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Thermodynamic properties of three adamantanols in the ideal gas state

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Abstract

The enthalpies of sublimation and the saturated vapor pressure of 1-adamantanol (1-Adol), 2-adamantanol (2-Adol) and 2-methyl-2-adamantanol (2-Me-2-Adol) were measured. Thermodynamic functions of the compounds under study in the ideal gas state between 100 and 1000 K were calculated by the statistical thermodynamic methods. The sets of wave numbers of normal vibrations for adamantanols were obtained by semi empirical calculation (MINDO3 И MNDO/d). The experimental entropies for gaseous adamantanols and the calculated values were in the satisfactory agreement.

Keywords: 1-Adamantanol; 2-Adamantanol; 2-Methyl-2-adamantanol; Enthalpy of sublimation; Saturated vapor pressure

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1. Introduction

The heat capacities in the range of 5–600 K and the enthalpies of solid-to-solid phase transitions and fusion for 1-adamantanol (1-Adol), 2-adamantanol (2-Adol) and 2-methyl-2-adamatnanols (2-Me-2-Adol) were reported in [1,2]. The results of further investigation of thermodynamic properties of these adamantanols are presented in this work. To obtain the experimental entropies of the compounds in the gas state, the enthalpies of sublimation and saturated vapor pressures were measured. Thermodynamic functions of 1-Adol, 2-Adol and 2-Me-2-Adol in the ideal gas state in the temperature intervals 100–1000 K were calculated by the statistical thermodynamics methods.

2. Experimental

Commercial samples of 1-Adol, 1-Adol and 2-Me-2-Adol (Aldrich) were additionally purified by sublimation. The mass fraction purity of the samples thus refined were 0.9994, 0.9998 and 0.9997 for 1-Adol, 2-Adol and 2-Me-2-Adol, respectively, as determined by g.l.c.

The saturated vapor pressures were determined by integral effusion Knudsen method. The samples were placed in a stainless steel chamber, which was sealed with a Teflon gasket. Membranes of nickel foil (thickness 0.05 mm) with diameters of effusion orifice 0.82543 ± 0.00010 mm (1-Adol, 2-Adol) and 0.80420 ± 0.00010 mm (2-Me-2-Adol) were used. It was assumed for calculation that the vapor has a monomolecular composition. The uncertainty in vapor pressures determination did not exceed ±5%. The apparatus construction and measuring procedure were described earlier [3,4].

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The sublimation enthalpies were determined in a differential heat-conducting microcalorimeter of Calvet type MID-200 with special calorimetric cells, described earlier [5]. The modernized MID-200 included a voltmeter with limits of measurements between 1×10^{-9} and 2 V and relaxation time between 2 and 30 s combined with an IBM PC. The samples were placed in hermetic cells of stainless steel supplied with a nickel membrane. After preliminary thermostating of the calorimeter, the membrane was pierced by a special demountable rod and the heating flux needed for evaporation was recorded. The calorimeter was calibrated by sublimation of benzoic acid ($K - 1$) and naphthalene and vaporization of *n*-decane and doubly distillated water. As a result, it was found that the uncertainty of evaporation enthalpy measurements did not exceed ±0.5%.

3. Thermodynamic properties of 1-Adol, 2-Adol and 2-Me-2-Adol

As it was reported earlier [2], 2-Adol undergoes solid-to-solid phase transition crIII–crII at 322.3 K. The limitation of the Knudsen method to determine saturated vapor pressures of compounds (0.03–30 Pa) and possibility of thermal decomposition of 2-Adol under vacuum and at the increasing of temperature allowed to obtain the reliable data only over phase crIII. The calorimetric determination of the enthalpy of sublimation of 2-Adol in the modified MID-200 was not possible due to low values of its saturated vapor pressure at $T \leq 322$ K and the solid-to-solid phase transition. That is why the enthalpy of sublimation for 2-adamantanol was obtained only from the data of the temperature dependence of the saturated vapor pressure.

