Thermodynamic Equilibria in Xylene Isomerization. 1. The Thermodynamic Properties of *p*-Xylene†

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Measurements and calculations leading to the determination of thermodynamic properties for the gaseous and condensed phases of *p*-xylene (Chemical Abstracts registry number (supplied by the authors) [106-42-3]) are reported. All measurement results reported were obtained with a differential-scanning calorimeter (DSC). The critical temperature was measured by DSC. Saturation heat capacities for the liquid phase between 370 K and 550 K, the critical density and the critical pressure were derived with fitting procedures involving the new DSC results and literature vapor pressures and densities. Results were combined with heat capacities reported in the literature obtained with adiabatic calorimetry and the enthalpy of combustion 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. Results are compared with literature values. Literature vapor pressures, enthalpies of vaporization, virial coefficients, densities, and heat capacities for the condensed and gaseous phases are checked for consistency with the values used in this research.

Introduction

Demand for *p*-xylene as a raw material for polyester fibers and films continues to drive the search for improved xylene isomerization catalysts. Worldwide production of *p*-xylene in 1994 was near 18 billion pounds per year (approximately 260 $kg{\cdot}s^{-1}$) with an anticipated increase of 5−6% per year into the late 1990s (Tomasula, 1994). Mobil Chemical alone plans to increase its production capacity to 1.63 billion pounds per year (C&EN, 1995).

The discovery of the shape-selective zeolite catalyst ZSM-5 has led to the development of new conversion processes yielding a distribution of aromatics, particularly methylbenzenes (Chen and Garwood, 1986). The term PATE (percent *p*-xylene approach-to-equilibrium) is often used to characterize the isomerization activity of a catalyst. As discussed by Amelse (1993), this quantity is very sensitive to errors in an assumed equilibrium xylene distribution, which has led to claims in the scientific and patent literature that isomerization to a *p*-xylene concentration in excess of equilibrium is possible (Seddon, 1986). Amelse (1993), in research for the Amoco Chemical Co., recently exploited the shape-selectivity of ZSM-5 to experimentally determine the equilibrium xylene distribution with high precision at 623 K and 673 K.

Amelse (1993) monitored the approach to equilibrium for xylene isomerization using both a non-shape-selective molecular sieve and the shape-selective ZSM-5. The differing approaches to the equilibrium distribution were used to extrapolate with high precision to the equilibrium value. Comparison with calculated equilibria based upon available standard thermodynamic properties for the xylenes (Stull et al., 1987) led Amelse (1993) to conclude that the existing thermodynamic data for the xylenes are in error.

Recently published standard Gibbs free energies for the xylenes used in equilibria calculations (Laesecke, 1993; Stull et al., 1987; Draeger, 1985a; Chao et al., 1984; Stull et al., 1969) all stem from experimental work completed in the 1940s by Pitzer and Scott (1943), Prosen et al. (1945), and Osborne and Ginnings (1947). Similarly, the source for enthalpies of formation is often given as Pedley (1994), Pedley et al. (1986), or Cox and Pilcher (1970). Values given in these compilations are, again, those determined by Prosen et al. (1945) and Osborne and Ginnings (1947). While the results by Prosen et al. (1945) and Osborne and Ginnings (1947) are of high quality, the values are restricted to the temperature 298.15 K.

Some high-precision thermodynamic-property results have been published in the intervening 50 years for *p*-xylene (Messerly et al., 1988; Hossenlopp and Scott, 1981; Osborn and Douslin, 1974; Ambrose et al., 1967), while little has been published concerning *o*-xylene (Ambrose et al., 1967; Archer and Hossenlopp, 1988) and *m*-xylene (Ambrose et al., 1967). Except for the work of Chao et al. (1984), who used the vapor-phase heat-capacity results of Hossenlopp and Scott (1981) to help force agreement between statistically and calorimetrically derived ideal-gas entropies, the new information has not been incorporated into the compilations of Gibbs free energies.

This is the first in a series of papers concerning the thermodynamic properties of the xylenes. New measurements were completed where necessary to fill gaps in the existing literature or to confirm key values. Extensive new results for *m*-xylene and *o*-xylene including heat capacities between 5 K and 420 K by adiabatic calorimetry, vapor pressures by comparative ebulliometry, high-temperature heat capacities by differential-scanning calorimetry (DSC), and results of vibrating-tube densitometry will be published separately (Chirico et al., 1996a,b). Such extensive new measurements were not required for *p*-xylene.

In the present paper, two-phase (liquid + vapor) heat capacities to the temperature $T \approx 0.9T_c$ by DSC are reported for *p*-xylene. Saturation heat capacities C_{sat} for the liquid phase are derived, and results are combined with literature values to derive standard entropies, enthalpy increments, and Gibbs free energies of formation for

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temperatures between 250 K and 550 K ($\approx 0.9T_c$) 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. DSC was also used to determine the critical temperature directly. The critical pressure was derived by fitting procedures.

p-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.

Much confusion exists in the literature concerning the precision with which equilibrium distributions for xylene isomerization can be calculated from thermodynamic information. Distribution percentages are often reported to ±0.1% or better (Amelse, 1993; Seddon, 1986), while others (Everdell, 1967) estimate uncertainties nearer ±10%. An important aspect of the present series of papers is the consideration of experimental uncertainties and their propagation through to the calculation of equilibrium distributions. Equilibria calculations based on the new calorimetric results will be published separately (Chirico and Steele, 1996a).

This research was completed at the National Institute for Petroleum and Energy Research (NIPER) 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 the accurate estimation of properties for broad families of alkyl-substituted aromatic compounds. Furthermore, if assignments of the fundamental vibrations for the xylenes can be well-established, comparisons between statistical and calorimetrically derived thermodynamic properties provide the means to define accurately many physical-property values for the very broad temperature range from the triple-point temperature T_{tp} to the critical temperature T_c, as reported recently for pyridine (Chirico et al., 1996c; Chirico and Steele, 1996b). Such physical-property values are required for the development and testing of structure-property correlations, which are essential for process development and optimization.

Experimental Procedure

Materials. The *p*-xylene used in this research was an American Petroleum Institute (API) research-grade hydrocarbon. The purity of the sample was determined to be 0.999 96 mole fraction *p*-xylene by fractional melting as part of adiabatic calorimetric studies (Messerly et al., 1988) completed at this laboratory. Following the heat-capacity studies, the sample was sealed in glass under vacuum and was stored at 285 K until used in the present research.

Physical Constants and Standards. Molar values are reported in terms of $M = 106.1674$ g·mol^{-1} for *p*-xylene and the gas constant, $R = 8.314\ 51$ J·K^{-1}·mol^{-1}, adopted by CODATA (Cohen and Taylor, 1988). All temperatures reported are in terms of ITS-90. Measurements of mass, time, electrical resistance, and potential difference were made in terms of standards traceable to calibrations at the National Institute of Standards and Technology.

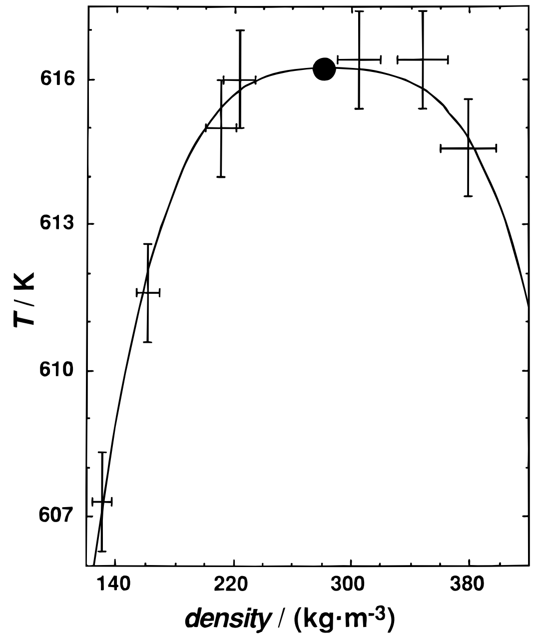

Figure 1. Vapor–liquid coexistence region for *p*-xylene. The crosses span the range of uncertainty for the measurement results of this research. (●) Critical temperature and critical density selected by Tsonopoulos and Ambrose (1995). The curve provides an aid to the eye.

Table 1. Densities ρ and Temperatures for the Conversion from Two Phases to One Phase for *p*-Xylene Measured by DSC

ρ/kg·m^{-3}	T/K	ρ/kg·m^{-3}	T/K
131	607.3	305	616.4
161	611.6	348	616.4
211	615.0	379	614.6
223	616.0		

Differential-Scanning Calorimetry. DSC measurements were made with a Perkin-Elmer DSC-2. Experimental methods were described previously (Knipmeyer et al., 1989; Chirico and Steele, 1994; Steele, 1995).

Experimental Results

Differential-Scanning Calorimetry. The *p*-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. Table 1 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. These results are shown graphically in Figure 1. Details of the method used were described recently (Steele, 1995). The cell volume was calculated with the equation

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

where $y = \{(T/\text{K}) - 298.15\}$, $a = 3.216 \times 10^{-5}$, and $b = 5.4 \times 10^{-8}$. The critical temperature derived from the DSC measurements is (616.4 ± 1.0) K, in excellent agreement with the value (616.2 ± 0.2) K selected by Tsonopoulos and Ambrose (1995) in their recent review. The selected value (616.2 ± 0.2) K was used in all subsequent procedures detailed in this paper.

