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CHEMICAL THERMODYNAMIC PROPERTIES OF TOLUENE, *o*-, *m*- AND *p*-XYLENES

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ABSTRACT

Employing recent molecular, spectroscopic and thermal constants, the ideal gas thermodynamic properties [C_p^0, S^0, $H^0(T) - H^0(0)$, ΔH_f^0 and ΔG_f^0] of toluene, *o*-xylene, *m*-xylene and *p*-xylene in the temperature range 0–3000 K are calculated by the statistical mechanical method. A potential function, formed by summation of internal rotational energy levels, is used for evaluating the internal rotational contributions to the thermodynamic properties caused by the presence of each CH_3 rotor in these molecules. The internal rotational energy levels for each rotor are calculated by solving the wave equation using the adopted internal rotational constant and potential function for the given rotor. The heat capacities and entropies obtained agree with the experimental values. The sources of molecular data and method of calculation are described in detail.

INTRODUCTION

The thermodynamic properties of toluene (methylbenzene, C_7H_8), *o*-xylene (1,2-dimethylbenzene, C_8H_{10}), *m*-xylene (1,3-dimethylbenzene, C_8H_{10}) and *p*-xylene (1,4-dimethylbenzene, C_8H_{10}) in the ideal gaseous state have been calculated by Pitzer and Scott [1], Taylor et al. [2], Scott et al. [3] and Draeger and Scott [4] using the molecular constants then available. Recently, new data on molecular structure, vibrational assignments and internal rotation potential barrier heights for the CH_3 rotor have been reported for these compounds. Therefore, we have employed the best values of the recent molecular, spectroscopic and thermal constants to recalculate the ideal gas thermodynamic properties of these alkyl benzenes. In these calculations, a standard statistical mechanical method based upon a rigid-rotor and a harmonic-oscillator molecular model was adopted.

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For computing the contributions to the thermodynamic properties caused by internal rotation of the methyl groups ($-CH_3$) in the molecules of the above compounds, we employed an internal rotation potential function formed by summation of internal rotational energy levels for each CH_3 rotor. These energy levels were obtained from the solutions of the torsional wave-equation for a molecule with n-fold symmetry

$$\left[-F\frac{\gamma^2}{\gamma\phi^2}+\frac{Vn}{2}(1-\cos n\phi)\right]\psi(\phi)=E\psi(\phi) \tag{1}$$

where F = internal rotation constant for the given rotor, ϕ = internal rotational angle, V_n = internal rotation barrier height and E = the required internal rotational energy levels. For the toluene molecule $n = 6$ and for the other alkyl benzene molecules $n = 3$. The method suggested by Lewis et al. [5] was adopted for generating the internal rotational energy levels using eqn. (1).

Each xylene molecule has two methyl ($-CH_3$) rotors. The two CH_3 groups in the *o*-xylene molecule attach to two adjacent carbon atoms in the benzene ring. Because of steric effects, the internal rotation of these two rotors in this molecule is hindered, i.e., the potential barrier is high for each rotor. However, the two CH_3 groups in the *m*- and *p*-xylene molecules are not so close to each other and consequently their potential barriers for internal rotation are much lower.

We estimated the CH_3 barrier height of the *m*- and *p*-xylene molecules to be comparable to that of the toluene molecule. In the statistical mechanical calculations for the thermodynamic properties of the three isomeric xylenes we assumed that the two CH_3 rotors are identical and independent; in other words, there was no interaction between these two rotors in each molecule. In all calculations the recent fundamental constants [6] and the 1975 Atomic Weights [7], C = 12.011 and H = 1.0079, were employed.