Table 1
Saturated vapor pressures P_{sat} over crystal 1-adamantanol; Δm is the sample mass decrease; τ is the duration of effusion

T (K)	kS ($\times 10^8$ m^2)	τ (s)	Δm (mg)	P_{sat} (Pa)
287.92	50.4406	36054	4.31	0.07450
292.90	50.4406	34264	7.71	0.1414
298.14	50.4406	28854	11.47	0.2521
303.30	50.4406	14454	10.59	0.4686
308.33	50.4406	9054	11.05	0.7870
313.34	50.4406	7254	14.59	1.308
313.61	50.4406	5454	11.89	1.418
313.73	50.4406	5454	11.93	1.423
318.70	50.4406	3654	13.02	2.336
323.31	50.4406	1854	10.47	3.729

Table 2
Saturated vapor pressures P_{sat} over crystal 2-adamantanol; Δm is the sample mass decrease; τ is the duration of effusion

T (K)	kS ($\times 10^8$ m^2)	τ (s)	Δm (mg)	P_{sat} (Pa)
303.54	50.4406	32454	9.76	0.1924
307.79	50.4406	14454	6.94	0.3094
312.87	50.4406	5454	4.61	0.5491
313.53	50.4406	9354	8.34	0.5798
315.40	50.4406	12654	13.79	0.7108
317.96	50.4406	7254	10.20	0.9208

The measured saturated vapor pressures for adamantanols are represented in Tables 1–3, respectively. Experimental data for 1-Adol (287.92–323.31 K), 2-Adol (303.35–317.96 K) and 2-Me-2-Adol (298.12–333.94 K) were described by the following equation:

$$\ln(P_{\text{sat}}\,(\text{Pa})) = (32.99 \pm 0.40) - (10242 \pm 122)\left(\frac{1}{T\,(\text{K})}\right) \tag{1.1}$$

$$\ln(P_{\text{sat}}\,(\text{Pa})) = (33.02 \pm 0.61) - (10523 \pm 191)\left(\frac{1}{T\,(\text{K})}\right) \tag{1.2}$$

Table 3
Saturated vapor pressures P_{sat} over crystal 2-methyl-2-adamantanol; Δm is the sample mass decrease; τ is the duration of effusion

T (K)	kS ($\times 10^8$ m^2)	τ (s)	Δm (mg)	P_{sat} (Pa)
298.12	47.8224	23754	9.91	0.2670
303.11	47.8224	12654	9.39	0.4789
308.48	47.8224	7256	10.39	0.9322
313.40	47.8224	5454	13.29	1.599
313.44	47.8224	3654	8.94	1.606
313.51	47.8224	4254	10.44	1.611
317.97	47.8224	2754	10.84	2.602
323.35	47.8224	1854	13.04	4.688
328.05	47.8224	1854	20.99	7.601
333.94	47.8224	1854	36.40	13.30

Table 4
The results of calorimetric determination of the enthalpy of sublimation for 1−adamantanol

Number	m (g)	T (K)	$\int_{\tau=0}^{\tau}\Delta V\,\mathrm{d}\tau$ (mV s)	Type of cell	ΔH (J)	$\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\circ}$ (kJ mol^{-1})[a]
1	0.02335	318.56	2457.73	A	13.22	86.16
2	0.02664	319.10	2808.96	A	15.10	86.31
3	0.02964	319.10	3120.33	A	16.78	86.17
4	0.02688	320.35	2820.75	A	15.17	85.90
5	0.02921	318.93	3071.71	A	16.52	86.08
6	0.02551	318.68	2733.54	B	14.52	86.67
7	0.02834	319.22	3023.19	B	16.06	86.28
8	0.02859	319.25	3042.21	B	16.16	86.06
9	0.02582	319.21	2770.14	B	14.72	86.78
10	0.02738	319.06	2932.23	B	15.58	86.62

