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Thermodynamic Equilibria in Xylene Isomerization. 2. The Thermodynamic Properties of *m*-Xylene†

R. D. Chirico,* S. E. Knipmeyer, A. Nguyen, J. W. Reynolds, and W. V. Steele

Bartlesville Thermodynamics Group, BDM Petroleum Technologies, P.O. Box 2543,
Bartlesville, Oklahoma 74005

Measurements leading to the calculation of the ideal-gas thermodynamic properties for *m*-xylene are reported. Experimental methods included adiabatic heat-capacity calorimetry (5 K to 430 K), vibrating-tube densitometry (323 K to 523 K), comparative ebulliometry (309 K to 453 K), and differential-scanning calorimetry (DSC). The critical temperature was measured by DSC. Saturation heat capacities for the liquid phase between 430 K and 550 K and the critical pressure were derived with the vapor-pressure 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 for the vapor phase. All results are compared with literature values.

Introduction

This is the second 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 distributions and those calculated with thermodynamic information (Amelse, 1993; Seddon, 1986).

Amelse (1993) monitored the approach to equilibrium for xylene isomerization using both a non-shape-selective molecular sieve and the shape-selective zeolite catalyst ZSM-5. The differing approaches to the equilibrium distribution were used to extrapolate with high precision to the equilibrium value. Comparison with calculated equilibria on the basis of 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.

Gibbs free energies of formation and enthalpies of formation for the xylenes published in numerous compilations and used in equilibria calculations (cf., Frenkel et al., 1994; Laesecke, 1993; Stull et al., 1987; Pedley et al., 1986; Draeger, 1985a; and Chao et al., 1984; Cox and Pilcher, 1970; 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). Some high-precision thermodynamic-property results have been published in the intervening 50 years for *p*-xylene (see 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) by vibrating-tube densitometry are reported for *m*-xylene. Saturation heat capacities C_{sat} for the liquid phase to $T \approx 0.9T_c \approx 550$ 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. DSC was used also to determine the critical temperature directly. The critical pressure was derived by fitting procedures.

m-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, 1997).

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 *m*-xylene (Chemical Abstracts registry number 108-38-3) used in this research was prepared by the Grignard reaction of a commercial sample of 3-bromotoluene (Aldrich Chemical Company; 98% purity) with magnesium, followed by reaction of the Grignard reagent

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† Contribution No. 361 from the Bartlesville Thermodynamics Group.
* To whom correspondence should be addressed.

with methyl sulfate. The *m*-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 of pressure. The sample was determined to be 0.9990 mole fraction *m*-xylene by fractional melting as part of the adiabatic calorimetric studies reported here.

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

Physical Constants and Standards. Molar values are reported in terms of $M = 106.1674\ \text{g·mol}^{-1}$ for *m*-xylene and the gas constant, $R = 8.31451\ \text{J·K}^{-1}\text{·mol}^{-1}$, adopted by CODATA (Cohen and Taylor, 1988). The platinum resistance thermometers used in these measurements were calibrated by comparison with standard 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 obtained in this research for *m*-xylene 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., 1993a). 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 (Swietoslawski, 1945; Osborn and Douslin, 1966). The ebulliometers were used to reflux the *m*-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 *m*-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).

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

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

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 $\text{d}p_{\text{ref}}/\text{d}T$ for the reference substances were calculated from vapor pressures of the reference materials (decane and water).

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

T/K	ρ/(kg·m^{-3})	T/K	ρ/(kg·m^{-3})
323.14	837.4	448.11	718.1
348.13	815.8	473.11	689.9
373.12	792.9	498.11	659.5
398.12	769.0	523.11	625.1
423.11	744.6		

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 cc) was filled with 42.208 g of *m*-xylene and sealed with a gold-gasketed screw-cap closure under a helium pressure of 7.8 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 *m*-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 methods were described previously (Knipmeyer et al., 1989; Chirico and Steele, 1994; Steele, 1995).

Experimental Results

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

Vapor Pressures. Vapor pressures for *m*-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 indicated 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 430 K were determined by adiabatic calorimetry. Crystallization of the *m*-xylene sample was initiated by cooling (approximately 7 mK·s^{-1}) the liquid sample to 30 K to 35 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 Wadding-

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

standard	T/K	p/kPa	Δp/kPa	σ/kPa	ΔT/K
decane	308.640	1.9992	−0.0003	0.0003	0.025
decane	322.290	3.9924	0.0004	0.0005	0.013
decane	328.459	5.336	0.000	0.001	0.013
decane	328.459	5.336	0.000	0.001	0.013
decane	337.564	8.001	0.001	0.001	0.010
decane	344.412	10.671	0.000	0.001	0.009
decane	349.946	13.335	0.000	0.002	0.009
decane	355.722	16.679	−0.001	0.002	0.009
decane	360.484	19.931	−0.001	0.002	0.009
decane	366.807	25.036	−0.001	0.002	0.008
water[b]	366.795	25.026	0.000	0.003	0.008
water	373.152	31.185	−0.001	0.003	0.007
water	379.540	38.561	−0.002	0.004	0.008
water	385.969	47.348	−0.002	0.005	0.007
water	392.455	57.780	−0.001	0.006	0.009
water	399.012	70.118	−0.001	0.007	0.011
water	405.601	84.545	−0.001	0.008	0.011
water	412.213	101.299	0.005	0.009	0.014
water	418.893	120.78	0.00	0.01	0.013
water	425.615	143.23	0.01	0.01	0.014
water	432.383	169.01	0.00	0.01	0.014
water	439.202	198.51	0.00	0.02	0.014
water	446.046	231.98	0.00	0.02	0.014
water	452.947	269.98	−0.01	0.02	0.013

[a] Water or decane refers to which material was used as the standard in the reference ebulliometer; T is the condensation temperature of the *m*-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 *m*-xylene. [b] This value was not included in the fits to the vapor pressures.

