Thermodynamic Properties of Normal and Deuterated Methanols

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Structural and spectroscopic data on CH_3OH, CH_3OD, CD_3OH, and CD_3OD were reviewed. The selected values were utilized to calculate the ideal gas thermodynamic properties in the temperature range of 0 to 1500 K, using the rigid-rotor and harmonic-oscillator model. Experimental data for the standard enthalpy of formation at 298.15 K, the heat capacities, and the third-law entropies at elevated temperatures are available only for CH_3OH in the vapor phase where intermolecular association occurs. The agreement between the observed thermal data and our calculated values is satisfactory within the experimental uncertainties. Finally, the standard chemical thermodynamic values for $\Delta Hf°$, $\Delta Gf°$, and log Kf were generated in the temperature range of 0 to 1500 K.

Key words: Enthalpy of formation; Gibbs energy of formation; ideal gas thermodynamic properties; intermolecular association; normal and deuterated methanols; potential barrier to internal rotation; principal and reduced moments of inertia; structural parameters; vibrational fundamentals; virial coefficients of the equation of state.

Contents

1. Introduction

The chemical thermodynamic properties of methanol and its deuterated species in the ideal gas state were calculated [1][^1] two decades ago. The values reported for methanol were included in a recent work on monohydroxy aliphatic alcohols [2]. However, many of the vibrational frequencies used then differed considerably from those recommended by Shimanouchi [3]. Moreover, numerous investigations [4–16], which were carried out prior to or contemporary with the thermodynamic calculations [1], led to greatly diverse values for the potential barrier to internal rotation and the torsional frequency. Only in recent years have extensive analyses [17, 18] of microwave and infrared spectra made available more accurate structural parameters, rotational constants, and potential barrier parameters. Consequently, the contribution of internal rotation to the thermodynamic properties can now be computed more accurately, using a partition function formed by a direct sum over energy levels [19].

[^1]: Figures in brackets indicate the literature references. Throughout this paper 1 cal = 4.1840 J, 1 amu $\cdot$ Å^2 = 1.66057 $\times$ 10^{-40} g $\cdot$ cm^2, and 1 atm = 1.01325 $\times$ 10^5 N $\cdot$ m^{-2}.

The availability of more accurate molecular parameters and related experimental thermodynamic properties stimulated this study. The selections of molecular parameters and the calculations of thermodynamic properties are described in the following sections.

2. Molecular Structure and Moments of Inertia

The molecular structure of methanol was investigated with x-ray diffraction [20], electron diffraction [21], and microwave [13–15, 17, 22, 23] techniques and was also reported in papers [24] primarily dealing with force field calculations. For the purpose of this paper, the deuterated methanols (CH_3OD, CD_3OH, and CD_3OD) will be considered to possess the same molecular dimensions as CH_3OH. Analyses of microwave spectra [13, 14, 17, 22, 25] provides accurate values for the rotational constants and, consequently, the moments of inertia for each of the four methanols. The extensive analyses of Lees, et al. [17] appeared to give more accurate structural parameters and rotational constants; those parameters and constants were adopted in this work. The principal moments of inertia were derived from rotational constants by using the conversion factor 505379 MHz $\cdot$ amu $\cdot$ Å^2 [26]. The selected values of the structural parameters and the principal moments are listed in table 1.

TABLE 1.   Selected values of physical and chemical constants of isotopic species of methanol