Note: The calorimetrically measured enthalpy change ΔH and molar enthalpies $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\circ}$ were calculated from expressions:

$$\Delta H = K^{-1}\int_{\tau=0}^{\tau}\Delta V\,\mathrm{d}\tau; \quad \Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\circ} = \Delta H\,M/m,$$

where m is the mass of a specimen; M the molar mass; K the calorimetric constant ($K_{\mathrm{A}} = 185.98$ and $K_{\mathrm{B}} = 188.22\,\mathrm{mV\,s\,K^{-1}}$); ΔV the thermocouple potential difference corresponding to the temperature difference between the cell and the calorimetric thermostat at time τ; τ the experiment duration; and T is the temperature of the calorimeter. The value of m is corrected for the mass of saturated vapor in the free volume of the ampoule immediately before the experiment.

[a] $\langle\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\circ}\langle 319.15\rangle\rangle = (86.30 \pm 0.21)\,\mathrm{kJ\,mol^{-1}}$.

$$\ln(P_{\mathrm{sat}}(\mathrm{Pa})) = (35.26 \pm 0.29) - (10904 \pm 92)\left(\frac{1}{T\,(\mathrm{K})}\right) \qquad (1.3)$$

respectively.

The enthalpies of sublimation of 1-Adol and 2-Me-2-Adol were determined in the series of calorimetric experiments (Tables 4 and 5) (and were listed at the average temperatures of the measurements). The enthalpies of sublimation of adamantanols calculated from the vapor pressure data and their weighted average values obtained from the results calorimetric and effusion measurements, are represented in Table 6. This enthalpies of sublimation for 1-Adol and 2-Adol are in the well agreement with values from [6] (Table 6).

4. Normal vibration frequencies, conformational composition and statistical calculation of the thermodynamic functions of 1-Adol, 2-Adol and 2-Me-2-Adol in the ideal gas state

The molecular structures of the compounds under study are shown in Fig. 1. There were no literature data for the sets of wave numbers and forms of

Table 5
The results of calorimetric determination of the enthalpy of sublimation for 2-methyl-2-adamantanol

Number	m (g)	T (K)	$\int_{\tau=0}^{\tau}\Delta V\,\mathrm{d}\tau$ (mV s)	Type of cell	ΔH (J)	$\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\circ}$ (kJ mol^{-1})[a]
1	0.04188	318.54	4237.89	A	22.77	91.51
2	0.04280	320.78	4329.60	A	23.27	90.38
3	0.04081	319.27	4146.11	A	22.88	90.77
4	0.04950	319.96	5117.17	B	27.11	91.04
5	0.04557	318.58	4688.98	B	24.84	90.62
6	0.04067	320.83	4187.58	B	22.18	90.68

$K_{\mathrm{A}} = 186.09$ and $K_{\mathrm{B}} = 188.79\,\mathrm{mV\,s\,K^{-1}}$.

[a] $\langle\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}\langle 319.66\rangle\rangle = (90.65 \pm 0.26)\,\mathrm{kJ\,mol^{-1}}$.

Table 6
The enthalpies of sublimation for 1-adamantanol, 2-adamantanol and 2-methyl-2-adamantanol

Compound	Transition type	T (K)	$\Delta_{\mathrm{cr}}^{\mathrm{g}}H$ (kJ mol^{-1})	Method of determination
1-Adamantanol	crII-to-gas	319.15	86.23 ± 0.21	Calorimetric
		298.15	86.8 ± 0.22	Calorimetric ($\Delta_{\mathrm{crII}}^{\mathrm{g}}C_p = -24.0 \pm 1.2$)
		305.62	85.16 ± 1.01	$P_{\mathrm{sat}} = f(T)$
		298.15	85.33 ± 1.02	$P_{\mathrm{sat}} = f(T)$ ($\Delta_{\mathrm{crII}}^{\mathrm{g}}C_p = -23.3 \pm 1.3$)
		298.15	86.73 ± 0.22	Weighted average value
		298.15	86.6 ± 2.5	$P_{\mathrm{sat}} = f(T)$ [6]
2-Adamantanol	crIII-to-gas	310.75	87.49 ± 1.59	$P = f(T)$
		298.15	88.14 ± 1.60	$P_{\mathrm{sat}} = f(T)$ ($\Delta_{\mathrm{crIII}}^{\mathrm{g}}C_p = -51.8 \pm 1.1$)
		298.15	88.7 ± 2.5	$P_{\mathrm{sat}} = f(T)$ [6]
2-Methyl-2-adamantanol	crII-to-gas	319.56	90.65 ± 0.26	Calorimetric
		298.15	91.41 ± 0.27	Calorimetric ($\Delta_{\mathrm{crII}}^{\mathrm{g}}C_p = -35.3 \pm 1.3$)
		316.03	90.66 ± 0.76	$P_{\mathrm{sat}} = f(T)$
		298.15	91.29 ± 0.77	$P_{\mathrm{sat}} = f(T)$ ($\Delta_{\mathrm{crII}}^{\mathrm{g}}C_p = -35.1 \pm 1.3$)
		298.15	91.40 ± 0.25	Weighted average value

