

# NIST-JANAF Thermochemical Tables. II. Three Molecules Related to Atmospheric Chemistry: $\text{HNO}_3$ , $\text{H}_2\text{SO}_4$ , and $\text{H}_2\text{O}_2$

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# NIST-JANAF Thermochemical Tables. II. Three Molecules Related to Atmospheric Chemistry: HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, and H<sub>2</sub>O<sub>2</sub>

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The structural, spectroscopic, and thermochemical properties of three polyatomic molecules with internal rotation—HNO<sub>3</sub>(g), H<sub>2</sub>SO<sub>4</sub>(g), and H<sub>2</sub>O<sub>2</sub>(g)—have been reviewed. Three revised ideal gas thermodynamic tables result from this critical examination. The revisions involved the consideration of new spectroscopic information and the use of theoretical results to model the internal rotation in the H<sub>2</sub>SO<sub>4</sub> molecule. Compared to previous calculations, the entropies at 298.15 K are unchanged for HNO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub>, but the high temperature values ( $T > 4000$  K) are significantly different. As for H<sub>2</sub>SO<sub>4</sub>, its thermodynamic functions differ significantly from values calculated earlier. © 2003 American Institute of Physics. [DOI: 10.1063/1.1547435]

Key words: critical evaluation; hydrogen peroxide; internal rotation; nitric acid; molecular structure; spectroscopic properties; sulfuric acid; thermodynamic properties.

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## 1. Introduction

The interest in the properties of gaseous HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, and H<sub>2</sub>O<sub>2</sub> is due to their role in the chemistry of the upper and lower stratosphere. These molecules are present in significant abundance in the earth's atmosphere and are in-

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volved in the formation of various atmospheric particles. These particles play a key role in atmospheric chemical reactions which influence climate and ozone depletion. The increased interest in these reactions and the field of atmospheric chemistry, in general, has stimulated the present re-evaluation of the thermodynamic properties for  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$ , and  $\text{H}_2\text{O}_2$ .

The thermodynamic properties of gaseous  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$ , and  $\text{H}_2\text{O}_2$  have been calculated earlier<sup>1,2</sup> (see also the references quoted within Chase<sup>1</sup> and Gurvich *et al.*<sup>2</sup>). In both cases, the statistical thermodynamics calculations were based on molecular constants determined prior to the 1980s. Since that time, a number of experimental and theoretical investigations have been performed in which the data on molecular structure, vibrational spectra, and internal rotation were substantially improved.

From the microwave data on eight isotopomers of  $\text{HNO}_3$ , the zero-point average structure has been derived.<sup>3</sup> High-resolution infrared, diode-laser, and Fourier transform spectroscopic investigations<sup>4–14</sup> have enabled the precise values for all the fundamental frequencies of  $\text{HNO}_3$  to be determined. In previous statistical calculations, the internal rotation in the  $\text{HNO}_3$  molecule was ignored or approximated by the potential barrier estimated from the torsional mode. The internal rotation can now be treated accurately, using the potential for the torsional motion of the O–H bond as determined from a recent analysis of the infrared spectrum of  $\text{HNO}_3$ .<sup>11</sup>

The thermodynamic properties of  $\text{H}_2\text{SO}_4(\text{g})$  were calculated earlier assuming this molecule had  $C_{2v}$  symmetry. However, the results of microwave spectra investigation<sup>15</sup> of four isotopic species of  $\text{H}_2\text{SO}_4$  indicate that the overall symmetry is not  $C_{2v}$  but  $C_2$ . This conclusion is of great importance for the thermodynamic function calculation. In comparison to  $C_{2v}$  symmetry, the  $C_2$  symmetry causes a  $R \ln 2$  contribution to be added to the entropy and Gibbs energy function because of the two optically isomeric forms present in the latter case. In addition, it now became possible to estimate the potential function for internal rotation with reasonable accuracy via high-level theoretical calculations.

The thermodynamic properties of hydrogen peroxide were calculated earlier using a fairly well defined structure with experimentally determined vibrational frequencies, including a torsional frequency. Early tabulations of the thermodynamic properties of hydrogen peroxide were generated by Giguere and co-workers.<sup>16</sup> A much improved statistical calculation is possible today, using detailed rotational–vibrational constants, anharmonicity constants, and a summation over the torsional energies (experimentally based below  $1000 \text{ cm}^{-1}$  and calculated for higher energies).

In the present study, the thermodynamic properties of gaseous nitric acid, sulfuric acid, and hydrogen peroxide were revised based on new data for the molecular constants of these molecules. The calculations were performed by standard statistical thermodynamics methods in which a rigid-rotor harmonic-oscillator model was modified for internal rotation. The statistical formulas for thermodynamic func-

tions are discussed in several textbooks, review articles, and reference books.<sup>1,2,17–20</sup> Molecular and spectroscopic constants needed for the calculations were selected from the literature or estimated from theoretical calculations (torsional potential function for  $\text{H}_2\text{SO}_4$  molecule).

To evaluate the internal rotational contributions to the thermodynamic functions, the internal rotational partition function was formed by the summation of internal rotational energy levels for each rotor. These energy levels were obtained by the diagonalization of the one dimensional Hamiltonian using the potential function of the general type

$$V(\varphi) = V_0 + \sum_n V_n \cos n\varphi + \sum_n V'_n \sin n\varphi, \quad (1)$$

where  $\varphi$  is the internal rotational angle. The method for generating the internal rotation energy levels has been described by Lewis *et al.*<sup>21,22</sup> The constant required to generate the internal rotational energy levels for each rotor is the internal rotational constant ( $F$ ) or reduced moment of inertia of the rotating group ( $I_r$ ). Where available, the  $V_n$  terms and internal rotational constant were taken from spectroscopic data. If the  $F$  value was unavailable, it was calculated from the reduced moment of inertia with the relationship

$$F = h/8\pi^2 c I_r. \quad (2)$$

Sources of uncertainties in the calculated thermodynamic functions arise from uncertainties in the molecular constants used in the calculations as well as deviations from the rigid-rotor harmonic-oscillator model. In this work uncertainties in the thermodynamic functions were estimated by the procedure developed by Gurvich *et al.*<sup>2</sup> This approach predicts the uncertainties in the thermodynamic functions  $S^\circ(T)$  and  $C_p^\circ(T)$  for simple molecules reasonably well. The total estimated uncertainties in the thermodynamic functions  $S^\circ(T)$  and  $C_p^\circ(T)$  in the range between 298.15 and 6000 K are given in the discussions for each molecule.

Based on the selected values of the molecular constants, the ideal gas thermodynamic functions, heat capacity  $C_p^\circ(T)$ , entropy  $S^\circ(T)$ , enthalpy [ $H^\circ(T) - H^\circ(298.15 \text{ K})$ ], and the Gibbs energy function  $\{[G^\circ(T) - H^\circ(298.15 \text{ K})]/T\}$ , have been calculated for selected temperatures up to 6000 K at the standard pressure  $p^\circ = 0.1 \text{ MPa}$ . The enthalpy of formation values  $\Delta_f H^\circ(298.15 \text{ K})$  were selected by analyzing experimental studies which may result in an enthalpy of formation determination. Accepted  $\Delta_f H^\circ(298.15 \text{ K})$  value and the calculated ideal gas values of the enthalpy difference [ $H^\circ(T) - H^\circ(298.15 \text{ K})$ ] and entropy  $S^\circ(T)$  were combined with values of the enthalpies and entropies of the elements in their reference states to derive values of enthalpy of formation  $\Delta_f H^\circ$ , Gibbs energy of formation  $\Delta_f G^\circ$ , and the logarithm of the equilibrium constant of formation  $\log K_f^\circ$  of the substances as a function of temperature over the range of 0–6000 K. Values used here of [ $H^\circ(T) - H^\circ(298.15 \text{ K})$ ] and  $S^\circ(T)$  for the elements in their reference states  $\text{H}_2(\text{g})$ ,  $\text{O}_2(\text{g})$ ,  $\text{N}_2(\text{g})$ ,  $\text{S}(\text{cr, liq}, 717 \text{ K} < T)$ ,  $\text{S}_2(\text{g}, T > 717 \text{ K})$  are those given JANAF Thermochemical Tables<sup>1</sup> (all elements except for sulfur) and TRC Thermodynamic Tables<sup>23</sup> (sulfur).