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

F	$T(F)$/K
0.1596	225.069
0.2587	225.158
0.4073	225.209
0.6550	225.242
0.8037	225.252
T_{tp}/K	(225.30 ± 0.01)
x	0.0010

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

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

N[a]	h[b]	T_{i}/K	T_{f}/K	T_{trs}/K	$\Delta_{\mathrm{tot}}U_{\mathrm{m}}$[c]/(kJ·mol^{-1})	$\Delta_{\mathrm{trs}}H_{\mathrm{m}}$[d]/(kJ·mol^{-1})
		Single-Phase Measurements in the Crystal Phase				
5	1	101.515	164.591		5.382	−0.001
5	1	164.599	211.048		4.986	−0.002
		Crystals to Liquid				
1	7	213.566	228.234	225.30	13.538	11.644
2	2	222.024	228.561		12.573	11.644
5	3	211.085	227.940		13.782	11.644
					Average:	11.644
		Single-Phase Measurements in the Liquid Phase				
5	1	227.941	310.367		14.244	−0.001
7	1	294.786	395.440		20.003	−0.003
7	1	395.410	427.130		7.118	−0.001

[a] Adiabatic series number. [b] Number of heating increments. [c] $\Delta_{\mathrm{tot}}U_{\mathrm{m}}$ is the molar energy input from the initial temperature T_{i} to the final temperature T_{f}. [d] $\Delta_{\mathrm{trs}}H_{\mathrm{m}}$ 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, $C_{\mathrm{sat,m}}$, at Vapor-Saturation Pressure for *m*-Xylene Measured with Adiabatic Calorimetry (R = 8.314 51 J·K^{-1}·mol^{-1})

N[a]	$\langle T\rangle$/K	ΔT/K	$C_{\mathrm{sat,m}}/R$[b]	N[a]	$\langle T\rangle$/K	ΔT/K	$C_{\mathrm{sat,m}}/R$[b]
			Crystals				
3	5.216	1.077	0.032	5	59.308	5.683	6.704
3	6.179	0.881	0.055	5	65.298	6.284	7.066
4	6.313	0.874	0.059	5	72.099	6.910	7.431
3	7.113	0.931	0.087	5	79.403	7.692	7.792
4	7.240	0.952	0.092	5	87.590	8.675	8.178
4	8.201	0.978	0.138	2	90.805	7.472	8.326
4	9.200	1.014	0.201	5	96.699	9.533	8.599
4	10.220	1.021	0.284	2	98.874	8.655	8.695
4	11.336	1.204	0.388	2	108.067	9.720	9.113
4	12.599	1.317	0.524	2	117.825	9.787	9.560
4	13.983	1.454	0.702	2	127.669	9.890	10.014
4	15.528	1.636	0.921	2	137.629	9.936	10.474
4	17.245	1.798	1.190	2	148.569	11.936	10.993
4	19.142	1.995	1.504	2	160.538	11.996	11.577
4	21.345	2.411	1.887	2	172.530	11.986	12.171
4	23.764	2.432	2.326	1	183.075	12.274	12.701
4	26.345	2.734	2.792	2	184.489	11.932	12.781
4	29.213	3.006	3.296	1	195.357	12.173	13.380
4	32.375	3.322	3.828	2	196.472	12.051	13.434
4	35.901	3.733	4.374	1	207.525	12.046	14.143
4	39.835	4.137	4.916	2	208.488	12.036	14.218
4	44.200	4.595	5.436	5	216.233	10.295	15.552
4	49.085	5.174	5.920	1	217.407	7.681	15.860
5	53.923	5.066	6.323	2	218.246	7.562	16.278
4	54.554	5.762	6.372				
			Liquid				
2	232.339	7.557	19.550	6	318.005	14.968	22.679
2	240.996	9.785	19.802	6	333.009	15.011	23.332
2	251.993	12.198	20.142	6	348.135	15.049	24.009
2	264.272	12.349	20.559	6	363.544	15.764	24.719
2	276.643	12.387	21.006	6	379.165	15.480	25.451
6	287.489	15.513	21.423	6	394.503	15.211	26.180
2	289.033	12.391	21.485	6	409.570	14.954	26.908
2	301.398	12.342	21.980	6	423.428	12.805	27.588
6	302.882	15.238	22.041				

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

ton, 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 4 mK of the calculated equilibrium temperatures for F values listed in Table 3. The presence of solid-soluble impurities was not indicated.

Experimental molar enthalpy results 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 and 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

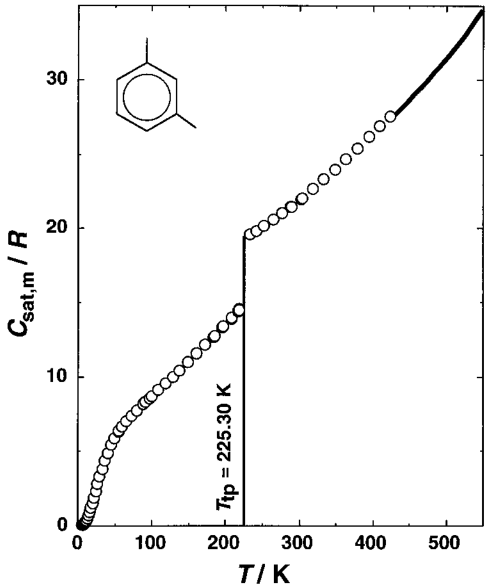

Figure 1. Heat capacity $C_{sat,m}$ against temperature for *m*-xylene. The vertical line indicates the triple-point temperature T_{tp}. (○) $C_{sat,m}$ values measured with adiabatic calorimetry and listed in Table 5. Premelting corrections were applied to the values in the figure. The curve for temperatures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

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

ρ/(kg·m^{-3})	T/K	ρ/(kg·m^{-3})	T/K
146	601.3	343	617.6
193	610.9	356	617.2
210	615.3	387	611.6
252	617.4	435	605.2
286	617.7		

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 *m*-xylene were less than 1 h for temperatures below 180 K and increased smoothly to 6 h near T_{tp} (225.30 K). Extrapolation of the heat-capacity results to $T \rightarrow 0$ K was made with a plot of $C_{sat,m}/T$ against T^2 for temperatures below 10 K.

Differential-Scanning Calorimetry. The *m*-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 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. Details of the method used were described recently (Steele, 1995). The cell volume was calculated with the equation

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

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 derived from the DSC measurements, (617.6 ± 1.0) K, is in good agreement with the value selected by Tsonopoulos and Ambrose (1995), (617.0 ± 0.5) K, in their recent review, as shown in the figure.