Table 7
Calculated wave numbers for the normal modes of intermolecular vibrations for the compound under study

Compound	Numerical values of wave numbers	Method of the calculation
1-Adamantanol	243, 250, 267, 308, 374, 378, 390, 391, 403, 441, 446, 534, 625, 626, 814, 814, 824, 825, 885, 891, 892, 907, 946, 946, 951, 977, 983, 998, 1013, 1014, 1023, 1055, 1058, 1061, 1064, 1073, 1073, 1082, 1176, 1198, 1205, 1257, 1265, 1288, 1302, 1310, 1310, 1313, 1316, 1329, 1343, 1344, 1355, 1355, 1360, 1364, 1365, 1365, 1447, 3363, 3363, 3364, 3374, 3377, 3383, 3384, 3387, 3389, 3396, 3397, 3402, 3403, 3405, 3412, 3952	MINDO3
2-Adamantanol	178, 251, 279, 318, 344, 355, 375, 412, 423, 431, 582, 674, 686, 735, 913, 956, 956, 957, 961, 965, 981, 1003, 1018, 1019, 1027, 1038, 1085, 1094, 1100, 1153, 1175, 1177, 1181, 1190, 1211, 1220, 1221, 1288, 1332, 1339, 1355, 1360, 1374, 1387, 1387, 1388, 1394, 1396, 1414, 1431, 1432, 1435, 1487, 1489, 1490, 1495, 1497, 1506, 1560, 3160, 3228, 3228, 3230, 3233, 3233, 3256, 3261, 3261, 3262, 3301, 3301, 3302, 3303, 3304, 4004	MNDO/d
2-Methyl-2-adamantanol	150, 174, 215, 270, 289, 312, 335, 370, 404, 416, 481, 502, 513, 530, 668, 685, 708, 823, 951, 955, 959, 962, 970, 978, 999, 1005, 1016, 1029, 1033, 1069, 1069, 1092, 1097, 1116, 1161, 1178, 1179, 1192, 1200, 1210, 1222, 1223, 1276, 1326, 1335, 1340, 1367, 1378, 1387, 1388, 1389, 1393, 1395, 1411, 1432, 1433, 1451, 1458, 1481, 1491, 1495, 1497, 1504, 1507, 1516, 1529, 3225, 3227, 3228, 3230, 3233, 3250, 3257, 3258, 3259, 3261, 3272, 3303, 3304, 3304, 3306, 3307, 3352, 4000	MNDO/d

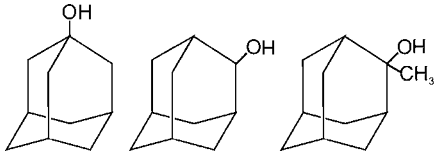

Fig. 1. The molecular structures of 1-adamantanol 2-adamantanol and 2-methyl-2-adamantanol.