TOLUENE

The molecular structure of gaseous toluene was determined by electron diffraction by Keidel and Bauer [8]. Later, Rudolph et al. [9] investigated the microwave rotational spectrum of toluene in the region 8–23 GHz. They determined the rotational constants and derived the three principal moments of inertia as $I_a = 88.23570$ uÅ^2, $I_b = 200.8198$ uÅ^2 and $I_c = 289.06118$ uÅ^2. From analysis of the spectral lines, they also obtained the internal rotation barrier height $V_6 = (13.94 \pm 0.1)$ cal mol^{-1} or (58.32 ± 0.42) J mol^{-1} for the CH_3 rotor in this molecule. The internal rotation constant (F) was reported to be 166.72646 GHz or 5.561 cm^{-1}. These values were adopted for

TABLE 1

Molecular constants for toluene, *o*-, *m*- and *p*-xylenes

	Toluene	*o*-Xylene	*m*-Xylene	*p*-Xylene
Molecular weight	92.1402	106.1670	106.1670	106.1670
Point group and total symmetry number	C_{2v}, 6	C_{2v}, 18	C_{2v}, 18	D_{2h}, 36
Ground-state configuration	A_1	A_1	A_1	A_g
Product of the three principal moments of inertia (g^3 cm^6)	23446.4×10^{-117}	66790.9×10^{-117}	77362×10^{-117}	66870×10^{-117}
Internal rotation of CH_3 rotor:				
Internal rotational constant, F(cm^{-1})	5.561	5.381	5.350	5.309
potential barrier height (J mol^{-1})	(58.32 ± 0.42)	6234	65.0	65.0
torsional wavenumber ($0 \rightarrow 1$) (cm^{-1})	51.28	162.0	48.21	47.85
Vibrational wavenumber (cm^{-1})	3063, 3055, 3003, 2921, ... [a]	3080, 3062, 2950, 1680, ... [a]	3062, 3047, 3046, 2950, ... [a]	3050, 2950, 1616, 1578, ... [a]
Enthalpy of formation at 298.15 K (kJ mol^{-1})	50.17	19.08	17.32	18.03

[a] See text for more information.

TABLE 2

Ideal gas thermodynamic properties

T (K)	C_p^0 (J K^{-1} mol^{-1})	S^0 (J K^{-1} mol^{-1})	$H^0(T)-H^0(0)$ (J mol^{-1})	ΔH_f^0 (kJ mol^{-1})	ΔG_f^0 (kJ mol^{-1})
Toluene [a]					
0	0	0	0	73.22	73.22
50	38.10	220.3	1876.0	66.63	73.15
100	44.57	248.3	3917.0	64.01	80.66
150	56.00	268.4	6414.0	60.86	89.64
200	70.72	286.5	9570.0	57.30	99.79
273.15	96.06	312.2	15650.0	51.92	116.2
298.15	105.2	321.0	18170.0	50.17	122.2
300	105.8	321.6	18360.0	50.04	122.6
400	141.2	357.0	30740.0	43.56	147.8
500	171.7	391.9	46430.0	38.22	174.5
600	196.9	425.5	64910.0	33.93	202.2
700	217.6	457.5	85670.0	30.53	230.5
800	234.8	487.7	108300.0	27.89	259.3
900	249.3	516.2	132500.0	25.95	288.4
1000	261.6	543.1	158100.0	24.70	317.8
1100	272.0	568.6	184800.0	23.98	346.7
1200	281.0	592.6	212400.0	23.60	376.4
1300	288.7	615.4	240900.0	23.51	405.7
1400	295.4	637.1	270200.0	23.67	435.4
1500	301.1	657.6	300000.0	24.03	464.7
1750	312.5	705.0	376800.0	25.55	537.5
2000	320.7	747.2	456000.0	27.58	610.6
2250	326.7	785.4	536900.0	29.81	683.7
2500	331.3	820.1	619200.0	32.07	755.6
2750	334.8	851.8	702500.0	35.41	827.5
3000	337.5	881.0	786500.0	38.89	899.0
o-Xylene [b]					
0	0	0	0	46.43	46.43
50	40.58	220.7	1740.0	37.59	48.47
100	61.32	255.4	4302.0	34.37	60.60
150	78.99	283.7	7816.0	30.91	74.45
200	96.27	308.8	12200.0	27.05	89.56
273.15	122.9	342.7	20200.0	21.07	113.3
298.15	132.3	353.8	23390.0	19.08	121.9
300	133.0	354.6	23640.0	18.93	122.6
400	170.5	398.1	38820.0	11.32	158.3
500	204.3	439.8	57600.0	4.81	195.8
600	233.2	479.7	79520.0	−0.53	234.5
700	257.6	517.6	104100.0	−4.83	274.1
800	278.3	553.4	130900.0	−8.17	314.2
900	296.0	587.2	159700.0	−10.50	354.6
1000	311.1	619.2	190000.0	−12.16	395.5
1100	324.0	649.4	221800.0	−13.02	435.8