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2. Nitric Acid, HONO<sub>2</sub>Nitric acid (HNO<sub>3</sub>)

Ideal gas

 $M_r = 63.0128$  $S^\circ(298.15\text{ K}) = 266.8 \pm 0.7\text{ J K}^{-1}\text{ mol}^{-1}$  $\Delta_f H^\circ(0\text{ K}) = -124.6 \pm 0.5\text{ kJ mol}^{-1}$  $\Delta_f H^\circ(298.15\text{ K}) = -134.3 \pm 0.5\text{ kJ mol}^{-1}$ 

Molecular constants

Point group:  $C_s$ Symmetry number:  $\sigma = 1$ Ground electronic state:  $\tilde{X}^1A'$ Energy:  $\epsilon_X = 0\text{ cm}^{-1}$ Quantum weight:  $g_X = 1$ Vibrational frequencies,  $\nu_i$ , and degeneracies,  $g_i$ 

Symmetry	$\nu_i, \text{cm}^{-1}$	$g_i$	Symmetry	$\nu_i, \text{cm}^{-1}$	$g_i$
$A'$	$\nu_1$	3550.00	$A''$	$\nu_6$	646.83
	$\nu_2$	1709.57		$\nu_7$	580.30
	$\nu_3$	1325.74		$\nu_8$	763.15
	$\nu_4$	1303.52		$\nu_9$	... <sup>a</sup>
	$\nu_5$	879.11			

<sup>a</sup>Instead of a torsional mode  $\nu_9 = 458.23\text{ cm}^{-1}$ , the contributions due to the internal rotation of OH group around the N–O bond were calculated from the potential:  $V(\varphi) = V_0 + V_1 \cos 2\varphi$ , where  $\varphi$  is the torsional angle,  $V_0 = 1134.4\text{ cm}^{-1}$ ,  $V_1 = -1369.2\text{ cm}^{-1}$ .

OH top: Reduced moment of inertia,  $I_r = 0.1329 \times 10^{-39}\text{ g cm}^2$ , Symmetry number,  $\sigma_m = 2$ 

Geometry

 $r(\text{O–H}) = 0.941 \pm 0.003\text{ \AA}$  $\angle \text{H–O–N} = 102.6 \pm 0.3^\circ$  $r(\text{N–OH}) = 1.410 \pm 0.002\text{ \AA}$  $\angle \text{O–N–O}_{cis} = 115.7 \pm 0.2^\circ$  $r(\text{N–O})_{cis} = 1.213 \pm 0.002\text{ \AA}$  $\angle \text{O–N–O}_{trans} = 114.1 \pm 0.2^\circ$  $r(\text{N–O})_{trans} = 1.198 \pm 0.002\text{ \AA}$ Rotational constants in  $\text{cm}^{-1}$ : $A_0 = 0.433\,999\,9$      $B_0 = 0.403\,608\,9$      $C_0 = 0.208\,832\,7$ Product of moments of inertia:  $I_A I_B I_C = 599.665 \times 10^{-117}\text{ g}^3\text{ cm}^6$ 

## 2.1. Enthalpy of Formation

The enthalpy of formation of nitric acid was determined from data on equilibria involving HNO<sub>3</sub>.<sup>1–8</sup> The JANAF Thermochemical Tables,<sup>9</sup> and the compilation of Gurvich *et al.*<sup>10</sup> provide an exhaustive analysis of these experimental data, resulting in the values from  $-129.7$  to  $-136.7\text{ kJ mol}^{-1}$  for  $\Delta_f H^\circ(\text{HNO}_3, g, 298.15\text{ K})$ . The value adopted here,  $-134.3 \pm 0.5\text{ kJ mol}^{-1}$ , is the average of experimental values. This value is in good agreement with the results of theoretical calculations based on *ab initio* calculation and the isodesmic reaction procedure,<sup>11</sup>  $-133.3\text{ kJ mol}^{-1}$ . In the present study, a similar value of  $-132.7\text{ kJ mol}^{-1}$  was calculated by the composite G3 method using the GAUSSIAN 98 system of programs.<sup>12</sup>

## 2.2. Heat Capacity and Entropy

The planar structure of  $C_s$  symmetry was determined for nitric acid in its  $\tilde{X}^1A'$  ground electronic state from microwave investigations.<sup>13–15</sup> The structural parameters give

above are the  $r_z$  parameters derived by Cox *et al.*<sup>13</sup> from a microwave study of eight isotopomers. These parameters agree with previous experimental data<sup>14,15</sup> and theoretical calculations.<sup>16–18</sup> The product of the principal moments of inertia was calculated using the ground state rotational constants determined from the microwave spectrum<sup>13</sup> of HNO<sub>3</sub>. These constants agree well with the results of earlier microwave studies.<sup>17,19–23</sup>

Vibrational spectra of HNO<sub>3</sub> have been analyzed at high resolution by infrared, diode-laser, and Fourier transform spectroscopy.<sup>24–35</sup> These investigations have led to precise line positions for normal modes of HNO<sub>3</sub> which were adopted in this work, namely:

Bands	Reference
$\nu_1$	24
$\nu_2$	25, 29
$\nu_3$ and $\nu_4$	28
$\nu_5$	26, 30, 31
$\nu_6$	27
$\nu_7$ and $\nu_8$	27, 33, and
$\nu_9$	34.



Experimental assignments of vibrational frequencies were confirmed by normal coordinate analyses<sup>36–38</sup> and *ab initio* calculations.<sup>16,17,39</sup>

The  $\nu_9$  vibrational mode of HNO<sub>3</sub> corresponds to the torsional motion of the O–H bond relative to the N–O bond. The internal rotational potential for nitric acid was determined from analysis of torsional region of gas phase infrared spectrum.<sup>32,40</sup> The torsional potential, adopted in this work, was obtained by Perrin *et al.*<sup>32</sup> by accurate description of the torsional splittings using Fourier transform spectra. The barrier to internal rotation, given by  $2 \times |V_1| = 2738 \pm 10 \text{ cm}^{-1}$ , is somewhat higher than that determined from previous analysis<sup>40</sup> ( $2432 \text{ cm}^{-1}$ ). Close estimates for the torsional barrier were obtained from theoretical calculations.<sup>41–43</sup> The reduced moment of inertia, used in this work, corresponds to a rotational constant,<sup>32</sup>  $F = 21.064 \pm 0.080 \text{ cm}^{-1}$ .

According to the experimental and theoretical data,<sup>44,45</sup> the excited electronic states of HNO<sub>3</sub> lie above  $30\,000 \text{ cm}^{-1}$ . These excited electronic states were not taken into account in the present calculation of thermodynamic functions.

The uncertainties in the calculated thermodynamic functions (see Table 1) are estimated to be 1, 2, 3, and  $4 \text{ J K}^{-1} \text{ mol}^{-1}$  for  $C_p^\circ(T)$  at 298.15, 1000, 3000, and 6000 K and 0.7, 2.5, 3, and  $5 \text{ J K}^{-1} \text{ mol}^{-1}$  for  $S^\circ(T)$  at 298.15, 1000, 3000, and 6000 K, respectively.

The calculated entropy value at 298.15 K ( $266.8 \text{ J K}^{-1} \text{ mol}^{-1}$ ) is in close agreement with the value of  $S^\circ(298.15 \text{ K}) = 266.2 \text{ J K}^{-1} \text{ mol}^{-1}$  obtained from calorimetric data.<sup>4</sup> The thermodynamic properties of nitric acid were calculated earlier (see Gurvich *et al.*<sup>10</sup> and references within). The discrepancies with results of Gurvich *et al.*<sup>10</sup> do not exceed  $0.7 \text{ J K}^{-1} \text{ mol}^{-1}$  for  $S^\circ(T)$  and  $C_p^\circ(T)$ . Because of differences in molecular constants used and consideration of internal rotation as a harmonic oscillation ( $\nu_9 = 465 \text{ cm}^{-1}$ ),  $S^\circ(T)$  and  $C_p^\circ(T)$  values given in JANAF Thermochemical Tables<sup>9</sup> are different from those obtained in this work up to 2.0 and  $3.8 \text{ J K}^{-1} \text{ mol}^{-1}$ , respectively.

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TABLE 1. Ideal gas thermochemical properties of nitric acid  $\text{HNO}_3(\text{g})$  at standard state pressure,  $p^\circ = 0.1 \text{ MPa}$  ( $T_r = 298.15 \text{ K}$ )

