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Thermodynamic Equilibria in Xylene Isomerization. 3. The Thermodynamic Properties of *o*-Xylene†

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Measurements leading to the calculation of the ideal-gas thermodynamic properties for *o*-xylene (Chemical Abstracts registry number [95-47-6]) are reported. Experimental methods included adiabatic heat-capacity calorimetry (5 K to 420 K), comparative ebulliometry (313 K to 459 K), differential-scanning calorimetry (DSC), and vibrating-tube densitometry (323 K to 523 K). The critical temperature was measured by DSC. Saturation heat capacities for the liquid phase between 420 K and 550 K, the critical density, and the critical pressure were derived with the vapor-pressure, density, and DSC results. Results were combined with an enthalpy of combustion reported in the literature to derive standard molar entropies, enthalpies, and Gibbs free energies of formation at selected temperatures between 250 K and 550 K. The standard state is defined as the ideal gas at the pressure $p = p° = 101.325$ kPa. Standard entropies are compared with those calculated statistically on the basis of assigned vibrational spectra from the literature for the vapor phase. A preliminary value for the barrier to methyl-group rotation is derived. All results are compared with literature values.

Introduction

This is the third in a series of papers concerning the thermodynamic properties of the xylenes. The background for this research was discussed in the first paper of this series concerning *p*-xylene (Chirico et al., 1997a). This work was initiated to investigate discrepancies between experimentally determined xylene isomerization product distributions (Amelse, 1993; Seddon, 1986) and those calculated with thermodynamic information. Comparison with calculated equilibria based upon available standard thermodynamic properties for the xylenes (i.e., Stull et al., 1987) led Amelse (1993) to conclude that the existing thermodynamic data for the xylenes are in error.

Gibbs free energies of formation for the xylenes published in numerous compilations and used in equilibria calculations (e.g., TRC, 1996; Daubert et al., 1996; Frenkel et al., 1994; Laesecke, 1993; Stull et al., 1987; Draeger, 1985a; Chao et al., 1984; Stull et al., 1969; Taylor et al., 1946) all stem primarily from experimental work completed in the 1940s by Pitzer and Scott (1943), Prosen et al. (1945), and Osborne and Ginnings (1947). Similarly, Pedley (1994), Pedley et al. (1986), or Cox and Pilcher (1970) are often cited as sources of enthalpies of formation for the liquid and gas phases. Values given in these compilations are, again, those determined by Prosen et al. (1945) and Osborne and Ginnings (1947). Some high-precision thermodynamic-property results have been published in the intervening 50 years for *p*-xylene (literature cited in Chirico et al. (1997a)), while little has been published concerning *m*-xylene and *o*-xylene. None of the new information has been incorporated into modern compilations of standard thermodynamic properties.

In the present paper, heat capacity and enthalpy increment determinations (5 K to 420 K) by adiabatic calorimetry, vapor pressures (313 K to 459 K) by comparative ebulliometry, two-phase (liquid + vapor) heat capacities to the temperature $T \approx 600$ K by differential-scanning calorimetry (DSC), and densities (323 K to 523 K) are reported for *o*-xylene. Saturation heat capacities C_{sat} for the liquid phase to $T \approx 0.9\ T_{\mathrm{c}} \approx 550$ K are derived with fitting procedures. These results are combined with a reliable literature value for the enthalpy of combustion to derive standard entropies, enthalpy increments, and Gibbs free energies of formation for temperatures between 250 K and 550 K based solely on the experimental thermophysical and thermochemical results. The standard state is defined as the ideal gas at the pressure $p = p° = 101.325$ kPa. The DSC was also used to determine the critical temperature directly. The critical pressure was derived by fitting procedures.

o-Xylene has been the subject of many thermodynamic and physical-property investigations including the determination of heat capacities, vapor pressures, densities, enthalpies of vaporization, second virial coefficients, critical properties, enthalpy of combustion, and vibrational assignment. Although routinely reported in isolation in the literature, these properties are closely interrelated through thermodynamic relationships and correlations. Consistency between the related properties, such as vapor pressure with enthalpy of vaporization and virial coefficients, has not been demonstrated in the literature and is emphasized here. Xylene isomerization equilibria calculations based on the new calorimetric results will be published separately (Chirico and Steele, 1997a).

A key feature of the *o*-xylene molecule is the steric interaction of the methyl groups. The nature and magnitude of the potential restricting the methyl-group rotation has been a continuous subject of research for more than 50 years. Much confusion exists in the literature concerning what information can be derived from thermodynamic analyses. In this paper, an attempt is made to clarify this issue. The analysis reported here shows that the new calorimetric results are in accord with spectroscopically derived information concerning the rotational barrier. However, a definitive analysis requires an accurate vibrational assignment for the vapor phase. As discussed later, such an assignment does not exist at this time. The vibrational assignment for *o*-xylene is presently under

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investigation at this laboratory.

This research was completed as part of a program, funded by the Department of Energy (DOE) Office of Fossil Energy, Oil Technology program, to provide thermochemical and thermophysical properties for key compounds related to the upgrading of fossil fuels. The determination of thermodynamic properties for every compound of importance to fossil fuel upgrading is an impossibly large task. Thermodynamic properties for the xylenes provide the basis for structure−property correlations for broad families of alkyl-substituted aromatic compounds, which are essential for process development and optimization.

Experimental Procedure

Materials. The *o*-xylene used in this research was prepared by the Grignard reaction of a commercial sample of 2-bromotoluene (Aldrich Chemical Company; 99% purity) with magnesium, followed by reaction of the Grignard reagent with methyl sulfate. The *o*-xylene was separated from the reaction mixture with a diethyl ether wash followed by fractional distillation to remove the ether. The sample used in the calorimetric studies was further purified by distillation on a Perkin-Elmer spinning band still near 0.1 MPa pressure. The sample was determined to be 0.9993 mole fraction *o*-xylene by fractional melting as part of the heat-capacity studies with adiabatic calorimetry reported here.

Purification of the water and decane used as reference materials in the ebulliometric vapor-pressure measurements has been described (Steele et al., 1988).

Physical Constants and Standards. Molar values are reported in terms of $M = 106.1674\ \mathrm{g{\cdot}mol^{-1}}$ for *o*-xylene and the gas constant, $R = 8.314\,51\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$, adopted by CODATA (Cohen and Taylor, 1988). The platinum resistance thermometers used in these measurements were calibrated by comparison with standard resistance thermometers whose constants were determined at the National Institute of Standards and Technology (NIST). All temperatures reported are in terms of ITS-90. The platinum resistance thermometer used in the adiabatic heat-capacity study was calibrated at $T < 13.81$ K using the method of McCrackin and Chang (1975) with subsequent conversion to ITS-90. Measurements of mass, time, electrical resistance, and potential difference were made in terms of standards traceable to calibrations at NIST.

Densitometry. Densities ρ at saturation pressure for the liquid phase for a range of temperatures were measured with a vibrating-tube densitometer. The densitometer design is essentially that used successfully by Dr. J. M. Simonson and his colleagues at Oak Ridge National Laboratory for the study of aqueous salt mixtures at high temperatures and pressures. The instrument and its operation have been described (Chirico et al., 1993). Test measurements of the density of benzene between the temperatures 310 K and 523 K were reported (Chirico and Steele, 1994). Results agreed with the values published by Hales and Townsend (1972) within $(1 \times 10^{-3})\rho$. The precision of the measurements was approximately $(5 \times 10^{-4})\rho$.

Vapor-Pressure Measurements. Vapor pressures were measured by comparative ebulliometry. The essential features of the ebulliometric equipment and procedures are described in the literature (Osborn and Douslin, 1966; Swietoslawski, 1945). The ebulliometers were used to reflux the *o*-xylene with a standard of known vapor pressure under a common helium atmosphere. The boiling and condensation temperatures of the two substances were determined, and the vapor pressure of the *o*-xylene sample was derived using the condensation temperature of the standard. In the pressure region 25 kPa to 270 kPa, water was used as the standard, and the pressures were derived using the international equation for ordinary water revised to ITS-90 (Wagner and Pruss, 1993). In the region 2 kPa to 25 kPa, decane was used as the standard. The equation used to define the decane vapor pressures in this region has been published (Steele et al., 1995a).

Table 1. Measured Density Values ρ at Saturation Pressure for *o*-Xylene

T/K	ρ/(kg·m^{-3})	T/K	ρ/(kg·m^{-3})
323.14	854.2	448.11	738.1
348.13	832.7	473.11	710.9
373.12	810.6	498.11	681.9
398.12	787.6	523.11	649.3
423.11	763.4		

The accuracy and precision of the temperature measurements for the ebulliometric vapor-pressure studies are estimated to be 0.002 K and 0.0005 K, respectively. Uncertainties in the pressures are adequately described by

$$\sigma(p) = (0.002\ \mathrm{K})\{(\mathrm{d}p_{\mathrm{ref}}/\mathrm{d}T)^2 + (\mathrm{d}p_x/\mathrm{d}T)^2\}^{0.5} \qquad (1)$$

where p_{ref} is the vapor pressure of the reference substance and p_x is the vapor pressure of the sample under study. Values of $\mathrm{d}p_{\mathrm{ref}}/\mathrm{d}T$ for the reference substances were calculated from vapor pressures of the reference materials (decane and water).

Adiabatic Heat-Capacity Calorimetry. Adiabatic heat-capacity and enthalpy measurements were made with a calorimetric system that has been described previously (Steele et al., 1988; Ruehrwein and Huffman, 1943). The platinum calorimeter (internal volume = 62.47 cm^3) was filled with 40.408 g of *o*-xylene and sealed with a gold-gasketed screw-cap closure under a helium pressure of 5.6 kPa at 297 K. Energy measurement procedures were the same as those described for studies on quinoline (Steele et al., 1988). Thermometer resistances were measured with self-balancing alternating-current resistance bridges (H. Tinsley & Co. Ltd.; Models 5840C and 5840D). Energies were measured to a precision of 0.01%, and temperatures were measured to a precision of 0.0001 K. The energy increments to the filled calorimeters were corrected for enthalpy changes in the empty calorimeter, for the helium exchange gas, and for vaporization of the sample. The maximum correction to the measured energy for the helium exchange gas was less than 0.4% near $T = 5$ K for *o*-xylene. The maximum correction for vaporization of the sample into the free space of the calorimeter was approximately 0.07% near 400 K.

