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PERFECT GAS THERMODYNAMIC PROPERTIES OF METHANAL, ETHANAL AND THEIR DEUTERATED SPECIES

JING CHAO, RANDOLPH C. WILHOIT and KENNETH R. HALL

Thermodynamics Research Center, Texas Engineering Experiment Station, Texas A&M University, College Station, TX 77840 (U.S.A.)

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ABSTRACT

Employing recent and reliable selected molecular, spectroscopic, and thermal constants, the perfect gas thermodynamic properties [$H^0 - H^0_0$, $(G^0 - H^0_0)/T$, S^0, C^0_p, ΔH^0_f, and ΔG^0_f], for methanal (formaldehyde), methanal-d_1, methanal-d_2, ethanal (acetaldehyde), ethanal-d_1, and ethanal-d_4 were evaluated over the temperature range from 0 to 1500 K and 1 atm by statistical mechanical methods using rigid-rotor and harmonic-oscillator approximations. The internal rotation contributions of —CH_3 and —CD_3 rotors to the thermodynamic properties were computed based on internal rotation partition functions formed by summation of calculated internal rotation energy levels. The results compare well with available experimental data.

INTRODUCTION

The perfect gas thermodynamic functions of methanal and ethanal have been calculated by statistical mechanical methods many times. Since ethanal has one degree of internal rotation, calculation of its thermodynamic properties require an evaluation of the internal rotation energy states. Values for methanal have been reported by Stevenson and Beach [1], Thompson [2], Dworjanyn [3], Antonov and Maslov [4], and Pillai and Cleveland [5]. These results were based upon available geometry and vibrational frequencies of the methanal molecule at the time of publication.

Thermodynamic properties of acetaldehyde have been evaluated by Thompson and Harris [6], Smith [7], Pitzer and Weltner [8], Antonov and Maslov [4], Vasil'ev and Vvedenskii [9], and Lippincott et al. [10]. Thompson and Harris studied the infrared spectrum of acetaldehyde vapor and assigned 14 of the 15 fundamental vibrational frequencies. They also made a rough evaluation of the specific heat of $CH_3CHO(g)$. Smith based his calculations on a vibrational assignment by Morris [11]. His C^0_p values did not agree with the vapor heat capacity measurements of Coleman and DeVries [12].

Pitzer and Weltner reassigned the vibrational frequencies for acetaldehyde to permit the calculated C^0_p to agree with the heat capacity of gaseous acetaldehyde in addition to the observed spectra and the product rule. A potential barrier to internal rotation of 1000 cal mole^{-1} or 4184 J mole^{-1} provided the best agreement with thermodynamic data which included the equilibrium with hydrogen and ethanol and the heat capacity of gaseous acetaldehyde [12,13].

Antonov and Maslov [4] calculated the perfect gas properties of methanal-d_1 and ethanal (as well as other compounds) by an approximation procedure [14,15]. Their technique generates the properties of derivatives of a parent compound by adding certain correction terms to the values for the parent compound. The parent compound for methanal-d_1 and ethanal was methanol. The values for methanol were taken from previously published reports.

Lippincott et al. [10] computed the perfect gas thermodynamic functions for acetaldehyde in the temperature range 200—2000 K and at 1 atm by the statistical mechanical method. The C_p^0 values obtained were in reasonable agreement with the available experimental data. They adopted the following molecular data for evaluation: the molecular structure of Kilb et al. [16] elucidated from microwave spectroscopy, fourteen fundamental frequencies assigned by Evans and Bernstein [17], and a torsional frequency of 150 cm^{-1} observed by Fateley and Miller [18].

Based upon the most recent and reliable molecular, spectroscopic and thermal constants, the thermodynamic properties [$H^0 - H_0^0$, $(G^0 - H_0^0)/T$, S^0, C_p^0, ΔH_f^0, and ΔG_f^0] for HCHO, HCDO, DCDO, CH_3CHO, CH_3CDO, and CD_3CDO in the perfect gaseous state in the temperature range from 0 to 1500 K and at 1 atm are evaluated in this work by the method of statistical mechanics [19]. In all calculations, the 1973 Fundamental Physical Constants recommended by the CODATA Task Group [20], and 1975 Atomic Weights [21,22] for C = 12.011, H = 1.0079, D = 2.0141, and O = 15.9994 were used. SI units were adopted for presenting the final calculated results. For comparison of the calculated values with the experimental data, the reported values, mostly in calories instead of joules, were taken directly to avoid confusion caused by changing units. For conversion to SI units, the conversion factors 1 cal = 4.184 joules and 1 atm = 101325 Nm^{-2} should be used.

