	33.06	51.83	25.96	-2.57
2300	19.85	82.90	67.67	35.04	51.75	24.66	-2.34
2400	19.92	83.75	68.32	37.02	51.67	23.45	-2.14
2500	19.99	84.56	68.95	39.02	51.59	22.32	-1.95
2600	20.05	85.35	69.57	41.02	51.50	21.12	-1.78
2700	20.10	86.10	70.17	43.03	51.40	20.01	-1.62
2800	20.15	86.84	70.75	45.04	51.30	18.82	-1.47
2900	20.20	87.54	71.32	47.06	51.20	17.71	-1.33
3000	20.24	88.23	71.87	49.08	51.08	16.52	-1.20

Table 10. Estimated Uncertainties and Anharmonic Effects in Tabulated Thermodynamic Properties of C_2D_2 .

Property	Uncertainty, (anharmonic effect) at		
	298K	1500K	3000K
C_p° , cal K^{-1} mol $^{-1}$.03(.04)	.01(.42)	.00(.91)
S° , cal K^{-1} mol $^{-1}$.03(.00)	.05(.30)	.06(.74)
$-(G^\circ-H^\circ_{298})/T$, cal K^{-1} mol $^{-1}$.03(.00)	.04(.11)	.05(.32)
$H^\circ-H^\circ_{298}$, kcal mol $^{-1}$.00(.00)	.02(.28)	.02(1.27)
ΔH°_f , kcal mol $^{-1}$.19(.00)	.19(.28)	.19(1.27)
ΔG°_f , kcal mol $^{-1}$.19(.00)	.21(.16)	.24(.96)
$\log K_p$.14(.00)	.03(.02)	.02(.07)

Table 11. Ideal Gas Thermodynamic Properties of Methane- d_4 (CD_4).

T, K	cal K^{-1} mol $^{-1}$			kcal mol $^{-1}$			$\log K_p$
	C_p°	S°	$-(G^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH°_f	ΔG°_f	
0	0.00	0.00	INF	-2.47	-19.22	-19.22	INF
100	7.85	29.44	55.20	-1.68	-19.75	-18.18	39.74
200	8.78	44.00	48.36	-0.87	-20.43	-16.36	17.87
298	9.63	47.53	47.53	-0.00	-21.09	-14.22	10.43
300	9.71	47.60	47.53	0.02	-21.10	-14.17	10.32
400	11.62	50.65	47.94	1.09	-21.68	-11.77	6.43
500	13.48	53.45	48.76	2.34	-22.14	-9.24	4.04
600	15.15	56.05	49.76	3.77	-22.50	-6.62	2.41
700	16.61	58.50	50.84	5.36	-22.76	-3.95	1.23
800	17.87	60.80	51.94	7.09	-22.94	-1.25	0.34
900	18.94	62.97	53.05	8.93	-23.05	1.46	-0.36
1000	19.84	65.02	54.14	10.87	-23.11	4.19	-0.92
1100	20.60	66.94	55.22	12.90	-23.14	6.92	-1.38
1200	21.24	68.76	56.27	14.99	-23.13	9.66	-1.76
1300	21.78	70.49	57.30	17.14	-23.10	12.39	-2.08
1400	22.23	72.12	58.30	19.34	-23.06	15.12	-2.36
1500	22.62	73.67	59.28	21.58	-23.00	17.86	-2.60
1600	22.95	75.14	60.22	23.86	-22.94	20.80	-2.84
1700	23.24	76.54	61.14	26.17	-22.87	23.52	-3.02
1800	23.49	77.87	62.03	28.51	-22.78	26.22	-3.18
1900	23.70	79.15	62.90	30.87	-22.70	28.91	-3.33
2000	23.89	80.37	63.74	33.25	-22.61	31.48	-3.44
2100	24.05	81.54	64.56	35.65	-22.52	34.23	-3.56
2200	24.20	82.66	65.36	38.06	-22.43	36.87	-3.66
2300	24.33	83.74	66.14	40.48	-22.34	39.53	-3.76
2400	24.44	84.78	66.89	42.92	-22.26	42.14	-3.84
2500	24.54	85.78	67.63	45.37	-22.18	44.91	-3.93
2600	24.63	86.74	68.34	47.83	-22.11	47.54	-4.00
2700	24.72	87.67	69.04	50.20	-22.04	50.32	-4.07
2800	24.79	88.57	69.72	52.77	-21.99	52.94	-4.13
2900	24.86	89.44	70.39	55.26	-21.95	55.72	-4.20
3000	24.92	90.29	71.04	57.74	-21.92	58.31	-4.25

Table 12. Estimated Uncertainties and Anharmonic Effects in Tabulated Thermodynamic Properties of CD₄.

