Thermodynamic Equilibria in Xylene Isomerization. 4. The Thermodynamic Properties of Ethylbenzene[†]

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Measurements leading to the calculation of the ideal-gas thermodynamic properties for ethylbenzene (Chemical Abstracts registry number [100-41-4]) are reported. Experimental methods included adiabatic heat-capacity calorimetry (5 K to 420 K), comparative ebulliometry (306 K to 450 K), and differential-scanning calorimetry (DSC). The critical temperature was measured by DSC. Saturation heat capacities for the liquid phase between 420 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 temperatures between 250 K and 550 K. The standard state is defined as the ideal gas at the pressure $p = p° = 101.325$ kPa. Results are compared with literature values for all properties. Problems associated with independent statistical calculation of ideal-gas properties for ethylbenzene are discussed.

Introduction

This is the fourth in a series of papers concerning the thermodynamic properties of compounds related to isomerization of the xylenes. The background for this research was discussed in the first paper in 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). The results published here for ethylbenzene complete our experimental research plan for the C_8H_{10} aromatic hydrocarbons.

Gibbs free energies of formation and enthalpies of formation for ethylbenzene published in numerous compilations and used in equilibria calculations (cf., Daubert et al., 1996; TRC, 1996; Pedley, 1994; Stull et al., 1987; Pedley et al., 1986; Cox and Pilcher, 1970; Stull et al., 1969) stem primarily from experimental work completed in the 1940s by Guthrie et al. (1944), Scott and Brickwedde (1945), Prosen et al. (1945), and Osborne and Ginnings (1947). Some high-precision thermodynamic and physical-property results have been published in the intervening 50 years for ethylbenzene (c.f. Hossenlopp and Scott, 1981; Osborn and Scott, 1980). These more recent results were exploited by Miller and Scott (1978) in the derivation of ideal-gas properties for ethylbenzene. The results reported here provide a stringent test of the values derived by Miller and Scott (1978). Previous papers in this series (Chirico et al., 1997a−c) have shown significant errors in the thermodynamic property information available in the literature, particularly for entropies of the condensed and gas phases for *m*-xylene (Chirico et al., 1997b) and *o*-xylene (Chirico et al., 1997c).

In the present paper, heat capacity and enthalpy increment determinations for the condensed phases (5 K to 420 K) by adiabatic calorimetry, vapor pressures (306 K to 450 K) by comparative ebulliometry, and two-phase (liquid + vapor) heat capacities to the temperature $T \approx 585$ K by differential-scanning calorimetry (DSC) are reported for ethylbenzene. Saturation heat capacities C_{sat} for the liquid phase from $T = 420$ K 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. The DSC was used also to determine the critical temperature directly. The critical pressure was derived by fitting procedures.

Ethylbenzene has been the subject of many thermodynamic and physical-property investigations including the determination of heat capacities for all phases, vapor pressures, densities, enthalpies of vaporization, critical properties, enthalpy of combustion, and vibrational assignment. Although routinely reported in isolation in the literature, these properties are closely related through thermodynamic relationships and correlations. Consistency between the related properties, through corresponding-states correlations or thermodynamic identities such as the Clapeyron equation, has not been demonstrated in the literature and is emphasized here. Excellent accord between the new results published here and key literature values will be demonstrated. The accord is consistently superior to that shown previously in this research for the xylenes (Chirico et al., 1997a−c).

Problems with statistical calculation of ideal-gas properties for ethylbenzene are discussed. Equilibria calculations for the isomerization of the four C_8H_{10} aromatic hydrocarbons based on the new calorimetric results will be published separately in the fifth paper of this series (Chirico and Steele, 1997a).

This research was completed as part of a program, funded by the Department of Energy (DOE) Office of Fossil Energy, Advanced Oil Recovery (AOR) 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 ethylbenzene and the xylenes provide the basis for structure−

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property correlations for broad families of alkyl-substituted aromatic compounds, which are essential for process development and optimization.