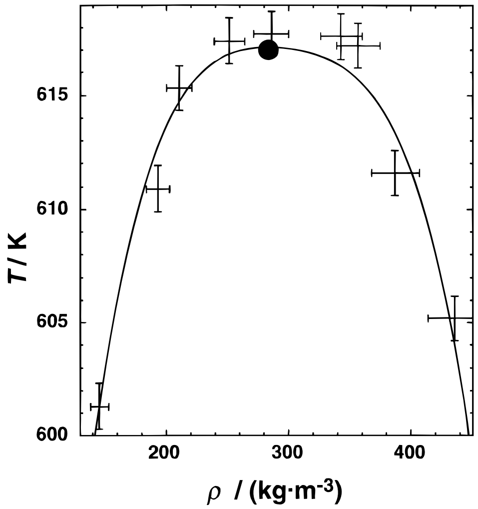

Figure 2. Vapor−liquid coexistence region for *m*-xylene. The crosses span the range of uncertainty for the measurement results of this research. (●) Critical temperature and critical density selected by Tsonopoulos and Ambrose (1995). The curve provides an aid to the eye.

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

T/K	$C^{II}_{x,m}/R$ for V(cell) = 0.052 17 cm^3 and m = 0.010 22 g	$C^{II}_{x,m}/R$ for V(cell) = 0.052 17 cm^3 and m = 0.015 14 g	$C^{II}_{x,m}/R$ for V(cell) = 0.052 19 cm^3 and m = 0.020 53 g
355.0	24.30	24.80	24.60
375.0	25.50	25.90	25.70
395.0	27.00	27.10	26.70
415.0	28.30	28.20	27.80
435.0	29.90	29.40	28.80
455.0	31.40	30.90	30.00
475.0	32.90	32.20	31.20
495.0	34.70	33.40	32.20
515.0	36.50	34.90	33.20
535.0	38.20	35.80	34.40
555.0	40.10	37.60	35.70
575.0	42.30	39.60	37.30
595.0	45.90	42.60	39.80

[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}).

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 (vapor + liquid) 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 *m*-xylene obtained for three cell fillings with 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 the $C_{sat,m}$ values determined by adiabatic calorimetry. The effect of vaporization of the sample into the free space of the cell as the temperature is increased 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,

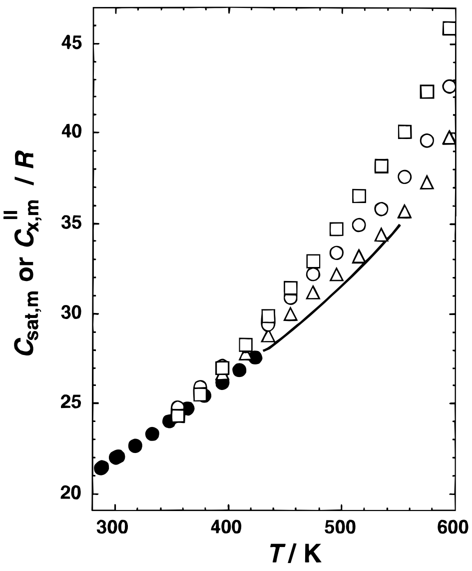

Figure 3. Curve of heat capacity against temperature for *m*-xylene. $C^{II}_{x,m}$ by DSC for three cell fillings: (□) 10.22 mg; (○) 15.14 mg; (△) 20.51 mg of sample. (●) $C_{sat,m}$ determined by adiabatic calorimetry in this research. The curve represents the saturation heat capacities derived in this research and listed in Table 9.

1994). $C_{sat,m}$ values determined by adiabatic calorimetry in this research for the temperature range $301 < (T/K) < 423$ 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.

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. 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 (Chirico et al., 1996) and *p*-xylene (Chirico et al., 1997a) also from T_{tp} to T_c. The T_c value measured in this research was in good accord with that selected by Tsonopoulos and Ambrose (1995) for *m*-xylene. The selected value, $T_c = 617.0$ K, 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 $C^{II}_{V,m}$ as follows:

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

where n is the number of moles of *m*-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 $(\partial p/\partial T)_{sat}$ 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

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

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

m-Xylene			
$A = -7.564\,368$		$b_0 = -0.447\,86$	
$B = 1.623\,819$		$b_1 = -0.277\,79$	
$C = -1.139\,601$		$b_2 = 0.155\,94$	
$D = -4.004\,004$		$b_3 = -0.380\,14$	
$T_c = 617.0$ K	$p_c = 3540$ kPa	$\rho_c = 283$ kg·m^{-3}	$\omega = 0.3261$

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

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

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):

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

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%. Derived $C_{sat,m}$ values for *m*-xylene are included in Figures 1 and 3. The derived critical pressure (3540 ± 40) kPa is in excellent agreement with that selected by Tsonopoulos and Ambrose, (3541 ± 40) kPa, and is included in Table 8.

Critical Density. The value of the critical density ρ_c selected by Tsonopoulos and Ambrose (1995) in their recent review, (283 ± 4) kg·m^{-3}, was used with eq 7. Comparisons of literature densities with values calculated with eq 7 are described later in this paper. Systematic deviations exist but do not exceed ±0.6%. Propagated errors due to a 0.6% uncertainty in densities calculated with eq 7 are negligible for all properties derived here.

Enthalpies of Vaporization. Molar enthalpies of vaporization $\Delta_l^g H_m$ were derived from the Wagner-equation fit to the vapor pressures by means of the Clapeyron equation:

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

$\Delta_l^g V_m$ 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

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

T/K	$C_{\mathrm{sat,m}}/R$	$\Delta_0^T S_m/R$	$\Delta_0^T H_m/RT$	T/K	$C_{\mathrm{sat,m}}/R$	$\Delta_0^T S_m/R$	$\Delta_0^T H_m/RT$
			Crystals				
5.00	0.028	0.009	0.007	90.00	8.292	8.281	4.699
10.00	0.265	0.082	0.062	100.00	8.745	9.178	5.081
15.00	0.844	0.287	0.217	120.00	9.654	10.853	5.767
20.00	1.651	0.637	0.472	140.00	10.577	12.410	6.388
30.00	3.431	1.645	1.163	160.00	11.535	13.885	6.971
40.00	4.937	2.849	1.928	180.00	12.521	15.300	7.533
50.00	6.002	4.073	2.643	200.00	13.527	16.671	8.082
60.00	6.749	5.237	3.268	220.00	14.582	18.009	8.624
70.00	7.322	6.322	3.808	225.30	14.880	18.359	8.768
80.00	7.821	7.333	4.279				
			Liquid				
225.30	19.362	24.575	14.984	400.00	26.444	37.351	18.308
240.00	19.772	25.812	15.264	420.00	27.419	38.665	18.719
260.00	20.410	27.419	15.635	440.00[b]	28.41	39.96	19.14
280.00	21.133	28.958	16.001	460.00[b]	29.44	41.25	19.56
298.15	21.848	30.307	16.335	480.00[b]	30.51	42.52	20.00
300.00	21.923	30.442	16.369	500.00[b]	31.65	43.79	20.44
320.00	22.765	31.884	16.743	520.00[b]	32.89	45.06	20.89
340.00	23.642	33.290	17.122	540.00[b]	34.30	46.33	21.36
360.00	24.554	34.667	17.510	550.00[b]	35.10	46.96	21.61
380.00	25.490	36.020	17.905				