Table 2. Summary of the Fit of the Wagner Equation to the Vapor-Pressure Results (Osborn and Douslin, 1974) for *p*-Xylene[a]

method	T/K	p/kPa	Δp/kPa	σ/kPa
IP	286.432	0.5817	−0.0006	0.0003
IP	288.150	0.6489	0.0004	0.0003
IP	290.620	0.7554	0.0002	0.0003
IP	293.160	0.8803	0.0000	0.0003
benzene	340.927	9.590	0.000	0.001
benzene	344.013	10.893	0.000	0.001
benzene	347.109	12.345	0.000	0.002
benzene	350.216	13.960	0.001	0.002
benzene	353.335	15.752	0.001	0.002
benzene	356.467	17.737	0.000	0.002
water	359.610	19.933	0.000	0.002
water	365.929	25.023	0.000	0.003
water	372.296	31.177	−0.001	0.003
water	378.708	38.565	−0.001	0.004
water	385.168	47.375	−0.003	0.005
water	391.672	57.818	0.002	0.006
water	398.228	70.121	−0.002	0.007
water	404.829	84.533	−0.002	0.008
water	411.476	101.325	0.001	0.009
water	418.170	120.79	0.01	0.01
water	424.914	143.25	0.00	0.01
water	431.701	169.02	0.00	0.01
water	438.537	198.49	0.00	0.02
water	445.418	232.02	−0.01	0.02
water	452.341	270.02	0.00	0.02

[a] IP refers to measurements performed with an inclined-piston gauge; water or benzene refers to which material was used as the standard in the reference ebulliometer; T is the condensation temperature of the p-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 2 and the parameters listed in Table 4, from the observed value of pressure; σ is the propagated error (Chirico et al., 1996c).

Table 3. Measured Two-Phase (Liquid + Vapor) Heat Capacities $C^{\mathrm{II}}_{\mathrm{x,m}}/R$ for *p*-Xylene[a]

T/K	$C^{\mathrm{II}}_{\mathrm{x,m}}/R$	$C^{\mathrm{II}}_{\mathrm{x,m}}/R$	$C^{\mathrm{II}}_{\mathrm{x,m}}/R$
V(cell)/cm^3	0.052 04	0.054 48	0.052 04
m/g	0.008 51	0.012 35	0.020 87
350.0	24.61	24.02	24.09
370.0	25.95	25.15	25.10
390.1	27.00	26.20	26.05
410.0	28.48	27.52	27.13
430.0	30.36	28.58	28.10
450.1	31.79	30.01	29.17
470.0	33.62	31.45	30.08
490.0	35.36	33.11	31.27
510.1	37.39	34.53	32.33
530.0	39.28	35.87	33.72
550.0	41.52	37.44	35.14
570.1	43.78	38.96	36.50
590.0	46.77	42.22	38.35

[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}).

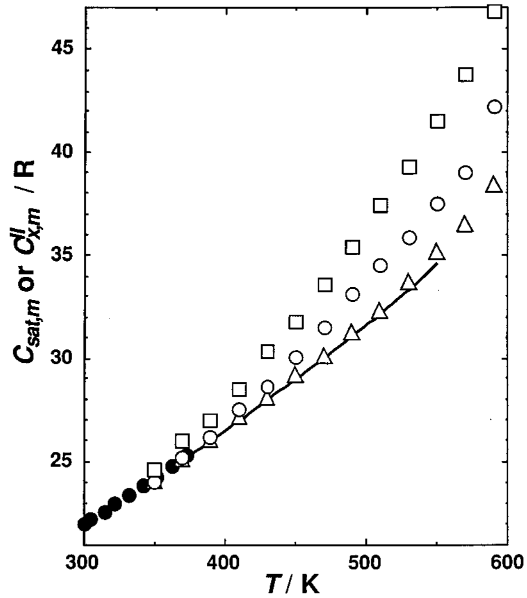

Figure 2. Heat capacity against temperature for p-xylene. $C^{\mathrm{II}}_{\mathrm{x,m}}$ by DSC for three cell fillings: (□) 8.51 mg; (○) 12.35 mg; and (△) 20.87 mg of sample. (●) $C_{\mathrm{sat,m}}$ determined by adiabatic calorimetry (Messerly et al., 1988). The curve represents the saturation heat capacities derived in this research and listed in Table 5.

The theoretical background for the determination of heat capacities for the liquid phase at vapor-saturation pressure C_{sat} from results obtained with a DSC has been described (Chirico and Steele, 1994; Steele, 1995). Measured two-phase (liquid + vapor) heat capacities for a minimum of two cell fillings, vapor pressures, and density values for the liquid phase are required. Osborn and Douslin (1974) completed vapor-pressure measurements with comparative ebulliometry and inclined-piston manometry in this laboratory (NIPER) for p-xylene in the liquid phase for the temperature range 286.4 < (T/K) < 452.3 K. These values were used in all vapor-pressure fits described in this paper. Values were converted to ITS-90 and are listed in Table 2.

Table 3 lists molar two-phase heat capacities $C^{\mathrm{II}}_{\mathrm{x,m}}$ for p-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 2 shows the $C^{\mathrm{II}}_{\mathrm{x,m}}$ values determined by DSC and $C_{\mathrm{sat,m}}$ values determined by adiabatic calorimetry (Messerly et al., 1988). The effect of vaporization of the sample into the free space of the cell as the temperature is increased is observed readily in the figure. The estimated uncertainty in the $C^{\mathrm{II}}_{\mathrm{x,m}}$ 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 $C^{\mathrm{II}}_{\mathrm{x,m}}$ values given in Table 3 was completed. The weighting of the $C^{\mathrm{II}}_{\mathrm{x,m}}$ and vapor-pressure values has been described with the fitting procedure (Steele, 1995; Chirico and Steele, 1994). $C_{\mathrm{sat,m}}$ values determined by adiabatic calorimetry (Messerly et al., 1988) for the temperature range 295 < (T/K) < 374 were included and weighted equally with the vapor pressures. These were included to ensure a smooth junction between the $C_{\mathrm{sat,m}}$ values determined with adiabatic calorimetry and those derived with the DSC results.

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

$$\ln(p/p_{\mathrm{c}}) = (1/T_{\mathrm{r}})\{A(1 - T_{\mathrm{r}}) + B(1 - T_{\mathrm{r}})^{1.5} + C(1 - T_{\mathrm{r}})^2 + D(1 - T_{\mathrm{r}})^4\} \quad (2)$$

where $T_{\mathrm{r}} = T/T_{\mathrm{c}}$. The designation (2,4) refers to the exponents of the last two terms in the equation. For several years, the (2.5,5) form, as recommended by Ambrose (1986), was used exclusively by this research group. Recently, Wagner and co-workers (Duschek et al., 1990) used the (2,4) form to represent the vapor pressures of carbon dioxide from the triple point to the critical temperature. Subsequently, the (2,4) form was used to represent successfully the vapor pressures of pyridine also from T_{tp} to T_{c} (Chirico et al., 1996c). In this research, the (2,4) form provides improved agreement between statistically and

Table 4. Parameters for Eqs 2 and 4, Critical Constants, and Acentric Factor

	p-Xylene		
A	−7.593 06	b_0	−0.415 99
B	1.779 64	b_1	−0.610 33
C	−1.245 26	b_2	1.226 51
D	−3.932 48	b_3	−1.504 06
$T_c = 616.2$ K	$p_c = 3510$ kPa	$\rho_c = 281$ kg·m^{-3}	$\omega = 0.3211$

calorimetrically derived standard entropies relative to those derived with the (2.5,5) form, particularly at low temperatures, as described later. The critical pressure was included as a variable in the fits.

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

$$C^{\mathrm{II}}_{\mathrm{V,m}} = C^{\mathrm{II}}_{\mathrm{x,m}} - T/n\{(\partial V_{\mathrm{x}}/\partial T)_{\mathrm{x}}(\partial p/\partial T)_{\mathrm{sat}}\} \qquad (3)$$

where *n* is the number of moles of *p*-xylene used for the particular cell filling, as listed in Table 3. Equation 1 was used to calculate $(\partial V_{\mathrm{x}}/\partial T)_{\mathrm{x}}$, the variation of the cell volume with temperature, and the vapor-pressure fit was used to calculate $(\partial p/\partial T)_{\mathrm{sat}}$. The values of $C^{\mathrm{II}}_{\mathrm{V,m}}$ and the vapor pressures were used in a weighted nonlinear least-squares fit to derive functions for $(\partial^2 p/\partial T^2)_{\mathrm{sat}}$ and $(\partial^2\mu/\partial T^2)_{\mathrm{sat}}$, 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

$$(\partial^2\mu/\partial T^2)_{\mathrm{sat}}/\mathrm{J{\cdot}K^{-2}{\cdot}mol^{-1}} = \sum_{i=0}^{n} b_i(1 - T/T_{\mathrm{c}})^i \qquad (4)$$

For compounds where sufficient information was available to evaluate reliably $(\partial^2\mu/\partial T^2)_{\mathrm{sat}}$, 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 4 lists the coefficients determined in the nonlinear least-squares fits. Deviations of the vapor pressures (Osborn and Douslin, 1974) from the fitted Wagner equation are included in Table 2.