Differential-Scanning Calorimetry. DSC measurements were made with a Perkin-Elmer DSC-2. Experimental measurement of two-phase (liquid + vapor) heat capacities and determination of the critical temperature T_c were described previously (Steele, 1995; Chirico and Steele, 1994; Knipmeyer et al., 1989).

Experimental Results

Densities. Measured densities ρ for *o*-xylene in the liquid phase at saturation pressure are listed in Table 1.

Vapor Pressures. Vapor pressures for *o*-xylene are reported in Table 2. The pressures, the condensation temperatures, and the difference between condensation and boiling temperatures for the sample are reported. The small differences obtained between the boiling and condensation temperatures indicate correct operation of the equipment and the high purity of the sample.

Adiabatic Calorimetry. The enthalpy of fusion and heat capacities for the temperature range 5 K to 420 K

Table 2. Summary of Vapor-Pressure Results for *o*-Xylene[a]

standard	T/K	p/kPa	Δp/kPa	σ/kPa	ΔT/K
decane	312.660	2.0064	−0.0002	0.0003	0.020
decane	326.514	4.0102	0.0002	0.0005	0.008
decane	332.634	5.328	0.000	0.001	0.006
decane	341.866	7.993	0.000	0.001	0.005
decane	348.781	10.650	0.000	0.001	0.005
decane	354.425	13.330	0.000	0.001	0.004
decane	360.242	16.653	0.000	0.002	0.003
decane	365.087	19.915	−0.001	0.002	0.003
decane	371.505	25.027	−0.001	0.002	0.002
water[b]	371.507	25.030	0.000	0.003	0.002
water	377.932	31.171	−0.003	0.003	0.002
water	384.408	38.551	−0.002	0.004	0.002
water	390.932	47.353	−0.001	0.005	0.003
water	397.511	57.798	0.001	0.006	0.003
water	404.147	70.121	0.000	0.007	0.003
water	410.812	84.522	0.002	0.008	0.003
water	417.527	101.305	0.003	0.009	0.003
water	424.304	120.80	0.00	0.01	0.003
water	431.115	143.25	0.00	0.01	0.003
water	437.963	168.98	0.00	0.01	0.003
water	444.877	198.48	0.00	0.02	0.004
water	451.825	231.99	0.00	0.02	0.004
water	458.822	269.99	−0.01	0.02	0.003

[a] Water or decane refers to which material was used as the standard in the reference ebulliometer; T is the condensation temperature of the *o*-xylene; the pressure p for ebulliometric measurements was calculated from the condensation temperature of the reference substance; Δp is the difference of the value of pressure, calculated with eq 3 and the parameters listed in Table 8, from the observed value of pressure; σ is the propagated error calculated from eq 1; ΔT is the difference between the boiling and condensation temperatures ($T_{\mathrm{boil}} - T_{\mathrm{cond}}$) for the *o*-xylene [b] This value was not included in the fits to the vapor pressures.

Table 3. Melting-Study Summary for *o*-Xylene[a]

F	$T(F)$/K
0.1564	247.820
0.2564	247.884
0.4063	247.922
0.6561	247.945
0.8060	247.953
T_{tp}/K	($247.98_5 \pm 0.01$)
x	0.0007

[a] F is the fraction melted at observed temperature $T(F)$; T_{tp} is the triple-point temperature; x is the mole-fraction impurity.

were determined by adiabatic calorimetry. Crystallization of the *o*-xylene sample was initiated by cooling (approximately 10 mK·s^{-1}) the liquid sample 10 K to 20 K below the triple-point temperature T_{tp}. The crystals were annealed by maintaining the sample under adiabatic conditions in the partially melted state (15% to 25% liquid) for approximately 3 h. No spontaneous warming, which would indicate incomplete crystallization or phase conversion, was observed. The sample was cooled at an effective rate of 1 mK·s^{-1} to crystallize the remaining liquid. As a final step, the sample was thermally cycled between $T <$ 100 K and within 2 K of the T_{tp}, where it was held for a minimum of 3 h to provide further tempering. All of the solid-phase measurements were performed upon crystals pretreated in this manner.

T_{tp} and the sample purity listed in Table 3 were determined from the measurement of the equilibrium melting temperatures $T(F)$ as a function of fraction F of the sample in the liquid state (McCullough and Waddington, 1957). Equilibrium melting temperatures were determined by measuring temperatures at approximately 300-s intervals for 1 h to 1.2 h after an energy input and extrapolating to infinite time by assuming an exponential decay toward the equilibrium value. The observed temperatures at 1 h after an energy input were invariably within 2 mK of the calculated equilibrium temperatures for F values listed in Table 3. The presence of solid-soluble impurities was not indicated. Fractions F were determined from the measured energies corrected for the energy required to heat the crystals from the initial temperature T_{i} to T_{tp} and from T_{tp} to the final temperature T_{f} in the liquid phase. T_{i} and T_{f} are listed in Table 4 (adiabatic series 1) together with the total measured energy and derived enthalpy of fusion.

Experimental molar enthalpy results for *o*-xylene are summarized in Table 4. The table includes both the enthalpy of fusion and results of measurements in single-phase regions, which serve as checks on the integration of the heat-capacity values. Corrections for premelting caused by impurities were made in these evaluations. Results with the same series number in Tables 4 and 5 were taken without interruption of adiabatic conditions.

The experimental molar heat capacities under vapor saturation pressure $C_{\mathrm{sat,m}}$ determined by adiabatic calorimetry are listed in Table 5 and shown in Figure 1. Values in Table 5 were corrected for effects of sample vaporization into the gas space of the calorimeter. The temperature increments were small enough to obviate the need for corrections for nonlinear variation of $C_{\mathrm{sat,m}}$ with temperature. The precision of the heat-capacity measurements ranged from approximately 5% at $T = 5$ K to 1% at $T = 10$ K, 0.2% near $T = 20$ K, and improved gradually to less than 0.1% above $T = 100$ K, except in the solid phase near T_{tp} where equilibration times were long. The heat capacities in Table 5 have not been corrected for premelting, but an independent calculation can be made with the temperature increments provided.

Equilibrium was reached in less than 1 h for heat-capacity measurements in the liquid phase. Equilibration times for the crystal phase of *o*-xylene were less than 1 h for temperatures below 210 K and increased smoothly to 12 h near T_{tp} (247.98_5 K). Extrapolation of the heat-capacity results to $T \rightarrow 0$ K was made with a plot of $C_{\mathrm{sat,m}}/T$ against T^2 for temperatures below 10 K.

Differential-Scanning Calorimetry. The *o*-xylene sample was sufficiently stable in the critical region to allow experimental determination of the critical temperature with DSC. The temperature of conversion from the two-phase (vapor + liquid) to the fluid-phase region was measured for a range of cell fillings. Details of the method

Table 4. Measurements of Molar Enthalpy Increment $\Delta_{tot}U_m$ for *o*-Xylene (R = 8.314 51 J·K^{-1}·mol^{-1})

N^a	h^b	T_i/K	T_f/K	T_{trs}/K	$\Delta_{tot}U_m{}^c$/(kJ·mol^{-1})	$\Delta_{trs}H_m{}^d$/(kJ·mol^{-1})
			Single-Phase Measurements in the Crystal Phase			
4	1	55.269	116.168		3.837	0.001
5	1	101.512	138.970		3.052	0.000
5	1	138.977	180.062		4.120	0.002
5	1	180.068	209.904		3.489	0.000
			Crystals to Liquid			
1	6	241.421	249.873	247.98$_5$	14.869	13.605
4	3	221.103	249.675		17.582	13.605
5	2	244.522	250.649		14.567	13.608
					average:	13.606
			Single-Phase Measurements in the Liquid Phase			
7	1	282.630	367.317		16.675	0.000
7	1	367.335	420.538		11.792	−0.001

[a] Adiabatic series number. [b] Number of heating increments. [c] $\Delta_{tot}U_m$ is the molar energy input from the initial temperature T_i to the final temperature T_f. [d] $\Delta_{trs}H_m$ is the net molar enthalpy of transition at the transition temperature T_{trs} or the excess enthalpy for single-phase measurements relative to the heat-capacity curve described in the text and defined in Table 9.