MOLECULAR AND THERMAL DATA

Methanal (HCHO)

The molecular structure of this compound is planar with C_{2v} symmetry as observed by electron diffraction and microwave spectroscopy. The bond distances and angles reported did not agree.

Recent, Chu et al. [23] observed the weak transitions of the type $\Delta J = \pm 1$, $\Delta K_a = \mp 2$, $\Delta K_c = \pm 3$ in HCHO and DCDO by the millimeterwave double resonance method and also by direct absorption with a Stark modulated spectrometer. Adding these new transitions into the previously known microwave and millimeterwave data, for a least-squares analysis, they obtained an improved set of rotational and distortion constants. Their reported ground state rotational constants for the HCHO molecule (in MHz): $A = 281968.61$, $B = 38835.3198$, and $C = 34002.9531$ were adopted to derive the three

TABLE 1

Molecular and thermal constants for methanal and its deuterated species

Molecular and thermal constant	HCHO	HCDO	DCDO
Molecular weight	30.0262	31.0324	32.0386
Point group	C_{2v}	C_s	C_{2v}
Symmetry number	2	1	2
Ground state configuration	$^1A_1$	$^1A'$	$^1A_1$
Product of the three principal moment of inertia (g^3 cm^6)	1.5874×10^{-117}	2.8906×10^{-117}	4.9357×10^{-117}
Vibrational wavenumbers (cm^{-1})	a_1: 2783, 1746, 1500 b_1: 2843, 1249 b_2: 1167	a': 2844, 2121 1723, 1400, 1041 a'': 1074	a_1: 2056, 1700, 1106 b_1: 2160, 990 b_2: 938
Enthalpy of formation at 298.15 K (kcal $mole^{-1}$)	—25.95	—26.59	—27.46

principal moments of inertia as: $I_A = 2.97626 \times 10^{-40}$ g cm^2, $I_B = 2.16096 \times 10^{-39}$ g cm^2, and $I_C = 2.46807 \times 10^{-39}$ g cm^2, respectively. The product, $I_A I_B I_C$ (as shown in Table 1) was employed to calculate the rotational contributions to perfect gas thermodynamic properties for HCHO molecules by the statistical mechanical method.

Numerous researchers investigated infrared spectra of the formaldehyde molecule. In this work, we adopted the vibrational assignments recommended by Shimanouchi [24] for evaluation of the vibrational contributions to the thermodynamic properties of this compound in the perfect gas state. Their numerical values appear in Table 1.

Reported values for the enthalpy of formation at 298.15 K for methanal gas range from —25.1 to —29.3 kcal mole^{-1} (see Table 2). It is interesting to note that different authors derived different values of ΔH_f° (HCHO, g, 298.15 K) from the same set of reported experimental thermal data, because of various choices of auxiliary data for evaluation.

Fletcher and Pilcher [25] measured the enthalpy of combustion of HCHO(g) as —136.42 ± 0.11 kcal mole^{-1} by flame calorimetry. The ΔH_f° (HCHO, g, 298.15 K) was calculated to be —25.95 ± 0.11 kcal mole^{-1}, which was used along with the thermodynamic functions for C(graphite), H_2(g), O_2(g) [26] and HCHO(g) from this work to compute ΔH_f° and ΔG_f°.

Methanal-d$_1$ *(HCDO)*

Oka [27] determined the rotational constants for the isotopic methanal molecules from the parameters used in the analysis of K-type doubling spectra and the frequencies of $1_{01} \leftarrow 0_{00}$ transitions. From the rotational constants, the zero-point structure of methanal molecule, r_z, was derived by a new method taking into account the zero-point vibration—rotation interaction and electronic interaction. The reported rotational constants for HCDO(g): $A = 198122 \pm 25$ MHz, $B = 34910.13 \pm 1$ MHz, and $C =$

TABLE 2

Reported enthalpy of formation at 298.15 K for methanal

ΔH_f° (kcal mole^{-1})	Method of determination
—25.1 ± 0.7	Solution calorimetry [a]
—25.3	Solution and flame calorimetry [b]
—25.90 ± 0.21	Reaction calorimetry [c]
—25.95 ± 0.11	Flame calorimetry [d]
—27.7	Flame calorimetry [e]
—28.44	Equilibrium measurement [f]
—28.69 ± 0.7	Equilibrium measurement [g]
—29.3 ± 1.0	Equilibrium measurement [h]
—25.97 ± 0.09	Average value [i]

[a] Ref. 45.

[b] Refs. 45—47.

[c] Ref. 50.

[d] Ref. 25.

[e] Ref. 46.

[f] Ref. 48; chemical reaction: $HCHO(g) + H_2(g) = CH_3OH(g)$.