Molar saturation heat capacities $C_{\mathrm{sat,m}}$ for *p*-xylene were derived with the equation

$$C_{\mathrm{sat,m}} = V_{\mathrm{m}}(l)T(\partial^2 p/\partial T^2)_{\mathrm{sat}} - T(\partial^2\mu/\partial T^2)_{\mathrm{sat}} + T(\partial p/\partial T)_{\mathrm{sat}}\{\mathrm{d}V_{\mathrm{m}}(l)/\mathrm{d}T\} \qquad (5)$$

Temperature derivatives of the pressure were calculated with the Wagner-equation parameters listed in Table 4. Molar volumes of the liquid $V_{\mathrm{m}}(l)$ were calculated with densities obtained with a form of the corresponding-states equation of Riedel (1954):

$$(\rho/\rho_{\mathrm{c}}) = 1 + 0.85\{1 - (T/T_{\mathrm{c}})\} + (1.6916 + 0.9846\omega)\{1 - (T/T_{\mathrm{c}})\}^{1/3} \qquad (6)$$

Values of $(\partial^2\mu/\partial T^2)_{\mathrm{sat}}$ were determined with the derived coefficients for eq 4, as listed in Table 4. The derived $C_{\mathrm{sat,m}}$ values are included in Table 5. The estimated uncertainty in the values is $1 \times 10^{-2}C_{\mathrm{sat,m}}$. Derived $C_{\mathrm{sat,m}}$ values for *p*-xylene are included in Figure 2. The derived critical pressure (3510 ± 40) kPa is in excellent agreement with that selected by Tsonopoulos and Ambrose (3511 ± 20) kPa, and is included in Table 4.

Critical Density. The value of the critical density ρ_{c} (281 ± 4) kg·m^{-3} selected by Tsonopoulos and Ambrose (1995) in their recent review was used in eq 6. Comparisons of literature densities with values calculated with eq 6 are described later in this paper. Systematic deviations exist, but these do not exceed ±1%. Propagated errors due to a 1% uncertainty in densities calculated with eq 6 are negligible for all properties derived here.

Enthalpies of Vaporization. Molar enthalpies of vaporization $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}$ were derived from the Wagner-equation fit to the vapor pressures by means of the Clapeyron equation:

$$\mathrm{d}p/\mathrm{d}T = \Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}/(T\Delta_{\mathrm{l}}^{\mathrm{g}}V_{\mathrm{m}}) \qquad (7)$$

$\Delta_{\mathrm{l}}^{\mathrm{g}}V_{\mathrm{m}}$ is the difference in molar volume between the liquid and the real vapor. Estimates of liquid-phase volumes were made with eq 6. Vapor-phase volumes were calcu-

Table 5. Molar Thermodynamic Functions at Vapor-Saturation Pressure for *p*-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				
10.00	0.155	0.052	0.039	120.00	10.226	9.636	5.464
15.00	0.522	0.175	0.131	140.00	11.284	11.293	6.221
20.00	1.115	0.402	0.299	160.00	12.247	12.864	6.915
30.00	2.523	1.118	0.804	180.00	13.203	14.361	7.560
40.00	3.874	2.032	1.406	200.00	14.167	15.802	8.173
50.00	5.039	3.025	2.018	220.00	15.171	17.199	8.763
60.00	6.047	4.035	2.608	240.00	16.220	18.564	9.340
70.00	6.926	5.034	3.163	260.00	17.344	19.906	9.913
80.00	7.701	6.011	3.683	280.00	18.531	21.235	10.485
90.00	8.410	6.959	4.169	286.40	18.925	21.658	10.670
100.00	9.056	7.879	4.626				
			Liquid				
250.00	19.979	26.038	17.448	400.00[b]	26.516	36.789	19.578
260.00	20.373	26.829	17.553	420.00[b]	27.501	38.107	19.932
280.00	21.175	28.368	17.783	440.00[b]	28.510	39.409	20.299
286.40	21.436	28.850	17.862	460.00[b]	29.541	40.699	20.678
298.15	21.922	29.721	18.012	480.00[b]	30.591	41.979	21.069
300.00	21.999	29.857	18.037	500.00[b]	31.664	43.249	21.472
320.00	22.847	31.304	18.311	520.00[b]	32.777	44.512	21.885
340.00	23.732	32.715	18.603	540.00[b]	33.977	45.771	22.310
360.00	24.633	34.098	18.913	550.00[b]	34.645	46.401	22.528
380.00[b]	25.559	35.454	19.239				

[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 (Messerly et al., 1988).

Table 6. Enthalpies of Vaporization $\Delta_l^g H_m$ for *p*-Xylene Obtained from the Wagner and Clapeyron Equations

T/K	$\Delta_l^g H_m/RT$	T/K	$\Delta_l^g H_m/RT$	T/K	$\Delta_l^g H_m/RT$
250.00[a]	45.15 ± 0.08	340.00	40.03 ± 0.06	460.00[a]	32.41 ± 0.17
260.00[a]	44.56 ± 0.08	360.00	38.90 ± 0.06	480.00[a]	30.81 ± 0.22
280.00[a]	43.39 ± 0.07	380.00	37.74 ± 0.07	500.00[a]	29.03 ± 0.27
298.15	42.36 ± 0.07	400.00	36.53 ± 0.08	520.00[a]	27.06 ± 0.32
300.00	42.26 ± 0.07	420.00	35.25 ± 0.10	540.00[a]	24.86 ± 0.38
320.00	41.14 ± 0.07	440.00	33.89 ± 0.13	550.00[a]	23.65 ± 0.42

[a] Values at this temperature were calculated with extrapolated vapor pressures determined from the fitted Wagner coefficients listed in Table 4.

lated 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 pyridine (Chirico et al., 1996c), benzene and methylbenzene (Chirico and Steele, 1994), and 2-methylaniline (Steele et al., 1994). Uncertainties in the virial coefficients were assumed to be 5%. Derived enthalpies of vaporization are reported in Table 6. 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 6 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 $T \to 0$ for the solid and liquid phases of *p*-xylene are listed in Table 5. The tabulated values were derived by integration of the measured heat capacities (Messerly et al., 1988) corrected for premelting, together with the entropies and enthalpies of fusion. Temperature increments provided with the experimental heat-capacity values (Messerly et al., 1988) were used to convert those results to ITS-90. 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 the results of Messerly et al. (1988) 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 (Westrum et al., 1968) for solid-insoluble impurities with the mole-fraction impurity value 0.000 04.

Thermodynamic Properties for the Standard State from Calorimetric Studies. The standard state is defined as the ideal gas at the pressure $p = p° = 101.325$ kPa. Standard enthalpies and entropies at selected temperatures were calculated for *p*-xylene using values in Tables 5 and 6 and are listed in columns 2 and 4 of Table 7. Standard entropies were calculated with the following summation:

$$\Delta_0^T S_m^\circ = \Delta_0^T S_m(\text{liquid}) + \Delta_l^g S_m + \Delta_{\text{comp}} S_m \qquad (8)$$

where $\Delta_0^T S_m^\circ$ is the entropy of *p*-xylene in the standard state, $\Delta_0^T S_m(\text{liquid})$ is the entropy of the liquid under its saturation pressure, $\Delta_l^g S_m$ is the entropy of vaporization to the real gas at the saturation pressure, and $\Delta_{\text{comp}} S_m$ is the entropy of compression of the real gas to the ideal gas at $p = 101.325$ kPa. The sum of terms used in the calculation of the standard enthalpies is analogous.

Entropies and enthalpies of compression to $p = 101.325$ 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 the entropy and enthalpy of compression are (Lewis and Randall, 1961)

$$\Delta_{\text{comp}} S_m = R \ln(p) + (\mathrm{d}B/\mathrm{d}T)p + (\mathrm{d}C'/\mathrm{d}T)(p^2/2) \qquad (10)$$

$$\Delta_{\text{comp}} H_m = \{B - T(\mathrm{d}B/\mathrm{d}T)\}p + \{C' - T(\mathrm{d}C'/\mathrm{d}T)\}(p^2/2) \qquad (11)$$

Temperature derivatives were estimated by numerical differentiation of the estimated virial coefficients (Pitzer and Curl, 1957; Orbey and Vera, 1983).