$T$ (K)	$C_p^\circ$ ( $\text{J K}^{-1} \text{ mol}^{-1}$ )	$S^\circ$ ( $\text{J K}^{-1} \text{ mol}^{-1}$ )	$-[G^\circ - H^\circ(T_r)]/T$ ( $\text{J K}^{-1} \text{ mol}^{-1}$ )	$H^\circ - H^\circ(T_r)$ ( $\text{kJ mol}^{-1}$ )	$\Delta_f H^\circ$ ( $\text{kJ mol}^{-1}$ )	$\Delta_f G^\circ$ ( $\text{kJ mol}^{-1}$ )	$\log K_f^\circ$
0	0.000	0.000	$\infty$	-11.866	-124.572	-124.572	$\infty$
25	33.258	175.597	616.987	-11.035	-125.450	-122.671	256.304
50	33.261	198.650	402.716	-10.203	-126.490	-119.505	124.845
75	33.377	212.148	337.094	-9.371	-127.555	-115.779	80.635
100	33.979	221.817	307.120	-8.530	-128.544	-111.703	58.347
150	37.385	236.144	281.197	-6.758	-130.356	-102.882	35.826
180	40.481	243.225	274.288	-5.591	-131.337	-97.293	28.233
190	41.605	245.444	272.712	-5.181	-131.644	-95.394	26.225
200	42.756	247.607	271.403	-4.759	-131.942	-93.478	24.414
210	43.924	249.722	270.320	-4.326	-132.229	-91.548	22.771
220	45.101	251.792	269.431	-3.881	-132.505	-89.604	21.274
230	46.281	253.823	268.708	-3.424	-132.770	-87.648	19.905
240	47.459	255.818	268.130	-2.955	-133.025	-85.680	18.648
250	48.631	257.779	267.677	-2.475	-133.270	-83.703	17.488
260	49.793	259.709	267.333	-1.982	-133.504	-81.715	16.417
270	50.942	261.610	267.086	-1.479	-133.727	-79.719	15.422
280	52.076	263.483	266.924	-0.964	-133.940	-77.715	14.498
290	53.194	265.330	266.837	-0.437	-134.142	-75.703	13.635
298.15	54.092	266.816	266.816	0.000	-134.300	-74.059	12.975
300	54.294	267.152	266.818	0.100	-134.335	-73.685	12.830
350	59.507	275.919	267.498	2.947	-135.156	-63.509	9.478
400	64.210	284.178	269.072	6.042	-135.761	-53.230	6.951
450	68.405	291.988	271.188	9.360	-136.182	-42.886	4.978
500	72.122	299.391	273.641	12.875	-136.449	-32.504	3.396
600	78.280	313.109	279.095	20.408	-136.610	-11.694	1.018
700	83.033	325.549	284.857	28.484	-136.407	9.113	-0.680
800	86.706	336.886	290.663	36.979	-135.948	29.874	-1.951
900	89.567	347.271	296.384	45.798	-135.313	50.564	-2.935
1000	91.818	356.829	301.957	54.872	-134.554	71.177	-3.718
1100	93.608	365.667	307.352	64.147	-133.711	91.710	-4.355
1200	95.049	373.876	312.558	73.582	-132.812	112.164	-4.882
1300	96.221	381.532	317.572	83.148	-131.879	132.542	-5.326
1400	97.184	388.699	322.400	92.819	-130.925	152.847	-5.703
1500	97.984	395.432	327.046	102.579	-129.967	173.082	-6.027
1600	98.654	401.778	331.521	112.412	-129.010	193.253	-6.309
1700	99.220	407.776	335.832	122.306	-128.063	213.364	-6.556
1800	99.701	413.462	339.988	132.253	-127.130	233.423	-6.774
1900	100.115	418.864	343.998	142.244	-126.220	253.429	-6.967
2000	100.471	424.008	347.871	152.274	-125.333	273.387	-7.140
2100	100.781	428.918	351.614	162.337	-124.474	293.302	-7.295
2200	101.052	433.612	355.236	172.429	-123.643	313.176	-7.436
2300	101.290	438.110	358.742	182.546	-122.845	333.012	-7.563
2400	101.499	442.425	362.139	192.686	-122.078	352.817	-7.679
2500	101.686	446.572	365.434	202.845	-121.344	372.587	-7.785
2600	101.852	450.564	368.632	213.022	-120.643	392.333	-7.882
2700	102.000	454.411	371.738	223.215	-119.976	412.048	-7.971
2800	102.133	458.123	374.758	233.422	-119.343	431.742	-8.054
2900	102.253	461.709	377.694	243.641	-118.742	451.415	-8.131
3000	102.362	465.177	380.553	253.872	-118.175	471.064	-8.202
3100	102.460	468.535	383.337	264.113	-117.641	490.695	-8.268
3200	102.549	471.789	386.051	274.364	-117.139	510.309	-8.330
3300	102.631	474.946	388.697	284.623	-116.667	529.912	-8.388
3400	102.706	478.011	391.279	294.890	-116.227	549.497	-8.442
3500	102.774	480.990	393.800	305.164	-115.814	569.073	-8.493

TABLE 1. Ideal gas thermochemical properties of nitric acid  $\text{HNO}_3(\text{g})$  at standard state pressure,  $p^\circ = 0.1 \text{ MPa}$  ( $T_r = 298.15 \text{ K}$ )—Continued

$T$ (K)	$C_p^\circ$ ( $\text{J K}^{-1} \text{ mol}^{-1}$ )	$S^\circ$ ( $\text{J K}^{-1} \text{ mol}^{-1}$ )	$-[G^\circ - H^\circ(T_r)]/T$ ( $\text{J K}^{-1} \text{ mol}^{-1}$ )	$H^\circ - H^\circ(T_r)$ ( $\text{kJ mol}^{-1}$ )	$\Delta_f H^\circ$ ( $\text{kJ mol}^{-1}$ )	$\Delta_f G^\circ$ ( $\text{kJ mol}^{-1}$ )	$\log K_f^\circ$
3600	102.837	483.886	396.262	315.444	-115.434	588.634	-8.541
3700	102.895	486.704	398.669	325.731	-115.080	608.188	-8.586
3800	102.948	489.449	401.022	336.023	-114.754	627.734	-8.629
3900	102.998	492.124	403.324	346.320	-114.456	647.270	-8.669
4000	103.044	494.732	405.576	356.622	-114.186	666.799	-8.707
4100	103.086	497.277	407.782	366.929	-113.941	686.316	-8.744
4200	103.126	499.761	409.942	377.240	-113.722	705.834	-8.778
4300	103.162	502.188	412.060	387.554	-113.529	725.344	-8.811
4400	103.197	504.560	414.135	397.872	-113.362	744.850	-8.842
4500	103.229	506.880	416.170	408.193	-113.220	764.352	-8.872
4600	103.259	509.149	418.167	418.518	-113.104	783.853	-8.901
4700	103.287	511.370	420.127	428.845	-113.014	803.351	-8.928
4800	103.314	513.545	422.050	439.175	-112.949	822.842	-8.954
4900	103.339	515.675	423.939	449.508	-112.911	842.339	-8.979
5000	103.362	517.763	425.795	459.843	-112.900	861.837	-9.003
5100	103.384	519.811	427.618	470.180	-112.916	881.336	-9.027
5200	103.405	521.818	429.411	480.520	-112.958	900.827	-9.049
5300	103.424	523.788	431.173	490.861	-113.031	920.325	-9.070
5400	103.443	525.721	432.906	501.204	-113.134	939.823	-9.091
5500	103.461	527.620	434.611	511.550	-113.264	959.320	-9.111
5600	103.477	529.484	436.288	521.896	-113.426	978.831	-9.130
5700	103.493	531.316	437.939	532.245	-113.621	998.333	-9.149
5800	103.508	533.116	439.565	542.595	-113.850	1017.842	-9.167
5900	103.522	534.885	441.166	552.946	-114.112	1037.356	-9.184
6000	103.535	536.625	442.742	563.299	-114.410	1056.871	-9.201



3. Sulfuric Acid, (HO)<sub>2</sub>SO<sub>2</sub>Sulfuric acid (H<sub>2</sub>SO<sub>4</sub>)

Ideal gas

 $M_r = 98.0734$  $S^\circ(298.15\text{ K}) = 311.3 \pm 1.5\text{ J K}^{-1}\text{ mol}^{-1}$  $\Delta_f H^\circ(0\text{ K}) = -720.8 \pm 2.0\text{ kJ mol}^{-1}$   
 $\Delta_f H^\circ(298.15\text{ K}) = -732.7 \pm 2.0\text{ kJ mol}^{-1}$ 

Molecular constants

Point group:  $C_2$ Symmetry number:  $\sigma = 2$ Ground electronic state:  $\tilde{X}^1A$ Energy:  $\epsilon_X = 0\text{ cm}^{-1}$ Quantum weight:  $g_X = 1$ Vibrational frequencies,  $\nu_i$ , and degeneracies,  $g_i$ 

Symmetry	$\nu_i, \text{cm}^{-1}$	$g_i$	Symmetry	$\nu_i, \text{cm}^{-1}$	$g_i$		
A	$\nu_1$	3563	1	B	$\nu_9$	3567	1
	$\nu_2$	1216	1		$\nu_{10}$	1452	1
	$\nu_3$	1136	1		$\nu_{11}$	1157	1
	$\nu_4$	831	1		$\nu_{12}$	882	1
	$\nu_5$	548	1		$\nu_{13}$	558	1
	$\nu_6$	[420]	1		$\nu_{14}$	[475]	1
	$\nu_7$	[355]	1		$\nu_{15}$	... <sup>a</sup>	1
	$\nu_8$	... <sup>a</sup>	1				

<sup>a</sup>Instead of the torsional modes  $\nu_8 = 240\text{ cm}^{-1}$  and  $\nu_{15} = 310\text{ cm}^{-1}$ , the contributions due to the internal rotation of OH groups around S–O bonds were calculated from the potential:  $V(\varphi) = V_0 + V_1 \cos \varphi + V_2 \cos 2\varphi + V_3 \cos 3\varphi + V_4 \cos 4\varphi + V'_1 \sin \varphi + V'_2 \sin 2\varphi + V'_3 \sin 3\varphi + V'_4 \sin 4\varphi$ , where  $\varphi$  is the torsional angle,  $V_0 = 534.8$ ,  $V_1 = -153.3$ ,  $V_2 = -342.0$ ,  $V_3 = -60.4$ ,  $V_4 = 23.1$ ,  $V'_1 = -283.4$ ,  $V'_2 = -1.8$ ,  $V'_3 = 106.3$ ,  $V'_4 = 9.0$  (in  $\text{cm}^{-1}$ ).