TABLE 2 (continued)

T (K)	C_p^0 (J K^{-1} mol^{-1})	S^0 (J K^{-1} mol^{-1})	$H^0(T)-H^0(0)$ (J mol^{-1})	ΔH_f^0 (kJ mol^{-1})	ΔG_f^0 (kJ mol^{-1})
1200	335.2	678.1	254800.0	−13.41	477.0
1300	344.8	705.3	288800.0	−13.41	517.8
1400	353.0	731.2	323700.0	−13.07	559.0
1500	360.2	755.8	359400.0	−12.46	599.7
1750	374.3	812.5	451300.0	−10.07	701.0
2000	384.4	863.1	546200.0	−6.98	802.5
2250	391.8	908.9	643300.0	−3.60	903.8
2500	397.3	950.4	741900.0	−0.19	1004.0
2750	401.5	988.5	841800.0	4.46	1104.0
3000	404.7	1024.0	942600.0	9.23	1203.0
m-Xylene[b]					
0	0	0	0	45.94	45.94
50	43.30	234.9	2092.0	37.46	47.62
100	55.77	268.4	4541.0	34.12	59.06
150	71.14	293.8	7709.0	30.31	72.33
200	87.94	316.6	11680.0	26.04	87.00
273.15	115.7	348.0	19110.0	19.49	110.3
298.15	125.7	358.5	22120.0	17.32	118.8
300	126.5	359.3	22360.0	17.16	119.4
400	166.3	401.2	37010.0	9.02	154.8
500	201.8	442.2	55460.0	2.18	192.0
600	231.6	481.8	77180.0	−3.37	230.5
700	256.6	519.4	101600.0	−7.80	269.8
800	277.4	555.0	128400.0	−11.22	309.8
900	295.2	588.8	157000.0	−13.74	350.1
1000	310.3	620.7	187300.0	−15.37	390.8
1100	323.2	650.9	219000.0	−16.31	431.0
1200	334.3	679.5	251900.0	−16.78	472.0
1300	343.9	706.6	285800.0	−16.86	512.7
1400	352.1	732.4	320600.0	−16.62	553.7
1500	359.3	757.0	356200.0	−16.10	594.3
1750	373.3	813.5	447900.0	−13.96	695.4
2000	383.5	864.0	542600.0	−11.10	796.6
2250	391.0	909.6	639400.0	−7.94	897.7
2500	396.6	951.2	737900.0	−4.72	997.5
2750	400.9	989.2	837600.0	−0.22	1097.1
3000	404.3	1024.2	938300.0	4.43	1196.2
p-Xylene[b]					
0	0	0	0	46.76	46.76
50	44.67	229.2	2116.0	38.30	48.75
100	54.98	263.0	4582.0	34.98	60.46
150	69.79	288.0	7690.0	31.11	74.00
200	87.00	310.4	11600.0	26.78	88.97
273.15	115.7	341.7	18990.0	20.20	112.7
298.15	126.0	352.2	22010.0	18.03	121.4

TABLE 2 (continued)