Table 7. Standard Molar Thermodynamic Properties in the Ideal-Gas State for *p*-Xylene at $p = p° = 101.325$ kPa ($R = 8.314\,51$ J·K^{-1}·mol^{-1})

T/K	$\Delta_0^T H_m^\circ/RT$	$\Delta_{imp} H_m^\circ$ [a]$/RT$	$\Delta_0^T S_m^\circ/R$	$\Delta_{imp} S_m^\circ$ [b]$/R$	$\Delta_f H_m^\circ/RT$	$\Delta_f S_m^\circ/R$	$\Delta_f G_m^\circ/RT$
250.00[c,d]	39.17 ± 0.04	0.00	39.90 ± 0.05	0.00	10.69 ± 0.22	−39.82 ± 0.05	50.51 ± 0.22
260.00[c,d]	38.17 ± 0.04	0.00	40.41 ± 0.05	0.00	9.86 ± 0.21	−40.24 ± 0.05	50.10 ± 0.21
280.00[c,d]	36.43 ± 0.04	0.00	41.44 ± 0.04	0.00	8.40 ± 0.20	−41.03 ± 0.04	49.42 ± 0.20
298.15	35.11 ± 0.03	0.01	42.36 ± 0.04	0.01	7.25 ± 0.19	−41.68 ± 0.04	48.93 ± 0.19
300.00	34.99 ± 0.03	0.01	42.46 ± 0.04	0.01	7.15 ± 0.18	−41.74 ± 0.04	48.89 ± 0.18
320.00	33.79 ± 0.03	0.02	43.48 ± 0.04	0.01	6.07 ± 0.17	−42.40 ± 0.04	48.46 ± 0.17
340.00	32.80 ± 0.03	0.03	44.50 ± 0.04	0.03	5.13 ± 0.16	−42.99 ± 0.04	48.12 ± 0.16
360.00	31.96 ± 0.03	0.06	45.52 ± 0.04	0.04	4.32 ± 0.15	−43.53 ± 0.04	47.85 ± 0.16
380.00	31.27 ± 0.03	0.09	46.54 ± 0.04	0.06	3.61 ± 0.15	−44.03 ± 0.04	47.64 ± 0.15
400.00	30.69 ± 0.03	0.13	47.55 ± 0.04	0.10	2.98 ± 0.14	−44.49 ± 0.04	47.47 ± 0.14
420.00	30.21 ± 0.04	0.19	48.56 ± 0.05	0.14	2.43 ± 0.13	−44.90 ± 0.05	47.33 ± 0.14
440.00	29.82 ± 0.05	0.26	49.56 ± 0.06	0.19	1.95 ± 0.13	−45.28 ± 0.06	47.23 ± 0.13
460.00[d]	29.50 ± 0.07	0.34	50.57 ± 0.07	0.25	1.51 ± 0.13	−45.63 ± 0.07	47.15 ± 0.13
480.00[d]	29.23 ± 0.09	0.45	51.56 ± 0.09	0.33	1.13 ± 0.14	−45.95 ± 0.09	47.08 ± 0.14
500.00[d]	29.02 ± 0.10	0.57	52.55 ± 0.11	0.41	0.79 ± 0.15	−46.25 ± 0.11	47.04 ± 0.14
520.00[d]	28.85 ± 0.12	0.71	53.52 ± 0.12	0.52	0.47 ± 0.16	−46.52 ± 0.12	47.00 ± 0.15
540.00[d]	28.71 ± 0.15	0.87	54.49 ± 0.14	0.64	0.19 ± 0.17	−46.78 ± 0.14	46.97 ± 0.16
550.00[d]	28.65 ± 0.16	0.95	54.96 ± 0.15	0.71	0.05 ± 0.18	−46.91 ± 0.15	46.96 ± 0.17

[a] Gas-imperfection correction included in the ideal-gas enthalpy. The ideal-gas enthalpy is calculated relative to that of the crystals at $T \to 0$. [b] Gas-imperfection correction included in the ideal-gas entropy. [c] Values at this temperature were calculated with extrapolated liquid-phase heat capacities. [d] Values at this temperature were calculated with extrapolated vapor pressures calculated from the fitted Wagner equation parameters listed in Table 4.

The *R* ln(*p*) term of eq 10 is the entropy of compression, if the gas were ideal. The uncertainty in this term is not significant. The sum of the second and third terms of eq 10 is the "gas-imperfection correction" to the entropy of compression. Equation 11 gives the "gas-imperfection correction" to the enthalpy of compression directly, as the ideal-gas value is zero. The gas-imperfection corrections are listed in Table 7. 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 *p*-xylene were combined with the enthalpy of formation of the liquid (-24.39 ± 0.91) kJ·mol^{-1} based on the enthalpy of combustion measurements of Prosen et al. (1945) to calculate the standard enthalpies, entropies, and Gibbs energies of formation listed in columns 6−8, respectively, of Table 7. Enthalpies and entropies for graphite and 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 7 represent one standard deviation and do not include uncertainties in the properties of the elements.

Comparisons with Literature Values

The physical and thermodynamic properties of *p*-xylene have been the subject of numerous investigations reported in the literature. Comparisons of the results used and derived in this 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 *p*-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 ortho and meta isomers. A preliminary energy of combustion for *o*-xylene was measured in this laboratory as part of this research on the xylenes and was found to be in excellent agreement with the value reported by Prosen et al. Consequently, the enthalpy of combustion for *p*-xylene was not determined in this research and the value reported by Prosen et al. was used in the calculations. Values reported by Prosen et al. (1945) were also used for *m*-xylene (Chirico et al., 1996a) and *o*-xylene (Chirico et al., 1996b).

Vapor Pressures. Reports of vapor pressures for *p*-xylene have appeared in the literature for more than 100 years. Vapor pressures for *p*-xylene were measured in this laboratory in the 1970s and were reported (Osborn and Douslin, 1974). No new measurement results are reported here. Extensive intercomparisons of literature vapor-pressure values for *p*-xylene have not been published previously. Comparisons of literature values with those calculated with the Wagner-type representation derived in this research for temperatures between T_{tp} and T_c follow.

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 Osborn and Douslin (1974) used in this research, as shown in Figure 3. All values are shown relative to vapor pressures calculated with eq 2 and the parameters listed in Table 4. Values reported by Osborn and Douslin (1974) for temperatures below 340 K were determined with an inclined-piston apparatus.

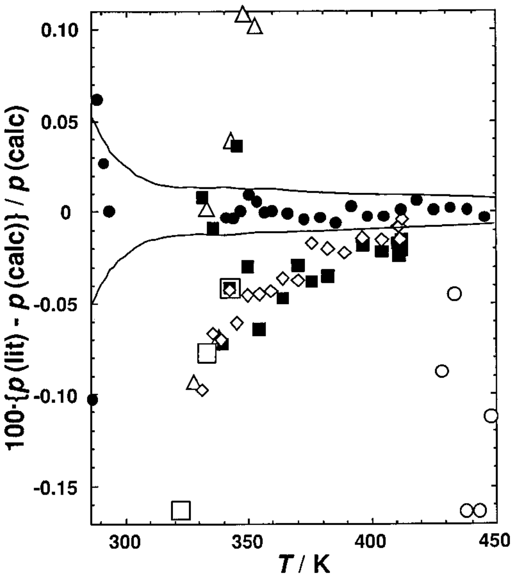

Figure 3. Deviation plot for *p*-xylene vapor pressures. *p*(calc) represents the values calculated with eq 2 and the parameters listed in Table 4. Values of *p*(lit): (●) fitted results by Osborn and Douslin (1974); (△) Díaz Peña et al. (1979); (□) Gaw and Swinton (1968) {values at 303 K and 313 K are not shown, these are 0.4% and 0.7% low, respectively}; (○) Ambrose et al. (1967) {most values from this reference are not shown; see Figure 4 for a complete comparison}; (■) Forziati et al. (1949); (◇) Willingham et al. (1945). The curves represent the $\sigma(p)$ values for results by Osborn and Douslin (1974) listed in Table 2.

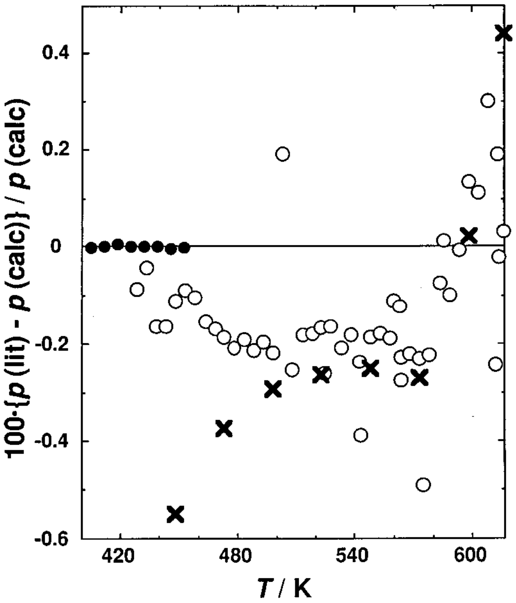

Figure 4. Deviation plot for *p*-xylene vapor pressures at high temperatures. *p*(calc) represents the values calculated with eq 2 and the parameters listed in Table 4. Values of *p*(lit): (●) fitted results by Osborn and Douslin (1974); (○) Ambrose et al. (1967); (×) Mamedov et al. (1970).

High-temperature vapor pressures for *p*-xylene were reported by Ambrose et al. (1967) for temperatures between 428 K and T_c and by Mamedov et al. (1970) for temperatures between 448 K and T_c. The small deviations of these high-temperature results from values calculated with eq 2 and the parameters listed in Table 4 are shown in Figure 4. The critical temperature reported by Mamedov et al. (1970) is approximately 2 K higher than the assessed value (Tsonopoulos and Ambrose, 1995). For the comparison with the results of Mamedov et al. near T_c, a value calculated by Mamedov et al. for $T = 616.2$ K was used.

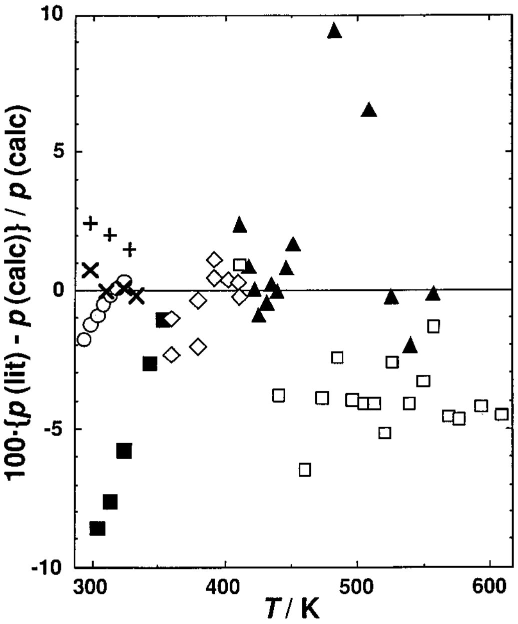

Figure 5. Low-resolution deviation plot for *p*-xylene vapor pressures. *p*(calc) represents the values calculated with eq 2 and the parameters listed in Table 4. Values of *p*(lit): (○) Smith (1990); (▲) Natarajan and Viswanath (1985); (+) Mentzer et al. (1982); (□) Glaser and Rüland (1957); (×) Pitzer and Scott (1943); (■) Kassel (1936); (◇) Neubeck (1887).