[g] Ref. 49; chemical process: $CH_2O(g) \rightleftharpoons 1/n(CH_2O)_n(c)$.

[h] Ref. 48; chemical reaction: $CO(g) + H_2(g) = CH_2O(g)$.

[i] This is the weighted average value. The last three experimental data are not used because determination by equilibrium measurement is less accurate than by the other techniques.

29562.36 ± 1 MHz were used to calculate $I_A = 4.23585 \times 10^{-40}$ g cm^2, $I_B = 2.40393 \times 10^{-39}$ g cm^2, $I_C = 2.83879 \times 10^{-39}$ g cm^2, and $I_A I_B I_C = 2.89065 \times 10^{-117}$ g^3 cm^6. The rotational constants B and C were later confirmed by analysis of millimeterwave spectrum of HCDO(g) by Takagi and Oka [28].

The fundamental vibrational wavenumbers used were those assigned by Shimanouchi [24]. The ΔH_f° (HCDO, g, 298.15 K) was derived from zero-point energies, ΔH_f° (HCHO, g, 0 K) and appropriate thermal functions for gaseous H_2, D_2, HCHO, and HCDO.

*Methanal-*d$_2$ *(DCDO)*

Chu et al. [23] observed frequencies of the $\Delta K_a = 2$ transitions in DCDO molecule and determined more accurately the rotational constant A and the centrifugal distortion constant. By adding the new transition to the known microwave and millimeterwave data in a least-squares analysis, they obtained the following ground state rotational constants: $A = 141653.48$ MHz, $B = 32283.204$ MHz, and $C = 26185.741$ MHz. These constants agree with those given by Tatematsu et al. [29]. Based upon these rotational constants, the moments of inertia are: $I_A = 5.9244 \times 10^{-40}$ g cm^2, $I_B = 2.5995 \times 10^{-39}$ g cm^2, and $I_C = 3.2048 \times 10^{-39}$ g cm^2. The value of $I_A I_B I_C$ was 4.9357×10^{-117} g^3 cm^6 which was used for statistical mechanical calculations.

Shimanouchi [24] recommended the six vibrational wavenumbers observed by Cossee and Schachtschneider [30] as the best values for DCDO(g). The vibrational assignments, shown in Table 1, were adopted in this work. The enthalpy of formation at 298.15 K was calculated following the same procedure as that described for HCDO(g).

Ethanal (CH_3CHO)

The molecular structure of ethanal has been studied by electronic diffraction [31—33] and microwave spectroscopy [34—37]. The two carbon atoms and the hydrogen and oxygen of the carbonyl group are in a single plane. In this work, the structural parameters determined by Nösberger et al. [37] from the moments of inertia of isotopically substituted species were employed to calculate the three principal moments of inertia as follows: $I_A = 1.4752 \times 10^{-39}$ g cm^2, $I_B = 8.2479 \times 10^{-34}$ g cm^2, and $I_C = 9.1889 \times 10^{-39}$ g cm^2. Based on these structural parameters, the reduced moment of the CH_3 top and the internal rotational constant were calculated to be 3.648×10^{-40} g cm^2 and 7.673 cm^{-1}, respectively.

The vibrational spectra of acetaldehyde have been studied by many investigators. Shimanouchi [24] critically reviewed the reported vibrational assignments for the CH_3CHO molecule and selected a complete set of fundamental vibrational wavenumbers for this compound. His selected values (see Table 3) were used for evaluation.

Table 4 indicates the reported torsional frequency and internal rotational

TABLE 3

Molecular and thermal constants for ethanal and its deuterated species

Molecular and thermal constant	CH_3CHO	CH_3CDO	CD_3CDO
Molecular weight	44.0530	45.0592	48.0778
Point group	C_s	C_s	C_s
Symmetry number	1	1	1
Ground state configuration	$^1A'$	$^1A'$	$^1A'$
Product of the three principal moments of inertia (g^3 cm^6)	1.1180×10^{-115}	1.4720×10^{-115}	2.6079×10^{-115}
Internal rotation constant (cm^{-1})	7.673	7.030	4.370
Torsional frequency ($0 \rightarrow 1$) (cm^{-1})	150	146	116
Potential barrier height (kcal mole^{-1})	1.178	1.211	1.161
Vibrational wavenumbers (cm^{-1})	a': 3005, 2917, 2822, 1743, 1441, 1400, 1352, 1113, 919, 509 a'': 2967, 1420, 867, 763	a': 3028, 2917, 2071, 1743, 1442, 1109, 1353, 1043, 849, 500 a'': 2970, 1420, 802, 668	a': 2265, 2130, 2060, 1737, 1045, 938, 1028, 1151, 747, 436 a'': 2225, 1028, 573, 670
Enthalpy of formation at 298.15 K, (kcal mole^{-1})	—39.51	—40.44	—43.16