[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 *m*-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]	45.54 ± 0.08	340.00	40.35 ± 0.06	460.00[a]	32.69 ± 0.17
260.00[a]	44.94 ± 0.08	360.00	39.22 ± 0.06	480.00[a]	31.06 ± 0.22
280.00[a]	43.76 ± 0.07	380.00	38.05 ± 0.07	500.00[a]	29.28 ± 0.27
298.15[a]	42.72 ± 0.07	400.00	36.83 ± 0.08	520.00[a]	27.30 ± 0.32
300.00[a]	42.61 ± 0.07	420.00	35.55 ± 0.10	540.00[a]	25.07 ± 0.38
320.00	41.48 ± 0.07	440.00	34.17 ± 0.13	550.00[a]	23.85 ± 0.42

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

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), pyridine (Chirico et al., 1996; Chirico and Steele, 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%. 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 *m*-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 (Westrum et al., 1968) for solid-insoluble impurities with the mole-fraction impurity value 0.001 25.

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 *m*-xylene using values 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:

$$pV_m = RT + Bp + C'p^2 \tag{9}$$

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). The gas-imperfection corrections are included 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 *m*-xylene were combined with the enthalpy of formation of the liquid phase $-(25.38 \pm 0.62)$ 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 one standard deviation and do not include uncertainties in the properties of the elements.

Comparisons with Literature Values

The thermophysical and thermochemical properties of *m*-xylene have been the subject of numerous investigations reported in the literature. Comparisons of the results of the present research with 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 *m*-xylene reported by Coops et al. (1946) is 2.3 kJ·mol^{-1} more positive than that reported by Prosen et al. (1945). Similar differences are observed for the ortho and para 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 values reported by Prosen et al. for the three xylenes were used in all calculations of this research.

Table 11. Standard Molar Thermodynamic Properties in the Ideal-Gas State for *m*-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	37.36 ± 0.04	0.00	40.59 ± 0.05	0.00	10.40 ± 0.15	−39.13 ± 0.05	49.53 ± 0.15
260.00^c	36.42 ± 0.04	0.00	41.10 ± 0.05	0.00	9.59 ± 0.15	−39.55 ± 0.05	49.14 ± 0.15
280.00^c	34.80 ± 0.04	0.00	42.12 ± 0.04	0.00	8.14 ± 0.14	−40.34 ± 0.04	48.48 ± 0.14
298.15^c	33.58 ± 0.03	0.01	43.04 ± 0.04	0.01	7.00 ± 0.13	−41.01 ± 0.04	48.01 ± 0.13
300.00^c	33.46 ± 0.03	0.01	43.13 ± 0.04	0.01	6.89 ± 0.13	−41.07 ± 0.04	47.96 ± 0.13
320.00	32.35 ± 0.03	0.02	44.14 ± 0.04	0.01	5.82 ± 0.12	−41.73 ± 0.04	47.56 ± 0.12
340.00	31.43 ± 0.03	0.03	45.15 ± 0.04	0.02	4.89 ± 0.11	−42.34 ± 0.04	47.23 ± 0.11
360.00	30.67 ± 0.03	0.05	46.17 ± 0.04	0.04	4.08 ± 0.11	−42.89 ± 0.04	46.98 ± 0.11
380.00	30.03 ± 0.03	0.09	47.18 ± 0.04	0.06	3.38 ± 0.10	−43.39 ± 0.04	46.77 ± 0.10
400.00	29.51 ± 0.03	0.13	48.18 ± 0.05	0.09	2.76 ± 0.10	−43.86 ± 0.05	46.61 ± 0.10
420.00	29.08 ± 0.04	0.18	49.18 ± 0.05	0.13	2.21 ± 0.10	−44.28 ± 0.05	46.49 ± 0.10
440.00	28.73 ± 0.05	0.25	50.18 ± 0.06	0.18	1.73 ± 0.10	−44.67 ± 0.06	46.39 ± 0.10
460.00^c	28.45 ± 0.06	0.34	51.17 ± 0.07	0.25	1.30 ± 0.10	−45.03 ± 0.07	46.32 ± 0.09
480.00^c	28.22 ± 0.07	0.44	52.16 ± 0.08	0.32	0.91 ± 0.11	−45.35 ± 0.08	46.27 ± 0.10
500.00^c	28.04 ± 0.09	0.56	53.14 ± 0.09	0.41	0.57 ± 0.12	−45.66 ± 0.09	46.23 ± 0.10
520.00^c	27.91 ± 0.11	0.70	54.11 ± 0.11	0.52	0.27 ± 0.13	−45.93 ± 0.11	46.20 ± 0.11
540.00^c	27.81 ± 0.13	0.86	55.08 ± 0.13	0.64	−0.01 ± 0.15	−46.19 ± 0.13	46.18 ± 0.13
550.00^c	27.77 ± 0.14	0.95	55.56 ± 0.14	0.70	−0.14 ± 0.16	−46.31 ± 0.14	46.17 ± 0.14

[a] Gas-imperfection correction included in the ideal-gas enthalpy. The ideal-gas enthalpy is calculated relative to that of the crystals at $T \rightarrow$ 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.

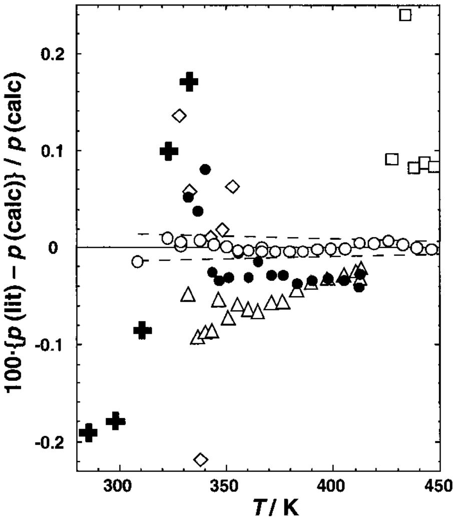

Figure 4. Deviation plot for *m*-xylene vapor pressures; p(calc) represents the values calculated with eq 3 and the parameters listed in Table 8. Values of p(expt): (○) Fitted values of this research (Table 2); (◇) Díaz Peña et al. (1979); (□) Ambrose et al. (1967), most values from this reference are not shown (See Figure 5 for a complete comparison); (●) Forziati et al. (1949); (△) Willingham et al. (1945); (+) Pitzer and Scott (1943). The dashed lines indicate the estimated experimental uncertainties (one standard deviation) for the values of this research (Table 2).