T (K)	C_p^0 (J K^{-1} mol^{-1})	S^0 (J K^{-1} mol^{-1})	$H^0(T)-H^0(0)$ (J mol^{-1})	ΔH_f^0 (kJ mol^{-1})	ΔG_f^0 (kJ mol^{-1})
300	126.8	353.0	22250.0	17.87	122.0
400	167.4	395.1	36980.0	9.81	158.0
500	203.3	436.5	55570.0	3.11	195.8
600	233.2	476.2	77440.0	−2.28	234.9
700	258.1	514.1	102000.0	−6.56	274.8
800	278.9	550.0	128900.0	−9.84	315.2
900	296.4	583.9	157700.0	−12.22	356.0
1000	311.4	615.9	188100.0	−13.74	397.2
1100	324.2	646.2	219900.0	−14.57	437.9
1200	335.2	674.9	252900.0	−14.95	479.4
1300	344.7	702.1	286900.0	−14.95	520.5
1400	352.8	728.0	321800.0	−14.63	562.0
1500	359.9	752.5	357400.0	−14.05	603.0
1750	373.8	809.1	449300.0	−11.76	705.2
2000	383.9	859.7	544000.0	−8.79	807.5
2250	391.3	905.4	641000.0	−5.54	909.7
2500	396.9	946.9	739500.0	−2.24	1011.0
2750	401.2	985.0	839300.0	2.33	1111.0
3000	404.6	1020.0	940100.0	7.06	1211.0

[a] 7 C (c, graphite) + 4 $H_2(g) = C_7H_8(g)$.

[b] 8 C (c, graphite) + 5 $H_2(g) = C_8H_{10}(g)$.

calculating the rotational and internal rotational contributions to the thermodynamic properties of gaseous toluene.

It is interesting to note that to obtain calculated heat capacities of gaseous toluene consistent with experimental values, Pitzer and Scott [1] found that the internal rotation of the methyl group in the molecule was relatively free, i.e., $V_6 = 500$ cal mol^{-1}. Taylor et al. [2] selected $V_6 = 750$ cal mol^{-1} and Kovner [19] adopted $V_6 = 873$ cal mol^{-1} as an empirical parameter for the potential barrier, on the basis of the entropy and heat capacity data. Scott et al. [3] treated the CH_3 group as a free rotor for calculation of the ideal gas thermodynamic properties of toluene by the statistical mechanical method. We adopted the experimental value $V_6 = 13.94$ cal mol^{-1} [9] for the statistical calculations.

The vibrational spectra of toluene have been observed by numerous researchers [10–17]. Based upon the reported Raman and IR spectra, Pitzer and Scott [1] and Scott et al. [3] made a complete set of vibrational assignments for toluene. Recently, Sverdlov et al. [18] analyzed the reported spectral data and assigned the complete fundamental vibrational frequencies for gaseous toluene. We adopted their values for evaluating the vibrational contributions to thermodynamic properties of this compound, because the use of their frequencies yielded C_p^0 and S^0 in better agreement with the experimental values.

Table 1 lists the molecular constants which we employ for calculating the heat capacity (C_p^0), entropy (S^0), enthalpy ($H^0(T) - H^0(0)$), enthalpy of formation (ΔH_f^0) and Gibbs energy of formation (ΔG_f^0) in the temperature range 0–3000 K and at atmospheric pressure (101.325 kPa) for gaseous toluene. The results appear in Table 2.

A value of ΔH_f^0(g, 298.15 K) = 50.17 kJ mol^{-1} [20–22] was selected for calculation of the ΔH_f^0 and ΔG_f^0 at the given temperatures. The required auxiliary data on $H^0(T) - H^0(0)$ and $(G^0(T) - H^0(0))/T$ for the elements C (graphite) and gaseous H_2 were taken from the TRC Hydrocarbon Project Tables [22].

o-XYLENE

Rudolph et al. [23] measured the microwave ground-state spectra of this compound and determined its molecular structure. They reported the three principal moments of inertia as $I_a = 2.65245 \times 10^{-38}$ g cm^2, $I_b = 3.90320 \times 10^{-38}$ g cm^2 and $I_c = 6.45133 \times 10^{-38}$ g cm^2. This was the only source of data on the molecular structure of *o*-xylene. Their results were adopted for calculating $I_a I_b I_c$ in this work.