OH tops: Reduced moment of inertia,  $I_r = 0.8097 \times 10^{-39}\text{ g cm}^2$ , Symmetry number,  $\sigma_m = 1$ 

Geometry

$$r(\text{O–H}) = 0.970 \pm 0.010 \text{ \AA}$$

$$r(\text{S–O}) = 1.574 \pm 0.010 \text{ \AA}$$

$$r(\text{S=O}) = 1.422 \pm 0.010 \text{ \AA}$$

$$\angle \text{O–S–O} = 101.3 \pm 1.0^\circ$$

$$\angle \text{O=S=O} = 123.3 \pm 1.0^\circ$$

$$\angle \text{H–O–S} = 108.5 \pm 1.5^\circ$$

$$\varphi(\text{H–O–S–O}) = 89.1 \pm 1.0^\circ$$

$$\tau(\text{O–S–O/O=S=O}) = 88.4 \pm 0.1^\circ$$

<sup>b</sup> $\tau$  is the dihedral angle between the O=S=O and O–S–O planesRotational constants in  $\text{cm}^{-1}$ :

$$A_0 = 0.172\ 139\ 2 \quad B_0 = 0.167\ 600\ 4 \quad C_0 = 0.162\ 813\ 3$$

Product of moments of inertia:  $I_A I_B I_C = 4669.95 \times 10^{-117}\text{ g}^3\text{ cm}^6$ 

## 3.1. Enthalpy of Formation

The equilibrium of the reaction  $\text{H}_2\text{SO}_4(\text{g}) = \text{H}_2\text{O}(\text{g}) + \text{SO}_3(\text{g})$  has been investigated by a number of authors.<sup>1–5</sup> From the detailed analysis of these experimental data, the value of  $-732.7 \pm 2.0\text{ kJ mol}^{-1}$  was recommended by Gurvich *et al.*<sup>6</sup> for  $\Delta_f H^\circ(\text{H}_2\text{SO}_4, \text{g}, 298.15\text{ K})$ . This value is accepted in this work. A value close to that,  $-735.1 \pm 8.4\text{ kJ mol}^{-1}$ , was recommended in the JANAF Thermochemical Tables,<sup>7</sup> but its uncertainty was much greater. The available experimental data do not permit the determination of a high accuracy  $\Delta_f H^\circ$  value. Because of this, it is of interest to estimate the enthalpy of formation of sulfuric acid from theoretical calculations. The results of calculations at different levels of theory are given in Table 2. From the atomization reaction,  $\Delta_f H^\circ$  values at sufficient accuracy can be obtained

from composite *ab initio* calculation methods, G3, G3B3, CBS-Q, and CBS-QB3. These methods were used in this work. For comparison, these methods were also applied to the SO<sub>2</sub> and SO<sub>3</sub> molecules whose enthalpies of formation are known with uncertainties of 0.2 and 0.7  $\text{kJ mol}^{-1}$ , respectively. We also used an isodesmic bond separation scheme based on a combination of theoretical and experimental data. This approach eliminates systematic errors in the quantum chemical methods and improves the results. Calculations were done with the GAUSSIAN 98 system of programs.<sup>8</sup> We do not present the total energies, zero-point energies, and thermal corrections for the species in Table 2 because most of these values are available via Internet.<sup>9</sup> As can be seen from Table 2, the CBS-QB3 theory leads to the best agreement between experimental and theoretical  $\Delta_f H^\circ$  values for SO<sub>2</sub> and SO<sub>3</sub>. However, the CBS-QB3 value for H<sub>2</sub>SO<sub>4</sub> is 6

TABLE 2. Enthalpies of formation of H<sub>2</sub>SO<sub>4</sub>, SO<sub>3</sub>, and SO<sub>2</sub> calculated at different levels of theory

Quantum chemical method	SO <sub>2</sub>		SO <sub>3</sub>		H <sub>2</sub> SO <sub>4</sub>	
	Deviation		Deviation		Deviation	
	$\Delta_f H^\circ(298.15\text{ K})$ (kJ mol <sup>-1</sup> )	(Expt—Theory) (kJ mol <sup>-1</sup> )	$\Delta_f H^\circ(298.15\text{ K})$ (kJ mol <sup>-1</sup> )	(Expt—Theory) (kJ mol <sup>-1</sup> )	$\Delta_f H^\circ(298.15\text{ K})$ (kJ mol <sup>-1</sup> )	(Expt—Theory) (kJ mol <sup>-1</sup> )
Enthalpies of formation from atomization reactions						
G3	-280.8	-16.0	-374.2	-21.7	-704.2	-28.6
G3B3	-286.2	-10.6	-377.3	-18.6	-702.4	-30.3
CBS-Q	-295.1	-1.7	-391.7	-4.2	-715.2	-17.5
CBS-QB3	-297.5	0.7	-395.2	-0.7	-726.7	-6.0
Enthalpy of formation of H <sub>2</sub> SO <sub>4</sub> from bond separation reaction: H <sub>2</sub> SO <sub>4</sub> =SO <sub>3</sub> +H <sub>2</sub> O						
B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d,p)					-707.2	-25.5
B3LYP/cc-pVTZ//B3LYP/6-31G(d,p)					-711.8	-20.9
MP2/cc-pVTZ//MP2/6-31G(d,p)					-713.0	-19.7
G3					-727.3	-5.4
G3B3					-721.8	-10.9
CBS-Q					-716.8	-15.9
CBS-QB3					-725.7	-7.0

kJ mol<sup>-1</sup> higher than the experimental value. The increased deviation for H<sub>2</sub>SO<sub>4</sub> can be due to both the accumulation of calculational errors in the larger molecule and the uncertainty in the experimental value. Values of the enthalpy of formation of H<sub>2</sub>SO<sub>4</sub> calculated from the bond separation reaction are also higher than the experimental value by at least 5 kJ mol<sup>-1</sup>. Thus, the results of theoretical calculations in Table 2 suggest a value of about -727 kJ mol<sup>-1</sup> for enthalpy of formation of H<sub>2</sub>SO<sub>4</sub>. It should be noted that uncertainties in similarly calculated values for molecules of this size are often in the range  $\pm 4$ –8 kJ mol<sup>-1</sup> with the experimental value falling within the range of the uncertainty of the calculated value. From the above, the authors believe that the value of the enthalpy of formation adopted in this work is reasonable.

### 3.2. Heat Capacity and Entropy

Early infrared studies of the vapor phase over liquid H<sub>2</sub>SO<sub>4</sub>,<sup>10–12</sup> electric deflection experiments,<sup>13</sup> and semi-empirical CNDO/2 calculation<sup>14</sup> were consistent with a structure of C<sub>2v</sub> symmetry for sulfuric acid. Later Kuczkowski *et al.*<sup>15</sup> investigated the microwave spectrum of four isotopic species of H<sub>2</sub>SO<sub>4</sub> and determined a detailed structure whose overall symmetry is not C<sub>2v</sub>, but C<sub>2</sub>. The structure with C<sub>2</sub> symmetry has the *gauche, gauche* conformation of the OH groups with dihedral angles  $\varphi(\text{H}_1\text{—O}_1\text{—S—O}_2) = \varphi(\text{H}_2\text{—O}_2\text{—S—O}_1) = 89.1^\circ$ . The C<sub>2</sub> symmetry for the equilibrium geometry of H<sub>2</sub>SO<sub>4</sub> was supported by *ab initio* calculations<sup>16–19</sup> and this symmetry was adopted in this work. The product of the principal moments of inertia was calculated using the rotational constants determined from microwave study.<sup>15</sup> Structural parameters of sulfuric acid given above are the experimental values.<sup>15</sup>

Vibrational spectra of H<sub>2</sub>SO<sub>4</sub> were studied in the gas phase,<sup>10,11,20</sup> liquid,<sup>10,21–23</sup> and solid state.<sup>10,24</sup> Experimental assignments have been confirmed by normal coordinate analysis<sup>25</sup> and theoretical calculations.<sup>19</sup> None of the above

experimental studies, however, gives a complete vibrational assignment for sulfuric acid and some uncertainty exists for a number of the vibrations. In this work, the values for vibrational frequencies  $\nu_1$ – $\nu_5$  and  $\nu_9$ – $\nu_{13}$  were taken from infrared matrix isolation study of H<sub>2</sub>SO<sub>4</sub>.<sup>20</sup> Unobserved fundamentals ( $\nu_6$ – $\nu_8$ ,  $\nu_{14}$ ,  $\nu_{15}$ ) were estimated using the results of *ab initio* calculations given in the Computational Chemistry Comparison and Benchmark DataBase which is available via the Internet.<sup>9</sup> From calculations at different levels of theory, we chose those theoretical vibrational assignments which were in best agreement with experiment. The accepted values of  $\nu_6$ – $\nu_8$ ,  $\nu_{14}$ , and  $\nu_{15}$  are the average values for such assignments.