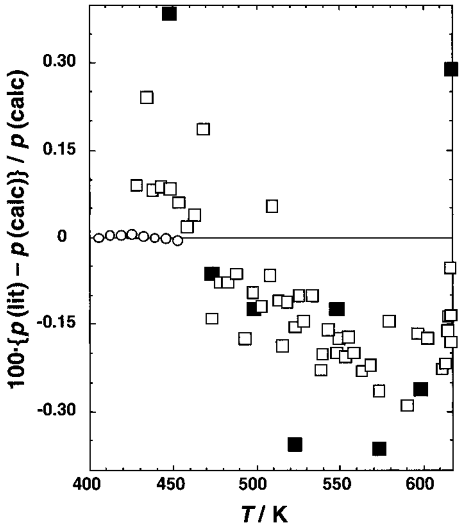

Figure 5. Deviation plot for *m*-xylene vapor pressures at high temperatures; p(calc) represents the values calculated with eq 3 and the parameters listed in Table 8. Values of p(expt): (○) Fitted values of this research (Table 2); (□) Ambrose et al. (1967); (■) Mamedov et al. (1967a).

Vapor Pressures. Reports of vapor pressures for *m*-xylene have appeared in the literature for more than one hundred 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 parameters listed in Table 8. Values reported by Pitzer and Scott (1943) above 273.15 K, measured with a mercury manometer, are included in the figure.

Ambrose et al. (1967) reported vapor pressures for *m*-xylene between the temperatures 428 K and 617 K. The small deviations of these high-temperature results from values calculated with eq 3 and the parameters listed in Table 8 are shown in Figure 5. Vapor pressures reported by Mamedov et al. (1967a) for temperatures between 448 K and T_c are also in good accord with those of this research, although the accuracy claimed (±0.05%) by Mamedov et al. is overstated by approximately an order of magnitude. The critical temperature reported by Mamedov et al. (1967a) for *m*-xylene is approximately 2 K higher than the assessed value (Tsonopoulos and Ambrose, 1995). For the vapor-pressure comparison near T_c a value calculated by Mamedov et al. for $T = 616.8$ K was used.

High-temperature values reported by Glaser and Rüland (1957) show large deviations from the values of this research, as shown in Figure 6. Similar large deviations were observed previously for *p*-xylene (Chirico et al., 1997a), while good accord was observed for *o*-xylene (Chirico et al., 1997b). The origin of the discord is not known. Deviations for values reported by Chao et al. (1980) obtained with a Heise gauge are near the claimed uncertainty of ±1%.

Comparisons with other literature values are shown also in Figure 6. The vertical axis in Figure 6 is expanded by a factor of approximately 30 relative to that of Figure 4. Values reported by Rintelen et al. (1937) for temperatures between 283 K and 323 K range from 34% to 6% lower than the calculated values and are not shown in Figure 6.

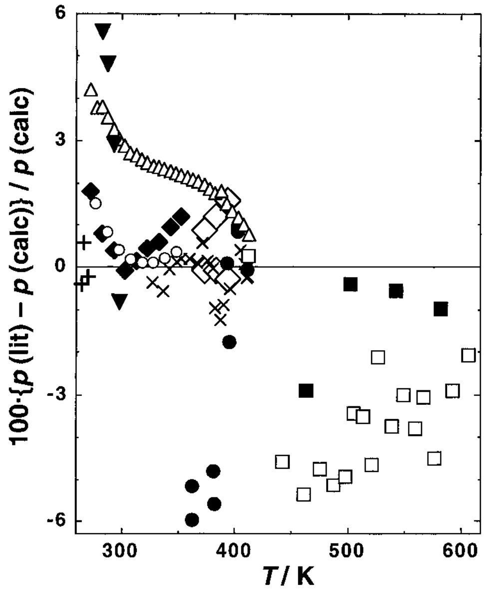

Figure 6. Low-resolution deviation plot for *m*-xylene vapor pressures; *p*(calc) represents the values calculated with eq 3 and the parameters listed in Table 8. Values of *p*(expt): (×) Park and Gmehling (1989); (◇) Willman and Teja (1985); (▼) Mato et al. (1986); (■) Chao et al. (1980); (□) Glaser and Rüland (1957); (○) Stuckey and Saylor (1940), values from this reference were provided in equation form only; (◆) Kassel (1936); (+) Linder (1931); (△) Woringer (1900); (●) Neubeck (1887). See text for additional citations.

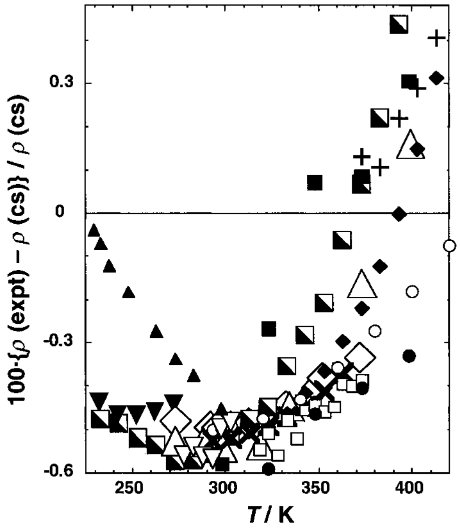

Figure 7. Deviation plot for *m*-xylene densities; *ρ*(cs) represents values calculated with the Riedel equation (eq 7). Values of *ρ*(expt): (●) this research (Table 1); (▲) Taravillo et al. (1994); (□) Garg et al. (1993); (▽) Serrano et al. (1990); (○) Hales and Townsend (1972); (◆) Shoitov et al. (1968); (■) Mamedov et al. (1967a,b); (▼) Ben'kovskii et al. (1966); (×) Shraiber and Pechenyuk (1965); (+) Francis (1957); (△) Massart (1936); (◩) Heil (1932); (◇) Tyrer (1914). See Figure 8 also. See text for additional citations.