Property	Uncertainty, (anharmonic effect) at		
	298K	1500K	3000K
C_p° , cal K ⁻¹ mol ⁻¹	.01(.01)	.01(.67)	.00(1.60)
S° , cal K ⁻¹ mol ⁻¹	.01(.00)	.01(.33)	.02(.63)
$-(G^\circ-H^\circ_{298})/T$, cal K ⁻¹ mol ⁻¹	.01(.00)	.02(.10)	.02(.40)
$H^\circ-H^\circ_{298}$, kcal mol ⁻¹	.00(.00)	.01(.35)	.02(2.07)
ΔH°_f , kcal mol ⁻¹	.10(.00)	.10(.35)	.10(2.07)
ΔG°_f , kcal mol ⁻¹	.10(.00)	.11(.15)	.12(1.20)
$\log K_p$.01(.00)	.02(.02)	.01(.09)

Table 13. Ideal Gas Thermodynamic Properties of Ethylene-d₄ (C₂D₄).

T, K	cal K ⁻¹ mol ⁻¹			kcal mol ⁻¹			$\log K_p$
	C_p°	S°	$-(G^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH°_f	ΔG°_f	
0	0.00	0.00	INF	-2.72	11.00	11.00	INF
100	7.99	44.91	64.17	-1.93	10.46	11.39	-24.90
200	9.51	50.78	56.13	-1.07	9.74	12.61	-13.78
298	12.40	55.09	55.09	-0.00	9.12	14.15	-10.38
300	12.46	55.18	55.09	0.02	9.11	14.18	-10.33
400	15.28	59.16	55.62	1.42	8.62	15.95	-8.72
500	17.67	62.83	56.70	3.07	8.23	17.83	-7.80
600	19.68	66.24	58.01	4.94	7.93	19.78	-7.21
700	21.39	69.40	59.41	6.99	7.72	21.78	-6.80
800	22.84	72.36	60.85	9.21	7.56	23.80	-6.50
900	24.05	75.12	62.28	11.55	7.46	25.83	-6.27
1000	25.07	77.71	63.70	14.01	7.41	27.87	-6.09
1100	25.92	80.14	65.08	16.56	7.40	29.92	-5.94
1200	26.64	82.42	66.43	19.19	7.41	31.97	-5.82
1300	27.24	84.58	67.75	21.88	7.43	34.02	-5.72
1400	27.76	86.62	69.02	24.63	7.46	36.06	-5.63
1500	28.19	88.55	70.26	27.43	7.51	38.12	-5.55
1600	28.56	90.38	71.46	30.27	7.56	40.38	-5.52
1700	28.88	92.12	72.63	33.14	7.62	42.42	-5.45
1800	29.16	93.78	73.76	36.05	7.69	44.43	-5.39
1900	29.40	95.36	74.85	38.97	7.76	46.44	-5.34
2000	29.61	96.88	75.92	41.92	7.84	48.33	-5.28
2100	29.80	98.33	76.95	44.89	7.92	50.40	-5.25
2200	29.96	99.72	77.95	47.88	7.99	52.36	-5.20
2300	30.10	101.05	78.93	50.89	8.07	54.34	-5.16
2400	30.23	102.34	79.88	53.90	8.13	56.28	-5.13
2500	30.35	103.57	80.80	56.93	8.19	58.37	-5.10
2600	30.45	104.76	81.70	59.97	8.24	60.32	-5.07
2700	30.54	105.91	82.57	63.02	8.29	62.43	-5.05
2800	30.62	107.03	83.43	66.08	8.33	64.37	-5.02
2900	30.70	108.10	84.26	69.14	8.35	66.48	-5.01
3000	30.77	109.14	85.07	72.22	8.36	68.40	-4.98

Table 14. Estimated Uncertainties and Anharmonic Effects in Tabulated Thermodynamic Properties of C_2D_4 .