Compound		CH_3OH	CH_3OD	CD_3OH	CD_3OD
Molecular weight, g · mol^{-1}		32.0424	33.0485	35.0607	36.0668
Symmetry number, dimensionless		3	3	3	3
Structural parameters					
r (C—H), 10^{-8} cm		1.0936			
r (C—O), 10^{-8} cm		1.4246			
r (O—H), 10^{-8} cm		0.9451	same as CH_3OH	same as CH_3OH	same as CH_3OH
∢HCH, degree		108.63			
∢COH, degree		108.53			
∢(methyl tilt), degree		3.27			
Principal moments of inertia					
I_a, 10^{-40} g · cm^2		6.578	7.671	11.854	12.956
I_b, 10^{-40} g · cm^2		34.004	35.803	42.283	44.418
I_c, 10^{-40} g · cm^2		35.306	38.174	43.541	46.750
Reduced moment of inertia					
Staggered configuration, 10^{-40} g · cm^2		0.993	1.576	1.097	1.856
Reduced inverse moment of inertia F, cm^{-1}		28.182	17.762	25.522	15.079
Vibrational fundamentals, cm^{-1}					
Symmetry species a'	ν_1	3681	2718	3690	2724
	ν_2	3000	3000	2260	2260
	ν_3	2844	2843	2077	2080
	ν_4	1477	1473	1047	1024
	ν_5	1455	1456	1134	1135
	ν_6	1345	864	1297	1060
	ν_7	1060	1230	858	776
	ν_8	1033	1040	988	983
Symmetry species a''	ν_9	2960	2960	2235	2228
	ν_{10}	1477	1473	1075	1080
	ν_{11}	1165	1160	877	892
	$\nu_{12}{}^a \begin{cases} E \\ A \end{cases}$	200 / 298	178 / 216	194 / 275	169 / 194
Potential barrier parameters					
V_3, cal · mol^{-1}		1067.06	1047.16	1058.60	1035.55
V_6, cal · mol^{-1}		−1.49	−3.57	−6.49	−6.63
Enthalpy of formation at 298.15 K (ideal gas), kcal · mol^{-1}		−48.06	−48.68[b]	−50.91[b]	−51.84[b]

[a] The torsional mode splits into singlet A and doublet E levels.

[b] Calculated from ΔH_0^0 (g) which was deduced from zero-point energies.

It is spectroscopically evident that the carbon-oxygen inter-nuclear axis in the methanol molecule does not coincide with the C_3 symmetry axis of the methyl group, which is taken as the axis of internal rotation. The observed angle between these two axes is 3.27° [17]. The reduced moment of inertia (I_r) and the reduced inverse moment of inertia ($F = h/8\pi^2cI_r$) were evaluated with the Kilpatrick-Pitzer procedure [28] and the values are reported in table 1.

3. Vibrational Fundamentals

Each of the normal and deuterated methanols belongs to the point group C_s and has eight of its twelve normal modes with a' symmetry and the other four with a'' symmetry. Falk and Whalley [29] reviewed the studies on vibrational assignments published prior to 1960. Using improved techniques, vibrational frequencies for the vapor [29–32] and condensed [29, 33–37] phases were determined from infrared [29, 31, 34–36] and Raman [29, 30, 32, 33, 37] spectra. Certain theoretical calculations have also been reported [24, 38]. Shimanouchi and coworkers have also analyzed and selected

[3] the values of the vibrational frequencies for the four methanols in both the gas and liquid phases.

Since our main concern is the calculation of thermodynamic properties in the gaseous state, the condensed-phase vibrational assignments will not be emphasized, unless information on the vapor phase is insufficient. For CH_3OH vapor, some of the vibrational frequencies reported among infrared [29, 31] and Raman [30, 32] investigations are conflicting. Shimanouchi's selected values have been adopted on the ground that his values were derived from thorough analyses of isotopic methanols; in addition, the resulting thermodynamic properties are in good agreement with their experimental counterparts. The adopted values for the vibrational fundamentals of the four methanols are listed in table 1.

4. Internal Rotation

Earlier investigations [4–16, 39] and quantum mechanical calculations [40] pertaining to the potential barrier to internal rotation showed considerable disagreement. In order to obtain a better fit to the observed data, it has been shown [18] that the barrier-shape parameter V_6, should also be included in

addition to V_3. The potential energy function can be adequately represented by $V(\phi) = \frac{1}{2}V_3(1 - \cos 3\phi) + \frac{1}{2}V_6(1 - \cos 6\phi)$ where ϕ is the angle of internal rotation. Based on the infrared data [41], $V_3 = 1072$ cal • mol^{-1} and $V_6 < 11$ cal • mol^{-1} were proposed [42] for methanol. A good fit to both infrared and microwave frequencies [22] was obtained with $V_3 = 1075$ cal • mol^{-1} and $V_6 = -2$ cal • mol^{-1} derived [43] from a semi-empirical energy function [44]. While 232 cm^{-1} proposed [45] from infrared data [41] as the torsional mode was a crude approximation, the assignment of 350 cm^{-1} from infrared data [34] to the methyl torsion was ruled out on the ground of the small isotopic shift factor [36].