TABLE 4

Reported torsional frequency and internal rotational barrier height of —CH_3 top in the CH_3CHO molecule

Torsional frequency (cm^{-1})	Barrier height (cal $mole^{-1}$) V_3	V_6	Investigators (year)
	1000	0	Pitzer and Weltner (1949) [a]
143.0	1112	0	Souter and Wood (1970) [b]
	1140 ± 40	~56	Lin and Kilb (1956) [c]
	1145 ± 7	—31 ± 9	Bauder and Günthard (1976) [d]
	1162 ± 30	~50	Kilb et al. (1957) [e]
148	1168 ± 30	0	Herschbach (1959) [f]
150	1178	0	This work
150 ± 1	1180 ± 15	0	Fateley and Miller (1961) [g]
	1232 ± 20	0	Iijima and Tsuchiya (1972) [h]

[a] Ref. 8.
[b] Ref. 51.
[c] Ref. 35.
[d] Ref. 36.
[e] Ref. 34.
[f] Ref. 43.
[g] Ref. 18.
[h] Ref. 44.

barrier height of the methyl top (—CH_3) in the CH_3CHO molecule. The torsional frequency of 150 cm^{-1} observed by Fateley and Miller [18] and the internal rotation constant derived from the molecular structure of Nösberger et al. [37] were employed for evaluating the internal rotational barrier height V_3 to be 1178 cal $mole^{-1}$, as shown in Table 4. Based upon a potential function $V = 0.5\ V_3\ (1 - \cos 3\theta)$, 96 energy levels (up to 17 000 cm^{-1}) were generated by an approximate solution of the Schrödinger wave equation [38, 39]. An internal rotation partition function formed by summation of the 96 internal rotation energy levels was used for computing the internal rotational contributions to the perfect gas thermodynamic properties for $CH_3CHO(g)$.

The enthalpy change for the reaction

$$CH_3CHO(g) + H_2(g) = CH_3CH_2OH(g)$$

was determined to be —16 752 ± 100 cal $mole^{-1}$ at 355 K by Dolliver et al. [40]. Employing appropriate enthalpy data at 355 and 298.15 K for $CH_3CHO(g)$ (from this work), $H_2(g)$ [26], and $CH_3CH_2OH(g)$ [26], the enthalpy change of the above reaction at 298.15 K was derived as —16.52 ± 0.10 kcal $mole^{-1}$. Using $\Delta H_f^0(CH_3CH_2OH, l, 298.15\ K) = -66.20 \pm 0.07$ kcal $mole^{-1}$ reported by Chao and Rossini [41] and $\Delta H_v^0(CH_3CH_2OH, l, 298.15\ K) = 10.17$ kcal $mole^{-1}$ [26], the value of $\Delta H_f^0(CH_3CHO, g, 298.15\ K)$ was calculated to be —39.51 kcal $mole^{-1}$ which was adopted for evaluation of the ΔH_f^0 and ΔG_f^0 over the temperature range from 0 to 1500 K and at 1 atm for gaseous acetaldehyde.

TABLE 5

Comparison of internal rotation energy levels (cm^{-1})

Transition	State	Observed (ref. 18)	Calculated
0 → 1	A	150.0	150.1
	E	147.6	147.7
1 → 2	A	111.0	111.9
	E	128.5	128.5
2 → 3	A	157.2	155.0
	E	79.9	78.0

A comparison of six calculated internal rotation energy levels with the observed ones is presented in Table 5. The agreement between our calculated energy levels and those reported by Fateley and Miller [18] is excellent.

Ethanal-d$_1$ *(CH_3CDO)*

The structural parameters determined by Nösberger et al. [37] for the acetaldehyde molecule were adopted for the calculation of the three principal moments of inertia: $I_A = 1.8621 \times 10^{-39}$ g cm^2, $I_B = 8.2517 \times 10^{-39}$ g cm^2, and $I_C = 9.5797 \times 10^{-39}$ g cm^2. The reduced moment and rotational constant for the CH_3 rotor in CH_3CDO were calculated to be 3.982×10^{-40} g cm^2 and 7.030 cm^{-1}, respectively.

A critical review of the reported spectra data on CH_3CDO was made by Shimanouchi [24]. A complete set of vibrational assignments for this compound was selected, which was consistent with that reported by Cossee and Schachtschneider [30], except for two frequencies, i.e. 3014 (2) cm^{-1} were reassigned as 3028 and 2917 cm^{-1} by Shimanouchi. The fundamental vibrational wavenumbers selected by Shimanouchi, as shown in Table 3, were used in this work for the evaluation of the perfect gas thermodynamic properties for $CH_3CDO(g)$.