Table 5. Molar Heat Capacities $C_{sat,m}$ at Vapor-Saturation Pressure for *o*-Xylene Measured with Adiabatic Calorimetry (R = 8.314 51 J·K^{-1}·mol^{-1})

N^a	$\langle T\rangle$/K	ΔT/K	$C_{sat,m}/R^b$	N^a	$\langle T\rangle$/K	ΔT/K	$C_{sat,m}/R^b$
			Crystals				
2	5.705	0.945	0.042	3	69.619	6.465	6.492
2	6.638	0.958	0.069	3	76.491	7.267	6.996
2	7.595	0.990	0.103	3	84.164	8.069	7.534
2	8.591	1.025	0.150	5	87.735	7.834	7.776
2	9.616	1.033	0.212	3	92.693	8.881	8.103
2	10.698	1.137	0.288	5	96.547	9.765	8.351
2	11.895	1.261	0.387	3	101.856	9.438	8.688
2	13.223	1.391	0.512	3	111.322	9.485	9.271
2	14.693	1.551	0.663	3	120.950	9.764	9.848
2	16.301	1.666	0.849	3	130.739	9.807	10.424
2	18.054	1.842	1.067	3	140.563	9.833	10.987
2	20.003	2.055	1.313	3	150.401	9.834	11.537
2	22.149	2.232	1.597	3	160.347	9.979	12.109
2	24.529	2.526	1.915	3	170.333	9.987	12.672
2	27.180	2.778	2.267	3	181.327	11.980	13.290
2	30.130	3.122	2.646	3	193.283	11.929	13.973
2	33.421	3.459	3.052	3	205.276	12.055	14.691
2	37.072	3.843	3.483	5	215.970	12.050	15.347
2	41.133	4.277	3.928	3	217.328	12.010	15.426
2	45.646	4.747	4.406	1	226.016	10.182	16.013
2	50.658	5.276	4.886	5	228.115	12.148	16.170
3	52.866	4.321	5.093	3	229.364	12.022	16.263
3	57.737	5.399	5.532	1	236.268	10.297	16.960
3	63.411	5.931	5.995	5	239.361	10.296	17.619
			Liquid				
4	251.989	4.628	20.974	6	300.840	15.358	22.687
1	253.558	7.390	21.018	6	316.394	15.741	23.304
5	255.571	9.846	21.082	6	332.520	16.508	23.966
4	259.422	10.237	21.206	6	349.043	16.519	24.670
1	262.249	9.996	21.297	6	365.632	16.233	25.393
1	273.303	12.120	21.675	6	381.746	15.963	26.107
1	285.471	12.227	22.110	6	397.595	15.706	26.819
6	287.053	12.206	22.167	6	413.184	15.459	27.533
1	297.742	12.327	22.569				

[a] Adiabatic series number. [b] Average heat capacity for a temperature increment of ΔT with a mean temperature $\langle T\rangle$.

used were described recently (Steele, 1995). Table 6 reports the filling densities, obtained from the mass of sample and the cell volume, and the temperatures at which conversion to a single phase was observed for all fillings. The cell volume was calculated with the equation:

$$V_x(T)/V_x(298.15\ \mathrm{K}) = 1 + ay + by^2 \qquad (2)$$

where $y = \{(T/\mathrm{K}) - 298.15\}$, $a = 3.216 \times 10^{-5}$, and $b = 5.4 \times 10^{-8}$. These results are shown graphically in Figure 2. The critical temperature for *o*-xylene derived from the DSC measurements, (630.5 ± 1.0) K, is in excellent agreement with the value selected by Tsonopoulos and Ambrose (1995), (630.3 ± 0.5) K, in their recent review. This selected value was used in all fitting procedures of the present research because of its higher precision.

The theoretical background for the determination of heat capacities for the liquid phase at vapor-saturation pressure C_{sat} from results obtained with DSC has been described (Chirico and Steele, 1994; Steele, 1995). Measured two-phase (liquid + vapor) heat capacities for a minimum of two fillings, vapor pressures, and reliable liquid-density values are required.

Table 7 lists molar two-phase heat capacities $C^{II}_{x,m}$ for *o*-xylene obtained for three cell fillings with the DSC. Heat capacities were determined at 20-K intervals with a heating rate of 0.083 K·s^{-1} and a 120-s equilibration period between heats. Figure 3 shows the $C^{II}_{x,m}$ values determined by DSC and $C_{sat,m}$ values determined by adiabatic calorimetry. The effect of vaporization of the sample into the free space of the cell as the temperature is increased

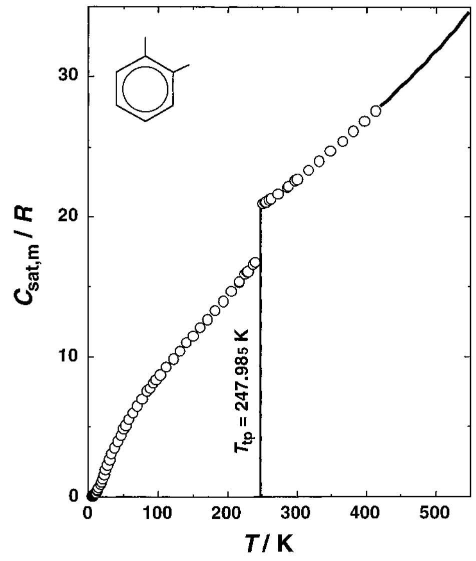

Figure 1. Curve of heat capacity $C_{sat,m}$ against temperature for *o*-xylene. The vertical line indicates the triple-point temperature T_{tp}. (○) $C_{sat,m}$ values measured with adiabatic calorimetry and listed in Table 5. Premelting corrections were applied to the values in the figure. The curve for temperatures $T > 420$ K was derived with results from the differential scanning calorimeter as described in the text.

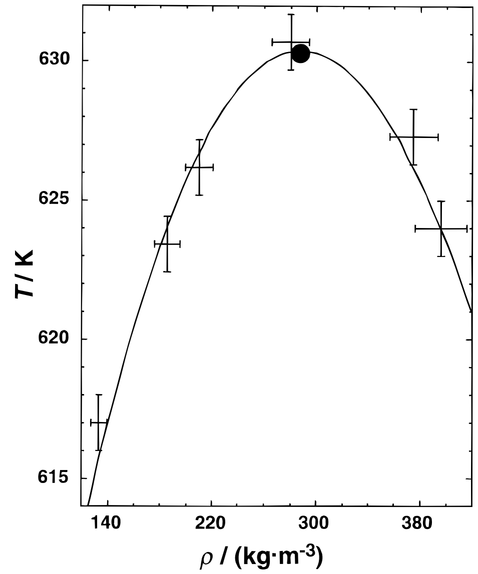

Figure 2. Vapor−liquid coexistence region for *o*-xylene. The crosses span the range of uncertainty for the temperatures measured with DSC and the filling densities ρ. (●) Critical temperature and critical density selected by Tsonopoulos and Ambrose (1995). The curve provides an aid to the eye.

Table 6. Densities ρ and Temperatures for the Conversion from Two Phases to One Phase for *o*-Xylene Measured by DSC

ρ/(kg·m^{-3})	T/K	ρ/(kg·m^{-3})	T/K
133	617.0	280	630.7
185	623.4	375	627.3
210	626.2	396	624.0

is observed readily in the figure. The estimated uncertainty in the $C^{II}_{x,m}$ values is 1%.

Derived Properties

Saturation Heat Capacities $C_{sat,m}$ from DSC Results. A simultaneous nonlinear least-squares fit to the vapor pressures listed in Table 2 and the $C^{II}_{x,m}$ values given in Table 7 was completed. The weighting of the $C^{II}_{x,m}$ and vapor-pressure values has been described with the fitting procedure (Steele, 1995; Chirico and Steele, 1994). $C_{sat,m}$ values determined by adiabatic calorimetry in this research for the temperature range $301 < (T/\mathrm{K}) < 413$ were included and weighted equally with the vapor pressures. These were included to ensure a smooth junction between the $C_{sat,m}$ values determined with adiabatic calorimetry and those derived with the DSC results.

Table 7. Measured Two-Phase (Vapor + Liquid) Heat Capacities $C^{II}_{x,m}$ for *o*-Xylene[a]

T/K	$C^{II}_{x,m}/R$ for V(cell) = 0.052 17 cm^3 m = 0.009 81 g	$C^{II}_{x,m}/R$ for V(cell) = 0.052 17 cm^3 m = 0.014 86 g	$C^{II}_{x,m}/R$ for V(cell) = 0.052 19 cm^3 m = 0.019 89 g
350.0	24.76	25.25	24.74
370.0	25.76	26.26	25.86
390.0	26.78	27.31	26.95
410.0	28.11	28.50	27.96
430.0	29.33	29.87	28.93
450.0	30.73	30.99	29.88
470.0	32.48	32.25	30.97
490.0	33.77	33.53	32.13
510.0	35.60	34.77	33.22
530.0	37.43	36.09	34.05
550.0	39.27	37.27	35.47
570.0	41.19	38.62	36.90
590.0	43.65	40.68	38.29
610.0	47.63		40.76

[a] *m* is the mass of sample, *V*(cell) is the volume of the DSC cell at $T = 298.15$ K after sealing ($R = 8.314\,51$ J·K^{-1}mol^{-1}).

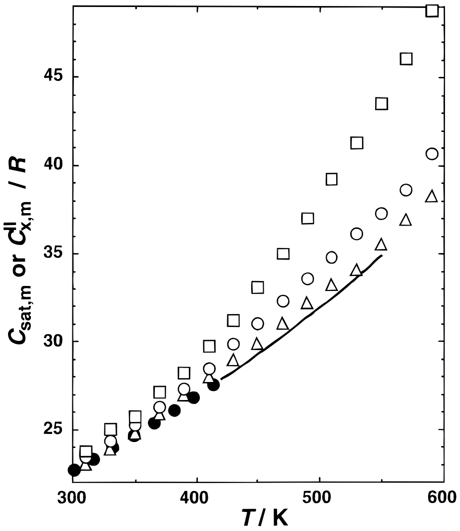

Figure 3. Curve of heat capacity against temperature for *o*-xylene. $C^{II}_{x,m}$ by DSC for three cell fillings: (□) 7.03 mg; (○) 14.86 mg; (△) 19.89 mg of sample. (●) $C_{sat,m}$ determined by adiabatic calorimetry in this research. The curve represents the saturation heat capacities derived in this research and listed in Table 9.

The (2,4) form of the Wagner equation (Wagner, 1973) was used to represent the vapor pressures:

$$\ln(p/p_c) = (1/T_r)\{A(1 - T_r) + B(1 - T_r)^{1.5} + C(1 - T_r)^2 + D(1 - T_r)^4\} \quad (3)$$

where $T_r = T/T_c$. The designation (2,4) refers to the exponents of the last two terms in the equation. The (2,4) form was used to represent successfully the vapor pressures from T_{tp} to T_c for carbon dioxide (Duschek et al., 1990), pyridine (Chirico et al., 1996), *p*-xylene (Chirico et al., 1997a), and *m*-xylene (Chirico et al., 1997b). The critical temperature selected by Tsonopoulos and Ambrose (1995)

Table 8. Parameters for Equations 3 and 5, Critical Constants, and Acentric Factor

o-Xylene	
$A = -7.457\,432$	$b_0 = -0.433\,23$
$B = 1.519\,744$	$b_1 = -0.478\,28$
$C = -1.030\,912$	$b_2 = 0.868\,45$
$D = -3.997\,287$	$b_3 = -1.262\,28$

$T_c = 630.3$ K $\quad p_c = 3730$ kPa $\quad \rho_c = 287$ kg·m^{-3} $\quad \omega = 0.3107$

was used in the fitting procedure. The critical pressure was included as a variable in the fits.