Except for the results of Chao et al. (1980) at high temperatures and those of Willman and Teja (1985), values obtained as part of vapor-liquid equilibria (VLE) studies were not included in the vapor-pressure comparisons. These are typically for one or two temperatures only and are often performed on materials of relatively low purity.

Densities. Densities for *m*-xylene are shown in Figures 7 and 8 relative to values calculated with the Riedel equation (eq 7) and the critical parameters listed in Table 8. Between the temperatures 280 K and 380 K, the densities of *m*-xylene are well established with numerous reported values within ±0.05%, as shown in Figure 7. Values reported for short temperature ranges between 280 K and 330 K by Jain et al. (1994), Naorem and Suri (1993), Aralaguppi et al. (1992), Ruiz et al. (1989), Suri and Ramakrishna (1975), Petro and Smyth (1958), Donaldson and Quayle (1950), and Timmermans and Hennaut-Roland (1930) are within 0.05% of those in Figure 7 but are not shown for clarity. Densities with larger scatter (approximately ±0.2%) and not shown in Figure 8 include those of Oshmyansky et al. (1986), Richards et al. (1924), Dutoit and Friederich (1900), Perkin (1896), and Neubeck (1887). Values reported by Azim et al. (1933) between 293 K and 348 K are anomalously high and are not shown. All references cited list densities for at least three temperatures.

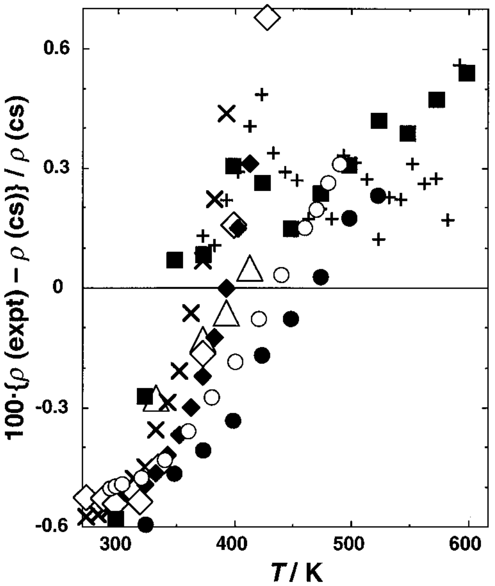

Figure 8. Deviation plot for *m*-xylene densities at high temperatures; *ρ*(cs) represents values calculated with the Riedel equation (eq 7). Values of *ρ*(expt): (●) this research (Table 1); (△) Chang et al. (1996); (○) Hales and Townsend (1972); (◆) Shoitov et al. (1968); (■) Mamedov et al. (1967a,b); (+) Francis (1957); (◇) Massart (1936); (×) Heil (1932).

Densities at low temperatures (230 K to 298 K) for a range of pressures were reported recently by Taravillo et al. (1994) with a claimed accuracy of better than 0.05%. Values represented in Figure 7 were calculated by short extrapolations to the saturation pressure. The claimed accuracy cannot be reconciled with the results of Serrano et al. (1990), Ben'kovskii et al. (1966), Geist and Cannon (1946), Massart (1936), Heil (1932), Timmermans and Hennaut-Roland (1930), and Tyrer (1914), which are in good accord with each other (within ±0.1%) between 273 K and 300 K.

There is less consistency at higher temperatures, as seen in Figure 8. Results reported by Shoitov et al. (1968), Mamedov et al. (1967a,b), Francis (1957), Massart (1936), and Heil (1932) are mutually consistent for temperatures below 450 K. However, the results of this research (Table 1) and Hales and Townsend (1972) clearly define a different curve between 380 K and 460 K. The origin of this discrepancy is not known.

The densities attributed to Mamedov et al. (1967a,b) 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 3 and the parameters given in Table 8. Mamedov et al. (1967a,b) reported *PVT* results for tem-

Table 12. Comparison of Enthalpies of Vaporization for *m*-Xylene Obtained from the Wagner and Clapeyron Equations, $\Delta_l^g H_m$(this research), with Literature Values, $\Delta_l^g H_m$(lit)

source	T/K	$\Delta_l^g H_m$(lit)/(kJ·mol^{-1})	$\Delta_l^g H_m$(this research)/(kJ·mol^{-1})
Osborne and Ginnings (1947)	298.15	42.66 ± 0.04	42.72 ± 0.07
Kusano and Saito (1974)	298.15	42.57 ± ?	42.72 ± 0.07
Mathews (1926)	411.43	36.36 ± 0.04	36.11 ± 0.09
Nagornow and Rotinjanz (1911)	413.05	36.56 ± 0.13	36.00 ± 0.09

peratures from 298 K to 673 K and pressures to 20 MPa. The extrapolation of the density/pressure values was done for all reported temperatures below T_c.

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., 1997b) and *p*-xylene (Chirico et al., 1997a). 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 *m*-xylene were reviewed recently by Tsonopoulos and Ambrose (1995). Their selected value for the critical temperature (617.0 ± 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, (617.6 ± 1.0) K, is in agreement with the selected value, as shown earlier in Figure 2.

The critical pressure derived in this research, (3540 ± 40) kPa, from the simultaneous fit of the vapor pressures and two-phase heat capacities is in excellent agreement with that selected, (3541 ± 40) kPa, by Tsonopoulos and Ambrose (1995), again on the basis of the measurements by Ambrose et al. (1967).

The critical density selected by Tsonopoulos and Ambrose (1995), (283 ± 4) kg·m^{-3}, is the average of values reported by Simon (1957) and Akhundov and Asadullaeva (1968). This value was used in the present research and is consistent with the available saturation densities and the corresponding-states equation (eq 7), as shown in Figures 7 and 8.

Enthalpies of Vaporization. The enthalpy of vaporization at 298.15 K for *m*-xylene was reported by Osborne and Ginnings (1947) of the National Bureau of Standards and by Kusano and Saito (1974). Values near the normal-boiling temperature were reported by Mathews (1926) and Nagornow and Rotinjanz (1911). The literature values are compared in Table 12 with those calculated in this research with the fitted Wagner equation (eq 3) and the Clapeyron equation (eq 8), as described earlier. The value reported by Osborne and Ginnings (1947) is in good agreement with that obtained in this research; the others are not.