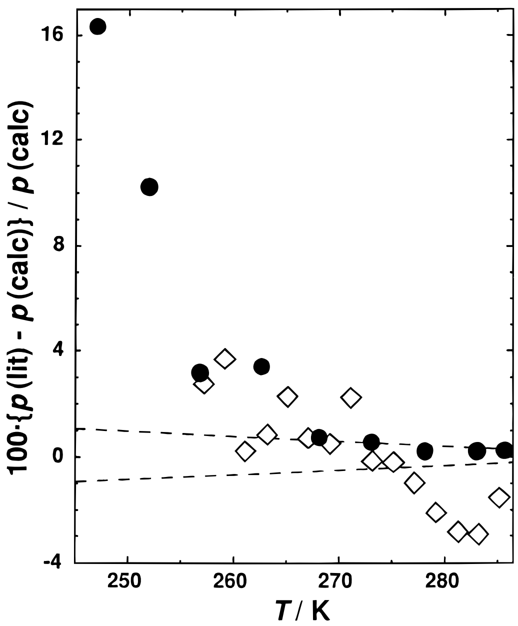

Figure 6. Deviation plot for *p*-xylene sublimation pressures. *p*(calc) represents the values calculated with eq 12. Values of *p*(lit): (●) Osborn and Douslin (1974); (◇) Hessler and Lichtenstein (1986). Hessler (1979) and Linder (1931) data are not shown (see text). The dashed lines represent the estimated uncertainty in the *p*(calc) values.

Comparisons with other literature values are shown in Figure 5. The vertical axis in Figure 5 is expanded by a factor of 70 relative to that in Figure 3. Values listed by Woringer (1900) for temperatures from 273 K to 413 K show large deviations except near the normal-boiling temperature (411.48 K) and are not shown in the figure. Values reported by Rintelen et al. (1937) for temperatures between 283 K and 323 K range from 34% to 1% lower than the calculated values and are not shown in Figure 5.

Results reported with vapor−liquid equilibria (VLE) studies generally were not considered in the vapor-pressure comparisons. VLE results are typically for one or two temperatures only and are often performed on materials of relatively low purity. Vapor pressures reported by Mentzer et al. (1982) show deviations approximately 2−3 times larger than their estimated uncertainty of ±0.03 kPa.

Sublimation Pressures. Sublimation pressures for *p*-xylene were reported by Hessler and Lichtenstein (1986), Hessler (1979), Osborn and Douslin (1974), and Linder (1931). The “third-law” method was employed to calculate sublimation pressures in this research for *p*-xylene from 245 K to T_{tp}. The “third-law” values were calculated from the tabulated thermodynamic functions of the ideal gas (Table 7) and the crystalline solid (Table 5). The method applied here was the same as that used previously for biphenyl (Chirico et al., 1989). The derived sublimation pressures were represented by the equation

$$\ln(p/p_x) = 28.476 - 5078.9(T/\mathrm{K})^{-1} - 4.576 \times 10^{5}(T/\mathrm{K})^{-2} + 2.822 \times 10^{7}(T/\mathrm{K})^{-3} \quad (12)$$

where p_x = 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 relatively short (from 286.43 K to 245 K). Osborn and Douslin (1974) measured vapor pressures (Table 2) for the liquid phase of *p*-xylene nearly to T_{tp} (286.40 K) with an inclined-piston apparatus. On the basis of results obtained previously with the (2,4) form of the Wagner equation for pyridine (Chirico et al., 1996c), uncertainties in the calculated sublimation pressures are estimated to be ≈0.2% near T_{tp} and <1% near 245 K. Comparisons between calorimetrically and statistically derived standard entropies described later support the validity of the extrapolated vapor pressures used here.

Deviations of the experimental values reported by Osborn and Douslin (1974) and Hessler and Lichtenstein (1986) from those calculated with eq 12 are shown in Figure 6. Deviations for values given by Linder (1931) range from 32% low near 264 K to 10% low near 273 K and are not shown in the figure. Above 265 K, the values reported by Osborn and Douslin are in excellent agreement with the calculated values. At lower temperatures, large deviations are observed. The values reported by Hessler and Lichtenstein (1986) show a larger scatter, but remain within ±4% of the calculated values. Earlier values reported by Hessler (1979) between 248 K and 273 K show large deviations, particularly at the lower temperatures. Hessler and Lichtenstein (1986) also reported sublimation pressures for *o*-xylene. In a separate paper (Chirico et al., 1996b) these are shown to be very inconsistent with calculated sublimation pressures. The qualitative difference in the results may be related to differences in sample purities, which were determined by gas chromatographic methods (Hessler and Lichtenstein, 1986).

Densities. Densities for *p*-xylene are shown in Figures 7 and 8 relative to values calculated with the Riedel equation (eq 6) and the critical parameters listed in Table 4. Between the temperatures 286.40 K (i.e., $T = T_{tp}$) and 380 K, the densities of *p*-xylene are well established with numerous reported values within ±0.05% of each other, as shown in Figure 7. Additional densities in this temperature range within approximately 0.05% of those shown in Figure 7 include those reported by Jain et al. (1994), Naorem and Suri (1993), Garg et al. (1993), Fukuchi et al. (1983), Suri and Ramakrishna (1975), Akhundov and Imanov (1969), Donaldson and Quayle (1950), Fairbrother (1934), and Neubeck (1887). Ruiz et al. (1989), Mamedov

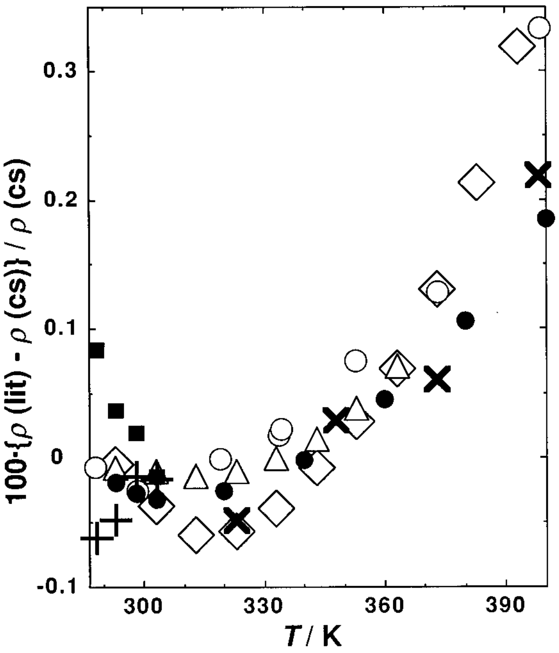

Figure 7. Deviation plot for *p*-xylene densities. ρ(cs) represents values calculated with the Riedel equation (eq 6). Values of ρ(lit): (■) Castro et al. (1994); (+) Serrano et al. (1990); (●) Hales and Townsend (1972); (×) Akhundov and Imanov (1969); (△) Shraiber and Pechenyuk (1965); (○) Massart (1936); (◇) Heil (1932). See text for additional citations.

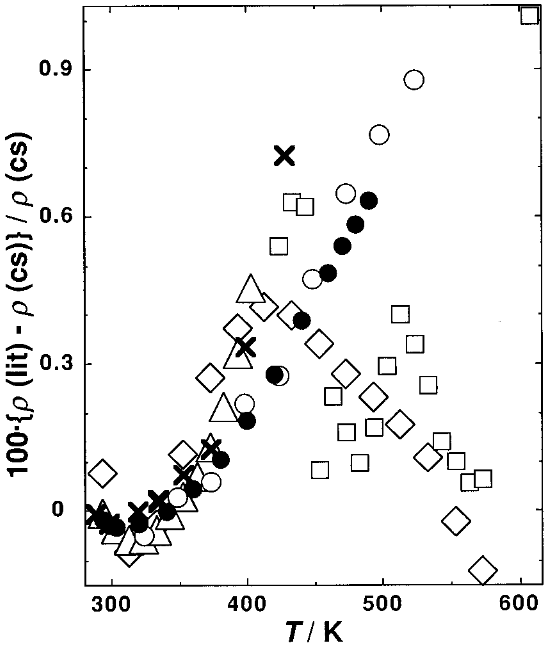

Figure 8. Deviation plot for *p*-xylene densities at high temperatures. ρ(cs) represents values calculated with the Riedel equation (eq 6). Values of ρ(lit): (◇) Mel'nikov et al. (1985); (●) Hales and Townsend (1972); (○) Akhundov and Imanov (1969); (□) Francis (1957); (×) Massart (1936); (△) Heil (1932).

and Panchenkov (1955), Richards et al. (1924), Auwers (1919), and Perkin (1896) reported values that differ by more than 0.1% from those shown. All references cited report densities for at least three temperatures.