Experimental $C^{II}_{x,m}$ values were converted to $C^{II}_{x,m}$ as follows:

$$C^{II}_{x,m} = C^{II}_{x,m} - T/n\,\{(\partial V_x/\partial T)_x(\partial p/\partial T)_{sat}\} \qquad (4)$$

where n is the number of moles of *o*-xylene used for the particular cell filling, as listed in Table 7. Equation 2 was used to calculate $(\partial V_x/\partial T)_x$, the variation of the cell volume with temperature, and the vapor-pressure fit was used for calculation of $(\partial p/\partial T)_{sat}$. The values of $C^{II}_{V,m}$ and the vapor pressures were used in a weighted nonlinear least-squares fit to derive functions for $(\partial^2 p/\partial T^2)_{sat}$ and $(\partial^2\mu/\partial T^2)_{sat}$, as described previously (Steele, 1995; Chirico and Steele, 1994). The form chosen for variation of the second derivative of the chemical potential with temperature was

$$(\partial^2\mu/\partial T^2)_{sat}/(\mathrm{J{\cdot}K^{-2}{\cdot}mol^{-1}}) = \sum_{i=0}^{n} b_i(1 - T/T_c)^i \qquad (5)$$

For compounds where sufficient information was available to evaluate reliably $(\partial^2\mu/\partial T^2)_{sat}$, e.g., benzene (Goodwin, 1988), four terms, i.e., expansion to $n = 3$, were required to represent the function. Four terms were used in this research. Table 8 lists the coefficients determined in the nonlinear least-squares fits. Deviations of the measured vapor pressures from the fitted Wagner equation are included in Table 2.

Molar heat capacities at saturation pressure $C_{sat,m}$ for *o*-xylene were derived with the equation

$$C_{sat,m} = V_m(l)T(\partial^2 p/\partial T^2)_{sat} - T(\partial^2\mu/\partial T^2)_{sat} + T(\partial p/\partial T)_{sat}\{dV_m(l)/dT\} \qquad (6)$$

Temperature derivatives of the pressure were calculated with the Wagner-equation parameters listed in Table 8. Molar volumes of the liquid V_m(l) were calculated with densities obtained with a form of the corresponding-states equation of Riedel (1954):

$$(\rho/\rho_c) = 1 + 0.85\{1 - (T/T_c)\} + (1.6916 + 0.9846\omega)\{1 - (T/T_c)\}^{1/3} \qquad (7)$$

Values of $(\partial^2\mu/\partial T^2)_{sat}$ were determined with the derived coefficients for eq 5, as listed in Table 8. The derived $C_{sat,m}$ values are included in Table 9. The estimated uncertainty in the values is $(1 \times 10^{-2})C_{sat,m}$. Derived $C_{sat,m}$ values for *o*-xylene are included in Figure 3. The derived critical pressure (3730 ± 40) kPa is in excellent agreement with that selected by Tsonopoulos and Ambrose (3732 ± 40) kPa and is included in Table 8.

Critical Density. The value of the critical density ρ_c = (287 ± 4) kg·m^{-3} selected by Tsonopoulos and Ambrose (1995) in their recent review was used in eq 7. Systematic deviations of eq 7 from reliable literature values exist, but do not exceed 1%. Propagated errors due to a 1% uncertainty in densities calculated with eq 7 are negligible for all properties derived here.

Enthalpies of Vaporization. Molar enthalpies of vaporization $\Delta_l^g H_m$ for *o*-xylene were derived from the Wagner-equation fit to the vapor pressures with the Clapeyron equation:

$$dp/dT = \Delta_l^g H_m/(T\Delta_l^g V_m) \qquad (8)$$

$\Delta_l^g V_m$ is the difference in molar volume between the liquid and the real vapor. Estimates of liquid-phase volumes were made with eq 7. Vapor-phase volumes were calculated with the virial equation of state truncated at the third virial coefficient. Second virial coefficients were estimated with the corresponding-states equation of Pitzer and Curl (1957), and third virial coefficients were estimated with the corresponding-states method of Orbey and Vera (1983). This formulation for third virial coefficients was applied successfully in analyses of the thermodynamic properties of *p*-xylene (Chirico, et al., 1997a), *m*-xylene (Chirico, et al., 1997b), pyridine (Chirico et al., 1996), benzene and methylbenzene (Chirico and Steele, 1994), and 2-methylaniline (Steele et al., 1994). Uncertainties in the virial coefficients were assumed to be 5% on the basis of the good agreement between calculated and experimental values shown for *p*-xylene (Chirico, et al., 1997a).

Derived enthalpies of vaporization are reported in Table 10. For $p > 0.1$ MPa, the uncertainties in the virial coefficients are the dominant contributions to the uncertainties in the derived enthalpies of vaporization. Uncertainties in the volumes of the liquid phase derived with eq 7 do not contribute significantly to the uncertainties in the $\Delta_l^g H_m$ values.

Thermodynamic Properties of Condensed Phases. Entropies and enthalpies under vapor saturation pressure relative to that of the crystals at $T \rightarrow 0$ K for the solid and liquid phases of *o*-xylene are listed in Table 9. The tabulated values were derived by integration of the smoothed heat capacities corrected for premelting, together with the entropies and enthalpies of fusion. The heat capacities were smoothed with cubic-spline functions by least-squares fits to six points at a time and by requiring continuity in value, slope, and curvature at the junction of successive cubic functions. Due to limitations in the spline-function procedure, some acceptable values from Table 5 were not included in the fit, while in other regions graphical values were introduced to ensure that the second derivative of the heat capacity with respect to temperature was a smooth function of temperature. Premelting corrections were made by means of published methods for solid-insoluble impurities (Westrum et al., 1968) with the mole-fraction impurity value 0.000 65.

Thermodynamic Properties for the Standard State from Calorimetric Studies. The standard state is defined as the ideal gas at the pressure p = 101.325 kPa. Standard enthalpies and entropies at selected temperatures were calculated for *o*-xylene with values listed in Tables 9 and 10 and are listed in columns 2 and 4 of Table 11. Entropies and enthalpies of compression to 101.325 kPa were calculated on the basis of the virial equation truncated after the third virial coefficient:

$$pV_m = RT + Bp + C'p^2 \qquad (9)$$

Formulations used to calculate "gas imperfection corrections" are given by Lewis and Randall (1961) and were discussed recently with results for *p*-xylene (Chirico et al., 1997a). Required temperature derivatives of virial coefficients were estimated by numerical differentiation of values estimated with the methods of Pitzer and Curl (1957) and Orbey and Vera (1983), for the second and third virial coefficients, respectively. The gas imperfection cor-

Table 9. Molar Thermodynamic Functions at Vapor-Saturation Pressure for *o*-Xylene[a] (R = 8.314 51 J·K^{-1}·mol^{-1})

T/K	$C_{\mathrm{sat,m}}/R$	$\Delta_0^T S_{\mathrm{m}}/R$	$\Delta_0^T H_{\mathrm{m}}/RT$	T/K	$C_{\mathrm{sat,m}}/R$	$\Delta_0^T S_{\mathrm{m}}/R$	$\Delta_0^T H_{\mathrm{m}}/RT$
			Crystals				
5.00	0.029	0.010	0.007	100.00	8.571	7.788	4.446
10.00	0.237	0.079	0.059	120.00	9.792	9.460	5.236
20.00	1.313	0.538	0.391	140.00	10.954	11.057	5.971
30.00	2.630	1.320	0.919	160.00	12.083	12.593	6.664
40.00	3.806	2.242	1.498	180.00	13.206	14.081	7.328
50.00	4.827	3.204	2.064	200.00	14.354	15.532	7.973
60.00	5.720	4.165	2.601	220.00	15.551	16.956	8.607
70.00	6.517	5.108	3.104	240.00	16.835	18.363	9.239
80.00	7.246	6.026	3.577	247.98_5	17.383	18.923	9.492
90.00	7.926	6.919	4.023				
			Liquid				
247.98_5	20.845	25.521	16.091	400.00	26.927	36.738	18.984
250.00	20.908	25.690	16.129	420.00	27.858	38.074	19.384
260.00	21.226	26.517	16.319	440.00[b]	28.83	39.39	19.79
280.00	21.910	28.114	16.694	460.00[b]	29.84	40.70	20.21
298.15	22.584	29.511	17.031	480.00[b]	30.87	41.99	20.63
300.00	22.655	29.651	17.066	500.00[b]	31.95	43.27	21.06
320.00	23.450	31.138	17.440	520.00[b]	33.08	44.54	21.50
340.00	24.282	32.585	17.818	540.00[b]	34.30	45.82	21.95
360.00	25.146	33.997	18.201	550.00[b]	34.95	46.45	22.18
380.00	26.029	35.380	18.589				

[a] Values listed in this table are reported with one digit more than is justified by the experimental uncertainty. This avoids round-off errors in calculations based on these results. [b] Values at this temperature are based on the fits of the DSC and vapor-pressure measurements described in the text. All other values are based on the adiabatic calorimetric results.