Property	Uncertainty, (anharmonic effect) at		
	298K	1500K	3000K
C_p° , cal K^{-1} mol $^{-1}$.12(.01)	.02(.50)	.01(1.15)
S° , cal K^{-1} mol $^{-1}$.07(.00)	.18(.28)	.19(1.36)
$-(G^\circ-H^\circ_{298})/T$ cal K^{-1} mol $^{-1}$.07(.00)	.14(.09)	.16(.33)
$H^\circ-H^\circ_{298}$, kcal mol $^{-1}$.00(.00)	.07(.29)	.08(1.54)
ΔH°_f , kcal mol $^{-1}$.07(.00)	.10(.29)	.11(1.54)
ΔG°_f , kcal mol $^{-1}$.07(.00)	.22(.14)	.49(.99)
$\log K_p$.05(.00)	.03(.02)	.04(.07)

Table 15. Ideal Gas Thermodynamic Properties of Ethane (C_2H_6).

T, K	cal K^{-1} mol $^{-1}$			kcal mol $^{-1}$			$\log K_p$
	C_p°	S°	$-(G^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH°_f	ΔG°_f	
0	0.00	0.00	INF	-2.84	-16.31	-16.31	INF
100	8.54	43.92	64.24	-2.03	-17.80	-14.83	32.42
200	10.13	50.31	55.82	-1.10	-18.84	-11.50	12.56
298	12.54	54.75	54.75	-0.00	-20.04	-7.65	5.61
300	12.60	54.84	54.75	0.03	-20.06	-7.56	5.51
400	15.64	58.89	55.31	1.44	-21.23	-3.23	1.76
500	18.62	62.69	56.39	3.15	-22.25	1.40	-0.61
600	21.31	66.32	57.74	5.15	-23.10	6.21	-2.26
700	23.69	69.79	59.22	7.40	-23.81	11.16	-3.48
800	25.79	73.10	60.75	9.87	-24.37	16.19	-4.42
900	27.65	76.24	62.30	12.55	-24.81	21.29	-5.17
1000	29.29	79.24	63.85	15.40	-25.12	26.43	-5.78
1100	30.73	82.10	65.38	18.39	-25.35	31.59	-6.28
1200	31.98	84.83	66.89	21.53	-25.49	36.78	-6.70
1300	33.08	87.43	68.37	24.78	-25.56	41.97	-7.06
1400	34.03	89.92	69.82	28.15	-25.58	47.17	-7.36
1500	34.87	92.30	71.24	31.59	-25.55	52.37	-7.63
1600	35.60	94.57	72.62	35.12	-25.50	57.55	-7.86
1700	36.25	96.75	73.98	38.71	-25.42	62.75	-8.07
1800	36.82	98.84	75.30	42.37	-25.31	67.93	-8.25
1900	37.32	100.84	76.59	46.08	-25.19	73.08	-8.41
2000	37.76	102.77	77.85	49.83	-25.05	78.28	-8.55
2100	38.16	104.62	79.09	53.63	-24.90	83.45	-8.68
2200	38.51	106.40	80.29	57.46	-24.74	88.60	-8.80
2300	38.82	108.12	81.46	61.33	-24.57	93.75	-8.91
2400	39.10	109.78	82.60	65.23	-24.40	98.90	-9.01
2500	39.36	111.38	83.72	69.15	-24.24	104.02	-9.09
2600	39.59	112.93	84.82	73.10	-24.07	109.16	-9.18
2700	39.79	114.43	85.89	77.07	-23.90	114.27	-9.25
2800	39.98	115.88	86.93	81.06	-23.73	119.39	-9.32
2900	40.15	117.29	87.95	85.06	-23.57	124.50	-9.38
3000	40.31	118.65	88.96	89.09	-23.41	129.60	-9.44

Table 16. Ideal Gas Thermodynamic Properties of Ethane-d₆ (C₂D₆).