Based upon the observed vibrational spectra, Pitzer and Scott [1] assigned a complete set of fundamental vibrational frequencies for gaseous *o*-xylene. Kovner and Bogomolov [25] and Bogomolov [26] calculated the fundamental frequencies theoretically for the *o*-xylene molecule, to interpret its vibrational spectrum. For computing the vibrational contributions to thermodynamic properties of gaseous *o*-xylene, we selected the vibrational assignments of Pitzer and Scott [1] as the best values.

Determination of the internal rotation barrier height of the two CH_3 rotors in the *o*-xylene molecule has occupied researchers for many years. From the low-temperature heat capacity measurements, Wulff [27] evaluated the value $V_3 = (1850 \pm 75)$ cal mol^{-1}. Haupt and Muller-Warmuth [28] studied the temperature dependence of the proton-spin relaxation times of crystalline *o*-xylene at low temperatures and derived $V_3 = (2200 \pm 100)$ cal mol^{-1} for the CH_3 rotor.

By inelastic neutron scattering and using a two-dimensional Fourier series to describe the potential energy interactions of the two methyl groups, Livingston et al. [29] obtained $V_3 = (2400 \pm 130)$ cal mol^{-1} and $V_{33} = (-540 \pm 80)$ cal mol^{-1} for the CH_3 top in crystalline *o*-xylene. The potential function they employed was $V(\phi_1,\phi_2) = V_3\,(1 - \cos 3\phi_1) + V_3\,(1 - \cos 3\phi_2) + V_{33}\,(1 - \cos 3\phi_1 \cos 3\phi_2) + V_{33}\,(1 - \sin 3\phi_1 \sin 3\phi_2)$.

Pitzer and Scott [1] chose $V_3 = 2000$ cal mol^{-1} for producing the calculated C_p^0 and S^0 of gaseous *o*-xylene consistent with the third-law entropy at 298.15 K and the vapor heat capacity measurements in the temperature range 393–463 K. Taylor et al. [2] selected the value 2100 cal mol^{-1} for V_3. Rush [30] reported $V_3 = (1.96 \pm 0.14)$ kcal mol^{-1} for this compound. Ingham and Strickler [31] investigated the UV absorption spectrum of *o*-xylene and assigned a barrier of internal rotation of (700 ± 50) cm^{-1} or (2.00 ± 0.14) kcal mol^{-1} in the ground state assuming the two CH_3 groups in the molecule were independent oscillators.

Rudolph et al. [23] derived $V_3 = (1490 \pm 50)$ cal mol^{-1} or (6.234 ± 0.209) kJ mol^{-1} for the CH_3 rotor of the *o*-xylene molecule, neglecting the top–top coupling and the higher than three-fold barrier terms. They determined the reduced moment of inertia (I_r) and internal rotational constant (F) of the CH_3 rotor as 5.203×10^{-40} g cm^2 and 5.381 cm^{-1}, respectively. Their results were the best values and were adopted. Based upon the adopted F and V_3, we generated 108 internal rotational energy levels (0–15 300 cm^{-1}) for each of the two CH_3 rotors, which were used to calculate the internal rotational contributions to the thermodynamic properties of this compound. We calculated the CH_3 torsional frequency $(0 \rightarrow 1)$ to be 162 cm^{-1} which agreed with the value 162 ± 5 cm^{-1} observed from the far IR spectrum of gaseous *o*-xylene by Pardoe et al. [24].

The enthalpy of formation at 298.15 K, as given in Table 1, was derived from the enthalpy of combustion of liquid *o*-xylene determined by Prosen et al. [20] and the enthalpy of vaporization measured by Osborne and Ginnings [21]. The calculated results are listed in Table 2.

m-XYLENE

The molecular structure of *m*-xylene has never been determined experimentally. Based upon an estimated molecular structure, Pitzer and Scott [1] calculated the three principal moments of inertia and the reduced moment of the CH_3 rotor of the molecule as $I_a = 2.61 \times 10^{-38}$ g cm^2, $I_b = 3.88 \times 10^{-38}$ g cm^2, $I_c = 6.39 \times 10^{-38}$ g cm^2, and $I_r = 5.23 \times 10^{-40}$ g cm^2, respectively. These values were adopted tentatively in this work.