Experimental Procedure

Materials. The ethylbenzene used in this research was obtained by distillation and drying of a commercial sample (Aldrich Chemical Company; "anhydrous" 99+% purity). The sample used in the calorimetric studies was purified by distillation on a spinning band still near 0.1 MPa pressure and dried over activated HPLC-grade silica in a nitrogen atmosphere. The sample was not exposed to oxygen or water after purification. The sample was determined to be 99.99% ethylbenzene 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 (Steele et al., 1988).

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

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 ethylbenzene 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 ethylbenzene 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., 1995).

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

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

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

Table 1. Summary of Vapor-Pressure Results for Ethylbenzene[a]

standard	T/K	p/kPa	Δp/kPa	σ/kPa	ΔT/K
decane	306.244	2.0026	−0.0003	0.0003	0.012
decane	319.752	3.9914	0.0003	0.0005	0.009
decane	325.860	5.3307	0.0005	0.0007	0.006
decane	334.958	8.013	0.001	0.001	0.003
decane	341.719	10.664	0.000	0.001	0.003
decane	347.270	13.353	0.000	0.002	0.003
decane	352.939	16.653	0.000	0.002	0.002
decane	357.739	19.945	−0.001	0.002	0.002
water[b]	363.991	25.016	−0.001	0.003	0.001
decane	364.003	25.025	−0.001	0.002	0.001
water	370.330	31.181	−0.001	0.003	0.001
water	376.709	38.574	−0.001	0.004	0.001
water	383.115	47.359	−0.002	0.005	0.001
water	389.608	57.835	−0.001	0.006	0.001
water	396.119	70.119	0.001	0.007	0.001
water	402.703	84.560	0.001	0.008	0.001
water	409.309	101.317	0.003	0.009	0.001
water	415.986	120.80	0.01	0.01	0.001
water	422.704	143.25	0.00	0.01	0.001
water	429.469	169.02	0.01	0.01	0.001
water	436.288	198.49	0.00	0.02	0.001
water	443.148	232.00	0.00	0.02	0.001
water	450.056	269.98	−0.02	0.02	0.001

[a] Water or decane refers to which material was used as the standard in the reference ebulliometer; T is the condensation temperature of the ethylbenzene; 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 7, 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 ($T_{\mathrm{boil}} - T_{\mathrm{cond}}$). [b] This value was not included in the fits to the vapor pressures.

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 = 60.1 cc) was filled with 43.764 g of ethylbenzene and sealed with a gold-gasketed screw-cap closure under a helium pressure of 5.7 kPa at 296 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 0.2% near $T = 5$ K for ethylbenzene. The maximum correction for vaporization of the sample into the free space of the calorimeter was approximately 0.09% near 410 K.

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

Experimental Results

Vapor Pressures. Vapor pressures for ethylbenzene are reported in Table 1. The pressures, the condensation temperatures, and the difference between condensation and boiling temperatures for the sample are reported. The small differences obtained between the boiling and condensation temperatures indicate correct operation of the equipment and the high purity of the sample.

Table 2. Melting-Study Summary for Ethylbenzene[a]

F	$T(F)$/K
0.2018	178.179
0.3351	178.187
0.6018	178.192
0.8018	178.194
T_{tp}/K	(178.20 ± 0.01)
x	0.0001

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

Table 3. Measurements of Molar Enthalpy Increment $\Delta_{tot}U_m$ for Ethylbenzene (R = 8.314 51 J·K^{-1}·mol^{-1})

N^a	h^b	T_i/K	T_f/K	T_{trs}/K	$\Delta_{tot}U_m{}^c$/(kJ·mol^{-1})	$\Delta_{trs}H_m{}^d$/(kJ·mol^{-1})
		Single-Phase Measurements in the Crystal Phase				
3	1	138.631	173.771		3.400	0.001
4	1	56.005	105.243		3.006	0.001
4	1	105.245	135.744		2.450	0.001
4	1	135.746	174.005		3.677	0.000
		Crystals to Liquid				
1	2	174.735	179.965	178.20	9.819	9.173
3	2	173.788	180.017		9.927	9.173
4	5	173.985	180.382		9.963	9.173
					Average:	9.173
		Single-Phase Measurements in the Liquid Phase				
4	1	180.381	300.591		20.393	−0.003
6	1	288.567	404.664		23.614	−0.002

[a] Adiabatic series number. [b] Number of heating increments. [c] $\Delta_{tot}U_m$ is the molar energy input from the initial temperature T_i to the final temperature T_f. [d] $\Delta_{trs}H_m$ is the net molar enthalpy of transition at the transition temperature T_{trs} or the excess enthalpy for single-phase measurements relative to the heat-capacity curve described in the text and defined in Table 8.