Table 10. Enthalpies of Vaporization $\Delta_l^g H_m$ for *o*-Xylene Obtained from the Wagner and Clapeyron Equations

T/K	$\Delta_l^g H_m$/ (kJ·mol^{-1})	T/K	$\Delta_l^g H_m$/ (kJ·mol^{-1})	T/K	$\Delta_l^g H_m$/ (kJ·mol^{-1})
250.00[a]	46.30 ± 0.08	340.00	41.12 ± 0.06	460.00[a]	33.66 ± 0.16
260.00[a]	45.70 ± 0.08	360.00	39.99 ± 0.06	480.00[a]	32.12 ± 0.19
280.00[a]	44.52 ± 0.07	380.00	38.85 ± 0.07	500.00[a]	30.43 ± 0.24
298.15[a]	43.48 ± 0.07	400.00	37.66 ± 0.07	520.00[a]	28.58 ± 0.29
300.00[a]	43.37 ± 0.07	420.00	36.41 ± 0.09	540.00[a]	26.51 ± 0.35
320.00	42.25 ± 0.07	440.00	35.08 ± 0.12	550.00[a]	25.39 ± 0.38

[a] Values at this temperature were calculated with extrapolated vapor pressures determined from the fitted Wagner coefficients listed in Table 8.

rections are listed in Table 11. Uncertainties in these values are difficult to assess because temperature derivatives of estimated values are involved. An uncertainty of 10% of the calculated correction was assumed.

The derived standard enthalpies and entropies for *o*-xylene were combined with the enthalpy of formation of the liquid −(24.38 ± 1.02) kJ·mol^{-1}, on the basis of the enthalpy of combustion measurements of Prosen et al. (1945), to calculate the standard enthalpies, entropies, and Gibbs energies of formation listed in columns 6, 7, and 8, respectively, of Table 11. Enthalpies and entropies for equilibrium hydrogen were determined from JANAF tables (Chase et al., 1985). Values for graphite were determined with the polynomial (Chirico et al., 1990) used to calculate the values from 298.15 K to 6000 K listed in the JANAF tables. Values for graphite for temperatures below 298.15 K were estimated by interpolation of values listed in the JANAF tables. All uncertainties in Table 11 represent 1 standard deviation and do not include uncertainties in the properties of the elements.

Comparisons with Literature Values

The physical and thermodynamic properties of *o*-xylene have been the subject of numerous investigations reported in the literature. Comparisons of the results of the present research with key literature values are described in the following sections.

Energy of Combustion. The energies of combustion of the three xylenes were measured by Coops et al. (1946) and Prosen et al. (1945). The enthalpy of combustion for the liquid phase of *o*-xylene reported by Coops et al. (1946) is 1.4 kJ·mol^{-1} more positive than that reported by Prosen et al. (1945). Similar differences are observed for the meta and para isomers. A preliminary energy of combustion for *o*-xylene was measured in this laboratory as part of this research and was found to be in excellent agreement with the value reported by Prosen et al. Consequently, the values reported by Prosen et al. for the three xylenes were used in all calculations.

Vapor Pressures. Reports of vapor pressures for *o*-xylene have appeared in the literature for more than 100 years. All of the reported ebulliometric studies (Díaz Peña et al., 1979; Forziati et al., 1949; Willingham et al., 1945) are in good accord with the results of this research as shown in Figure 4. The values are shown relative to vapor pressures calculated with eq 3 and the fitted parameters listed in Table 8.

Ambrose et al. (1967) reported vapor pressures for *o*-xylene between the temperatures 432 K and 630.3 K. The small systematic deviations of these high-temperature results from values calculated with eq 3 and the parameters listed in Table 8 are shown in Figures 4 and 5. High-temperature values reported by Mamedov et al. (1970) and Glaser and Rüland (1957) are also in good accord with the values derived in the present research, as shown in Figure 5. The critical temperature reported by Mamedov et al. (1970) for *o*-xylene is approximately 1 K higher than the assessed value (Tsonopoulos and Ambrose, 1995). For the comparison near T_c a vapor pressure value calculated by Mamedov et al. for T = 630.2 K was used. Values reported by Glaser and Rüland for *m*-xylene and *p*-xylene show large deviations (2% to 5% low) from measurements completed in this laboratory (Chirico et al., 1997a; Chirico et al., 1997b; Osborn and Douslin, 1974) and by Ambrose et al. (1967). The origin of these deviations is not known.

Comparisons with other literature values are shown in Figure 6. The vertical axis in Figure 6 is expanded by a factor of 50 relative to that in Figure 4. Results derived from vapor−liquid equilibria (VLE) studies were not considered in the vapor-pressure comparisons. Results from VLE studies are typically for one or two temperatures only and are often performed on materials of relatively low purity. Values reported by Linder (1931) for temperatures

Table 11. Standard Molar Thermodynamic Properties in the Ideal-Gas State for *o*-Xylene at $p = p^\circ = 101.325$ kPa ($R = 8.314\,51$ J·K^{-1}·mol^{-1})

T/K	$\Delta_0^T H_m^\circ/RT$	$\Delta_{imp}H_m^\circ/RT^a$	$\Delta_0^T S_m^\circ/R$	$\Delta_{imp}S_m^\circ/R^b$	$\Delta_f H_m^\circ/RT$	$\Delta_f S_m^\circ/R$	$\Delta_f G_m^\circ/RT$
250.00^c	38.40 ± 0.04	0.00	39.74 ± 0.05	0.00	11.10 ± 0.25	−39.98 ± 0.05	51.08 ± 0.25
260.00^c	37.46 ± 0.04	0.00	40.28 ± 0.05	0.00	10.29 ± 0.24	−40.37 ± 0.05	50.66 ± 0.24
280.00^c	35.82 ± 0.04	0.00	41.36 ± 0.04	0.00	8.85 ± 0.22	−41.10 ± 0.04	49.95 ± 0.22
298.15^c	34.58 ± 0.03	0.01	42.33 ± 0.04	0.01	7.71 ± 0.21	−41.72 ± 0.04	49.43 ± 0.21
300.00^c	34.46 ± 0.03	0.01	42.42 ± 0.04	0.01	7.60 ± 0.21	−41.78 ± 0.04	49.38 ± 0.21
320.00	33.33 ± 0.03	0.02	43.48 ± 0.04	0.01	6.53 ± 0.19	−42.40 ± 0.04	48.93 ± 0.19
340.00	32.39 ± 0.03	0.03	44.53 ± 0.04	0.02	5.60 ± 0.18	−42.96 ± 0.04	48.56 ± 0.18
360.00	31.61 ± 0.03	0.05	45.58 ± 0.04	0.04	4.78 ± 0.17	−43.48 ± 0.04	48.26 ± 0.17
380.00	30.96 ± 0.03	0.07	46.62 ± 0.04	0.05	4.07 ± 0.16	−43.95 ± 0.04	48.02 ± 0.17
400.00	30.42 ± 0.03	0.11	47.66 ± 0.04	0.08	3.44 ± 0.16	−44.38 ± 0.04	47.83 ± 0.16
420.00	29.97 ± 0.04	0.16	48.68 ± 0.05	0.12	2.89 ± 0.15	−44.78 ± 0.05	47.67 ± 0.15
440.00	29.60 ± 0.04	0.22	49.70 ± 0.05	0.16	2.40 ± 0.14	−45.14 ± 0.05	47.54 ± 0.15
460.00^c	29.31 ± 0.06	0.30	50.72 ± 0.06	0.22	1.96 ± 0.14	−45.48 ± 0.06	47.44 ± 0.14
480.00^c	29.07 ± 0.07	0.39	51.73 ± 0.07	0.28	1.58 ± 0.14	−45.78 ± 0.07	47.36 ± 0.14
500.00^c	28.88 ± 0.08	0.50	52.73 ± 0.09	0.36	1.23 ± 0.15	−46.06 ± 0.09	47.30 ± 0.14
520.00^c	28.74 ± 0.10	0.63	53.73 ± 0.10	0.46	0.93 ± 0.16	−46.32 ± 0.10	47.24 ± 0.15
540.00^c	28.62 ± 0.12	0.77	54.72 ± 0.12	0.57	0.65 ± 0.17	−46.55 ± 0.12	47.20 ± 0.15
550.00^c	28.58 ± 0.13	0.85	55.20 ± 0.13	0.62	0.52 ± 0.17	−46.66 ± 0.13	47.18 ± 0.16

[a] Gas imperfection correction included in the ideal-gas enthalpy. The ideal-gas enthalpy is calculated relative to that of the crystals at $T \rightarrow 0$ K. [b] Gas imperfection correction included in the ideal-gas entropy. [c] Values at this temperature were calculated with extrapolated vapor pressures calculated from the fitted Wagner-equation parameters listed in Table 8.

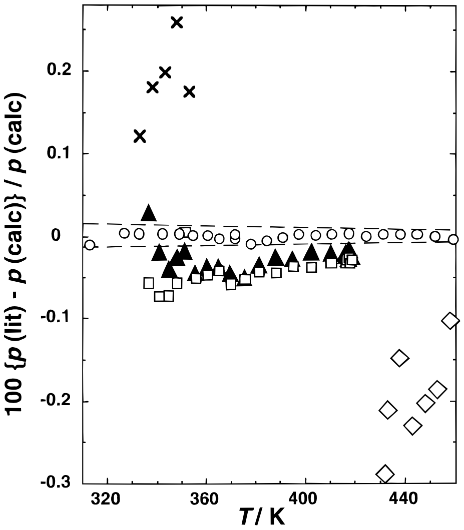

Figure 4. Deviation plot for *o*-xylene vapor pressures; p(calc) represents the values calculated with eq 3 and the parameters listed in Table 8. Values of p(expt): (○) fitted values of this research (Table 2); (×) Díaz Peña et al. (1979); (◇) Ambrose et al. (1967), most values from this reference are not shown (see Figure 5 for a complete comparison); (▲) Forziati et al. (1949); (□) Willingham et al. (1945). The dashed lines indicate the estimated experimental uncertainties (1 standard deviation) for the values of this research (Table 2).

