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Thermodynamic Properties of Methoxybenzene in the Ideal Gas State

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Calculation of thermodynamic properties of methoxybenzene (anisole) in the ideal gas state using the spectral data was carried out in the temperature region from 250 K up to 2000 K. The results were compared with the values of molar heat capacity, obtained from calorimetric measurements.

Introduction

Thermodynamic properties of methoxybenzene (anisole) in the ideal gas state are not available in widely used collections.[1,2] Estimation of thermodynamic properties of methoxybenzene can be carried out only by means of estimation methods. The most common Benson estimation method[3,4] does not include the contribution $O-(C_B),(C)$, describing an ether group between a methyl group and an aromatic ring. The aim of this work is therefore to calculate the thermodynamic properties of methoxybenzene in the ideal gas state from spectroscopic data.

Sources of Thermochemical and Spectral Data

The standard formation enthalpy of gaseous methoxybenzene, obtained from combustion calorimetry, was published by Lebedyeva and Katin[5] and by Fenwick and coworkers.[6] The values, presented in these two papers, differ by more than 14 kJ mol^{-1}. The values of formation and evaporation enthalpies, published in the literature, are summarized in Table 1. It follows from this table that the main reason for the difference of formation enthalpies in the ideal gas state is the different values of evaporation enthalpies, whereas the difference between formation enthalpies in the liquid state is only 5 kJ mol^{-1}. The evaporation enthalpy used in the paper by Fenwick[6] agrees well with the value reported by Hales and co-workers.[7] Thus, the formation enthalpy by Fenwick[6] was used for calculation of thermodynamic properties.

The molecular geometry of methoxybenzene was studied using electronic diffraction[8] and microwave spectra.[9] The following rotational constants[9] was used in this paper: A = 5028.867 MHz, B = 1569.375 MHz, and C = 1205.836 MHz.

Complete assignment of vibrational frequencies of gaseous methoxybenzene was carried out in the paper by Bogatyreva and co-workers[10] and later in the paper by Owen and Hester.[11] The published vibrational assignment[11] was used for calculations in this work. Because some vibrational frequencies are missing in ref 11, they were completed using the values from other works.[10,12] Two alternative values of vibrational wavenumbers are reported in the paper.[11] In these cases those value were chosen which agree better with the values reported in the previous paper.[10]

Table 1. Formation and Evaporation Enthalpies at 298 K

$\Delta_f H$(l)/kJ mol^{-1}	ΔH_{ev}/kJ mol^{-1}	$\Delta_f H$(g)/kJ mol^{-1}	ref
−120.08 ± 0.84	38.07 ± 0.84	−82.01 ± 1.26	5
−114.77 ± 1.18	46.84 ± 0.22	−67.93 ± 1.20	6
	46.79 ± 2.93		7

Table 2. Wavenumbers (wn) of Vibrations in Methoxybenzene, Used for Calculations of Thermodynamic Values

type	wn/cm^{-1}	ref	type	wn/cm^{-1}	ref
group OCH_3	3000	10	aromatic ring	1076	10
group OCH_3	2834	9, 10	aromatic ring	1246	10
group OCH_3	1452	10	aromatic ring	3032	10
group OCH_3	1440	10	aromatic ring	994	10
group OCH_3	1039	10	aromatic ring	783	10
group OCH_3	1076	9	aromatic ring	615	9, 10
group OCH_3	2955	10	aromatic ring	447	10
group OCH_3	1466	10	aromatic ring	264	10
group OCH_3	1151	10	aromatic ring	1019	10
aromatic ring	3105	10	aromatic ring	971	9
aromatic ring	3092	10	aromatic ring	757	10
aromatic ring	3062	10	aromatic ring	882	10
aromatic ring	3032	10	aromatic ring	852	10
aromatic ring	1599	10	aromatic ring	690	10
aromatic ring	1585	10	aromatic ring	553	10
aromatic ring	1496	10	aromatic ring	508	10
aromatic ring	1485	10	aromatic ring	754	10
aromatic ring	1334	10	aromatic ring	225	10
aromatic ring	1301	10	group COC	285	estimated
aromatic ring	1179	10	group COC	209	9
aromatic ring	1171	10	torsion COC	108	10

The value of the wavenumber, corresponding to one of the torsional vibrations of the group COC, is not reported in any papers mentioned above. The required wavenumber was therefore estimated. Owen and Hester[11] reported wavenumbers of these torsional vibrations for halogenated derivates of methoxybenzene. The wavenumbers of these vibrations depend linearly on the atomic mass of the substituted atom. Extrapolation to the atomic mass of hydrogen leads to the value 285 cm^{-1}. This extrapolation can be considered as satisfactory, because calculation of the correlation coefficient, from the noticed dependence of wavenumbers on the atomic mass of the substituent, gave the value of 0.992. The estimated value of the wavenumber also agrees well with the value obtained for this torsional vibration from Raman spectra in the solid state.[13] The

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Table 3. Thermodynamic Properties of Methoxybenzene in the Ideal Gas State