Employing the torsional frequency $\nu_{15} = 145$ cm^{-1} of Shimanouchi [24] and the calculated rotational constant, the internal rotation barrier height (V_3) was evaluated to be 1211 cal mole^{-1}. By use of the same procedure as that described for acetaldehyde, 96 internal rotation energy levels (0—16 000 cm^{-1}) were generated, which were adopted for computing the internal rotational contributions to the thermodynamic properties for ethanal-d_1.

Ethanal-d$_4$ *(CD_3CDO)*

The three principal moments of inertia of ethanal-d_4 and the reduced moment of the CD_3 top were calculated to be: $I_A = 2.4015 \times 10^{-39}$ g cm^2, $I_B = 9.7752 \times 10^{-39}$ g cm^2, $I_C = 1.1109 \times 10^{-38}$ g cm^2, and $I_\alpha = 6.407 \times 10^{-40}$ g cm^2, respectively, using an assumption that the structural parameters of $CD_3CDO(g)$ were the same as those [37] for $CH_3CHO(g)$. The product $I_A I_B I_C$ and the internal rotation constant were derived from the above calculated quantities. Their numerical values are given in Table 3.

The infrared and Raman spectra of acetaldehyde-d_4 were measured and assigned by Cossee and Schachtschneider [30]. Normal-coordinate calculations have been carried out for this compound and many other isotopic species of acetone, acetaldehyde, and formaldehyde. Their complete set of 14 fundamental assignments were adopted in this work. The missing frequency, ν_{14}, was assigned to be 670 cm^{-1} by Shimanouchi [24].

The torsional frequency (ν_{15}) has been reported to be 116 cm^{-1} [24,30, 42]. The barrier height for internal rotation of CD_3 top was given as: $V_3 = 1100 \pm 70$, $V_6 = 89$ cal mole^{-1} by Lin and Kilb [35]; $V_3 = 1151 \pm 30$, $V_6 = 58$ cal mole^{-1} by Kilb et al. [34]; $V_3 = 1163 \pm$ cal mole^{-1} by Herschbach [43]; and $V_3 = 1209 \pm 100$ cal mole^{-1} by Iijima and Tsuchiya [44].

Using the reported torsional frequency, 116 cm^{-1}, and our own calculated internal rotational constant, 4.370 cm^{-1}, a value of $V_3 = 1161$ cal mole^{-1} was obtained for the CD_3 top internal rotation potential barrier height in the CD_3CDO molecule. Employing these data, 120 internal rotation energy levels (0—16 000 cm^{-1}) were generated by the method described previously.

CALCULATION OF RESULTS AND DISCUSSION

Employing the selected molecular, spectroscopic, and thermal constants listed in Tables 1 and 3 for HCHO, HCDO, DCDO, CH_3CHO, CH_3CDO, and

TABLE 6

Perfect gas thermodynamic properties for methanal

T (K)	$H^0-H^0_0$ (J mole^{-1})	$-(G^0-H^0_0)/T$ (J K^{-1} mole^{-1})	S^0 (J K^{-1} mole^{-1})	C^0_p (J K^{-1} mole^{-1})	ΔH^0_f (kJ mole^{-1})	ΔG^0_f (kJ mole^{-1})
0	0.00	0.00	0.00	0.000	−104.74	−104.74
50	1663.00	125.60	158.86	33.258	−105.91	−105.65
100	3326.00	148.66	181.91	33.258	−106.10	−105.33
150	4989.00	162.14	195.40	33.280	−106.48	−104.87
200	6657.00	171.71	205.00	33.499	−107.07	−104.25
273.15	9144.00	182.11	215.58	34.699	−108.17	−103.07
298.15	10 020.00	185.05	218.65	35.388	−108.58	−102.56
300	10 085.00	185.25	218.87	35.444	−108.61	−102.52
400	13 809.00	195.04	229.56	39.242	−110.31	−100.23
500	17 956.00	202.88	238.79	43.737	−111.95	−97.53
600	22 554.00	209.57	247.16	48.183	−113.44	−94.50
700	27 581.00	215.50	254.90	52.281	−114.75	−91.23
800	32 996.00	220.88	262.13	55.942	−115.88	−87.80
900	38 754.00	225.85	268.91	59.157	−116.83	−84.22
1000	44 813.00	230.48	275.29	61.952	−117.62	−80.54
1100	51 132.00	234.83	281.31	64.368	−118.28	−76.85
1200	57 676.00	238.94	287.00	66.453	−118.83	−73.02
1300	64 413.00	242.85	292.39	68.251	−119.31	−69.19
1400	71 318.00	246.57	297.51	69.803	−119.72	−65.27
1500	78 367.00	250.13	302.37	71.146	−120.08	−61.39