T, K	cal K ⁻¹ mol ⁻¹			kcal mol ⁻¹			Log K _p
	C _p ^o	S ^o	-(G ^o -H ^o ₂₉₈)/T	H ^o -H ^o ₂₉₈	ΔH ^o _f	ΔG ^o _f	
0	0.00	0.00	INF	-3.16	-22.17	-22.17	INF
100	9.07	46.17	69.44	-2.33	-23.34	-19.84	43.35
200	11.57	53.12	59.67	-1.31	-24.60	-15.83	17.30
298	15.43	58.43	58.41	0.01	-25.66	-11.31	8.29
300	15.52	58.54	58.41	0.04	-25.67	-11.21	8.17
400	19.53	63.56	59.07	1.79	-26.50	-6.26	3.42
500	22.99	68.30	60.45	3.92	-27.11	-1.12	0.49
600	25.92	72.76	62.14	6.37	-27.53	4.12	-1.50
700	28.38	76.94	63.95	9.09	-27.80	9.42	-2.94
800	30.44	80.87	65.83	12.03	-27.95	14.74	-4.03
900	32.16	84.56	67.71	15.17	-28.00	20.08	-4.88
1000	33.58	88.02	69.57	18.45	-27.97	25.42	-5.56
1100	34.77	91.28	71.40	21.87	-27.88	30.75	-6.11
1200	35.76	94.35	73.18	25.39	-27.75	36.08	-6.57
1300	36.59	97.24	74.92	29.02	-27.58	41.39	-6.96
1400	37.29	99.98	76.61	32.72	-27.40	46.70	-7.29
1500	37.88	102.50	78.26	36.40	-27.21	52.00	-7.58
1600	38.39	105.04	79.86	40.29	-27.00	57.61	-7.87
1700	38.82	107.38	81.41	44.15	-26.78	62.88	-8.08
1800	39.20	109.61	82.91	48.06	-26.55	68.10	-8.27
1900	39.52	111.74	84.37	51.99	-26.31	73.31	-8.43
2000	39.81	113.77	85.79	55.96	-26.07	78.33	-8.56
2100	40.06	115.72	87.17	59.95	-25.83	83.62	-8.70
2200	40.27	117.59	88.51	63.97	-25.59	88.73	-8.81
2300	40.47	119.38	89.81	68.01	-25.36	93.87	-8.92
2400	40.64	121.11	91.08	72.07	-25.13	98.95	-9.01
2500	40.79	122.77	92.32	76.14	-24.92	104.24	-9.11
2600	40.93	124.37	93.52	80.22	-24.71	109.32	-9.19
2700	41.06	125.92	94.69	84.32	-24.52	114.63	-9.28
2800	41.17	127.41	95.83	88.43	-24.34	119.69	-9.34
2900	41.27	128.86	96.95	92.55	-24.18	124.98	-9.42
3000	41.36	130.26	98.03	96.69	-24.04	130.00	-9.47

Table 17. Estimated Uncertainties and Anharmonic Effects in Tabulated Thermodynamic Properties of C₂H₆ and C₂D₆.

Property	Uncertainty, (anharmonic effect) at		
	298K	1500K	3000K
C _p ^o , cal K ⁻¹ mol ⁻¹	.03(.02)	.02(1.09)	.01(2.60)
S ^o , cal K ⁻¹ mol ⁻¹	.04(.00)	.07(.58)	.08(1.81)
-(G ^o -H ^o ₂₉₈)/T, cal K ⁻¹ mol ⁻¹	.02(.00)	.05(.18)	.06(.68)
H ^o -H ^o ₂₉₈ , kcal mol ⁻¹	.00(.01)	.04(.60)	.06(3.34)
ΔH ^o _f , kcal mol ⁻¹	.06(.00)	.07(.60)	.08(3.39)
ΔG ^o _f , kcal mol ⁻¹	.06(.00)	.09(.27)	.19(2.04)
log K _p	.44(.00)	.13(.04)	.13(.15)

Table 18. Ideal Gas Thermodynamic Properties of Azomethane ($\text{CH}_3\text{N}_2\text{CH}_3$).