There are no experimental data on internal rotation in H<sub>2</sub>SO<sub>4</sub> molecule. The potential energy surface with respect to the pair of torsion angles  $\varphi(\text{H—O—S—O})$  was studied by *ab initio* calculations at the HF/STO-3G and HF/4-31G levels.<sup>16</sup> The global minimum on this surface was the *gauche, gauche* structure of C<sub>2</sub> symmetry. The rotation of OH groups about S—O bonds leads to conformations of C<sub>s</sub>(*gauche, gauche*), C<sub>1</sub>(*gauche, trans*), C<sub>1</sub>(*gauche, cis*), C<sub>2v</sub>(*trans, trans*), C<sub>s</sub>(*trans, cis*), and C<sub>2v</sub>(*cis, cis*) symmetry. According to the results of *ab initio* calculations,<sup>16</sup> only the C<sub>s</sub>(*gauche, gauche*) structure with an energy of about 500 cm<sup>-1</sup> is the shallow minimum, whereas the other structures are maxima or saddle points (C<sub>1</sub> symmetry) structures with energies from 1000 to 8500 cm<sup>-1</sup>. Since HF calculations with small basis sets such as STO-3G and 4-31G fail to produce reasonable transition state energies, we calculated the energies of conformations of sulfuric acid at the B3LYP/cc-pVTZ density functional theory level using the GAUSSIAN 98 program package.<sup>8</sup> Our calculations predict only one stable C<sub>2</sub>(*gauche, gauche*) conformation for H<sub>2</sub>SO<sub>4</sub>. The optimized geometry of C<sub>2</sub> conformer was utilized to perform a relaxed potential surface scan. In this potential surface scan the torsional dihedral angle  $\varphi(\text{H—O—S—O})$  was varied in 10° increments from 0° to 360° while all other structural param-

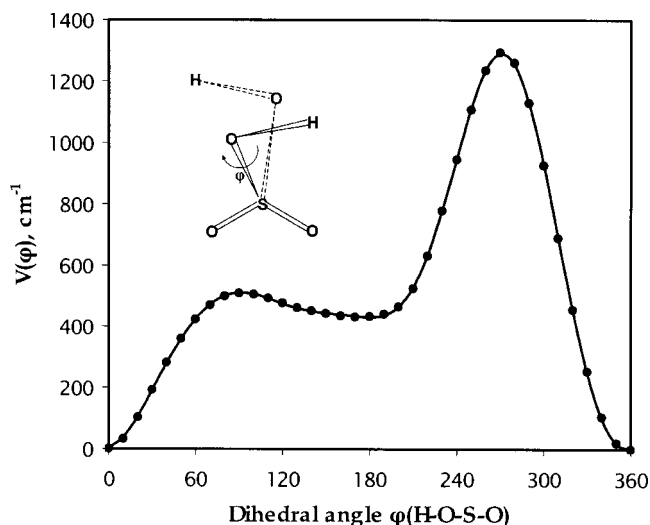


FIG. 1. Potential function governing internal rotation of sulfuric acid as determined at the B3LYP/cc-pVTZ level of theory.

eters were optimized. The resulting potential function is given in Fig. 1. Two maxima on this curve at  $\sim 90^\circ$  and  $270^\circ$  correspond to  $C_1(\textit{gauche,trans})$  and  $C_1(\textit{gauche,cis})$  conformations. The potential energy of sulfuric acid  $V(\varphi)$  as a function of torsional angle  $\varphi$  was approximated by a Fourier series of the form

$$V(\varphi) = V_0 + \sum_{n=1}^4 V_n \cos n\varphi + \sum_{n=1}^4 V'_n \sin n\varphi. \quad (3)$$

This potential function was used in this work to derive the contributions in the thermodynamic functions due to the internal rotation around two S–O bonds. The value of the reduced moment of inertia for the OH tops was calculated from structural parameters given above.

The uncertainties in the calculated thermodynamic functions (see Table 3) are estimated to be 1.5, 3, 4, and 5  $\text{JK}^{-1}\text{mol}^{-1}$  for  $C_p^\circ(T)$  at 298.15, 1000, 3000, and 6000 K and 2, 4, 6, and 7  $\text{JK}^{-1}\text{mol}^{-1}$  for  $S^\circ(T)$  at 298.15, 1000, 3000, and 6000 K, respectively.

Previous calculations of thermodynamic functions (refer to Gurvich *et al.*<sup>6</sup> and references within) were based on the  $C_{2v}$  symmetry for equilibrium geometry of sulfuric acid and did not take into account the internal rotation in sulfuric acid. Maximum deviations with two other earlier critical

reviews<sup>6,7</sup> are 6–8  $\text{JK}^{-1}\text{mol}^{-1}$  for  $C_p^\circ(T)$  and 12  $\text{JK}^{-1}\text{mol}^{-1}$  for  $S^\circ(298.15\text{ K})$ .

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TABLE 3. Ideal gas thermochemical properties of sulfuric acid  $\text{H}_2\text{SO}_4(\text{g})$  at standard state pressure,  $p^\circ = 0.1 \text{ MPa}$  ( $T_r = 298.15 \text{ K}$ )

$T$ (K)	$C_p^\circ$ ( $\text{J K}^{-1} \text{ mol}^{-1}$ )	$S^\circ$ ( $\text{J K}^{-1} \text{ mol}^{-1}$ )	$-[G^\circ - H^\circ(T_r)]/T$ ( $\text{J K}^{-1} \text{ mol}^{-1}$ )	$H^\circ - H^\circ(T_r)$ ( $\text{kJ mol}^{-1}$ )	$\Delta_f H^\circ$ ( $\text{kJ mol}^{-1}$ )	$\Delta_f G^\circ$ ( $\text{kJ mol}^{-1}$ )	$\log K_f^\circ$
0	0.000	0.000	$\infty$	-18.391	-720.845	-720.845	$\infty$
25	33.263	183.884	886.266	-17.560	-722.023	-718.548	1501.286
50	34.373	207.119	541.522	-16.720	-723.612	-714.493	746.407
75	39.496	221.877	432.622	-15.806	-725.264	-709.569	494.176
100	48.028	234.356	381.520	-14.716	-726.668	-704.118	367.784
150	65.558	257.290	336.346	-11.858	-728.805	-692.347	241.091
180	73.184	269.952	324.237	-9.771	-729.794	-684.960	198.765
190	75.253	273.965	321.487	-9.029	-730.091	-682.463	187.617
200	77.132	277.874	319.208	-8.267	-730.377	-679.948	177.580
210	78.851	281.679	317.331	-7.487	-730.650	-677.419	168.495
220	80.437	285.384	315.795	-6.690	-730.915	-674.879	160.233
230	81.913	288.993	314.552	-5.879	-731.170	-672.326	152.686
240	83.299	292.509	313.560	-5.052	-731.416	-669.763	145.766
250	84.611	295.936	312.787	-4.213	-731.654	-667.188	139.398
260	85.862	299.279	312.204	-3.360	-731.885	-664.605	133.517
270	87.063	302.542	311.786	-2.496	-732.108	-662.013	128.071
280	88.221	305.729	311.512	-1.619	-732.324	-659.414	123.012
290	89.344	308.845	311.367	-0.731	-732.534	-656.804	118.300
298.15	90.235	311.333	311.332	0.000	-732.700	-654.676	114.694
300	90.435	311.892	311.334	0.167	-732.737	-654.190	113.902
350	95.509	326.221	312.454	4.818	-733.654	-641.028	95.666
400	100.041	339.276	315.003	9.709	-736.647	-627.648	81.960
450	104.065	351.297	318.377	14.814	-737.959	-613.957	71.264
500	107.606	362.448	322.233	20.108	-739.212	-600.107	62.691
600	113.427	382.605	330.652	31.172	-740.975	-572.109	49.805
700	117.952	400.444	339.372	42.750	-742.195	-543.861	40.582
800	121.583	416.439	348.023	54.733	-747.467	-520.481	33.983
900	124.596	430.938	356.442	67.046	-749.779	-485.898	28.200
1000	127.160	444.202	364.565	79.637	-749.972	-451.399	23.578
1100	129.382	456.428	372.367	92.467	-795.070	-416.984	19.800
1200	131.326	467.771	379.851	105.504	-794.096	-382.654	16.656
1300	133.037	478.352	387.026	118.724	-793.066	-348.409	13.999
1400	134.549	488.267	393.906	132.105	-791.993	-314.242	11.724
1500	135.888	497.597	400.512	145.628	-790.895	-280.157	9.756
1600	137.077	506.406	406.857	159.278	-789.778	-246.146	8.036
1700	138.134	514.748	412.960	173.039	-788.658	-212.205	6.520
1800	139.077	522.671	418.837	186.901	-787.537	-178.325	5.175
1900	139.918	530.213	424.502	200.851	-786.428	-144.511	3.973
2000	140.671	537.410	429.969	214.882	-785.332	-110.752	2.892
2100	141.347	544.290	435.251	228.983	-784.262	-77.051	1.916
2200	141.954	550.880	440.358	243.149	-783.213	-43.401	1.030
2300	142.502	557.202	445.301	257.372	-782.195	-9.795	0.222
2400	142.996	563.277	450.091	271.647	-781.208	23.767	-0.517
2500	143.444	569.124	454.736	285.970	-780.254	57.283	-1.197
2600	143.850	574.758	459.244	300.335	-779.335	90.773	-1.824
2700	144.220	580.194	463.624	314.738	-778.452	124.217	-2.403
2800	144.557	585.445	467.882	329.178	-777.604	157.638	-2.941
2900	144.865	590.523	472.024	343.649	-776.795	191.028	-3.441
3000	145.146	595.439	476.056	358.150	-776.024	224.383	-3.907
3100	145.405	600.203	479.985	372.677	-775.292	257.715	-4.342
3200	145.643	604.823	483.814	387.230	-774.597	291.025	-4.750
3300	145.862	609.308	487.549	401.805	-773.940	324.320	-5.133
3400	146.064	613.666	491.194	416.402	-773.319	357.589	-5.494
3500	146.251	617.902	494.755	431.018	-772.734	390.848	-5.833