Condensed-Phase Heat Capacities and Entropies. Heat capacities for *m*-xylene by adiabatic calorimetry were first reported by Huffman et al. (1930) for temperatures between 95.9 K and 275.3 K. The sample of *m*-xylene used in those early studies was very impure. Although the purity was not determined, the authors noted "considerable premelting" and a large excess heat capacity approximately 50 K below the melting temperature. The melting temperature reported by Huffman et al. (1930), 219.6 K, is very close to the melting temperature of the *m*-xylene/*p*-xylene eutectic reported by Pitzer and Scott (1943). In spite of the low purity, the enthalpy of fusion for *m*-xylene reported by Huffman et al. is only 2% lower than that found in the present research. The reported heat capacities are typically within 1% of the results of the present research. However, between 160 K and 170 K deviations of the reported values increase from 3% to 28%. Deviations are shown in Figure 9. Huffman et al. (1930) estimated the entropy increment between 0 K and 95.9 K. The entropy for the liquid at 298.15 K reported by Huffman et al. is only 0.1% higher than that found in the present research. This result is serendipitous.

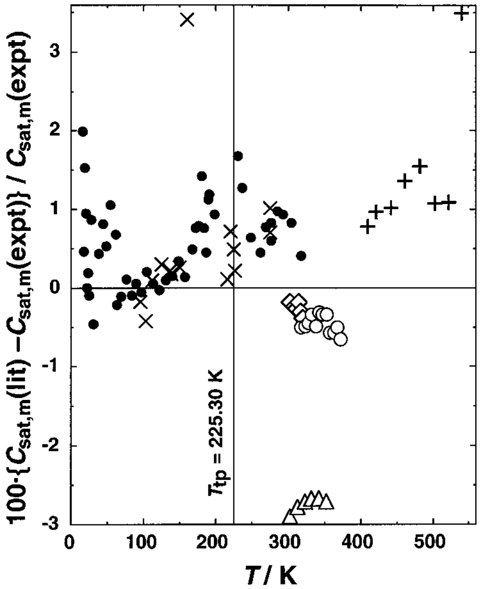

Figure 9. Deviation plot for *m*-xylene heat capacities. $C_{sat,m}$(expt) are the results of the present research (Table 9). Values of $C_{sat,m}$(lit): (○) Garg et al. (1993), the number of values shown is reduced for clarity; (◇) Jain et al. (1992), the number of values shown is reduced for clarity; (+) José et al. (1976); (●) Pitzer and Scott (1943); (×) Huffman et al. (1930); (△) Williams and Daniels (1924). The vertical line indicates the triple-point temperature.

Pitzer and Scott (1943) measured heat capacities for *m*-xylene for the temperature range 14.6 K to 318.2 K. The sample used by Pitzer and Scott was also very impure. On the basis of the results of a fractional-melting study, Pitzer and Scott estimated their *m*-xylene sample to contain 2.3% impurity, of which 2.1% was *p*-xylene. The heat-capacity values were "corrected" by assuming the results for *m*- and *p*-xylene were additive. Deviations of their results from those of the present research are shown in Figure 9. For temperatures between 50 K and 150 K, the deviations are in accord with the 0.2% uncertainty claimed by Pitzer and Scott. At lower and higher temperature their results are typically high by 0.5% to 1.5%.

The enthalpy of fusion reported by Pitzer and Scott (1943) for *m*-xylene is 0.7% lower than that found in the present research. Their value for T_{tp}, (225.30 ± 0.15) K, is in accord with the value obtained here, (225.30 ± 0.01) K. The entropy for the liquid at 298.15 K reported by Pitzer and Scott is 0.3% higher than that found in the present research.

José et al. (1976) measured isobaric heat capacities as a function of pressures with a closed-loop flow calorimeter for *m*-xylene for temperatures between 410 K and 540 K with a claimed uncertainty of ±1%. $C_{sat,m}$ values were obtained by José et al. (1976) by extrapolation to the saturation pressure. The extrapolated values are shown in Figure 9 to be in accord with those of this research except at the highest temperature, where uncertainties associated with the extrapolation are greatest. A possible source of discrepancy is the sample used by José et al., which was a commercial chemical used as received without analysis or purification.

Heat capacity values for the liquid phase for short temperature ranges between 300 K and 380 K have been reported by Garg et al. (1993), Jain et al. (1992), and Williams and Daniels (1924). Garg et al. (1993) and Jain et al. (1992) claimed accuracies of 0.1% or better in their measured values. These assessments are overly optimistic, as shown in Figure 10. Values reported by Williams and Daniels (1924) are approximately 3% lower than all other values reported for this temperature region.

Kurbatov (1947) reported heat capacities for *m*-xylene in the liquid phase derived from enthalpy increment measurements between $T = 288$ K and $T = 457$ K. Deviations of values calculated with the linear equation provided by Kurbatov from the values of this research (calculated with values in Table 9) range from 1% high near 288 K to 6% high near 457 K. Swietoslawski and Zielenkiewicz (1958) reported an enthalpy increment from near 294 K to 379 K. Their result is 2% higher than that of this research. Similar results were found for *p*-xylene (Chirico et al., 1997a) and *o*-xylene (Chirico et al., 1997b).

Standard Entropies and Heat Capacities from Spectroscopic Studies and Statistical Thermodynamics. Assignments for the 48 fundamental vibrational modes of *m*-xylene have been reported for more than fifty years (Pitzer and Scott, 1943; Green, 1970; La Lau and Snyder, 1971; Sverdlov et al., 1974; 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 five vibrational modes below 450 cm^{-1} was reached. For wavenumber values above 450 cm^{-1}, differences between the various assignments are significant, but relatively small, with differences typically near 10 cm^{-1} and not exceeding 40 cm^{-1}.

Wavenumber values for the vapor phase were reported first by Draeger (1985b). Recently, Selco and Carrick (1995) reported results of jet-cooled emission spectroscopic studies for the xylenes. Selco and Carrick reported wavenumbers for 13 of the 34 fundamental vibrational modes between 272.7 cm^{-1} and 1600 cm^{-1} and anharmonicity parameters, ω_e and $\omega_e\chi_e$, for three of these (529.4 cm^{-1}, 723.6 cm^{-1}, and 1000.0 cm^{-1}). The wavenumbers reported by Selco and Carrick (1995) are in good accord with those of Draeger (1985b) except for a value at 382.8 cm^{-1}, which Draeger (1985b) and all earlier researchers assigned to a band near 402 cm^{-1} for both the vapor and liquid phases.