T, K	cal K ⁻¹ mol ⁻¹			kcal mol ⁻¹			
	C _P ^o	S ^o	-(G ^o -H ^o ₂₉₈)/T	H ^o -H ^o ₂₉₈	ΔH _f ^o	ΔG _f ^o	Log K _P
0	0.00	0.00	INF	-3.95	40.24	40.24	INF
100	11.55	53.24	83.56	-3.03	38.16	44.01	-96.18
200	15.48	62.55	70.88	-1.67	36.86	50.35	-55.02
298	18.64	69.23	69.23	-0.00	35.54	57.26	-41.99
300	18.71	69.36	69.24	0.04	35.52	57.40	-41.82
400	22.44	75.24	70.02	2.09	34.30	64.89	-35.45
500	26.12	80.65	71.62	4.52	33.29	72.65	-31.76
600	29.42	85.71	73.55	7.30	32.50	80.60	-29.36
700	32.31	90.47	75.63	10.38	31.90	88.66	-27.68
800	34.81	94.95	77.77	13.75	31.49	96.80	-26.45
900	36.98	99.18	79.91	17.34	31.21	104.99	-25.49
1000	38.86	103.18	82.04	21.14	31.07	113.20	-24.74
1100	40.49	106.96	84.13	25.11	31.03	121.41	-24.12
1200	41.91	110.54	86.18	29.23	31.08	129.63	-23.61
1300	43.13	113.94	88.19	33.49	31.19	137.84	-23.17
1400	44.20	117.18	90.14	37.86	31.37	146.04	-22.80
1500	45.13	120.26	92.05	42.33	31.58	154.23	-22.47
1600	45.94	123.20	93.90	46.88	31.82	162.39	-22.18
1700	46.64	126.01	95.71	51.51	32.10	170.55	-21.93
1800	47.27	128.69	97.47	56.21	32.40	178.68	-21.70
1900	47.81	131.26	99.18	60.96	32.72	186.77	-21.48
2000	48.30	133.73	100.84	65.77	33.06	194.91	-21.30
2100	48.72	136.10	102.47	70.63	33.40	202.99	-21.13
2200	49.11	138.37	104.05	75.52	33.75	211.06	-20.97
2300	49.45	140.56	105.59	80.44	34.10	219.11	-20.82
2400	49.75	142.67	107.09	85.40	34.46	227.15	-20.68
2500	50.03	144.71	108.56	90.38	34.81	235.16	-20.56
2600	50.28	146.68	109.99	95.39	35.17	243.17	-20.44
2700	50.50	148.58	111.38	100.43	35.52	251.16	-20.33
2800	50.71	150.42	112.74	105.49	35.88	259.13	-20.23
2900	50.89	152.20	114.07	110.57	36.23	267.11	-20.13
3000	51.06	153.93	115.37	115.66	36.58	275.05	-20.04

Table 19. Ideal Gas Thermodynamic Properties of Azomethane-d₆ (CD₃N₂CD₃).

T, K	cal K ⁻¹ mol ⁻¹			kcal mol ⁻¹			Log K _P
	C _P ^o	S ^o	-(G ^o -H ^o ₂₉₈)/T	H ^o -H ^o ₂₉₈	ΔH _f ^o	ΔG _f ^o	
0	0.00	0.00	INF	-4.34	32.88	32.88	INF
100	12.56	55.36	89.05	-3.37	31.16	37.56	-82.09
200	17.02	65.38	74.83	-1.89	29.67	44.58	-48.71
298	21.63	73.01	73.01	-0.00	28.50	52.14	-38.24
300	21.73	73.15	73.01	0.04	28.48	52.30	-38.10
400	26.45	80.06	73.93	2.45	27.61	60.38	-32.99
500	30.60	86.42	75.80	5.31	27.02	68.65	-30.00
600	34.12	92.32	78.07	8.55	26.68	77.01	-28.05
700	37.06	97.80	80.51	12.10	26.52	85.40	-26.66
800	39.49	102.92	82.99	15.94	26.52	93.82	-25.63
900	41.50	107.69	85.47	20.00	26.65	102.22	-24.82
1000	43.17	112.15	87.91	24.24	26.85	110.61	-24.17
1100	44.55	116.33	90.31	28.63	27.13	118.98	-23.64
1200	45.69	120.26	92.64	33.14	27.45	127.32	-23.19
1300	46.65	123.96	94.91	37.76	27.80	135.63	-22.80
1400	47.46	127.45	97.11	42.47	28.17	143.92	-22.47
1500	48.14	130.74	99.24	47.25	28.56	152.19	-22.17
1600	48.72	133.87	101.31	52.10	28.95	160.76	-21.96
1700	49.22	136.84	103.31	56.99	29.36	168.96	-21.72
1800	49.65	139.66	105.25	61.94	29.78	177.11	-21.50
1900	50.02	142.36	107.14	66.92	30.22	185.25	-21.31
2000	50.34	144.93	108.96	71.94	30.65	193.18	-21.11
2100	50.62	147.40	110.73	76.99	31.09	201.36	-20.96
2200	50.87	149.76	112.45	82.07	31.52	209.37	-20.80
2300	51.09	152.02	114.13	87.16	31.94	217.39	-20.66
2400	51.29	154.20	115.75	92.28	32.36	225.34	-20.52
2500	51.47	156.30	117.33	97.41	32.76	233.50	-20.41
2600	51.62	158.32	118.87	102.56	33.15	241.44	-20.29
2700	51.76	160.27	120.37	107.73	33.53	249.59	-20.20
2800	51.89	162.15	121.83	112.91	33.90	257.50	-20.10
2900	52.00	163.97	123.25	118.10	34.25	265.63	-20.02
3000	52.11	165.74	124.64	123.30	34.58	273.48	-19.92