By considering torsion-vibration-rotation interactions as empirically adjusted parameters, the values of V_3 for CH$_3$OH, CH$_3$OD, CD$_3$OH, and CD$_3$OD were derived [17] from microwave and infrared data as 1074, 1059, 1063, and 1037 cal • mol^{-1}, respectively, with V_6 lying between 0 and -2.3 cal • mol^{-1}. When the perturbation terms for asymmetric rotor, first order deviation from a sinusoidal potential, and effects of centrifugal distortion were considered, Kwan and Dennison [18] obtained the values of V_3 (and V_6 in parentheses) as 1067.06 ± 0.23 (-1.49 ± 0.40), 1047.16 ± 0.14 (-3.57 ± 0.31), 1058.60 ± 0.69 (6.49 ± 2.12) and 1035.55 ± 0.17 (-6.63 ± 0.23) cal • mol^{-1}, respectively, for the four isotopic methanols. The values were derived from a nonlinear least squares fit to the observed microwave and infrared data. In view of the rigorous theoretical analysis by Kwan and Dennison [18], their values for V_3 and V_6, as listed in table 1, were used in this work to calculate, as previously described [19], the internal rotational energy levels.

5. Corrections for Gas Imperfection

From the nonlinear trend of heat capacity versus pressure [46, 47], from P-V-T studies [48], and from infrared absorption spectra [49], it was concluded that monomers, dimers, and cyclic tetramers of methanol mutually exist in a vapor mixture. The 1-2-4 model was also proposed [50] from the infrared absorption spectrum for CH$_3$OD. On analyses of the experimental vapor pressure and P-V-T data for CH$_3$OH, the 1-2 model [51] and the 1-3-8 model [52] were suggested. It

appears that the 1-3 model based on vapor-density measurements [58] is doubtful because of errors caused by condensation.

Although Kretschmer and Wiebe [48] accepted the 1-2-4 model, which was first proposed by Weltner and Pitzer [46] in the form of $PV = RT + BP + DP^3$, the corrections for nonideality to C_p and S of the real gas using their own virial coefficients, B and D, are quite different from those in [46]. The differences in $C_p - C_p^\circ$ and in $S - S^\circ$, calculated at temperatures where experimental data of C_p and S [46, 54–56] are available, can be compared in tables 2 and 3.

6. Results and Comparisons

From the selected values of the molecular constants in table 1 for the four methanols of interest, the ideal gas thermal functions, namely, C_p°, S°, $- (G^\circ - H_0^\circ)/T$, and $H^\circ - H_0^\circ$ at temperatures of $0 \sim 1500$ K, were calculated according to rigid-rotor and harmonic-oscillator approximations. The most recent fundamental constants [26] with the atomic masses, C $= 12.011$, O $= 15.9994$, H $= 1.0079$, and D $= 2.0141$ [57], were used throughout this work. The calculated results are given in tables 4, 5, 6, and 7. Only for ordinary CH$_3$OH is $\Delta H^\circ_{298.15}$ (g) $= - 48.06$ kcal• mol^{-1} available and well defined [2]. This enables one to compute the enthalpy (ΔH_f°), the Gibbs energy (ΔG_f°), and logarithmic equilibrium constant (log K_f) of formation at various temperatures, using $H^\circ - H_0^\circ$ and $(G^\circ - H^\circ)/T$ for the constituting chemical elements [58]. The calculated values are listed in table 4. For the deuterated species CH$_3$OD, CD$_3$OH, and CD$_3$OD, it is necessary to estimate ΔHf° at 0 K from the corresponding calculated zero-point energies. The thermodynamic quantities for the deuterated species thus obtained are given in tables 5, 6, and 7.

The condensed-phase heat capacities [59–62] which are essential for deriving the third-law entropy in the gas phase were experimentally measured for CH$_3$OH [59–62] and CH$_3$OD [61]. The value of S° for liquid CH$_3$OH at 298.15 K was independently obtained as 32.26 ± 0.2 cal•mol^{-1}•K^{-1} [59] and 30.40 ± 0.03 cal•mol^{-1}•K^{-1} [62]. Wilhoit and Zwolinski [2] have carefully studied the reported thermal data [59–62] and obtained 30.41 ± 0.05 cal•mol^{-1}•K^{-1} after a

TABLE 2. Comparisons of the third-law entropies (in cal • mol^{-1} • K^{-1}) with calculated values for CH$_3$OH (g)

T/K	S (Experimental)			S (Calculated)
	Real gas at saturation	Ideal gas at one atmosphere		
		W-P[a]	K-W[b]	This work
313.1	59.38[c]	57.81	57.69	57.81
327.9	58.48[c]	58.34	58.25	58.31
337.8	57.94[c]	58.73	58.66	58.64
323.15	58.76[d]	58.19	58.08	58.15
337.85	57.91[d]	58.72	58.65	58.64
363.15	56.62[d]	59.49	59.51	59.47
383.15	55.74[d]	60.07	60.17	60.10

[a] Weltner-Pitzer [46] virial coefficients, B and D, were applied to corrections for gas imperfection.