TABLE 3. Ideal gas thermochemical properties of sulfuric acid  $\text{H}_2\text{SO}_4(\text{g})$  at standard state pressure,  $p^\circ = 0.1 \text{ MPa}$  ( $T_r = 298.15 \text{ K}$ )—Continued

$T$ (K)	$C_p^\circ$ ( $\text{J K}^{-1} \text{ mol}^{-1}$ )	$S^\circ$ ( $\text{J K}^{-1} \text{ mol}^{-1}$ )	$-[G^\circ - H^\circ(T_r)]/T$ ( $\text{J K}^{-1} \text{ mol}^{-1}$ )	$H^\circ - H^\circ(T_r)$ ( $\text{kJ mol}^{-1}$ )	$\Delta_f H^\circ$ ( $\text{kJ mol}^{-1}$ )	$\Delta_f G^\circ$ ( $\text{kJ mol}^{-1}$ )	$\log K_f^\circ$
3600	146.424	622.025	498.233	445.651	-772.191	424.074	-6.153
3700	146.584	626.039	501.633	460.302	-771.680	457.304	-6.456
3800	146.733	629.950	504.959	474.968	-771.208	490.517	-6.742
3900	146.872	633.763	508.213	489.648	-770.772	523.720	-7.014
4000	147.002	637.483	511.398	504.342	-770.374	556.906	-7.272
4100	147.122	641.115	514.518	519.048	-770.014	590.075	-7.517
4200	147.235	644.661	517.574	533.766	-769.687	623.247	-7.751
4300	147.341	648.127	520.570	548.495	-769.400	656.407	-7.974
4400	147.440	651.516	523.508	563.234	-769.148	689.558	-8.186
4500	147.533	654.830	526.390	577.983	-768.936	722.710	-8.389
4600	147.620	658.074	529.217	592.740	-768.763	755.857	-8.583
4700	147.702	661.249	531.993	607.507	-768.628	789.004	-8.769
4800	147.779	664.360	534.719	622.281	-768.531	822.131	-8.946
4900	147.852	667.408	537.395	637.062	-768.478	855.269	-9.117
5000	147.921	670.395	540.025	651.851	-768.463	888.417	-9.281
5100	147.986	673.325	542.610	666.646	-768.492	921.561	-9.438
5200	148.048	676.199	545.152	681.448	-768.560	954.694	-9.590
5300	148.106	679.020	547.651	696.256	-768.677	987.822	-9.735
5400	148.161	681.789	550.110	711.069	-768.838	1020.976	-9.876
5500	148.213	684.508	552.529	725.888	-769.044	1054.118	-10.011
5600	148.263	687.179	554.909	740.712	-769.297	1087.282	-10.141
5700	148.310	689.804	557.253	755.540	-769.601	1120.428	-10.267
5800	148.355	692.383	559.561	770.374	-769.953	1153.594	-10.389
5900	148.397	694.920	561.833	785.211	-770.358	1186.755	-10.506
6000	148.438	697.414	564.072	800.053	-770.814	1219.926	-10.620



4. Hydrogen Peroxide, H<sub>2</sub>O<sub>2</sub>Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>)

Ideal gas

 $M_r = 34.0146$  $S^\circ(298.15\text{ K}) = 234.5 \pm 0.1\text{ J K}^{-1}\text{ mol}^{-1}$  $\Delta_f H^\circ(0\text{ K}) = -129.9 \pm 0.2\text{ kJ mol}^{-1}$   
 $\Delta_f H^\circ(298.15\text{ K}) = -135.9 \pm 0.2\text{ kJ mol}^{-1}$ 

Molecular constants

Point group:  $C_2$ Symmetry number:  $\sigma = 2$ Ground electronic state:  $\tilde{X}^1A$ Energy:  $\epsilon_X = 0\text{ cm}^{-1}$ Quantum weight:  $g_X = 1$ Vibrational frequencies,  $\nu_i$ , and degeneracies,  $g_i$ 

Symmetry	$\nu_i, \text{cm}^{-1}$	$g_i$	Symmetry	$\nu_i, \text{cm}^{-1}$	$g_i$
A	$\nu_1$	3598.7	B	$\nu_4$	... <sup>a</sup>
	$\nu_2$	1387.5		$\nu_5$	3610.7
	$\nu_3$	875		$\nu_6$	1266

<sup>a</sup>Instead of a torsional mode  $\nu_4$ , the contributions due to the internal rotation of OH group around the O–O bond were calculated using the following experimental and calculated (above 1000  $\text{cm}^{-1}$ ) torsional energies ( $E_{\text{tor}}^i$ ), multiplicities ( $g_i$ ), and the products of moments of inertia ( $I_A^i I_B^i I_C^i \times 10^{117}, \text{g}^3 \text{cm}^6$ ):

$E_{\text{tor}}^i$	$g_i$	$I_A^i I_B^i I_C^i$	$E_{\text{tor}}^i$	$g_i$	$I_A^i I_B^i I_C^i$	$E_{\text{tor}}^i$	$g_i$	$I_A^i I_B^i I_C^i$	$E_{\text{tor}}^i$	$g_i$	$I_A^i I_B^i I_C^i$
0.000	1	2.9760	3257.3	1	3.14	19 713	2	3.26	54 554	2	3.28
11.437	1	2.9749	3259.3	1	3.14	21 484	2	3.26	57 507	2	3.28
254.550	1	3.0069	3903.8	2	3.16	23 334	2	3.26	60 538	2	3.28
370.893	1	3.0089	4636.8	2	3.17	25 263	2	3.26	63 649	2	3.28
569.743	1	3.0264	5453.2	2	3.18	27 270	2	3.27	66 838	2	3.29
776.115	1	3.0410	6351.2	2	3.20	29 356	2	3.27	70 106	2	3.29
1000.882	1	3.0589	7329.9	2	3.21	31 522	2	3.27	73 453	2	3.29
1235.2	1	3.0706	8388.6	2	3.21	33 766	2	3.27	76 878	2	3.29
1474.7	1	3.0830	9526.9	2	3.22	36 088	2	3.27	80 383	2	3.29
1718.0	1	3.0942	10 745	2	3.23	38 490	2	3.28	83 966	2	3.29
1947.2	1	3.1037	12 042	2	3.24	40 970	2	3.28	87 628	2	3.29
2201.0	1	3.1133	13 418	2	3.24	43 529	2	3.28	91 368	2	3.29
2341.7	1	3.1182	14 873	2	3.25	46 167	2	3.28	95 188	2	3.29
2697.7	1	3.1296	16 408	2	3.25	48 884	2	3.28	99 086	2	3.29
2724.7	1	3.1304	18 021	2	3.25	51 679	2	3.28	100 669	2	3.29

The potential of the form

$$V(\varphi) = V_0 + V_1 \cos \varphi + V_2 \cos 2\varphi + V_3 \cos 3\varphi + V_4 \cos 4\varphi,$$

where  $\varphi$  is the H–O–O–H torsional angle,  $V_0 = 645.1$ ,  $V_1 = 1036.97$ ,  $V_2 = 657.53$ ,  $V_3 = 50.89$ ,  $V_4 = 2.524$  (in  $\text{cm}^{-1}$ ), was used for calculating the energy levels above 1000  $\text{cm}^{-1}$ .