Densities for temperatures above 380 K for the three xylenes were reported by Heil (1932), Massart (1936), Francis (1957), Akhundov and Imanov (1969), Hales and Townsend (1972), and Mel'nikov et al. (1985). As part of the research on the xylenes at this laboratory, densities of *o*-xylene and *m*-xylene were measured with a vibrating-tube densimeter for temperatures between 323 K and 523 K (Chirico et al., 1996a,b). These were found to be in accord with the results of Hales and Townsend (1972). The values reported by Hales and Townsend (1972), determined by measurements involving a magnetically controlled float (Hales, 1970), are here assumed to be the most reliable for *p*-xylene at high temperatures. Densities reported by Heil (1932) and Massart (1936) deviate high for temperatures above 400 K. Analogous deviations for densities reported by Heil (1932) and Massart (1936) were found for *o*-xylene (Chirico et al., 1996b) and *m*-xylene (Chirico et al., 1996a). Values reported by Francis (1957) measured with a glass dilatometer and those measured by Mel'nikov et al. (1985) by an acoustical method deviate low for temperatures above the normal boiling point.

The densities attributed to Akhundov and Imanov (1969) in Figure 8 were calculated in this research by extrapolation of the reported density/pressure values to the saturation pressure at each temperature. The saturation pressures were calculated with eq 2 and the parameters given in Table 4. Akhundov and Imanov (1969) reported *PVT* results for temperatures from 323 K to 673 K and pressures to 40 MPa. The extrapolation of the density/pressure values to the saturation pressure could not be done reliably for temperatures above 523 K. The agreement shown in Figure 8 between the results of Hales and Townsend (1972) and Akhundov and Imanov (1969) is excellent.

It is apparent from Figures 7 and 8 that the deviations from the corresponding-states correlation of Riedel (1954) far exceed the experimental uncertainties for the best available density values. Analogous systematic deviations were obtained for *o*-xylene (Chirico et al., 1996b) and *m*-xylene (Chirico et al., 1996a). Modifications to the corresponding-states correlation, which require additional empirical information, have been proposed by many researchers (cf., Campbell and Thodos, 1985; Joffe and Zudkevitch, 1974). 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 *p*-xylene were reviewed recently by Tsonopoulos and Ambrose (1995). Their selected value for the critical temperature (616.2 ± 0.2) K, based on the measurements by Ambrose and Grant (1957), was used in this research because of its high precision. The value obtained here by DSC (616.4 ± 1.0) K is in excellent agreement with the selected value, as shown earlier in Figure 1. The critical pressure derived in this research (3510 ± 40) kPa from the simultaneous fit of the vapor pressures and high-temperature two-phase heat capacities is in excellent agreement with that selected (3511 ± 20) kPa by Tsonopoulos and Ambrose (1995), based on the measurements by Ambrose et al. (1967).

The critical density selected by Tsonopoulos and Ambrose (1995), 281 ± 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 within the stated uncertainty with the available saturation densities and the corresponding-states equation (eq 6), as shown in Figures 7 and 8.

Enthalpies of Vaporization. Enthalpies of vaporization measured calorimetrically for *p*-xylene were reported by Nagornow and Rotinjanz (1911), Mathews (1926), Osborne and Ginnings (1947), Saito and Kusano (1973), Hossenlopp and Scott (1981), and Natarajan and Viswanath (1985). The literature values are compared in Figure 9 with those calculated in this research (Table 6) with the fitted Wagner equation (eq 2) and the Clapeyron equation (eq 7), as described earlier. The differences are generally

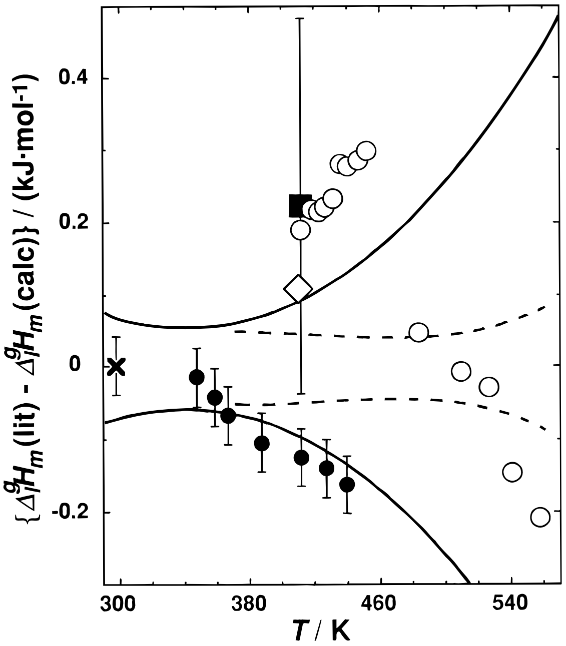

Figure 9. Deviation plot for *p*-xylene enthalpies of vaporization $\Delta_l^g H_m$. $\Delta_l^g H_m$(calc) represents values derived with the Clapeyron equation and listed in Table 6. (—) Error limits (one standard deviation) assigned to the calculated $\Delta_l^g H_m$ values. (- - -) Error limits without uncertainty in virial coefficients. Values of $\Delta_l^g H_m$(lit): (○) Natarajan and Viswanath (1985); (●) Hossenlopp and Scott (1981); (×) Osborne and Ginnings (1947); (◇) Mathews (1926); (■) Nagornow and Rotinjanz (1911). The value reported by Saito and Kusano (1973) at 298.15 K is 0.7 kJ·mol^{-1} lower than the calculated value and is not shown.

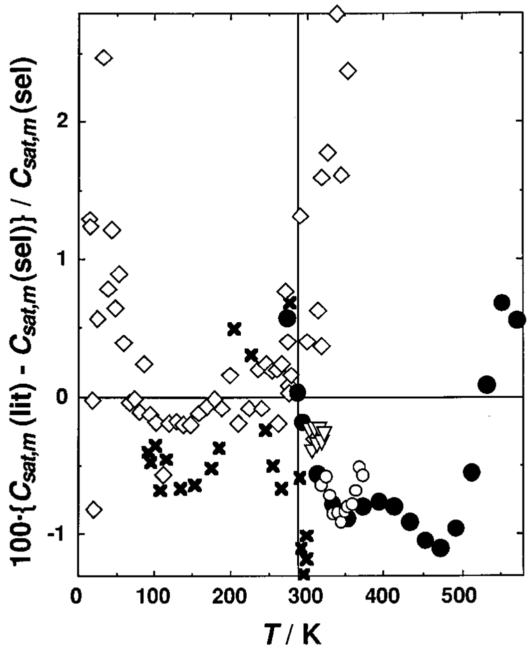

Figure 10. Deviation plot for *p*-xylene heat capacities. $C_{sat,m}$(sel) are the combined values of Messerly et al. (1988) and this research. Values of $C_{sat,m}$(lit): (○) Garg et al. (1993); (▽) Jain et al. (1992); (●) Corruccini and Ginnings (1947) from enthalpy increment measurements; (◇) Pitzer and Scott (1943); (×) Huffman et al. (1930). The vertical line indicates T_{tp} = 286.40 K.

within the combined uncertainties of the experimental and calculated values. The value reported by Osborne and Ginnings (1947) of the National Bureau of Standards (now NIST) is in excellent accord with the value calculated here. The single value at T = 298.2 K by Saito and Kusano (1973) is 0.7 kJ·mol^{-1} lower than the calculated value, and is not shown in Figure 9.

Natarajan and Viswanath (1985) claim an uncertainty in $\Delta_l^g H_m$ of only ±15 J·mol^{-1}. This corresponds approximately to the size of the symbol used to represent their results in Figure 9. The claimed uncertainty seems approximately 1 order of magnitude too small. Natarajan and Viswanath (1985) also greatly underestimated the uncertainty in their vapor pressure results. Uncertainties of 0.1% to 1% were claimed. Figure 5 shows deviations as large as 9% for these results.

Condensed-Phase Heat Capacities and Entropies. Heat capacities for *p*-xylene by adiabatic calorimetry have been reported by Huffman et al. (1930), Pitzer and Scott (1943), and by Messerly et al. (1988) of this laboratory. Values reported by Messerly et al. (1988) have an uncertainty of approximately 0.1% for all temperatures above 50 K. Deviations of the earlier results from those of Messerly et al. (1988) are shown in Figure 10. Some of the differences, particularly near T_{tp}, may be attributed to the high purity (>99.99% pure) of the sample used by Messerly et al. Agreement between the results of Pitzer and Scott (1943) and Messerly et al. (1988) for the triple-point temperature and enthalpy of fusion is excellent, with differences of 0.03 K and 0.01 kJ·mol^{-1} (0.1%), respectively.

Corruccini and Ginnings (1947) reported enthalpy increments and heat capacities for the temperature range 273.15 K to 573.15 K, and the enthalpy of fusion for *p*-xylene based upon drop calorimetric studies. The reported enthalpy of fusion is 0.1% lower than that measured by Messerly et al. (1988). $C_{sat,m}$ values for the liquid phase derived by Corruccini and Ginnings (1947) are compared with those derived in this research (Table 5) from the combined DSC and vapor-pressure results, described earlier. Agreement is excellent with differences not exceeding ±1% for the entire temperature range.