[b] Kretschmer-Wiebe [48] virial coefficients, B and D, were applied to corrections for gas imperfection.

[c] Derived from heats of vaporization [46] and C_l [62] with the estimated error of 0.3 cal•mol^{-1}•K^{-1}.

[d] Derived from heats of vaporization [54] and C_l [62] with presumably the same uncertainty as in footnote c.

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TABLE 3. Comparisons of C_p^o (g) derived from observed C_p (g) with calculated C_p^o (g) for CH_3OH

T/K	C_p/cal · mol⁻¹ · K⁻¹	C_p^o /cal · mol⁻¹ · K⁻¹			
	Experiment	Correlation [a]	W-P [b]	K-W [c]	This work
349.65	17.37 [d]		11.01	11.30	11.39
358.15	14.29 [d] (?)		11.17 (?)	10.87 (?)	11.55
358.85	14.48 [d]		11.52	11.20	11.54
359.85	14.42 [d]		11.67	11.33	11.58
368.15	13.62 [d]		12.02	11.63	11.73
382.15	13.10 [d]		12.26	11.96	11.99
401.15	13.01 [d]		12.51	12.33	12.36
420.15	13.07 [d]		12.72	12.62	12.73
442.65	13.62 [d]		13.36	13.32	13.17
341	27.00 [d]		12.29	14.83	11.23
363	14.00 [d]		11.80	11.41	11.63
405	13.03 [d]		12.57	12.41	12.43
345.6	12.18 ± 0.2 [e]		11.44 [f]	11.20 [f]	11.32
403.2	12.58 ± 0.05 [e]		12.43 [g]	12.37 [g]	12.40
464.0	13.74 ± 0.1 [e]		13.67 [g]	13.67 [g]	13.58
521.2	14.48 ± 0.2 [e]		14.44 [f]	14.45 [f]	14.66
347.35	20.76 [h]	11.19	12.60	13.29	11.35
356.55	15.92 [h]	11.37	12.27	12.03	11.51
373.35	13.43 [h]	11.71	12.19	11.81	11.83
398.95	12.66 [h]	12.22	12.13	11.94	12.32
401.15	12.91 [h]	12.27	12.41	12.22	12.36
401.35	12.94 [h]	12.27	12.44	12.26	12.36
431.45	13.33 [h]	12.88	13.03	12.96	12.95
442.15	13.39 [h]	13.09	13.13	13.08	13.16
457.35	13.62 [h]	13.39	13.41	13.38	13.45
477.75	13.68 [h]	13.80	13.51	13.50	13.84
485.05	13.52 [h] (?)	13.95	13.36 (?)	13.36 (?)	13.98
498.95	14.37 [h]	14.23	14.24	14.24	14.25
521.35	14.71 [h]	14.68	14.60	14.61	14.66
555.95	15.28 [h]	15.37	15.20	15.21	15.29
581.35	15.86 [h]	15.88	15.80	15.81	15.74
585.35	15.97 [h]	15.96	15.91	15.92	15.81

[a] $C_p^o = 2.444$ $(1.73 + 8.20 \times 10^{-3} T)$ with the average deviation of ± 0.32 cal · mol⁻¹ · K⁻¹ [56].

[b] See footnote a of table 2.

[c] See footnote b of table 2.

[d] Observed at 750 mm Hg with the uncertainty of about 1 percent [55].

[e] Observed at 260 mm Hg [46].

[f] With the estimated error of ± 0.3 cal · mol⁻¹ · K⁻¹.

[g] With the estimated error of ± 0.1 cal · mol⁻¹ · K⁻¹.

[h] Observed at 1 atm [56]. (Note 1 atm = 760 mm Hg = 101325 N · m⁻²).