Table 20. Estimated Uncertainties and Anharmonic Effects in Tabulated Thermodynamic Properties of CH₃N₂CH₃ and CD₃N₂CD₃.

Property	Uncertainty, (anharmonic effect) at		
	298K	1500K	3000K
C _P ^o , cal K ⁻¹ mol ⁻¹	.29(.10)	.08(1.45)	.02(3.23)
S ^o , cal K ⁻¹ mol ⁻¹	.46(.04)	.15(.92)	.11(2.48)
-(G ^o -H ^o ₂₉₈)/T, cal K ⁻¹ mol ⁻¹	.46(.01)	.23(.34)	.19(1.01)
H ^o -H ^o ₂₉₈ , kcal mol ⁻¹	.00(.01)	.25(.88)	.33(4.40)
ΔH _f ^o , kcal mol ⁻¹	1.23(.01)	1.26(.88)	1.27(4.41)
ΔG _f ^o , kcal mol ⁻¹	1.24(.00)	1.27(.50)	1.34(3.04)
log K _P	.91(.00)	.19(.08)	.10(.22)

4. Discussion

The computer program developed in the present study was general in nature and can be used for obtaining thermodynamic functions, using spectroscopic and other molecular data, of any gaseous molecule.

The accuracy of the tables is limited mainly by the assumption of the RRHO approximation, since the molecular dimensions and the vibrational spacings ($v = 0$ to $v = 1$) are quite well known. In table 5 we have compared harmonic oscillator and anharmonic oscillator calculations for C_2H_2 , the former being our calculations and the latter those of the JANAF tables. As expected, the differences are small at low temperatures, but increase at higher temperatures, exceeding 2% for the enthalpy at 3000 K. Fortunately, there is some cancellation of errors in obtaining the free energy functions and equilibrium constant of formation. In combining tabulated values to obtain thermodynamic data for reactions, it would clearly be best to use data obtained via the same set of assumptions, in order to get the greatest possible cancellation of errors.

The tables for azomethane and azomethane- d_6 are believed to be the first to present the thermodynamic properties of these compounds. Chiltz et al. [57] have calculated the functions $(H_T^\circ - H_0^\circ)/RT$, and $G_T^\circ - H_0^\circ/RT$ as a temperature series with respectively 5 and 6 terms. These are in disagreement with our results because their calculations were made before the data of references [34], [32], [14], and [53] were available, and their estimate of $51.2 \text{ kcal mol}^{-1}$ for $\Delta H_f^\circ(298.15 \text{ K})$ azomethane is much higher than the experimental value.

5. Acknowledgments

Calculations for the azomethanes were supported by the U.S. National Science Foundation under Grant ENG-7704115. The other calculations were supported by the U.S. Department of Energy under Contract DE-AC02-76ER02944. The authors wish to acknowledge very helpful discussions with Dr. Alexander Burcat of Technion, Israel Institute of Technology, Haifa, Israel, and with Dr. Graham L. Pratt of The University of Sussex, Brighton, U.K.

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