Adiabatic Calorimetry. The enthalpy of fusion and heat capacities for the temperature range 5 K to 420 K were determined by adiabatic calorimetry. Crystallization of the ethylbenzene sample was initiated by cooling (approximately 3 mK·s^{-1}) the liquid sample 15 K to 20 K below the triple-point temperature T_{tp} = 178.20 K. The crystals were annealed by maintaining the sample under adiabatic conditions in the partially melted state (15% to 25% liquid) for approximately 6 h. No spontaneous warming, which would indicate incomplete crystallization or phase conversion, was observed. The sample was cooled at an effective rate of 0.8 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 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 2 were determined from the measurement of the equilibrium melting temperatures $T(F)$ as a function of fraction F of the sample in the liquid state (McCullough and Waddington, 1957). This fractional-melting procedure has been described (Chirico et al., 1997c). The presence of solid-soluble impurities was not indicated.

Experimental molar enthalpy results are summarized in Table 3. 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 3 and 4 were taken without interruption of adiabatic conditions.

Table 4. Molar Heat Capacities $C_{sat,m}$ at Vapor-Saturation Pressure for Ethylbenzene Measured with Adiabatic Calorimetry (R = 8.31451 J·K^{-1}·mol^{-1})

N^a	$\langle T\rangle$/K	ΔT/K	$C_{sat,m}/R^b$	N^a	$\langle T\rangle$/K	ΔT/K	$C_{sat,m}/R^b$
			Crystals				
2	5.194	1.049	0.027	2	47.954	5.021	4.897
2	6.146	0.907	0.046	2	53.266	5.603	5.390
2	7.073	0.937	0.073	3	53.691	4.818	5.429
2	8.026	0.959	0.108	3	58.956	5.558	5.872
2	9.009	0.995	0.158	2	59.180	6.224	5.886
2	10.022	1.034	0.221	3	64.747	6.014	6.317
2	11.123	1.175	0.303	3	71.133	6.757	6.773
2	12.359	1.301	0.408	3	78.250	7.477	7.241
2	13.723	1.431	0.553	3	86.131	8.286	7.731
2	15.229	1.585	0.722	3	94.828	9.108	8.243
2	16.889	1.735	0.934	3	104.220	9.674	8.773
2	18.726	1.940	1.178	3	113.957	9.750	9.306
2	20.761	2.130	1.462	1	123.147	9.848	9.801
2	23.028	2.407	1.790	3	123.783	9.896	9.839
2	25.562	2.662	2.159	1	133.060	9.838	10.342
2	28.392	2.996	2.565	3	133.678	9.888	10.378
2	31.546	3.315	3.000	1	143.976	11.969	10.942
2	35.037	3.667	3.457	1	156.066	12.194	11.631
2	38.899	4.054	3.928	1	168.451	12.435	12.386
2	43.185	4.518	4.407				
			Liquid				
1	183.433	6.928	18.955	1	291.730	15.474	22.091
3	184.435	8.832	18.970	5	292.068	15.473	22.106
1	191.827	9.851	19.098	5	307.928	16.199	22.751
1	202.937	12.363	19.303	5	323.984	15.898	23.436
1	215.497	12.751	19.584	5	340.732	17.540	24.167
1	229.458	15.137	19.942	5	358.576	18.136	24.973
1	244.630	15.206	20.396	5	376.991	18.694	25.818
1	260.244	16.024	20.910	5	395.484	18.311	26.678
1	276.124	15.751	21.485	5	412.430	15.621	27.480