the normal vibrations for adamantanols. Therefore these sets (Table 7) were calculated using semi empirical methods (bases MINDO3 and MNDO/d). The comparison of the calculated wave numbers for 1-adamantanol, 2-adamantanol and 2-methyl-2-adamantanol with the wave numbers of 1-methylcyclohexanol, 1-cyclohexanols [7] and far-IR-spectra of 1-adamantanol [8] allow to interpret the obtained sets as justified and to use them in the statistical calculations. The internal rotation of hydroxyl

Table 8
Molecular and geometrical parameters used for the statistical calculation of thermodynamic functions of 1-adamantanol (1-Adol), 2-adamantanol (2-Adol) and 2-methyl-2-adamantanol (2-Me-2-Adol)

Compound	M (g mol^{-1})	I_{ABC} ($\times 10^{135}$ kg^3 m^6)	σ	Number of conformers	$\Delta_{conf} H_i$ (kJ mol^{-1})
1-Adol	152.23580	254.4	1	1	0
2-Adol	152.23580	249.1	1	3	0; 3.6
2-Me-2-Adol	166.26260	422.4	1	3	0; 2.2

I_{ABC}, a principal moment of inertia products (were calculated from geometrical parameters obtained by molecular mechanics method MM2 force-field [9]); σ, a symmetry number of internal rotation of molecule; $\Delta_{conf} H_i$, the energy difference of conformers.

and methyl tops was taking into account by the wave numbers corresponding to their librations.

To analyze the conformational compositions of gaseous 1-Adol, 2-Adol and 2-Me-2-Adol and to obtain the geometric parameters and energy characteristics of internal rotation, the molecular mechanics methods (MM2 force-field [2]) were used (Table 8). It was found that there are three conformers for 2-Adol

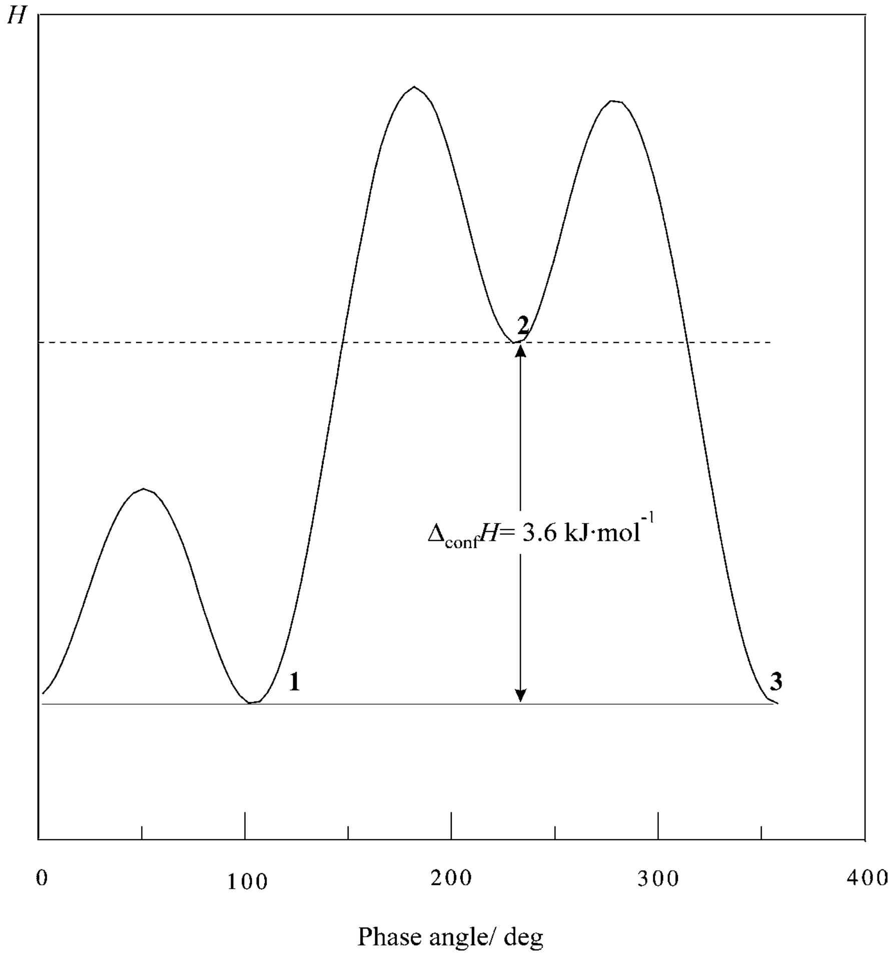

Fig. 2. The potential energy function for pseudorotation of hydroxyl top for 2-adamantanol: 1, 2, 3 denote the conformers.