OH top: Reduced moment of inertia,  $I_r = 0.071\,093 \times 10^{-39}\text{ g cm}^2$ , Symmetry number,  $\sigma_m = 1$ 

Geometry

$r(\text{O–H}) = 0.965 \pm 0.005\text{ \AA}$

$\angle\text{H–O–O} = 99.04^\circ \pm 1.20^\circ$

$r(\text{O–O}) = 1.464 \pm 0.003\text{ \AA}$

$\varphi(\text{H–O–O–H}) = 120.3^\circ \pm 0.7^\circ$

Rotational constants in  $\text{cm}^{-1}$ :

$A_0 = 10.069\,428$     $B_0 = 0.874\,351$     $C_0 = 0.837\,202$

Product of moments of inertia:  $I_A I_B I_C = 2.976\,026 \times 10^{-117}\text{ g}^3 \text{cm}^6$ Centrifugal distortion constants in  $\text{cm}^{-1}$ :

$\Delta_J = 3.517 \times 10^{-6}$     $\Delta_{JK} = 3.729 \times 10^{-5}$     $\Delta_K = 3.981 \times 10^{-4}$

Anharmonicity constants in  $\text{cm}^{-1}$ :

$x_{11} = 90.9$	$x_{15} = 167.6$	$x_{23} = 7$	$x_{33} = 10$	$x_{55} = 90.2$
$x_{12} = 11$	$x_{16} = 3$	$x_{25} = 11.5$	$x_{35} = 11.1$	$x_{56} = 3$
$x_{13} = 11$	$x_{22} = 10$	$x_{26} = 4$	$x_{36} = 2$	$x_{66} = 3$

Rotational–vibrational constants in  $\text{cm}^{-1}$ :

$\alpha_1^A = 0.234$	$\alpha_5^A = 0.234$	$\alpha_6^B = 0.004$	$\alpha_6^B = 0.003$	$\alpha_3^C = 0.013$
$\alpha_2^A = -0.104$	$\alpha_6^A = -0.174$	$\alpha_3^B = 0.007$	$\alpha_1^C = -0.001$	$\alpha_5^C = -0.001$
$\alpha_3^A = -0.034$	$\alpha_1^B = 0.003$	$\alpha_5^B = 0.003$	$\alpha_2^C = 0.004$	$\alpha_6^C = 0.007$

#### 4.1. Enthalpy of Formation

The enthalpy of formation is based on the selected value of the enthalpy of formation of liquid hydrogen peroxide  $\Delta_f H^\circ(\text{H}_2\text{O}_2, \text{liq}, 298.15 \text{ K}) = -187.78 \pm 0.08 \text{ kJ mol}^{-1}$ , which was obtained by Giguere *et al.*,<sup>1,2</sup> and on the value of  $\Delta_v H^\circ(\text{H}_2\text{O}_2, \text{liq}, 298.15 \text{ K}) = 51.9 \pm 0.2 \text{ kJ mol}^{-1}$ . The latter is the weighted mean value, calculated by Third Law method<sup>3</sup> from the results of vapor pressure determinations of  $\text{H}_2\text{O}_2(\text{liq})$ , obtained in several studies.<sup>4-6</sup> The uncertainty of this value involves the inaccuracy of the thermodynamic functions used in the calculation.<sup>3</sup> The adopted value of the enthalpy of formation is in good agreement with the results of mass-spectrometric investigations<sup>7-9</sup> and theoretical calculations.<sup>10</sup>

#### 4.2. Heat Capacity and Entropy

The molecular structure of hydrogen peroxide has been studied by infrared<sup>11-13</sup> and microwave<sup>14-17</sup> spectroscopy and quantum mechanical calculations.<sup>18-20</sup> In the ground electronic state,  $\tilde{X}^1A$ , the molecule has a *gauche* configuration with  $C_2$  symmetry.<sup>21</sup> In this work, the product of the principal moments of inertia of hydrogen peroxide was calculated using the rotational constants determined from the microwave spectrum study.<sup>17</sup> These rotational constants are in good agreement with those obtained from infrared spectra. The structural parameters given above are the  $r_o$  parameters, recommended by Khachkuruzov and Przheval'skii.<sup>22</sup> These parameters agree well with the corresponding parameters determined from the experimental studies<sup>11-17</sup> and theoretical calculations.<sup>18-20</sup> Centrifugal distortion constants were also accepted from microwave data.<sup>17</sup>

The values of the vibrational and vibrational-rotational constants are based on a critical analysis<sup>23,24</sup> of the results of investigations of the vibrational and the rotational-vibrational spectra of  $\text{H}_2\text{O}_2$  vapor obtained in several studies.<sup>12,25-31</sup> The torsional energy levels and products of moments of inertia for the levels have been adopted from the far infrared spectrum study.<sup>32</sup> Above  $1000 \text{ cm}^{-1}$  the levels were calculated<sup>33</sup> using the potential function of the form<sup>32</sup>

$$V(\varphi) = V_0 + V_1 \cos \varphi + V_2 \cos 2\varphi + V_3 \cos 3\varphi + V_4 \cos 4\varphi \quad (4)$$

and the inertial rotational constant  $F = 39.37544 \text{ cm}^{-1}$ . The values of *trans* barrier height  $V_{trans} = 387.07 \pm 0.2 \text{ cm}^{-1}$ , the *cis* barrier height  $V_{cis} = 2562.8 \pm 60 \text{ cm}^{-1}$ , and the HOOH dihedral angle  $\varphi_e = 111.9^\circ \pm 0.4^\circ$  correspond to this potential function. The products of moments of inertia were extrapolated by empirical formula.

From the analysis of spectroscopic data, the vibrational-rotational levels for the ground electronic state of  $\text{H}_2\text{O}_2$  can be presented by the following equation:

$$E_{v,j,K} = \sum_{i=1, i \neq 4}^6 \nu_i v_i - \sum_{i, i \neq 4}^6 x_{ii} v_i (v_i - 1) - \sum_{i < k, i \neq 4}^6 x_{ik} v_i v_k + E_{\text{tor}}(v_4) + 1/2(B_v + C_v)J(J+1) + (A_v - 1/2(B_v + C_v))K^2 - \Delta_J J^2 (J+1)^2 - \Delta_{JK} J(J+1)K^2 - \Delta_K K^4, \quad (5)$$

where

$$A_v = A_0 - \sum_{i=1, i \neq 4}^6 \alpha_i^A v_i, \quad B_v = B_0 - \sum_{i=1, i \neq 4}^6 \alpha_i^B v_i, \\ C_v = C_0 - \sum_{i=1, i \neq 4}^6 \alpha_i^C v_i,$$

and  $v$  denotes a set of vibrational quantum numbers of normal modes  $v_1, v_2, v_3, v_4, v_5, v_6$ .

Thermodynamic functions of  $\text{H}_2\text{O}_2$  were calculated taking into account the anharmonicity of the vibrations and the vibrational-rotational interaction,<sup>3,34</sup> the centrifugal distortion,<sup>35,36</sup> and the low-temperature correction.<sup>37</sup> The contribution of internal rotation was calculated by direct summation over energy levels taking into account interaction between the internal rotation and overall rotation

$$Q_{\text{int.rot.}} = \sum_i \frac{Q_{RR}^i}{Q_{RR}} g_i \exp(-hcE_{\text{tor}}^i/kT) \\ = \sum_i \sqrt{\left( \frac{I_A^i I_B^i I_C^i}{I_A I_B I_C} \right)} g_i \exp(-hcE_{\text{tor}}^i/kT). \quad (6)$$

The coefficients of these equations are given above.

According to the theoretical calculation,<sup>38</sup> the excited electronic states of  $\text{H}_2\text{O}_2$  lie above  $35000 \text{ cm}^{-1}$ . They are not taken into account in the present calculation of the thermodynamic functions.

Uncertainties in the calculated thermodynamic functions are estimated to be 0.3, 1.0, 2.0, and  $3.0 \text{ J K}^{-1} \text{ mol}^{-1}$  for  $C_p^o(T)$  at 298.15, 1000, 3000, and 6000 K and 0.1, 1.0, 2.0, and  $4.0 \text{ J K}^{-1} \text{ mol}^{-1}$  for  $S^o(T)$  at 298.15, 1000, 3000, and 6000 K, respectively.

The calculated thermodynamic functions of hydrogen peroxide (see Table 4) are in agreement with results of the best previous calculations.<sup>3,39</sup> The differences with calculated  $C_p^o(T)$  and  $S^o(T)$  values<sup>3,39</sup> do not exceed 1.7 and 1.2  $\text{J K}^{-1} \text{ mol}^{-1}$ , respectively. The value of  $S^o(298.15 \text{ K}) = 234.54 \text{ J K}^{-1} \text{ mol}^{-1}$  does not agree with the calorimetric value<sup>40,41</sup> of  $232.88 \pm 0.50 \text{ J K}^{-1} \text{ mol}^{-1}$  within the limits of the experimental accuracy. According to Giguere,<sup>42</sup> the most likely source of the discrepancy is the use in the calculations of an underestimated value for the enthalpy of vaporization of  $\text{H}_2\text{O}_2(\text{liq})$  at 298.15 K, obviously due to catalytic decomposition of the hydrogen peroxide during the calorimetric measurements.