Heat capacities for the liquid over short temperature ranges have been reported by Garg et al. (1993), Jain et al. (1992), and Ott et al. (1979). Garg et al. (1993) and Jain et al. (1992) claimed accuracies of 0.1% or better. These assessments are overly optimistic, as demonstrated in Figure 10. Measurements reported by Ott et al. (1979) were completed on a sample of relatively low purity (99.39%). Nonetheless, their listed values range from 0.5% low near 288 K to 0.3% high near 328 K. Heat-capacity values measured by Williams and Daniels (1924) for *p*-xylene between 303 K and 353 K are approximately 3% lower than those listed in Table 5.

Castro-Gomez et al. (1990) measured enthalpy increments for liquid *p*-xylene for the approximate temperature ranges 298 K to 361 K and 298 K to 396 K. Deviations from enthalpy increments calculated from values in Table 5 are 0.5% to 1.3% for the shorter temperature interval and 0.04% to 0.15% for the longer interval. Castro-Gomez et al. (1990) claimed an uncertainty of ±0.5%. Enthalpy increments reported by Kurbatov (1947) and Swietoslawski and Zielenkiewicz (1958) for similar temperature ranges show deviations of 2% to 4% high and 1% high, respectively, from values derived with Table 5.

Standard Entropies and Heat Capacities from Spectroscopic Studies and Statistical Thermodynamics. Assignments for the 48 fundamental vibrational modes of *p*-xylene have been reported for more than 50 years (Pitzer and Scott, 1943; Green, 1970; La Lau and Snyder, 1971; Sverdlov et al., 1974; Draeger and Scott, 1981; Draeger, 1985b). The assignment proposed by Pitzer and Scott (1943) is of historical interest only. Beginning with Green (1970) and some work in the 1960s cited by Sverdlov (1974), general agreement on the wavenumber values for the nine vibrational modes below 700 $\mathrm{cm^{-1}}$ was reached. For wavenumber values above 700 $\mathrm{cm^{-1}}$, differences between the various assignments are significant, but relatively small, with differences not exceeding 40 $\mathrm{cm^{-1}}$.

Wavenumber values for the vapor phase were reported first by Draeger and Scott (1981). Recently, Selco and Carrick (1995) reported results of jet-cooled emission spectroscopic studies for the xylenes. Selco and Carrick reported wavenumbers for six fundamental vibrational modes (381.8 $\mathrm{cm^{-1}}$, 646.8 $\mathrm{cm^{-1}}$, 454.3 $\mathrm{cm^{-1}}$, 824.3 $\mathrm{cm^{-1}}$, 1208.2 $\mathrm{cm^{-1}}$, and 1656.7 $\mathrm{cm^{-1}}$) and anharmonicity parameters, ω_e and $\omega_e\chi_e$, for three of these (646.8 $\mathrm{cm^{-1}}$, 824.3 $\mathrm{cm^{-1}}$, and 1208.2 $\mathrm{cm^{-1}}$). The wavenumbers for the vapor phase reported by Draeger and Scott (1981) combined with the small modifications reported by Selco and Carrick (1995) were used to calculate the standard entropies and standard heat capacities of *p*-xylene between 250 K and 550 K. Two of the fundamental vibrations are associated with internal rotation of the methyl groups, which can be treated as free rotors in the vapor phase (Breen et al., 1987).

The moment of inertia (6.719×10^{-134} $\mathrm{kg^3{\cdot}m^6}$) was calculated with bond distances (r_g) reported by Tamagawa et al. (1976) for atoms in the aromatic ring. C−H bond distances within the methyl groups were assumed equal to those for methane, as reported by Bartell et al. (1961). The aromatic-carbon to methyl-carbon distance was estimated from a crystal structure of *p*-xylene reported by Koningsveld et al. (1986). All bond angles within the ring were assumed to be $2\pi/3$, and methyl groups were assumed to be tetrahedral. The internal rotation constant F was calculated to be 5.29 $\mathrm{cm^{-1}}$ for the methyl groups. 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 $\Delta_0^T S_m^\circ$(cal) (Table 7) are shown in Figure 11. Good accord between the independently derived $\Delta_0^T S_m^\circ$ values is apparent, but a systematic deviation with temperature remains. Draeger and Scott (1981) and Chao et al. (1984) forced agreement between calorimetric and statistically derived $\Delta_0^T S_m^\circ$ values and ideal-gas heat-capacity $C_{p,m}^\circ$ values. Draeger and Scott (1981) added an empirical “anharmonicity correction” to the statistical calculations, while Chao et al. (1984) reassigned wavenumber values for two fundamental vibrations. These adjustments are not supported by experimental spectroscopic evidence and were not used here.

The lowest fundamental vibration in *p*-xylene undergoes a liquid-to-vapor shift from 152 $\mathrm{cm^{-1}}$ to 132 $\mathrm{cm^{-1}}$ (Draeger, 1985a). The $\Delta_0^T S_m^\circ$(stat) values were recalculated with 152 $\mathrm{cm^{-1}}$ substituted for the gas-phase value. Large deviations between $\Delta_0^T S_m^\circ$(stat) and $\Delta_0^T S_m^\circ$(cal) result. These are shown also in Figure 11. This demonstrates that large errors can occur in $\Delta_0^T S_m^\circ$(stat) values calculated with wavenumber values for the incorrect phase. Liquid-to-vapor wavenumber shifts of 10 $\mathrm{cm^{-1}}$ to 20 $\mathrm{cm^{-1}}$ are common, particularly for low-wavenumber modes.

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 by Pitzer and Scott (1943) with the Bertholet equation. 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 1% of the statistically calculated values based on the results of Draeger and Scott (1981) and Selco and Carrick (1995), described earlier. Estimation of the temperature derivatives of the second virial coefficient with the correlation of Pitzer and Curl (1957) rather than the Bertholet equation did not alter the results significantly.

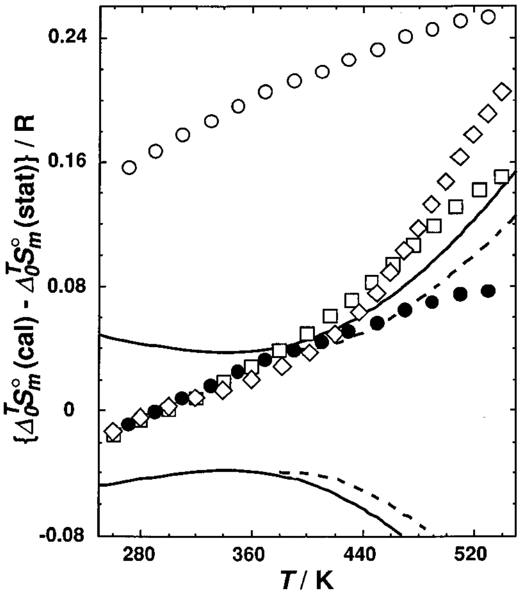

Figure 11. Deviation plot for *p*-xylene standard entropies: (—) error limits (one standard deviation) assigned to the calorimetric values $\Delta_0^T S_m^\circ$(cal); (- - -) error limits without uncertainty in the virial coefficients; (●) $\Delta_0^T S_m^\circ$(cal) values (Table 7) calculated with estimated second virial coefficients of Pitzer and Curl (1957) and $\Delta_0^T S_m^\circ$(stat) calculated with the vapor-phase assignment of Draeger and Scott (1981) with the modifications of Selco and Carrick (1995), as described in the text; (○) same as (●) except the lowest wavenumber from Draeger and Scott (1981) is replaced with the value for the liquid phase (152 $\mathrm{cm^{-1}}$ is substituted for 132 $\mathrm{cm^{-1}}$); (◇) same as (●) except second virial coefficients of Bich et al. (1981) were used in the calculation of $\Delta_0^T S_m^\circ$(cal) values; (□) same as (●) except second virial coefficients estimated with the method of Tsonopoulos (1974) were used in the calculation of $\Delta_0^T S_m^\circ$(cal) values.

Vapor heat capacities for several pressures between 12 kPa and 203 kPa and six temperatures between 398 K and 523 K were measured with vapor-flow calorimetry and reported by Hossenlopp and Scott (1981). The apparent gas-phase isobaric heat capacity was measured at four flow rates through the calorimeter at each temperature and pressure. These apparent heat capacities were fitted against inverse flow rate to obtain the gas-phase isobaric heat capacity at infinite flow rate. This method was used to correct for energy losses in the calorimeter (McCullough and Waddington, 1968). Heat capacities for the ideal-gas state $C_{p,m}^\circ$ were then calculated by linear extrapolation of the isobaric heat capacities at each temperature to zero pressure. Plots of the gas-phase isobaric heat capacities against pressure {from Table 3 of Hossenlopp and Scott (1981) and adjusted as described by McCullough et al. (1957)} show obvious nonlinearity for temperatures below 498 K. The extrapolations for these temperatures were redone in the present research without assuming linearity, and new values of $C_{p,m}^\circ$ were calculated. The new $C_{p,m}^\circ/R$ values are 20.07, 21.18, 22.34, and 23.36 for the temperatures 398.15 K, 423.15 K, 448.15 K, and 473.15 K, respectively. These values are approximately 0.2% higher than those reported by Hossenlopp and Scott (1981) for $C_{p,m}^\circ$.