For evaluation of the internal rotational contributions of the two CH_3 rotors in the *m*-xylene molecule to the thermodynamic properties of this substance, we employed $F = 5.35$ cm^{-1}, which was derived from the adopted I_r, and $V_3 = 65$ J mol^{-1} [32] for generating 108 internal rotational energy levels for each rotor.

To produce the calculated C_p^0 and S^0 for gaseous *m*-xylene in agreement with the experimental values, Pitzer and Scott [1] selected $V_3 = 500$ cal mol^{-1} and Taylor et al. [2] chose $V_3 = 750$ cal mol^{-1}. Using recent molecular constants for statistical calculations, we found that a value of $V_3 = 65$ J

TABLE 3

Comparison of experimental and calculated C_p^0 and S^0 (1 cal = 4.184 J)

T (K)	C_p^0/(cal K^{-1} mol^{-1}) Expt.	Calc.	Δ	S^0/(cal K^{-1} mol^{-1}) Expt.	Calc.	Δ
Toluene						
298.15				76.77 ± 0.15 [a]	76.72	−0.05
341.27				80.39 ± 0.15 [a]	80.36	−0.03
361.06				82.04 ± 0.15 [a]	82.04	0.00
371.20	31.09 [a]	31.40	0.31			
383.77				83.92 ± 0.15 [a]	83.96	0.04
390	33.5 [b]	32.94	−0.56			
393	32.8 ± 0.3 [c]	33.18	0.38			
396.20	33.19 [a]	33.44	0.25			
410	35.0 [b]	34.53	−0.47			
410.11				86.08 ± 0.15 [a]	86.16	0.08
427.20	35.65 [a]	35.86	0.21			
428	35.7 ± 0.4 [c]	35.92	0.22			
462.20	38.32 [a]	38.44	0.12			
463	38.0 ± 0.4 [c]	38.50	0.50			
500.20	40.98 [a]	41.06	0.08			
o-Xylene						
298.15				84.50 + 0.3 [c]	84.57	0.07
393	40.2 ± 0.4 [c]	40.13	−0.07			
428	43.5 ± 0.4 [c]	43.12	−0.38			
463	46.0 ± 0.5 [c]	45.98	−0.02			
m-Xylene						
298.15				85.60 + 0.3 [c]	85.69	0.09
393	39.1 ± 0.4 [c]	39.10	0.00			
428	42.4 ± 0.4 [c]	42.25	−0.15			
463	45.4 ± 0.4 [c]	45.24	−0.16			
p-Xylene						
298.15				84.27 + 0.3 [c]	84.19	−0.08
393	39.0 ± 0.4 [c]	39.37	0.37			
398.15	39.80 [d]	39.85	0.05			
423.15	42.02 [d]	42.13	0.11			
428	42.6 ± 0.4 [c]	42.56	−0.04			
448.15	44.31 [d]	44.33	0.02			
463	45.2 ± 0.4 [c]	45.59	0.39			
473.15	46.41 [d]	46.43	0.02			
498.15	48.50 [d]	48.44	−0.06			
523.15	50.45 [d]	50.37	−0.08			

[a] Ref. 3.
[b] Ref. 38.
[c] Ref. 1.
[d] Ref. 4.

mol^{-1} provided C_p^0 and S^0 values in better agreement with the experimental data, as shown in Table 3.

The vibrational assignments of Pitzer and Scott [1] were adopted for calculating the vibrational contributions to the thermodynamic properties of this substance. Fundamental frequencies and characteristic vibrations of *m*-xylene were calculated by Kovner and Bogomolov [33] and Bogomolov [35], respectively, using the force constants of the benzene ring [34].