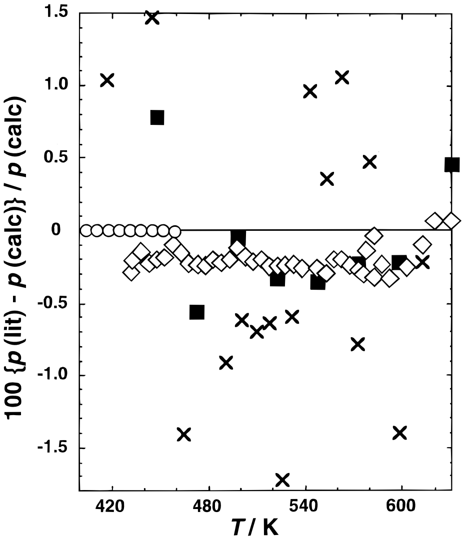

Figure 5. Deviation plot for *o*-xylene vapor pressures at high temperatures; p(calc) represents the values calculated with eq 3 and the parameters listed in Table 8. Values of p(expt): (○) fitted values of this research (Table 2); (◇) Ambrose et al. (1967); (■) Mamedov et al. (1970); (×) Glaser and Rüland (1957).

from 256 K to 273 K are 20% to 40% low relative to the calculated values and are not shown in Figure 6. Values reported by Rintelen et al. (1937) for temperatures between 283 K and 323 K range from 39% to 2% lower than the calculated values and also are not shown.

Sublimation Pressures. Sublimation pressures for *o*-xylene were reported by Hessler and Lichtenstein (1986) for temperatures from 241 K to 247 K. Sublimation pressures were calculated in the present research with the thermodynamic functions for the condensed phases (Table 9) and the fitted Wagner equation (eq 3 and Table 8). Sublimation pressures p_s were calculated with the following equation

$$\ln\{p_s(T)/p(T)\} = \{\Delta_0^T\Phi_m(\text{cr}) - \Delta_0^T\Phi_m(\text{liquid})\}/RT \quad (10)$$

where $\Delta_0^T\Phi_m = \{\Delta_0^T H_m - T\Delta_0^T S_m\}$ and $p(T)$ is the extrapolated vapor pressure of the liquid calculated with the fitted Wagner-equation coefficients (Table 8). The derived sublimation pressures were represented by the equation

$$\ln(p/p_\theta) = 25.93 - 4131(T/\text{K})^{-1} - 3.7834 \times 10^5 (T/\text{K})^{-2} \quad (11)$$

for the temperature range 241 K to 247 K, where $p_\theta = 1$ Pa. The primary source of uncertainty in the derived sublimation pressures stems from uncertainties associated with the extrapolation of vapor pressures for the liquid phase below the range of the measured values. In the present case this extrapolation is from 312.7 K to 241.2 K. On the basis of results obtained previously with the (2,4)-form of the Wagner equation for pyridine (Chirico et al., 1996), uncertainties in the calculated sublimation pressures are estimated to be <2% between 240 K and T_{tp} (247.98$_5$ K). Comparisons between calorimetrically and statistically derived standard entropies described later support the validity of the extrapolated vapor pressures used here. $\Delta_0^T\Phi_m$(liquid) is calculated with extrapolated values of $C_{sat,m}$ for the liquid; however, this extrapolation is short (from T_{tp} to 240 K) and can be done with high precision.

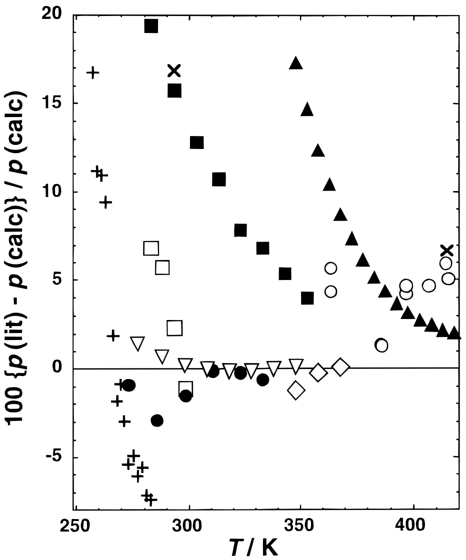

Figure 6. Low-resolution deviation plot for *o*-xylene vapor pressures; *p*(calc) represents the values calculated with eq 3 and the parameters listed in Table 8. Values of *p*(expt): (+) Hessler and Lichtenstein (1986), deviations for values from this reference extend to near 50% at T_{tp}; (□) Mato et al. (1986); (●) Pitzer and Scott (1943); (▽) Stuckey and Saylor (1940), values from this reference were provided in equation form only; (■) Kassel (1936); (×) Richards and Mathews (1908); (▲) Woringer (1900), deviations for values from this reference extend to near 200% at 273 K; (○) Neubeck (1887).

Sublimation pressures reported by Hessler and Lichtenstein (1986) show large deviations from eq 11. The deviations increase from 20% high near 241 K to 38% high near 247 K. Hessler and Lichtenstein (1986) also reported sublimation pressures for *p*-xylene between 257 K and 285 K. These were shown to be in good accord (within ±3%) with sublimation pressures derived analogously with those of eq 11 (Chirico et al., 1997a). The origin of the difference is not known. Vapor pressures for the liquid phase of *o*-xylene by Hessler and Lichtenstein (1986) also show large deviations from those of the present research, as shown in Figure 6.

Densities. Densities for *o*-xylene have been reported in the literature from near T_{tp} to near T_c. This extensive literature will be reviewed in a separate paper concerning the densities of the xylenes and related compounds (Chirico and Steele, 1997b). The Riedel equation (eq 7) will be shown to provide values in good accord with the experimental values (within ±1%); however, the deviations far exceed the experimental uncertainties for the best available density values. Alternative density representations such as those suggested by Campbell and Thodos (1985) and Spencer and Danner (1972) will be discussed separately (Chirico and Steele, 1997b). These approaches were not used here because the correlation of Riedel (1954) provides values of adequate precision for the calculations of this research.

Critical Properties. The critical properties for *o*-xylene were reviewed recently by Tsonopoulos and Ambrose (1995). Their selected value for the critical temperature (630.3 ± 0.5) K, based on the measurements by Ambrose et al. (1967), was used in this research because of its high precision. The value obtained here by DSC, (630.5 ± 1.0) K, is in excellent agreement with the selected value, as shown earlier in Figure 1. The critical pressure p_c derived here, (3730 ± 40) kPa, from the simultaneous fit of the vapor pressures and high-temperature two-phase heat capacities is in excellent agreement with that selected, (3732 ± 40) kPa, by Tsonopoulos and Ambrose (1995), again based on measurements by Ambrose et al. (1967). The critical pressure obtained in the present research, (3730 ± 40) kPa, was used in all calculations. Use of the p_c value selected by Tsonopoulos and Ambrose (1995) would not alter any of the property values derived here. The small difference is not significant.

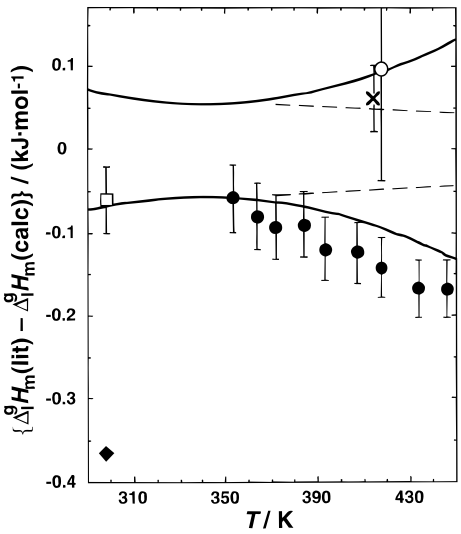

Figure 7. Deviation plot for *o*-xylene enthalpies of vaporization $\Delta_l^g H_m$. $\Delta_l^g H_m$(calc) represents values derived with the Clapeyron equation and listed in Table 10. —, Error limits (1 standard deviation) assigned to the calculated $\Delta_l^g H_m$ values; - - -, error limits without uncertainty in virial coefficients. Values of $\Delta_l^g H_m$(lit): (●) Archer and Hossenlopp (1988); (□) Osborne and Ginnings (1947); (◆) Saito and Kusano (1973); (×) Mathews (1926); (○) Nagornow and Rotinjanz (1911). The value reported by Kiselev et al. (1977) {(42.4 ± 0.5) kJ·mol^{-1} for T = 343.8 K} is 1.5 kJ·mol^{-1} higher than $\Delta_l^g H_m$(calc) and is not shown.

The critical density selected by Tsonopoulos and Ambrose (1995), ρ_c = (287 ± 4) kg·m^{-3}, is the average of values reported by Simon (1957) and Akhundov and Imanov (1970). This value was used in the present research and is consistent with the available saturation densities and the corresponding-states equation (eq 7).

Enthalpies of Vaporization. Enthalpies of vaporization from the literature are compared in Figure 7 with those calculated in this research with the fitted Wagner equation (eq 3 and coefficients of Table 8) and the Clapeyron equation (eq 8). The enthalpy of vaporization at 298.15 K for *o*-xylene was reported by Osborne and Ginnings (1947) of the National Bureau of Standards and by Saito and Kusano (1973). Values near the normal-boiling temperature were reported by Mathews (1926) and Nagornow and Rotinjanz (1911). Only the value reported by Saito and Kusano (1973) is not in accord with the calculated values of this research.

Archer and Hossenlopp (1988) reported enthalpies of vaporization for *o*-xylene for the temperature range 353 K to 446 K. The reported values are slightly lower than those derived in this research, as seen in Figure 7. The sample used by Archer and Hossenlopp (1988) was "a Research-Grade material obtained from Phillips Petroleum Company and was used without further purification". A sample from the same source was obtained originally for the present research and was found to contain ≈0.2% organic impurity in addition to some water. (The sample used in the present research was later synthesized, as described earlier.) Sample purity differences may account for some of the differences between the experimental (Archer and Hossenlopp, 1988) and derived enthalpies of vaporization.