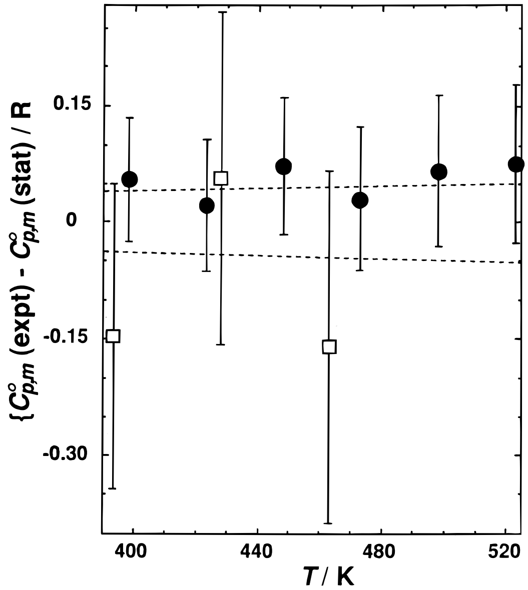

Figure 12. Comparison of experimental calorimetric $C^\circ_{p,\mathrm{m}}$(expt) values with statistically calculated $C^\circ_{p,\mathrm{m}}$(stat) values for *p*-xylene. $C^\circ_{p,\mathrm{m}}$(stat) values were calculated with the vapor-phase assignment of Draeger and Scott (1981) with the modifications of Selco and Carrick (1995), as described in the text. (- - -) ±0.2% of $C^\circ_{p,\mathrm{m}}$(stat). Values of $C^\circ_{p,\mathrm{m}}$(expt): (□) Pitzer and Scott (1943); (●) Hossenlopp and Scott (1981) recalculated in this research. See text.

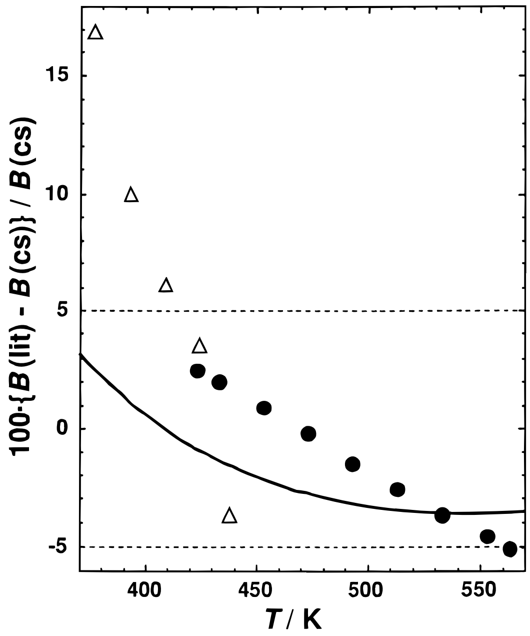

Figure 13. Deviation plot for *p*-xylene second virial coefficients *B*. *B*(cs) values were calculated with the corresponding-states method of Pitzer and Curl (1957). (- - -) ±5% of *B*(cs). Values of B(lit): (●) Bich et al. (1981); (△) Cox and Andon (1958), Andon et al. (1957); (—) corresponding-states method of Tsonopoulos (1974).

Hossenlopp and Scott (1981) estimated the uncertainty in the experimental $C^\circ_{p,\mathrm{m}}$ values to be ±0.2%. Their assessment is overly optimistic. There is a ±0.2% uncertainty associated with the extrapolation of the isobaric heat capacities to zero pressure. There is an additional uncertainty associated with the extrapolation to infinite flow rate used in the calculation of the isobaric heat capacities. A review of the original data (Hossenlopp and Scott, unpublished) showed this uncertainty to be at least as large as that associated with the extrapolation to zero pressure. Consequently, the uncertainties in the $C^\circ_{p,\mathrm{m}}$ values are estimated here to be ±0.4%. The recalculated "experimental" $C^\circ_{p,\mathrm{m}}$ values $\{C^\circ_{p,\mathrm{m}}$(expt)$\}$ for *p*-xylene are compared in Figure 12 with values calculated statistically with the assignment and structural parameters $\{C^\circ_{p,\mathrm{m}}$(stat)$\}$ described above. The $C^\circ_{p,\mathrm{m}}$(expt) values are slightly higher than those calculated statistically, but all differences remain within the combined estimated uncertainties of the two methods.

Vibrational analyses for *p*-xylene (Draeger and Scott, 1981; Green, 1970) show 18 fundamental modes between 1000 cm^{-1} and 1550 cm^{-1}. The small systematic deviations between the calorimetric and statistically derived $\Delta_0^T S^\circ_\mathrm{m}$ and $C^\circ_{p,\mathrm{m}}$ values shown in Figures 11 and 12 could be eliminated almost entirely by shifting some combination of these wavenumber values lower by a total of 150 cm^{-1}. A definitive vibrational assignment for *p*-xylene is not available. Changes to the assignment continue. Selco and Carrick (1995) observed only six of the 48 fundamental vibrations of *p*-xylene and made significant changes to two of them. (Bands at 389 cm^{-1} and 1616 cm^{-1} were reassigned to 381.8 cm^{-1} and 1656.7 cm^{-1}, respectively.) Furthermore, Selco and Carrick (1995) reported previously unknown anharmonicity constants for three others. Further refinements to the vibrational assignment are probable as experimental and computational methods develop.

Second Virial Coefficients. Second virial coefficients for *p*-xylene between the temperatures 377 K and 438 K were determined with vapor compressibility measurements at the Chemical Research Laboratory (also known as the National Physical Laboratory) of England (Cox and Andon, 1958; Andon et al., 1957). The imprecision of the reported values was near 2%. A comparison of the experimental values with those calculated with the corresponding states method of Pitzer and Curl (1957) is shown in Figure 13. Deviations between the experimental and calculated values decrease rapidly from 17% near 377 K to less than 4% above 420 K. Recently, for pyridine (Chirico and Steele, 1996b), excellent accord was demonstrated between second virial coefficients calculated with corresponding states (Pitzer and Curl, 1957) and those reported by Cox and Andon (1958; Andon et al., 1957). The origin of the inconsistency for *p*-xylene is not known.

Bich et al. (1981) reported second virial coefficients for *p*-xylene for the temperature range $423 < (T/\mathrm{K}) < 563$ by pressure measurements (53.3 kPa to 172 kPa) at constant volume. These are compared in Figure 13 with values calculated in this research with corresponding states (Pitzer and Curl, 1957). The values reported by Bich et al. (1981) show small systematic deviations from the corresponding states values; from 3% high near 419 K to 5% low near 573 K. Although these deviations are within the ±5% claimed for the second virial coefficients estimated with corresponding states (Pitzer and Curl, 1957), the systematic deviations lead to significant differences in entropy of compression values (eq 10) arising from differences in dB/dT for $p > 0.1$ MPa. Standard entropies $\Delta_0^T S^\circ_\mathrm{m}$(cal) were calculated from the calorimetric results as described earlier, but with the second virial coefficients by Bich et al. (1981) substituted for those derived with the Pitzer and Curl (1957) correlation. Comparisons with $\Delta_0^T S^\circ_\mathrm{m}$(stat) values are shown in Figure 11. For temperatures above the normal boiling temperature (411.5 K), significant deviations are apparent between the derived results.

Enthalpies of vaporization $\Delta_\mathrm{l}^\mathrm{g} H_\mathrm{m}$ calculated with the Clapeyron equation (eq 7) together with the second virial coefficients by Bich et al. (1981) substituted for those derived with the Pitzer and Curl (1957) correlation, show slightly improved agreement with the experimental values of Hossenlopp and Scott (1981). Differences shown in Figure 9 are decreased by approximately 0.04 $kJ{\cdot}mol^{-1}$. However, agreement with values reported by Natarajan and Viswanath (1985) is worse, particularly at high temperatures where differences increase to 0.9 $kJ{\cdot}mol^{-1}$.

Tsonopoulos (1974) published a modification to the second virial coefficient correlation of Pitzer and Curl (1957) based on new experimental information for argon, krypton, carbon dioxide, and several alkanes. Second virial coefficients calculated with the Tsonopoulos (1974) modifications are included in Figure 13. Differences between the Tsonopoulos (1974) and Pitzer and Curl (1957) correlations are small in the temperature region shown. Substitution of second virial coefficients estimated with the Tsonopoulos (1974) correlation for those derived with the Pitzer and Curl (1957) correlation yields standard entropy differences similar to those derived with the values of Bich et al. (1981), as shown in Figure 11. Enthalpies of vaporization $\Delta_l^g H_m$ derived with the Tsonopoulos (1974) correlation show slightly poorer agreement with the experimental values (Hossenlopp and Scott, 1981; Natarajan and Viswanath 1985) relative to values calculated with the Pitzer and Curl (1957) correlation.

The results shown here for *p*-xylene do not provide a means to ascertain unequivocally which second virial coefficient representation (Bich et al., 1981; Tsonopoulos, 1974; Pitzer and Curl, 1957) is best. The Pitzer and Curl (1957) correlation was used to derive all tabulated values because it provided slightly better accord with statistically derived $\Delta_0^T S_m^\circ$ values in Figure 11 and good accord with experimental $\Delta_l^g H_m$ values for all temperatures, as shown in Figure 9.

Conclusions

Standard thermodynamic properties for *p*-xylene based on calorimetric and physical-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, virial coefficients, enthalpies of vaporization, and critical properties. Results are in accord with the available vibrational assignment for the vapor phase; however, a systematic deviation with temperature indicates that slight inconsistencies remain. The calorimetrically derived values will be used to calculate xylene isomerization equilibria over a broad temperature. These results will be published separately (Chirico and Steele, 1996a).

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