Table 9

Standard molar thermodynamic functions for 1-adamantanol in the ideal gas state ($R = 8.31451\,\mathrm{J\,K^{-1}mol^{-1}}$; $p^{\mathrm{o}} = 101,325\,\mathrm{Pa}$)

T (K)	$C^{\circ}_{p,\mathrm{m}}/R$	$\Delta_0^T S^{\circ}_{\mathrm{m}}/R$	$\Delta_0^T H^{\circ}_{\mathrm{m}}/RT$	$\Phi^{\circ}_{\mathrm{m}}/R$	$\Delta_f H^{\circ}_{\mathrm{m}}$ (kJ mol^{-1})[a]	$\Delta_f G^{\circ}_{\mathrm{m}}$ (kJ mol^{-1})[a]
100	6.130	31.60	4.484	27.12	−275.7	−211.8
200	12.78	37.80	6.906	30.90	−294.2	−140.5
298.15	20.91	44.38	10.14	34.23	−310.9	−61.48
300	21.07	44.51	10.21	34.30	−311.2	−59.93
400	29.59	51.75	14.00	37.75	−325.0	26.00
500	36.83	59.16	17.87	41.29	−335.5	115.0
600	42.59	66.40	21.53	44.88	−343.2	205.9
700	47.16	73.33	24.88	48.45	−348.6	297.9
800	50.89	79.87	27.90	51.97	−352.3	391.0
900	54.00	86.05	30.63	55.42	−354.5	483.5
1000	56.66	91.88	33.11	58.78	−355.5	576.7

[a] Calculated on the basis of $\Delta_f H^{\circ}_{\mathrm{m}}(\mathrm{g}; 298.15) = (-310.87 \pm 3.35)\,\mathrm{kJ\,mol^{-1}}$ [6]. The thermodynamic properties of C (graphite) and H_2 (gas) between 100 and 1000 K were taken from [11].

and 2-Me-2-Adol (Fig. 2) and one conformer for 1-Adol. Conformational contributions to the entropy of gaseous 2-Adol and 2-Me-2-Adol were calculated by the equation:

$$S_{\mathrm{conf}}(\mathrm{g}) = \sum_i - R x_i \ln x_i \tag{2}$$

where x_i is the equilibrium molar fraction of equilibrium conformer. It was assumed at this calculation that $\Delta_{\mathrm{conf}} G_i \approx \Delta_{\mathrm{conf}} H_i$.

Statistical calculations of thermodynamic properties of adamantanols in the ideal gas state were made using the procedures and relations given in [10]. The experimental values for 1-Adol and 2-Adol [6] were used for the calculation of the temperature dependence of $\Delta_f H^{\circ}_{\mathrm{m}}(\mathrm{g}; 298.15)$ and Gibbs energy. Since there is no experimental data of the standard enthalpy of formation of 2-Me-2-Adol, therefore the value $\Delta_f H^{\circ}_{\mathrm{m}}(\mathrm{g}; 298.15) = (-327.31 \pm 3)\,\mathrm{kJ\,mol^{-1}}$ obtained by molecular mechanics methods (MM2) were used for the statistical calculation. One of the criteria for the validity using of such value of the standard enthalpy of formation for 2-Me-2-Adol can be well agreement of the experimental [6] and calculated values of $\Delta_f H^{\circ}_{\mathrm{m}}(\mathrm{g}; 298.15)$ for 1-Adol:

Table 10

Standard molar thermodynamic functions for 2-adamantanol in the ideal gas state ($R = 8.31451\,\mathrm{J\,K^{-1}\,mol^{-1}}$; $p^{\mathrm{o}} = 101,325\,\mathrm{Pa}$)

T (K)	$C^{\mathrm{o}}_{p,\mathrm{m}}/R$	$\Delta_0^T S^{\circ}_{\mathrm{m}}/R$	$\Delta_0^T H^{\circ}_{\mathrm{m}}/RT$	$\Phi^{\circ}_{\mathrm{m}}/R$	$\Delta_f H^{\circ}_{\mathrm{m}}$ (kJ mol^{-1})[a]	$\Delta_f G^{\circ}_{\mathrm{m}}$ (kJ mol^{-1})[a]
100	6.370	32.45	4.602	27.85	−262.8	−199.5
200	12.08	38.61	6.904	31.70	−281.4	−129.0
298.15	18.82	44.63	9.672	34.96	−299.2	−50.40
300	18.96	44.75	9.729	35.02	−299.5	−48.86
310.75	19.78	45.43	10.06	35.37	−301.2[b]	−39.61[b]
400	26.73	51.27	13.01	38.26	−315.5	37.17
500	33.89	58.02	16.48	41.53	−328.4	126.9
600	39.90	64.75	19.90	44.84	−338.4	218.9
700	44.85	71.28	23.12	48.16	−346.0	312.4
800	48.97	77.55	26.10	51.44	−351.4	407.4
900	52.43	83.52	28.84	54.68	−355.1	501.9
1000	55.38	89.20	31.35	57.85	−357.2	597.3

[a] Calculated on the basis of $\Delta_f H^{\circ}_{\mathrm{m}}(\mathrm{g}; 298.15) = (-299.16 \pm 4.60)\,\mathrm{kJ\,mol^{-1}}$ [6].

[b] Obtained by linear interpolation.

Table 11
Standard molar thermodynamic functions for 2-methyl-2-adamantanol in the ideal gas state ($R = 8.31451\,\mathrm{J\,K^{-1}\,mol^{-1}}$; $p^{\mathrm{o}} = 101,325\,\mathrm{Pa}$)

T (K)	$C^\circ_{p,\mathrm{m}}/R$	$\Delta_0^{\mathrm{T}} S^\circ_{\mathrm{m}}/R$	$\Delta_0^{\mathrm{T}} H^\circ_{\mathrm{m}}/RT$	$\Phi^\circ_{\mathrm{m}}/R$	$\Delta_{\mathrm{f}} H^\circ_{\mathrm{m}}$ (kJ mol^{-1})[a]	$\Delta_{\mathrm{f}} G^\circ_{\mathrm{m}}$ (kJ mol^{-1})[a]
100	7.525	33.50	5.061	28.44	−287.6	−215.1
200	14.00	40.69	7.903	32.79	−308.0	−134.6
298.15	21.55	47.63	11.11	36.53	−327.3	−45.31
300	21.71	47.77	11.17	36.60	−327.7	−43.56
400	30.27	55.19	14.88	40.31	−344.9	53.83
500	38.12	62.81	18.76	44.05	−358.8	155.2
600	44.71	70.36	22.56	47.80	−369.6	259.1
700	50.14	77.67	26.12	51.55	−377.7	364.5
800	54.66	84.67	29.41	55.26	−383.4	471.5
900	58.47	91.34	32.44	58.90	−387.2	578.0
1000	61.73	97.67	35.21	62.46	−389.3	685.4

[a] Calculated on the basis of $\Delta_{\mathrm{f}} H^\circ_{\mathrm{m}}(\mathrm{g}; 298.15) = (-327.3 \pm 3)\,\mathrm{kJ\,mol^{-1}}$ obtained by molecular mechanics calculation.