The small discrepancies between the results of Archer and Hossenlopp (1988) and those derived with the Clap-

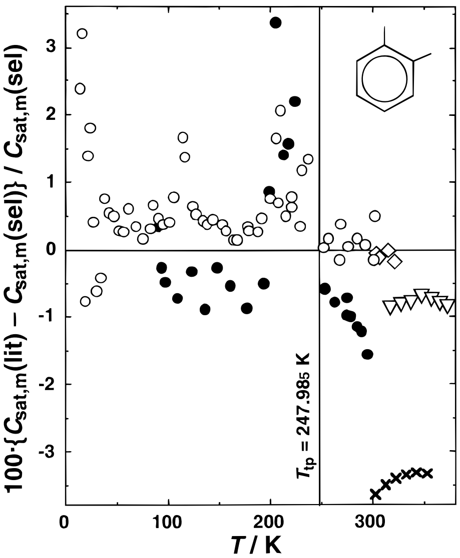

Figure 8. Deviation plot for *o*-xylene heat capacities. $C_{sat,m}$(sel) are the results of the present research (Table 9). Values of $C_{sat,m}$ (lit): (▽) Garg et al. (1993), the number of values shown is reduced for clarity; (◇) Jain et al. (1992), the number of values shown is reduced for clarity; (○) Pitzer and Scott (1943); (●) Huffman et al. (1930); (×) Williams and Daniels (1924). The vertical line indicates the triple-point temperature.

eyron equation could also result from errors in the estimated virial coefficients. If the second virial coefficients determined by Cox and Andon (1958) are substituted for those derived with corresponding states, the agreement between the experimental and calculated values is improved. However, analogous calculations for *p*-xylene substantially degrade the agreement between the experimental and calculated values.

Kiselev et al. (1977) reported an enthalpy of vaporization at the temperature 343.8 K for *o*-xylene determined with a gas chromatographic technique. Their value is approximately 1.5 kJ·mol^{-1} lower than that calculated in this research. Kiselev et al. (1977) claimed an uncertainty of ±0.5 kJ·mol^{-1}, which was clearly optimistic.

Condensed-Phase Heat Capacities and Entropies. Heat capacities for *o*-xylene by adiabatic calorimetry were first reported by Huffman et al. (1930) for temperatures between 90 K and 295 K. The sample of *o*-xylene used in those early studies was very impure. Although the purity was not determined, the authors noted an excess heat capacity near 208 K, which Pitzer and Scott (1943) later associated with the melting of an *o*-xylene/*m*-xylene eutectic. Pitzer and Scott (1943) observed an excess heat capacity near 210 K; however, the excess was approximately half that observed by Huffman et al. The enthalpy of fusion for *o*-xylene reported by Huffman et al. (1930) is approximately 4% lower than that found in the present research. The reported heat capacities are typically within 2% of the results reported here; however, between 200 K and 210 K deviations increase to 12%. Huffman et al. (1930) estimated the entropy increment between 0 K and 90 K. The entropy for the liquid at 298.15 K reported by Huffman et al. is 1% (≈0.3R) higher than that found in the present research.

Pitzer and Scott (1943) measured heat capacities for *o*-xylene for the temperature range 14.4 K to 301.9 K. The sample used by Pitzer and Scott was 99.88% pure *o*-xylene, based upon the results of a fractional-melting study. Deviations of their results from those of the present research are shown in Figure 8. The deviations are slightly larger than the 0.2% uncertainty claimed by Pitzer and Scott for temperatures above 50 K. At lower temperatures the deviations increase to from 1% to 4%.

The enthalpy of fusion reported by Pitzer and Scott (1943) for *o*-xylene, (13.60 ± 0.04) kJ·mol^{-1}, is in excellent accord with that found in the present research, (13.60 ± 0.01) kJ·mol^{-1}. Their value for the triple-point temperature, T_{tp} = (247.84 ± 0.10) K, is slightly lower than that obtained here, (247.98$_5$ ± 0.01) K. The entropy for the liquid at 298.15 K reported by Pitzer and Scott is 0.3% higher (≈0.08R) than that found in the present research (Table 9).

Kurbatov (1947) reported heat capacities for *o*-xylene in the liquid phase derived from enthalpy increment measurements between 288 K and 405 K. Deviations of values calculated with the linear equation provided by Kurbatov from the values of this research (Table 9) range from 2.7% low near 288 K to within 0.1% near 405 K. Swietoslawski and Zielenkiewicz (1958) reported an enthalpy increment from near 295 K to 400 K. Their result is 1% higher than that of this research, as was found previously for *p*-xylene (Chirico et al., 1997a).

Standard Entropies and Heat Capacities from Spectroscopic Studies. Numerous assignments for the 48 fundamental vibrational modes of *o*-xylene have been reported within the last 50 years (Draeger, 1985b; Sverdlov et al., 1974; Green, 1970; Hastings and Nicholson, 1957; Pitzer and Scott, 1943). Only Draeger (1985b) reported wavenumber values for the vapor phase. It has been demonstrated repeatedly that vapor-phase wavenumber values are essential for comparisons of calorimetric and statistically derived standard properties (Chirico et al., 1997a; Chirico et al., 1996; Klots and Collier, 1995a,b).

Two of the fundamental modes for the xylenes are associated with internal rotation of the methyl groups. For *m*-xylene and *p*-xylene these can be treated as free rotors in the vapor phase (Breen et al., 1987). Rotation of the methyl groups in the ortho isomer is restricted considerably, and numerous estimates of the size of the rotational barrier exist in the literature. Much of the confusion in the literature stems from a failure to recognize that the rotational barriers can arise from both intra- and intermolecular interactions. It is common (cf. Chao et al., 1984) for researchers to assume that barrier values determined for solids, liquids, or gases are equivalent.

Recent determinations of the barrier heights for xylenes in the vapor phase (Breen et al., 1987) and in the solid phase (Prager et al., 1990) show that intermolecular interactions make a large contribution to the observed rotational barriers for the xylenes in the crystalline state. Recently, calorimetric results for the six dimethylpyridines (Chirico et al., 1994; Steele et al., 1995b) were used to show that the size of the intermolecular contribution to the rotational barriers in the dimethylpyridines was similar to that of the ortho interaction for the isolated molecules.

Pitzer and Scott (1943) estimated the barrier to methyl group rotation for *o*-xylene by comparison of their calorimetric and statistically derived entropies for the gas phase. Their value (8.4 kJ·mol^{-1}) is often quoted in the literature as being “thermodynamic” or derived from “calorimetry”. The method used by Pitzer and Scott (1943) requires an accurate vibrational assignment together with calorimetrically derived standard entropies to derive a rotational barrier. The vibrational assignment proposed by Pitzer and Scott (1943) has long been shown to contain numerous errors (Draeger, 1985b; Green, 1970) although it is still used in many thermodynamic property compilations (cf. TRC, 1996; Frenkel et al., 1994; Laesecke, 1993; Stull et al., 1987; Chao et al., 1984). Furthermore, Pitzer and Scott (1943) used an enthalpy of vaporization derived from their low-precision vapor-pressure studies to derive the standard entropy at T = 298.15 K for *o*-xylene. Subsequent measurements by Ginnings and Osborne (1947) showed this

Table 12. Wavenumbers (cm^{-1}) for the Fundamental Vibrations of *o*-Xylene in the Vapor Phase

Draeger (1985b)	Selco and Carrick (1995)	this research[a]
163		163
245	246.1	246.1
245	322.9	322.9
405		405
434		434
482		482
506	502.6	502.6
584	581.0	581.0
702		702
738		738
738	739.5	739.5
826		826
862		862
930	928.5	928.5
966		966
989	982.4	982.4
989		989
1020		1020
1054		1054
1054	1056.4	1056.4
1120		1120
1164		1164
1221	1180.8	1180.8
1221	1220.0	1220.0
1290		1290
1290	1292.7	1292.7
1390		1390
1390		1390
1448		1448
1461		1461
1461		1461
1461		1461
1461		1461
1496		1496
1587		1587
1608		1608
2927		2927
2927		2927
2936		2936
2936		2936
2936		2936
2936		2936
3041		3041
3045		3045
3052		3052
3064	3075.7	3075.7

[a] Results of Draeger (1985b) modified with those of Selco and Carrick (1995).

$\Delta_l^g H_m$ value to be in error. The erroneous standard entropy at $T = 298.15$ K listed by Pitzer and Scott (1943) is still quoted by reviewers (cf. Frenkel, 1994; Chao et al., 1984) as the "best" calorimetrically derived value.

A definitive vibrational assignment for *o*-xylene is not available. Large differences exist between the available assignments (Draeger, 1985b; Sverdlov et al., 1974; Green, 1970; Hastings and Nicholson, 1957; Pitzer and Scott, 1943), particularly for wavenumber values below 500 cm^{-1}. The low-wavenumber fundamentals make large contributions to the thermodynamic properties in the temperature range considered here; 250 K to 550 K. The complete assignment reported by Draeger (1985b) is the only assignment available for the vapor phase. The wavenumber values reported by Draeger (1985b) for the gas phase are reproduced in Table 12.

Recently, Selco and Carrick (1995) reported results of jet-cooled emission spectroscopic studies for the xylenes, giving wavenumbers for 12 fundamental vibrational modes with slight anharmonicity for one mode only (739.5 cm^{-1} with $\omega_e\chi_e = 0.5\ cm^{-1}$). The wavenumber values reported by Selco and Carrick (1995) listed in Table 12 are in good accord with those of Draeger (1985b) except for the mode at 322.9 cm^{-1}, which Draeger assigned to 245 cm^{-1} on the basis of force-field calculations. The mode near 322.9 cm^{-1} was observed at 325 cm^{-1} in the liquid phase by Green (1970). The best assignment available presently is that of Draeger (1985b) augmented with the results of Selco and Carrick (1995). This combined assignment was used in all statistical calculations in the present research and is listed in the third column of Table 12 (labeled "this research").