TABLE 4. Ideal thermodynamic functions of methanol, CH_3OH

T	C_p^o	S^o	$-(G^o-H_0^o)/T$	$H^o-H_0^o$	ΔHf^o	ΔGf^o	log Kf
K	cal·mol⁻¹·K⁻¹				kcal·mol⁻¹		
0	0	0	0	0	−45.46	−45.46	∞
100	8.82	46.99	38.60	0.839	−46.50	−44.23	96.65
150	9.22	50.65	42.04	1.291	−46.82	−43.02	62.68
200	9.48	53.34	44.55	1.759	−47.21	−41.70	45.57
273.15	10.17	56.38	47.32	2.474	−47.84	−39.58	31.67
298.15	10.53	57.29	48.12	2.733	−48.06	−38.82	28.45
300	10.55	57.35	48.18	2.753	−48.08	−38.76	28.24
400	12.34	60.63	50.89	3.894	−48.93	−35.52	19.41
500	14.27	63.59	53.14	5.224	−49.68	−32.08	14.02
600	16.06	66.35	55.11	6.742	−50.31	−28.50	10.38
700	17.65	68.95	56.90	8.429	−50.84	−24.82	7.75
800	19.06	71.40	58.56	10.267	−51.28	−21.07	5.76
900	20.31	73.72	60.12	12.236	−51.62	−17.28	4.20
1000	21.40	75.91	61.59	14.323	−51.89	−13.44	2.94
1100	22.37	78.00	62.99	16.512	−52.09	−9.60	1.91
1200	23.21	79.98	64.32	18.792	−52.25	−5.72	1.04
1300	23.96	81.87	65.60	21.151	−52.36	−1.84	0.31
1400	24.61	83.67	66.83	23.580	−52.43	+2.07	−0.32
1500	25.19	85.39	68.01	26.071	−52.48	5.95	−0.87

TABLE 5. Ideal gas thermodynamic functions of methanol-d_1, CH_3OD

T	C_p°	S°	$-(G^\circ - H_0^\circ)/T$	$H^\circ - H_0^\circ$	ΔHf°	ΔGf°	$\log Kf$
K	cal·mol⁻¹·K⁻¹				kcal·mol⁻¹		
0	0	0	0	0	− 46.13	− 46.13	∞
100	9.13	47.56	39.16	0.840	− 47.11	− 44.77	97.85
150	9.51	51.35	42.63	1.308	− 47.46	− 43.53	63.42
200	9.76	54.11	45.17	1.789	− 47.85	− 42.16	46.07
273.15	10.52	57.26	48.00	2.528	− 48.47	− 39.98	31.99
298.15	10.90	58.19	48.82	2.795	− 48.68	− 39.20	28.73
300	10.93	58.26	48.87	2.816	− 48.70	− 39.14	28.51
400	12.76	61.65	51.65	3.997	− 49.51	− 35.82	19.57
500	14.70	64.70	53.96	5.371	− 50.21	− 32.32	14.13
600	16.51	67.55	55.99	6.933	− 50.81	− 28.69	10.45
700	18.13	70.22	57.84	8.666	− 51.30	− 24.96	7.79
800	19.56	72.73	59.54	10.552	− 51.69	− 21.17	5.78
900	20.83	75.11	61.14	12.573	− 52.00	− 17.33	4.21
1000	21.94	77.36	62.65	14.713	− 52.23	− 13.46	2.94
1100	22.91	79.50	64.09	16.956	− 52.40	− 9.59	1.91
1200	23.75	81.53	65.46	19.290	− 52.51	− 5.68	1.03
1300	24.48	83.46	66.77	21.702	− 52.59	− 1.78	0.30
1400	25.12	85.30	68.03	24.183	− 52.64	+ 2.15	− 0.34
1500	25.68	87.05	69.24	26.723	− 52.66	4.55	− 0.66