TABLE 7

Perfect gas thermodynamic properties for methanal-d_1

T (K)	$H^0-H^0_0$ (J mole^{-1})	$-(G^0-H^0_0)/T$ (J K^{-1} mole^{-1})	S^0 (J K^{-1} mole^{-1})	C^0_p (J K^{-1} mole^{-1})	ΔH^0_f (kJ mole^{-1})	ΔG^0_f (kJ mole^{-1})
0	0.00	0.00	0.00	0.000	—107.44	—107.44
50	1663.00	134.27	167.53	33.258	—108.22	—108.25
100	3326.00	157.32	190.58	33.258	—108.59	—108.16
150	4990.00	170.81	204.07	33.328	—109.12	—107.83
200	6665.00	180.38	213.71	33.779	—109.77	—107.30
273.15	9194.00	190.81	224.47	35.618	—110.86	—106.25
298.15	10 096.00	193.77	227.63	36.541	—111.25	—105.79
300	10 164.00	193.98	227.86	36.614	—111.28	—105.75
400	14 046.00	203.88	238.99	41.177	—112.83	—103.66
500	18 412.00	211.89	248.72	46.153	—114.26	—101.21
600	23 267.00	218.78	257.55	50.873	—115.50	—98.48
700	28 570.00	224.91	265.72	55.091	—116.56	—95.56
800	34 267.00	230.49	273.32	58.754	—117.44	—92.50
900	40 303.00	235.65	280.43	61.888	—118.17	—89.33
1000	46 629.00	240.46	287.09	64.553	—118.76	—86.07
1100	53 200.00	244.99	293.35	66.812	—119.23	—82.83
1200	59 980.00	249.27	299.25	68.728	—119.64	—79.46
1300	66 936.00	253.33	304.82	70.358	—119.98	—76.12
1400	74 043.00	257.19	310.08	71.748	—120.28	—72.68
1500	81 279.00	260.89	315.07	72.940	—120.54	—69.29

TABLE 8

Perfect gas thermodynamic properties for methanal-d_2

T (K)	$H^0-H^0_0$ (J mole^{-1})	$-(G^0-H^0_0)/T$ (J K^{-1} mole^{-1})	S^0 (J K^{-1} mole^{-1})	C^0_p (J K^{-1} mole^{-1})	ΔH^0_f (kJ mole^{-1})	ΔG^0_f (kJ mole^{-1})
0	0.00	0.00	0.00	0.000	—111.15	—111.15
50	1663.00	131.13	164.39	33.258	—111.54	—111.27
100	3326.00	154.18	187.44	33.261	—112.09	—110.81
150	4991.00	167.67	200.94	33.420	—112.76	—110.02
200	6679.00	177.25	210.65	34.235	—113.47	—109.00
273.15	9272.00	187.73	221.68	36.927	—114.54	—107.21
298.15	10 210.00	190.72	224.96	38.136	—114.90	—106.51
300	10 281.00	190.93	225.20	38.229	—114.93	—106.45
400	14 371.00	201.00	236.93	43.647	—116.28	—103.42
500	19 011.00	209.24	247.26	49.095	—117.43	—100.07
600	24 173.00	216.37	256.66	54.057	—118.38	—96.51
700	29 800.00	222.75	265.32	58.360	—119.13	—92.80
800	35 823.00	228.58	273.36	61.993	—119.73	—88.99
900	42 178.00	233.98	280.84	65.017	—120.19	—85.12
1000	48 809.00	239.02	287.82	67.521	—120.54	—81.17
1100	55 668.00	243.75	294.36	69.594	—120.80	—77.29
1200	62 716.00	248.23	300.49	71.316	—121.01	—73.28
1300	69 922.00	252.47	306.26	72.752	—121.19	—69.31
1400	77 259.00	256.51	311.70	73.958	—121.35	—65.26
1500	84 707.00	260.36	316.83	74.977	—121.50	—61.26