Methyl group rotation barrier heights for the vapor phase have been determined by Breen et al. (1987) with laser jet spectroscopy ($V_3 = 5.08\ kJ{\cdot}mol^{-1}$ and $V_6 = 0.22\ kJ{\cdot}mol^{-1}$), Rudolph et al. (1972) from an analysis of microwave spectra $\{V_3 = (6.2 \pm 0.2)\ kJ{\cdot}mol^{-1}\}$, and Ingham and Strickler (1970) from hot bands in the UV spectrum $\{V_3 = (8.4 \pm 0.6)\ kJ{\cdot}mol^{-1}\}$. Chao et al. (1984) estimated the rotational barrier ($V_3 \approx 7.5\ kJ{\cdot}mol^{-1}$) from far-infrared spectra by Pardoe et al. (1970). Chao et al. (1984) mistakenly assumed that the band observed by Pardoe et al. (1970) at $(162 \pm 5)\ cm^{-1}$ was associated with the $0 \rightarrow 1$ torsional transition. The band observed by Pardoe et al. (1970) is the lowest vibrational fundamental for *o*-xylene in the vapor phase, as reported by Draeger (1985b) at 163 cm^{-1}.

The wavenumber assignments of this research (Table 12) were used to calculate standard entropies and standard heat capacities for *o*-xylene between 250 K and 550 K. Rotational energy levels for the hindered methyl groups were estimated from solutions of the torsional wave equation for a rotor subject to a potential of combined 3-fold and 6-fold symmetry:

$$-F(d^2\Psi(\phi)/d\phi^2) + \{(V_3/2)(1 - \cos 3\phi) + (V_6/2)(1 - \cos 6\phi)\}\Psi(\phi) = E\Psi(\phi) \quad (12)$$

where F is the internal rotation constant for the rotor, ϕ is the rotation angle, V_3 and V_6 are the rotation barrier heights, and E represents the rotational energy levels. The method of Lewis et al. (1972) was used to calculate the energy levels with eq 12, and the methods of statistical mechanics were used to calculate the heat capacity arising from their thermal population. The restricting potentials reported by Breen et al. (1987), Rudolph et al. (1972) and Ingham and Strickler (1970) were used with eq 12. The moment of inertia for *o*-xylene ($6.634 \times 10^{-134}\ kg^3{\cdot}m^6$) was calculated with estimated bond distances and angles described previously (Chirico et al., 1997a). The reduced moments of inertia for rotation of the methyl groups were $5.375 \times 10^{-39}\ kg{\cdot}m^{-2}$. Effects due to centrifugal distortion were not considered in the calculations. Uncertainties in the calculated standard entropies resulting from this neglect were estimated to be very small (less than $0.02R$ near 550 K).

Differences between the statistically calculated standard entropies $\Delta_0^T S_m^\circ$(stat) and those derived from the calorimetric studies of this research $\Delta_0^T S_m^\circ$(cal) (Table 11) are shown in Figure 9. Deviations for $\Delta_0^T S_m^\circ$(stat) values calculated with the barrier reported by Ingham and Strickler (1970) range from $0.40R$ near 250 K to $0.25R$ near 550 K and are not shown in the figure. Agreement between $\Delta_0^T S_m^\circ$(stat) and $\Delta_0^T S_m^\circ$(cal) is optimized for $V_3 = (5.8 \pm 0.4)\ kJ{\cdot}mol^{-1}$ if the vibrational assignment is assumed to be correct. This barrier is in accord with that reported by Rudolph et al. (1972) $\{V_3 = (6.2 \pm 0.2)\ kJ{\cdot}mol^{-1}\}$ but is significantly higher than that determined by Breen et al. (1987), ($V_3 = 5.08\ kJ{\cdot}mol^{-1}$ and $V_6 = 0.22\ kJ{\cdot}mol^{-1}$). Inclusion in the calculations of the V_6 term reported by Breen et al. (1987) makes little contribution ($\approx 0.01R$) to the $\Delta_0^T S_m^\circ$(stat) values.

The assignment of this research (Table 12) is in general accord with the assignment for the liquid phase by Green

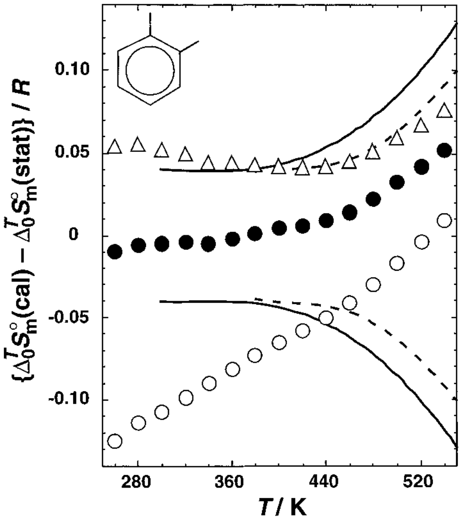

Figure 9. Deviation plot for *o*-xylene standard entropies. —, Error limits (1 standard deviation) assigned to the calorimetric values $\Delta_0^T S^\circ$(cal); - - -, error limits without uncertainty in the virial coefficients. $\Delta_0^T S^\circ$(stat) was calculated with the vapor-phase assignment of this research, as described in the text and listed in Table 12. $\Delta_0^T S^\circ$(stat) was calculated with three different rotational barriers: (△) $V_3 = 6.2$ kJ·mol^{-1} (Rudolph et al., 1972); (○) $V_3 = 5.08$ kJ·mol^{-1} and $V_6 = 0.22$ kJ·mol^{-1} (Breen et al., 1987); (●) $V_3 = 5.8$ kJ·mol^{-1}. See text.

(1970); however, important discrepancies remain in the 900 cm^{-1} to 1200 cm^{-1} region. Until a definitive vibrational assignment for *o*-xylene in the vapor phase is available, the size of the rotational barrier cannot be derived unequivocally from the calorimetric studies.

Raman and infrared spectroscopic studies for *o*-xylene in the vapor phase are in progress in this laboratory. Analysis of these spectral results and a more detailed discussion of rotational barriers in the xylenes will by published separately (Chirico et al., to be published).

Ideal-Gas Heat Capacities. Heat capacities for the gas phase were measured by Pitzer and Scott (1943) for all of the xylenes for the temperatures 393 K, 428 K, and 493 K. Values were obtained for a single pressure at each temperature. Differences between the measured heat capacities of the real gas and that of the ideal-gas $C_{p,m}^\circ$ were estimated with the Bertholet equation by Pitzer and Scott. Large uncertainties are associated with this estimation because the second derivative with temperature of the second virial coefficient B is required. Nonetheless, the $C_{p,m}^\circ$ values reported by Pitzer and Scott (1943) are within 0.5% of the values calculated statistically with the assignment of this research (Table 12) and the methyl rotation barrier $V_3 = 5.8$ kJ·mol^{-1} derived here by comparison with the calorimetrically derived standard entropies. Pitzer and Scott (1943) “somewhat arbitrarily” estimated the uncertainties in their experimental $C_{p,m}^\circ$ values to be near 1%. Estimation of the temperature derivatives of the second virial coefficient with the correlation of Pitzer and Curl (1957) rather than the Bertholet equation does not alter the results significantly.

Second Virial Coefficients. Second virial coefficients for *o*-xylene between the temperatures 377 K and 438 K were determined with vapor compressibility measurements at the Chemical Research Laboratory (a.k.a. the National Physical Laboratory) of England (Cox and Andon, 1958; Andon et al., 1957). The imprecision of the reported values was near 2%. Deviations between these experimental values and those calculated with the corresponding states method of Pitzer and Curl (1957) decrease rapidly from 16% near 377 K to 1.3% at 438 K. Similar deviations are observed from values derived with the correlation by Tsonopoulos (1974). The origin of the inconsistency at low temperatures for *o*-xylene is not known. Similar inconsistencies between experimental (Cox and Andon, 1958; Andon et al., 1957) and calculated second virial coefficients were shown previously for *p*-xylene (Chirico et al., 1997a) and *m*-xylene (Chirico et al., 1997b).

Cox, Andon, and co-workers (Cox, 1960; Cox and Andon, 1958; Andon et al., 1957) reported second virial coefficients for many single-ring aromatic compounds including benzene, toluene, the three xylenes, pyridine, the three methylpyridines, and the six dimethylpyridines. The deviations of these measured values from those calculated with corresponding states (Pitzer and Curl, 1957) do not form a consistent pattern, which can be related to an underlying physical phenomenon such as association in the liquid state. In contrast to the results for the xylenes, values reported by Andon et al. (1957) for benzene show deviations which increase with temperature from the corresponding-states values, while those for pyridine are in excellent accord (see Chirico and Steele, 1996).

Bich et al. (1981) reported second virial coefficients for *p*-xylene for the temperature range $423 < (T/\mathrm{K}) < 563$. These experimental values were shown (Chirico et al., 1997a) to be in excellent accord (within ±5%) with values derived with the method of Pitzer and Curl (1957). On the basis of this result, the correlation by Pitzer and Curl (1957) was used for all calculations in the present research for *o*-xylene.

Conclusions

Standard thermodynamic properties for *o*-xylene based on thermochemical and thermophysical property studies are reported for temperatures between 250 K and 550 K. Thermodynamic consistency was demonstrated for heat capacities for condensed and vapor phases, vapor pressures, enthalpies of vaporization, and critical properties. Available experimental virial coefficients were shown to be inconsistent with these results, and values derived with a corresponding states correlation were used. The single available vibrational assignment for the vapor phase was modified with a recent partial assignment based on jet-cooled emission spectra. The calorimetric results are in accord with this modified vibrational assignment and a 3-fold barrier to methyl group rotation $V_3 = (5.8 \pm 0.4)$ kJ·mol^{-1}. This value is preliminary until a definitive vibrational assignment for *o*-xylene in the vapor phase is determined. The calorimetrically derived thermodynamic property values will be used to calculate xylene isomerization equilibria over a broad temperature. These results will be published separately (Chirico and Steele, 1997a).

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