TABLE 6. Ideal gas thermodynamic functions of methanol-d_3-ol, CD_3OH

T	C_p°	S°	$-(G^\circ - H_0^\circ)/T$	$H^\circ - H_0^\circ$	ΔHf°	ΔGf°	$\log Kf$
K	cal · mol⁻¹ · K⁻¹				kcal · mol⁻¹		
0	0	0	0	0	−48.37	−48.37	∞
100	8.89	48.31	39.93	0.838	−49.26	−46.74	102.14
150	9.36	52.01	43.37	1.295	−49.68	−45.38	66.12
200	9.89	54.77	45.89	1.775	−50.11	−43.89	47.96
273.15	11.24	58.03	48.72	2.544	−50.71	−41.52	33.22
298.15	11.81	59.04	49.54	2.832	−50.91	−40.66	29.81
300	11.85	59.11	49.60	2.854	−50.92	−40.60	29.58
400	14.29	62.86	52.45	4.161	−51.61	−37.05	20.24
500	16.55	66.29	54.88	5.705	−52.15	−33.34	14.57
600	18.48	69.49	57.05	7.459	−52.56	−29.54	10.76
700	20.11	72.46	59.04	9.391	−52.86	−25.67	8.02
800	21.48	75.24	60.90	11.473	−53.08	−21.77	5.95
900	22.64	77.84	62.64	13.680	−53.22	−17.85	4.33
1000	23.61	80.27	64.28	15.994	−53.31	−13.91	3.04
1100	24.44	82.56	65.84	18.397	−53.35	−9.98	1.98
1200	25.14	84.72	67.32	20.877	−53.36	−6.03	1.10
1300	25.75	86.76	68.74	23.422	−53.35	−2.09	0.35
1400	26.26	88.68	70.10	26.023	−53.32	+1.87	−0.29
1500	26.71	90.51	71.40	28.672	−53.28	1.30	−0.19

TABLE 7.   Ideal gas thermodynamic functions of methanol-d_4, CD$_3$OD

T	C_p°	S°	$-(G^\circ - H_0^\circ)/T$	$H^\circ - H_0^\circ$	ΔHf°	ΔGf°	$\log Kf$
K	cal·mol^{-1}·K^{-1}				kcal · mol^{-1}		
0	0	0	0	0	−49.36	−49.36	∞
100	9.24	48.85	40.40	0.844	−50.20	−47.60	104.03
150	9.67	52.68	43.90	1.318	−50.64	−46.21	67.32
200	10.19	55.53	46.46	1.813	−51.06	−44.67	48.81
273.15	11.59	58.89	49.36	2.606	−51.66	−42.24	33.79
298.15	12.19	59.94	50.20	2.903	−51.85	−41.36	30.31
300	12.34	60.01	50.26	2.926	−51.86	−41.29	30.08
400	14.72	63.87	53.19	4.274	−52.51	−37.66	20.58
500	16.99	67.41	55.68	5.862	−53.01	−33.89	14.81
600	18.94	70.68	57.91	7.662	−53.37	−30.03	10.94
700	20.60	73.73	59.96	9.641	−53.63	−26.12	8.16
800	21.99	76.57	61.86	11.772	−53.80	−22.18	6.06
900	23.17	79.23	63.64	14.032	−53.91	−18.21	4.42
1000	24.15	81.73	65.33	16.399	−53.96	−14.24	3.11
1100	24.98	84.07	66.93	18.857	−53.96	−10.29	2.04
1200	25.68	86.27	68.45	21.391	−53.94	−6.31	1.15
1300	26.27	88.35	69.90	23.990	−53.89	−2.34	0.39
1400	26.78	90.32	71.29	26.643	−53.83	+1.64	−0.26
1500	27.20	92.18	72.62	29.342	−53.76	−0.42	+0.06

slight adjustment for internal consistency. This basic quantity was then used, in conjunction with the observed heat capacities of the liquid [62] and enthalpies of vaporization [46, 54], to derive the third-law entropies of the vapor with an estimated error of ±0.03 cal·mol^{-1}·K^{-1}. The reported values [8, 10, 63] of S° for the vapor at 298.15 K are less accurate, whereas Carlson and Westrum's 57.24 cal·mol^{-1}·K^{-1} [62] is fairly reliable. Comparisons with our calculated S° are shown in table 2 and the agreement, when the Weltner-Pitzer [46] corrections for gas imperfection were used, is remarkably within ±0.04 cal·mol^{-1}·K^{-1}, except at 337.8 K at which the deviation is 0.08 cal·mol^{-1}·K^{-1}. The Kretschmer-Wiebe [48] corrections for gas imperfection differ from those of Weltner and Pitzer [46] by ±0.1 cal·mol^{-1}·K^{-1}. These differences, however, are within the estimated overall experimental uncertainty ±0.3 cal·mol^{-1}·K^{-1} for S° and thus do not affect our calculated values of S°.