T/K	$C°_{pm}$/(J K^{-1} mol^{-1})	$S°$/(J K^{-1} mol^{-1})	$(G° - H°_{298})/T$/(J K^{-1} mol^{-1})	$H° - H°_{298}$/(kJ mol^{-1})	$(\Delta_f H°)_{298}$/(kJ mol^{-1})	$(\Delta_f G°)_{298}$/(kJ mol^{-1})
250.00	105.37	324.63	−346.36	−5.43	−64.70	6.24
273.15	114.23	333.96	−344.79	−2.96	−66.16	19.86
298.15	124.09	344.49	−344.49	0.00	−67.93	27.77
300.00	124.80	345.23	−344.49	0.22	−68.06	28.37
400.00	162.76	386.28	−349.27	14.80	−72.15	63.26
500.00	195.49	426.86	−361.31	32.77	−78.28	95.76
600.00	222.06	464.85	−375.55	53.58	−81.82	130.83
700.00	243.58	500.50	−390.77	76.80	−84.38	166.67
800.00	260.83	534.56	−406.97	102.07	−86.04	202.25
900.00	275.84	565.72	−422.55	128.85	−87.11	235.13
1000.00	287.82	595.74	−438.77	156.97	−87.60	274.51
1100.00	298.60	623.36	−453.78	186.53	−87.30	311.33
1200.00	307.02	650.14	−469.32	216.99	−86.69	347.19
1300.00	314.97	674.80	−483.87	248.21	−85.83	383.74
1400.00	321.82	698.18	−498.06	280.17	−84.72	420.25
1500.00	327.74	720.39	−511.88	312.77	−83.39	456.69
1600.00	331.83	742.20	−526.48	345.16	−82.68	491.21
1700.00	336.32	762.34	−539.56	378.74	−81.14	527.39
1800.00	340.25	781.57	−552.27	412.74	−79.61	563.45
1900.00	343.70	799.96	−564.64	447.11	−77.88	601.46
2000.00	346.74	817.57	−576.67	481.81	−76.19	655.56

Table 4. Comparison of the Calculated Values of Molar Heat Capacity with the Calorimetric Values

	$C°_{pm}$/(J K^{-1} mol^{-1})		
T/K	ref 14	this work	difference/%
400	166.33	162.76	2.14
500	196.52	195.49	0.52

Table 5. Values of Contribution O−(C$_B$),(C) in the Benson Contribution Method

		$C°_{pm}$/(J K^{-1} mol^{-1})					
$(\Delta_f H°)_{298}$/(kJ mol^{-1})	$S°_{298}$/(J K^{-1} mol^{-1})	T = 300 K	T = 400 K	T = 500 K	T = 600 K	T = 800 K	T = 1000 K
−87.19	24.50	14.78	14.88	16.02	17.50	19.69	21.20

wavenumbers used for the calculation of the thermodynamic properties are summarized in Table 2.

The barrier to the internal rotation of methoxybenzene was reported by Owen and Hester[11] to be 25.2 kJ mol^{-1}. This value corresponds to torsional frequency 108 cm^{-1}, and the corresponding reduced moment of inertia of the methyl group was 2.03×10^{-46} kg m^{-2}. Konschin, Tylli, and Grundfelt-Forsius[13] found for solid anisole the rotational barrier 22.1 kJ mol^{-1} (planar conformation) and 20.3 kJ mol^{-1} (orthogonal conformation). The values reported by Owen and Hester[11] were used in this work.

Calculation of Thermodynamic Properties

Thermodynamic properties of methoxybenzene were calculated from noticed molecular parameters using the model of rigid rotator and harmonic oscillator. The constants of centrifugal distortion have been reported.[9] The contribution of centrifugal distortion to the values of thermodynamic properties is a second-order effect in comparison with the contribution of anharmonicity of molecular vibrations. On the other hand, the influence of anharmonicity of vibrations could not be included into the calculations, because necessary spectral data are not available. The contribution of centrifugal distortion was thus not taken into account in the calculations.

The contributions of internal rotation were calculated by means of the tables by Pitzer and Gwinn.[14] The torsion COC vibration (108 cm^{-1}), presented in Table 2, was therefore not taken into account.

Values of entropies of the elements at 298 K were taken from the JANAF tables.[15] The calculated values of thermodynamic properties are reported in Table 3.

Calculated values of molar heat capacity were compared with those obtained from calorimetric measurements.[7] The comparisons of the calculated and measured values at the temperatures 400 K and 500 K are reported in Table 4. It follows from this table that agreement of calculated and measured values can be considered as satisfactory.

Evaluation of the Additional Benson Group Contribution

The values of contribution O−(C$_B$),(C) which are not included into the Benson contribution method were evaluated from thermodynamic properties, reported in Table 3. The following contribution was taken into account: 5 C$_B$−(H), 1 C$_B$−(O), 1 C−(H)$_3$,(O), and 1 O−(C$_B$),(C). The number of external symmetry was considered as unity, and the number of internal symmetry as 2. The values of contribution O−(C$_B$),(C) are reported in Table 5.

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