TABLE 9

Perfect gas thermodynamic properties for ethanal

T (K)	$H^0-H^0_0$ (J mole^{-1})	$-(G^0-H^0_0)/T$ (J K^{-1} mole^{-1})	S^0 (J K^{-1} mole^{-1})	C^0_p (J K^{-1} mole^{-1})	ΔH^0_f (kJ mole^{-1})	ΔG^0_f (kJ mole^{-1})
0	0.00	0.00	0.00	0.000	−154.83	−154.83
50	1689.00	153.94	187.73	35.532	−158.09	−154.09
100	3595.00	178.01	213.96	40.269	−159.16	−151.30
150	5686.00	192.96	230.87	43.263	−160.44	−147.10
200	7926.00	204.11	243.74	46.474	−161.98	−142.42
273.15	11 545.00	216.84	259.11	52.795	−164.46	−134.91
298.15	12 896.00	220.58	263.84	55.318	−165.31	−132.13
300	12 999.00	220.85	264.18	55.510	−165.37	−131.92
400	19 085.00	233.90	281.62	66.282	−168.65	−120.25
500	26 241.00	245.06	297.54	76.675	−171.54	−107.82
600	34 382.00	255.06	312.36	85.942	−173.99	−94.85
700	43 390.00	264.24	326.23	94.035	−176.03	−81.47
800	53 154.00	272.81	339.26	101.07	−177.69	−67.85
900	63 574.00	280.88	351.52	107.19	−179.00	−54.04
1000	74 565.00	288.53	363.10	112.49	−179.97	−40.05
1100	86 049.00	295.81	374.04	117.08	−180.68	−26.13
1200	97 961.00	302.71	384.40	121.06	−181.19	−11.98
1300	110 240.00	309.43	394.23	124.50	−181.55	+2.12
1400	122 850.00	315.82	403.57	127.49	−181.76	16.35
1500	135 730.00	321.97	412.46	130.09	−181.87	30.46

TABLE 10

Perfect gas thermodynamic properties for ethanal-d_1

T (K)	$H^0-H^0_0$ (J mole^{-1})	$-(G^0-H^0_0)/T$ (J K^{-1} mole^{-1})	S^0 (J K^{-1} mole^{-1})	C^0_p (J K^{-1} mole^{-1})	ΔH^0_f (kJ mole^{-1})	ΔG^0_f (kJ mole^{-1})
0	0.00	0.00	0.00	0.000	−158.97	−158.97
50	1691.00	155.38	189.20	35.641	−161.83	−158.57
100	3603.00	179.48	215.51	40.446	−163.08	−154.84
150	5713.00	194.49	232.58	43.939	−164.48	−150.42
200	8006.00	205.71	245.75	47.950	−166.04	−145.50
273.15	11 775.00	218.64	261.74	55.324	−168.41	−137.64
298.15	13 192.00	222.46	266.71	58.108	−169.20	−134.75
300	13 300.00	222.73	267.07	58.317	−169.26	−134.53
400	19 702.00	236.15	285.41	69.688	−172.23	−122.48
500	27 211.00	247.70	302.12	80.292	−174.77	−109.75
600	35 717.00	258.07	317.60	89.606	−176.87	−96.55
700	45 090.00	267.62	332.03	97.647	−178.56	−83.01
800	55 208.00	276.52	345.53	104.56	−179.91	−69.27
900	65 968.00	284.90	358.20	110.49	−180.92	−55.37
1000	77 279.00	292.83	370.11	115.58	−181.64	−41.33
1100	89 061.00	300.37	381.34	119.95	−182.13	−27.39
1200	101 250.00	307.57	391.94	123.71	−182.44	−13.22
1300	113 780.00	314.45	401.97	126.94	−182.63	+0.87
1400	126 620.00	321.04	411.49	129.73	−182.70	15.08
1500	139 720.00	327.37	420.52	132.14	−182.70	29.17

TABLE 11

Perfect gas thermodynamic properties for ethanal-d_4

T (K)	$H^0-H_0^0$ (J mole^{-1})	$-(G^0-H_0^0)/T$ (J K^{-1} mole^{-1})	S^0 (J K^{-1} mole^{-1})	C_p^0 (J K^{-1} mole^{-1})	ΔH_f^0 (kJ mole^{-1})	ΔG_f^0 (kJ mole^{-1})
0	0.00	0.00	0.00	0.000	−171.04	−171.04
50	1716.00	158.76	193.08	37.024	−172.70	−169.20
100	3699.00	183.39	220.38	41.898	−174.42	−165.07
150	5900.00	198.83	239.16	46.253	−176.17	−160.01
200	8343.00	210.47	252.19	51.699	−177.79	−154.37
237.15	12 468.00	224.04	269.68	61.243	−179.92	−145.48
298.15	14 041.00	228.10	275.19	64.640	−180.58	−142.27
300	14 161.00	228.39	275.59	64.890	−180.63	−142.02
400	21 310.00	242.80	296.07	77.859	−182.88	−128.79
500	29 678.00	255.34	314.70	89.214	−184.56	−115.08
600	39 097.00	266.68	331.84	98.906	−185.78	−101.06
700	49 408.00	277.14	347.72	107.08	−186.60	−86.87
800	60 467.00	286.89	362.48	113.90	−187.12	−72.58
900	72 149.00	296.07	376.23	119.55	−187.37	−58.23
1000	84 346.00	304.73	389.08	124.24	−187.39	−43.83
1100	96 970.00	312.95	401.11	128.12	−187.25	−29.61
1200	109 950.00	320.77	412.40	131.36	−187.02	−15.20
1300	123 220.00	328.23	423.02	134.06	−186.72	−0.92
1400	136 750.00	335.37	433.04	136.33	−186.39	+13.48
1500	150 480.00	342.20	442.51	138.26	−186.04	27.69