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TABLE 4. Ideal gas thermochemical properties of hydrogen peroxide  $\text{H}_2\text{O}_2(\text{g})$  at standard state pressure,  $p^\circ = 0.1 \text{ MPa}$  ( $T_r = 298.15 \text{ K}$ )

$T$ (K)	$C_p^\circ$ ( $\text{J K}^{-1} \text{ mol}^{-1}$ )	$S^\circ$ ( $\text{J K}^{-1} \text{ mol}^{-1}$ )	$-[G^\circ - H^\circ(T_r)]/T$ ( $\text{J K}^{-1} \text{ mol}^{-1}$ )	$H^\circ - H^\circ(T_r)$ ( $\text{kJ mol}^{-1}$ )	$\Delta_f H^\circ$ ( $\text{kJ mol}^{-1}$ )	$\Delta_f G^\circ$ ( $\text{kJ mol}^{-1}$ )	$\log K_f^\circ$
0	0.000	0.000	$\infty$	-11.162	-129.891	-129.891	$\infty$
25	34.073	145.429	556.919	-10.287	-130.272	-129.204	269.953
50	33.664	168.829	357.706	-9.444	-130.987	-127.890	133.604
75	34.361	182.586	297.187	-8.595	-131.752	-126.169	87.871
100	35.452	192.618	269.844	-7.723	-132.355	-124.214	64.882
150	37.406	207.382	246.707	-5.899	-133.334	-119.924	41.761
180	38.366	214.288	240.743	-4.762	-133.873	-117.192	34.008
190	38.676	216.370	239.406	-4.377	-134.050	-116.260	31.962
200	38.987	218.362	238.304	-3.988	-134.226	-115.319	30.118
210	39.302	220.272	237.400	-3.597	-134.402	-114.369	28.447
220	39.623	222.107	236.664	-3.202	-134.576	-113.411	26.927
230	39.951	223.876	236.070	-2.804	-134.749	-112.446	25.537
240	40.288	225.583	235.597	-2.403	-134.921	-111.472	24.261
250	40.634	227.235	235.230	-1.999	-135.091	-110.492	23.086
260	40.989	228.836	234.953	-1.591	-135.259	-109.504	21.999
270	41.352	230.389	234.756	-1.179	-135.425	-108.511	20.992
280	41.724	231.900	234.627	-0.764	-135.589	-107.511	20.056
290	42.102	233.371	234.558	-0.344	-135.750	-106.505	19.183
298.15	42.416	234.542	234.542	0.000	-135.880	-105.681	18.515
300	42.487	234.804	234.543	0.078	-135.909	-105.494	18.368
350	44.475	241.502	235.067	2.252	-136.661	-100.364	14.978
400	46.482	247.572	236.257	4.526	-137.339	-95.132	12.423
450	48.416	253.160	237.828	6.899	-137.944	-89.819	10.426
500	50.229	258.356	239.624	9.366	-138.481	-84.442	8.822
600	53.441	267.806	243.549	14.554	-139.381	-73.548	6.403
700	56.166	276.254	247.629	20.038	-140.090	-62.518	4.665
800	58.523	283.911	251.693	25.775	-140.642	-51.396	3.356
900	60.608	290.927	255.668	31.733	-141.064	-40.214	2.334
1000	62.481	297.411	259.522	37.890	-141.374	-28.991	1.514
1100	64.175	303.447	263.244	44.224	-141.587	-17.742	0.842
1200	65.713	309.098	266.832	50.719	-141.719	-6.477	0.282
1300	67.109	314.414	270.290	57.361	-141.781	4.797	-0.193
1400	68.377	319.435	273.623	64.137	-141.782	16.074	-0.600
1500	69.529	324.192	276.837	71.033	-141.736	27.347	-0.952
1600	70.576	328.713	279.939	78.039	-141.648	38.616	-1.261
1700	71.528	333.021	282.936	85.145	-141.528	49.877	-1.533
1800	72.395	337.134	285.833	92.342	-141.380	61.134	-1.774
1900	73.187	341.070	288.638	99.622	-141.212	72.380	-1.990
2000	73.911	344.843	291.354	106.977	-141.029	83.618	-2.184
2100	74.576	348.465	293.988	114.402	-140.836	94.845	-2.359
2200	75.187	351.949	296.544	121.890	-140.635	106.063	-2.518
2300	75.752	355.303	299.026	129.438	-140.429	117.271	-2.663
2400	76.274	358.539	301.439	137.039	-140.222	128.471	-2.796
2500	76.759	361.662	303.786	144.691	-140.015	139.662	-2.918
2600	77.211	364.682	306.070	152.390	-139.810	150.847	-3.031
2700	77.633	367.604	308.295	160.133	-139.609	162.020	-3.134
2800	78.029	370.434	310.464	167.916	-139.412	173.190	-3.231
2900	78.400	373.179	312.580	175.737	-139.222	184.352	-3.320
3000	78.751	375.843	314.644	183.595	-139.038	195.505	-3.404
3100	79.083	378.430	316.660	191.487	-138.862	206.653	-3.482
3200	79.397	380.946	318.630	199.411	-138.694	217.795	-3.555
3300	79.696	383.394	320.556	207.366	-138.534	228.934	-3.624
3400	79.981	385.777	322.439	215.350	-138.382	240.067	-3.688
3500	80.254	388.100	324.282	223.362	-138.238	251.197	-3.749

TABLE 4. Ideal gas thermochemical properties of hydrogen peroxide  $\text{H}_2\text{O}_2(\text{g})$  at standard state pressure,  $p^\circ=0.1$  MPa ( $T_r=298.15$  K)—Continued

$T$ (K)	$C_p^\circ$ ( $\text{J K}^{-1} \text{mol}^{-1}$ )	$S^\circ$ ( $\text{J K}^{-1} \text{mol}^{-1}$ )	$-[G^\circ - H^\circ(T_r)]/T$ ( $\text{J K}^{-1} \text{mol}^{-1}$ )	$H^\circ - H^\circ(T_r)$ ( $\text{kJ mol}^{-1}$ )	$\Delta_f H^\circ$ ( $\text{kJ mol}^{-1}$ )	$\Delta_f G^\circ$ ( $\text{kJ mol}^{-1}$ )	$\log K_f^\circ$
3600	80.515	390.364	326.087	231.400	-138.105	262.318	-3.806
3700	80.765	392.574	327.854	239.464	-137.979	273.444	-3.860
3800	81.006	394.731	329.585	247.553	-137.863	284.560	-3.912
3900	81.239	396.838	331.283	255.665	-137.756	295.678	-3.960
4000	81.464	398.898	332.948	263.800	-137.659	306.790	-4.006
4100	81.681	400.912	334.581	271.958	-137.571	317.898	-4.050
4200	81.892	402.883	336.184	280.136	-137.493	329.006	-4.092
4300	82.097	404.812	337.757	288.336	-137.424	340.112	-4.131
4400	82.296	406.702	339.303	296.556	-137.365	351.215	-4.169
4500	82.491	408.553	340.821	304.795	-137.317	362.320	-4.206
4600	82.680	410.369	342.314	313.054	-137.279	373.424	-4.240
4700	82.866	412.149	343.781	321.331	-137.252	384.524	-4.273
4800	83.047	413.895	345.223	329.627	-137.234	395.622	-4.305
4900	83.224	415.609	346.642	337.940	-137.229	406.723	-4.336
5000	83.399	417.293	348.038	346.271	-137.234	417.828	-4.365
5100	83.570	418.946	349.413	354.620	-137.250	428.932	-4.393
5200	83.738	420.570	350.765	362.985	-137.277	440.031	-4.420
5300	83.903	422.167	352.098	371.367	-137.317	451.133	-4.446
5400	84.066	423.737	353.410	379.766	-137.369	462.237	-4.471
5500	84.227	425.281	354.702	388.180	-137.432	473.340	-4.495
5600	84.385	426.800	355.976	396.611	-137.508	484.452	-4.519
5700	84.541	428.295	357.232	405.057	-137.597	495.555	-4.541
5800	84.695	429.766	358.470	413.519	-137.699	506.661	-4.563
5900	84.848	431.216	359.691	421.996	-137.814	517.774	-4.584
6000	84.999	432.643	360.895	430.489	-137.942	528.881	-4.604

## 5. Conclusions

The spectroscopic and thermodynamic properties of three ideal gas species—nitric acid, sulfuric acid, and hydrogen peroxide—have been reviewed. The user of this data needs to assess whether the error bounds on the recommended values for the entropy and the enthalpy of formation are sufficient for the specific intended end use. Although the thermodynamic functions are greatly improved over the previous evaluations, the formation data have not changed. This is due to the fact that there are no recent experimental measurements, which directly pertain to the determination of the formation properties. For nitric acid, the latest experimental measurement was in 1962; for sulfuric acid, 1966; and for hydrogen peroxide, 1957 (although there are supporting mass spectrometric results dating to 1962 and a theoretical calculation dated 1995).

The next step in the evaluation of the thermodynamic properties of these species would be to confirm the properties of the condensed phases and the consistency of that data with the presently reported ideal gas data.

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## 7. Extended Bibliographies

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