Only for CH$_3$OH have heat capacities of real gas been measured [46, 55, 56] in the temperature range of 341 ~ 585.35 K. The observed values of C_p at 358.15 K [55] and at 485.05 K [56] given in table 3 are apparently questionable. The differences in the corrections for gas imperfection by the Weltner-Pitzer [46] and Kretschmer-Weibe [48] viral coefficients are larger than ±0.2 cal·mol^{-1}·K^{-1} at temperatures below 400 K. This is probably due to the formation of polymeric species larger than dimers at lower temperatures, and may also be attributed to the inadequacy of the viral coefficients procedure to describe the complex state of the actual mixture. When the temperature is increased, the discrepancies diminish, indicating the predominance of dimers in the small amount of intermolecular association occurring.

As shown in table 3, comparisons of our calculated C_p° (g) with the three sets of values derived from the observed C_p (g) [46, 55, 56] for CH$_3$OH are encouraging. Except at the lowest

temperature, 341 K, each of our calculated values lies close to one of the three sets or among them. While the deviation throughout the entire temperature range falls within the experimental uncertainty of ±0.3 cal·mol^{-1}·K^{-1}, the agreement is particularly satisfactory at temperatures over 400 K.

Additional evidence in favor of our calculated C_p° at lower temperatures is also on hand. The values of C_v° for CH$_3$OH (g) derived from experimental measurements were found to be 7.46 ± 0.11 cal·mol^{-1}·K^{-1} at 200 K [9] and 8.38 ± 0.08 cal·mol^{-1}·K^{-1} [9] or 8.14 ± 0.18 cal·mol^{-1}·K^{-1} [16] at 279 K. The discrepancy at 279 K is due mainly to corrections for gas imperfection. These C_v° values correspond to C_p° values of 9.45, 10.13, and 10.37 cal·mol^{-1}·K^{-1}, respectively. Our calculated C_p° values are 9.49 cal·mol^{-1}·K^{-1} at 200 K and 10.25 cal·mol^{-1}·K^{-1} at 279 K. Our calculated value conveniently falls between the experimental values of 10.13 and 10.37 cal·mol^{-1}·K^{-1} at 279 K.

Errors in the thermodynamic properties of species calculated for the rigid-rotor harmonic-oscillator model with restricted internal rotation arise only because of errors in the molecular parameters used. In the case of methanol and its deuterated species the only significant sources of error are in the values of the fundamental frequencies and the barrier for internal rotation. Table 8 lists the uncertainties in the calculated thermodynamic functions which result from these sources. These were calculated from the usual formula for the propagation of random independent errors [64]. Errors in the fundamentals were taken as the maximum uncertainties assigned by Shimanouchi [3], and the error in the internal rotation barrier was assumed to be 100 cal·mol^{-1}. The effect of change in the internal rotation barrier was estimated from the tables of Pitzer and Gwinn [65]. Uncertainties in the thermodynamic functions for CD$_3$OD are very nearly the same as those for CD$_3$OH.

TABLE 8. Uncertainties in calculated ideal gas thermodynamic functions

T	C_p°	S°	$(G^\circ - H_0^\circ)/T$	$H^\circ - H_0^\circ$
K	cal·mol^{-1}·K^{-1}			kcal·mol^{-1}
	CH$_3$OH			
200	0.045	0.068	0.047	0.004
298	0.053	0.040	0.040	0.002
400	0.042	0.029	0.031	0.004
700	0.024	0.026	0.028	0.014
1000	0.014	0.029	0.023	0.018
1500	0.007	0.031	0.023	0.021
	CH$_3$OD			
200	0.049	0.070	0.048	0.004
298	0.057	0.043	0.048	0.002
400	0.044	0.027	0.047	0.007
700	0.022	0.014	0.035	0.018
1000	0.016	0.013	0.025	0.022
1500	0.006	0.013	0.020	0.027
	CD$_3$OH[a]			
200	0.053	0.071	0.049	0.004
298	0.070	0.046	0.050	0.004
400	0.057	0.038	0.039	0.010
700	0.036	0.044	0.041	0.024
1000	0.029	0.051	0.038	0.032
1500	0.018	0.057	0.041	0.042

[a] Uncertainties in the thermodynamic functions of CD$_3$OH and CD$_2$OD are nearly the same.

In addition, the values in tables 4–7 may differ from the properties of the real molecules because of limitations in the model. These include the effects of anharmonicity, vibration-rotation interaction, centrifugal stretching of bonds, and deviation of the potential for internal rotation from the two-term cosine formula. In general, the magnitude of these effects will increase with increasing temperature.

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8. References

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