Prosen et al. [20] measured the enthalpy of combustion of liquid *m*-xylene. The enthalpy of vaporization of this compound was determined by Osborne and Ginnings [21]. From their results we calculated the value ΔH_f (g, 298.15 K) = 17.32 kJ mol^{-1}, as indicated in Table 1, for computing the ΔH_f^0 and ΔG_f^0 at the given temperatures. The calculated ideal gas thermodynamic properties for *m*-xylene are presented in Table 2.

p-XYLENE

The thermodynamic properties of gaseous *p*-xylene have been reported by Pitzer and Scott [1] and Taylor et al. [2]. Recently, Draeger and Scott [4] employed new molecular data and recalculated the thermodynamic properties of this compound. In their recent calculations, Draeger and Scott assumed that the two methyl groups in the *p*-xylene molecule were free rotors and utilized a semi-empirical method [36,37] for estimating the anharmonicity corrections such that the calculated thermodynamic functions like C_p^0 and S^0 agreed with the experimental values.

As mentioned previously, we considered that the two CH_3 groups in the *p*-xylene molecule were not free rotors and that the potential barrier to internal rotation of each rotor was similar to the internal rotation potential barrier of the CH_3 rotor in the toluene molecule. We employed $V_3 = 65.0$ J mol^{-1} and $F = 5.309$ cm^{-1} [3] for generating 180 internal rotational energy levels for each CH_3 rotor, which were used for evaluation of the internal rotational contributions to thermodynamic properties of gaseous *p*-xylene.

The molecular structure of gaseous *p*-xylene has not been thoroughly investigated. The product of the three principal moments of inertia and the fundamental vibrational assignments reported by Draeger and Scott [4] were adopted for calculating the rotational and vibrational contributions to thermodynamic properties of gaseous *p*-xylene, respectively. To produce C_p^0 and S^0 of *p*-xylene in better agreement with the experimentally measured vapor heat capacity and third-law entropy values, we changed two vibrational wavenumbers from 972 and 700 cm^{-1} to 936 and 680 cm^{-1}, respectively. The calculated thermodynamic properties appear in Table 2.

DISCUSSION

The statistically calculated heat capacities and entropies of gaseous toluene, *o*-, *m*- and *p*-xylenes are compared with the experimental data in Table 3. The agreement in C_p^0 and S^0 between the calculated and experimental values indicates that our selected molecular constants and method of calculation are appropriate and reasonable.

In calculation of ideal gas thermodynamic properties of toluene and *p*-xylene, Scott et al. [3] and Draeger and Scott [4] employed a molecular model in which the methyl groups in these two molecules were treated as free rotors. They adopted a semi-empirical method for evaluation of the anharmonicity corrections to make the statistically calculated C_p^0 and S^0 agree with the experimental values. In our statistical mechanical calculations we treated the methyl groups in the alkyl benzene molecules as hindered rotors. For evaluation of internal rotational contributions to thermodynamic properties we adopted an internal rotation partition function formed by summation of internal rotational energy levels.

Due to the difference in the method of calculation, there are some differences in our calculated property values and those reported by Scott and his coworkers. For example, the C_p of *p*-xylene was reported to be 316.1 J K^{-1} mol^{-1} at 1000 K by Draeger and Scott [4] while our value is 311.4 J K^{-1} mol^{-1}. The values reported by Pitzer and Scott [1] and Taylor et al. [2] were 310.0 and 309.7 J K^{-1} mol^{-1}, respectively. The C_p^0 of *p*-xylene at 1000 K is estimated to be 311.7 J K^{-1} mol^{-1} using the methylene increment method, which is based upon the following formula: C_p^0(*p*-xylene, g, 1000 K) = C_p^0(toluene, g, 1000 K) + [C_p^0(toluene, g, 1000 K) − C_p^0(benzene, g, 1000 K)], where C_p^0(benzene, g, 1000 K) = 211.41 J K^{-1} mol^{-1}.

Because of the approximations involved in our molecular model for calculating the thermodynamic properties of these four alkyl benzenes, the property values evaluated at high temperatures, e.g., above 1000 K, may not be as accurate as those calculated at lower temperatures; however, they are still useful for approximate calculations.

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