The wavenumbers for the vapor phase reported by Draeger (1985b) were used alone and in combination with the modifications reported by Selco and Carrick (1995) to calculate standard entropies and standard heat capacities of *m*-xylene between $T = 250$ K and $T = 550$ K by statistical methods. The two fundamental vibrations associated with internal rotation of the methyl groups were treated as free rotors. The validity of this approximation is confirmed by the experiments of Breen et al. (1987). Contributions to $\Delta_0^T S^\circ_\mathrm{m}$ values due to the anharmonicity observed by Selco and Carrick were calculated to be very small, $0.01R$ or less for all temperatures. The harmonic oscillator approximation was used for all other modes.

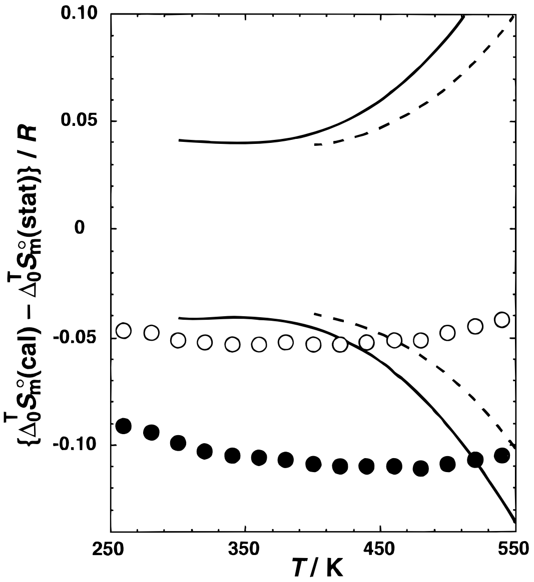

Figure 10. Deviation plot for *m*-xylene standard entropies. (—) Error limits (one standard deviation) assigned to the calorimetric values $\Delta_0^T S^\circ_\mathrm{m}$(cal); (- - -) error limits without uncertainty in the virial coefficients. (○) $\Delta_0^T S^\circ_\mathrm{m}$(stat) was calculated with the vapor-phase assignment of Draeger (1985b); (●) $\Delta_0^T S^\circ_\mathrm{m}$(stat) was calculated with the assignment of Draeger (1985b) with the modifications of Selco and Carrick (1995), as described in the text.

The moment of inertia (7.839×10^{-134} $\mathrm{kg}^3\cdot\mathrm{m}^6$) was calculated with estimated bond distances and angles described previously for *p*-xylene (Chirico et al., 1997a). 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). The internal rotation constant F was calculated to be 5.21 cm^{-1} for the methyl groups.

Differences between the statistically calculated standard entropies, $\Delta_0^T S^\circ_\mathrm{m}$(stat), and those derived from the calorimetric studies, $\Delta_0^T S^\circ_\mathrm{m}$(cal) (Table 11), are shown in Figure 10. Agreement between the $\Delta_0^T S^\circ_\mathrm{m}$(cal) values and those derived with the assignment of Draeger (1985b) alone is fair, with differences near the uncertainty limit (one standard deviation) of the calorimetrically derived values. The modifications proposed by Selco and Carrick (1995) worsen considerably the accord between $\Delta_0^T S^\circ_\mathrm{m}$(stat) and $\Delta_0^T S^\circ_\mathrm{m}$(cal). Nearly all of the increased divergence stems from the reassignment of the band near 402 cm^{-1} to 382.8 cm^{-1} by Selco and Carrick.

Raman and infrared spectroscopic studies for *m*-xylene in the vapor phase are in progress in this laboratory. Analysis of these spectral results, new comparisons of the $\Delta_0^T S^\circ_\mathrm{m}$(stat) and $\Delta_0^T S^\circ_\mathrm{m}$(cal) values, and a more detailed discussion of rotational barriers in the xylenes for all phases will by published separately (Chirico et al., 1997c).

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, $C^\circ_{p,\mathrm{m}}$, were estimated by Pitzer and Scott 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 $C^\circ_{p,\mathrm{m}}$ values reported by Pitzer and Scott (1943) are within ±0.6% of values calculated statistically here. Pitzer and Scott (1943) "somewhat arbitrarily" estimated the uncertainties in their experimental $C^{\circ}_{p,\mathrm{m}}$ values to be near ±1%. This uncertainty is too large to distinguish between the $\Delta_0^T S^{\circ}_{\mathrm{m}}$(stat) values calculated above (and shown in Figure 10). 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.

Second Virial Coefficients. Second virial coefficients for *m*-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%. Deviations between the experimental and calculated values decrease rapidly from 20% near 377 K to less than 2% above 420 K. Analogous inconsistencies were shown previously for *p*-xylene (Chirico et al., 1997a) and will be shown for *o*-xylene (Chirico et al., 1997b). Similar deviations are observed from second virial coefficients calculated with the correlation of Tsonopoulos (1974). For pyridine (Chirico and Steele, 1996), excellent accord was demonstrated between second virial coefficients calculated with corresponding states (Pitzer and Curl, 1957) and those reported by Andon and co-workers (Cox and Andon, 1958; Andon et al., 1957). The origin of these inconsistencies is not known.

Akhundov (1971) reported second virial coefficients for *m*-xylene for temperatures from 573 K to 673 K at 25-K intervals. Values calculated for temperatures below T_c (573.15 K and 598.15 K) with the corresponding-states method of Pitzer and Curl (1957) are in excellent accord (approximately 2.5% lower) with the experimental values. Values calculated with the corresponding-states method of Tsonopoulos (1974) show slightly larger deviations (approximately 6% lower).

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 these results, the correlation by Pitzer and Curl (1957) was used for all calculations in the present research.

Conclusions

Standard thermodynamic properties for *m*-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, enthalpies of vaporization, densities, and critical properties. Available experimental virial coefficients at low temperatures (Cox and Andon, 1958; Andon et al., 1957) are 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 (Draeger, 1985b) was shown to be in fair accord with the calorimetrically derived standard entropies. Modification of the vibrational assignment with results of recent jet-cooled emission spectral studies (Selco and Carrick, 1995) worsened the agreement. Raman and infrared spectroscopic studies for *m*-xylene in the vapor phase are in progress and will be published separately (Chirico et al., 1997c). The calorimetrically derived thermodynamic property values for *m*-xylene will be used to calculate xylene isomerization equilibria over a broad temperature range. These results will be published separately (Chirico and Steele, 1997).

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