TABLE 12

Comparison of vapor heat capacities for ethanal

T (K)	C_p (exptl.)[a] at 1 atm (cal K^{-1} mole^{-1})	C_p^0 (exptl.) (cal K^{-1} mole^{-1})		C_p^0 (calc.) (cal K^{-1} mole^{-1})	C_p^0 (exptl.)—C_p^0 (exptl.)	
		TRCDP[b]	P—W[c]		TRCDP[d]	P—W[e]
298.1	14.8	13.34	13.14	13.22	−0.12 (−0.9%)	0.08 (+0.6%)
322.9	14.8	14.02	13.87	13.84	−0.18 (−1.3%)	−0.03 (−0.2%)
372.7	15.2	14.90	14.92	15.13	+0.23 (+1.5%)	+0.21 (+1.4%)
422.4	16.3	16.15	16.12	16.42	+0.27 (+1.7%)	+0.30 (+1.9%)

[a] Ref. 12.

[b] Use second virial coefficient data from ref. 26 for conversion to C_p^0.

[c] Use second virial coefficient data from ref. 8 for conversion to C_p^0.

[d] C_p^0 (exptl.) values are those listed in the third column of this table.

[e] C_p^0 (exptl.) values are those listed in the fourth column of this table.

TABLE 13

Comparison of calculated C_p^0, S^0 and H^0—H_0^0 with reported values for ethanal

T (K)	C_p^0 (cal K^{-1} mole^{-1})				H^0—H_0^0 (cal mole^{-1})				S^0 (cal K^{-1} mole^{-1})			
	P—W [a]	A—M [b]	L—N—K [c]	This work	P—W [a]	A—M [b]	L—N—K [c]	This work	P—W [a]	A—M [b]	L—N—K [c]	This work
100				9.624				859.00				51.136
298.15	13.06	13.18	13.216	13.221	3070.00			3082.00	63.15	63.50	63.012	63.059
500	18.27	18.17	18.371	18.326	6240.00			6272.00	71.14	71.50	71.140	71.114
1000	26.96	26.98	26.950	26.886	17 810.00			17 821.00	86.84	87.12	86.662	86.782
1500		31.36		31.091				32 440.00		99.23		98.579

[a] Ref. 8.
[b] Ref. 4.
[c] Ref. 10.

CD_2CDO, the perfect gas thermodynamic properties for these compounds were evaluated by the method of statistic mechanics, based on a rigid-rotor harmonic-oscillator molecular model. The calculated results are presented in Table 6—11.

For the calculation of the three principal moments of inertia for the deuterated species, an assumption was made that the molecular structure of each was the same as that of the corresponding undeuterated species. The errors caused by this assumption in the calculated thermodynamic properties are insignificant.

The value of ΔH^0_f(g, 298.15 K) for the deuterated species was derived from the zero point energies of the given pair of deuterated and undeuterated species, the ΔH^0_f at 0 K for the undeuterated one, and the auxiliary enthalpy data for the species involved.

In Table 12, a comparison of heat capacities calculated in this work with some experimental data is given for ethanal(g). The C_p values listed in column 2 of this table were determined by Coleman and DeVries [12], which are the only experimental measurements available for ethanal. Two sets of second virial coefficients for ethanal(g) were reported [8,26]. These two sets of data were employed separately to derive the corresponding $C_p - C^0_p$ values at four temperatures, 298.1, 322.9, 372.7, and 422.4 K. The derived heat capacities at these temperatures were presented in columns 3 and 4 of Table 12. The differences between calculated and experimental heat capacities are listed in the last two columns of that table. In general, the agreement is good. The average deviations for the values in columns 6 and 7 are 0.05 and 0.14 cal K^{-1} $mole^{-1}$, respectively (0.2% and 0.9%). The calculated C^0_p, $H^0 - H^0_0$, and S^0 are compared with the reported literature values [4,8,10] at 298.15, 500, 1000, and 1500 K, which are presented in Table 13.

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