Table 12
The standard molar entropies of 1-adamantanol, 2-adamantanol and 2-adamantanol in the ideal gas state obtained from experimental data and using statistical calculations

Compound	T (K)	$\Delta_{\mathrm{cr}}^{\mathrm{g}} H_{\mathrm{m}}$ (kJ mol^{-1})	$\Delta_{\mathrm{cr}}^{\mathrm{g}} S_{\mathrm{m}}$ (J mol^{-1} K^{-1})[a]	P_{sat} (Pa)	$\Delta_{\mathrm{cr}}^{\mathrm{g}} S^{\mathrm{o}}_{\mathrm{m}}$ (J mol^{-1} K^{-1})[b]	S°_{m}(cr) (J mol^{-1} K^{-1})	$S^\circ_{\mathrm{m}}(\mathrm{g})_{\mathrm{exp}}$ (J mol^{-1} K^{-1})[c]	$S^\circ_{\mathrm{m}}(\mathrm{g})_{\mathrm{calc}}$ (J mol^{-1} K^{-1})[c]
1-Adamantanol	298.15	86.73 ± 0.22	290.9 ± 0.7	0.256 ± 0.013	183.7 ± 0.8	185.0 ± 0.8	368.7 ± 1.1	369.0 ± 1.8
2-Adamantanol	310.75	87.49 ± 1.59	281.5 ± 5.1	0.430 ± 0.022	178.7 ± 5.1	199.9± 0.9	378.6 ± 5.2	377.7 ± 1.9
2-Methyl-2-adamantanol	298.15	91.40 ± 0.25	306.6 ± 0.8	0.269 ± 0.014	199.9 ± 0.9	197.6 ± 0.9	397.5 ± 1.3	396.1 ± 2.0

[a] $\Delta_{\mathrm{cr}}^{\mathrm{g}} S_{\mathrm{m}} = (\Delta_{\mathrm{cr}}^{\mathrm{g}} H_{\mathrm{m}}/T)$.
[b] $\Delta_{\mathrm{cr}}^{\mathrm{g}} S^{\mathrm{o}}_{\mathrm{m}} = \Delta_{\mathrm{cr}}^{\mathrm{g}} S_{\mathrm{m}} - R\ln(p^{\mathrm{o}}/p_{\mathrm{sat}}), \quad p^{\mathrm{o}} = 101325\,\mathrm{Pa}$.
[c] $S^\circ_{\mathrm{m}}(\mathrm{g})_{\mathrm{exp}} = \Delta_{\mathrm{cr}}^{\mathrm{g}} S^\circ_{\mathrm{m}} + S^\circ_{\mathrm{m}}(\mathrm{cr})$.

$$\Delta_{\mathrm{f}} H^\circ_{\mathrm{m}}(\mathrm{g}; 298.15)_{\mathrm{exp}} = (-310.87 \pm 3.5)\,\mathrm{kJ\,mol^{-1}}$$

$$\Delta_{\mathrm{f}} H^\circ_{\mathrm{m}}(\mathrm{g}; 298.15)_{\mathrm{calc}} = (-311.1 \pm 3)\,\mathrm{kJ\,mol^{-1}}$$

and for 2-Adol:

$$\Delta_{\mathrm{f}} H^\circ_{\mathrm{m}}(\mathrm{g}; 298.15)_{\mathrm{exp}} = (-299.16 \pm 4.6)\,\mathrm{kJ\,mol^{-1}}$$

$$\Delta_{\mathrm{f}} H^\circ_{\mathrm{m}}(\mathrm{g}; 298.15)_{\mathrm{calc}} = (-298.6.6 \pm 3)\,\mathrm{kJ\,mol^{-1}}$$

Thermodynamic functions of the compounds under study in the ideal gas state between 100 and 1000 K are given in Tables 9–11.

The experimental and calculated values of $S^\circ_{\mathrm{m}}(\mathrm{g})$ are represented in Table 12. The standard entropies of crystalline adamantanols were evaluated from the data of low-temperature measurements [1,2]. As can be see, the satisfactory agreement between the experimental and calculated values of $S^\circ_{\mathrm{m}}(\mathrm{g})$ is observed for adamantanols.

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