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

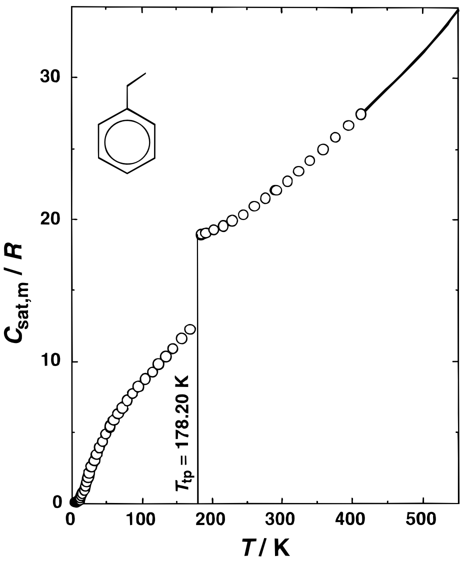

Figure 1. Heat capacity $C_{sat,m}$ against temperature for ethylbenzene. The vertical line indicates the triple-point temperature T_{tp}. (○) $C_{sat,m}$ values measured with adiabatic calorimetry and listed in Table 4. The curve for temperatures T > 420 K was derived with results from the DSC as described in the text.

The experimental molar heat capacities under vapor saturation pressure $C_{sat,m}$ determined by adiabatic calorimetry are listed in Table 4 and shown in Figure 1. Values in Table 4 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 $C_{sat,m}$ with temperature. The precision of the heat-capacity measurements ranged from approximately 5% at T = 5 K to 1% at T = 10 K, 0.2% near T = 20 K, and improved gradually to less than 0.1% above T = 100 K, except in the solid phase near

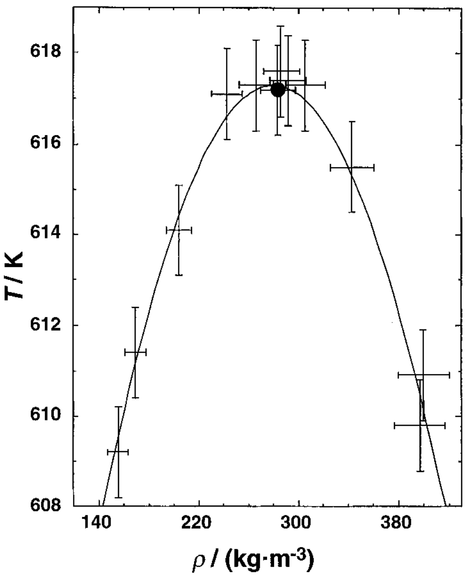

Figure 2. Vapor–liquid coexistence region for ethylbenzene. The crosses span the range of uncertainty for the measurement results of this research. (●) Critical temperature (Ambrose et al., 1960) and critical density (Simon, 1957) selected by Tsonopoulos and Ambrose (1995). The curve provides an aid to the eye.

Table 5. Densities ρ and Temperatures for the Conversion from Two Phases (Liquid + Vapor) to One Phase (Fluid) for Ethylbenzene Measured by DSC

ρ/(kg·m^{-3})	T/K	ρ /(kg·m^{-3})	T/K
138	607.2	287	617.6
156	609.2	292	617.4
170	611.4	306	617.3
205	614.1	343	615.5
243	617.1	397	609.8
267	617.3	400	610.9

T_{tp} where equilibration times were long. The heat capacities in Table 4 have not been corrected for premelting, but an independent calculation can be made with the temperature increments provided.

Equilibrium was reached in less than 1 h for heat-capacity measurements in the liquid phase. Equilibration times for the crystal phase of ethylbenzene were less than 1 h for temperatures below 165 K and increased smoothly to 12 h near T_{tp} = 178.20 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 ethylbenzene 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 5 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 2. Details of the method used were described recently (Steele, 1995). The critical temperature derived from the DSC measurements, (617.3 ± 1.0) K, is in excellent accord with the value selected by Tsonopoulos and Ambrose (1995) (617.15 ± 0.10) K in their recent review, as shown in the figure. The more precise value measured by Ambrose et al. (1960) and selected by Ambrose and Tsonopoulos (1995) was used in all calculations of this research.

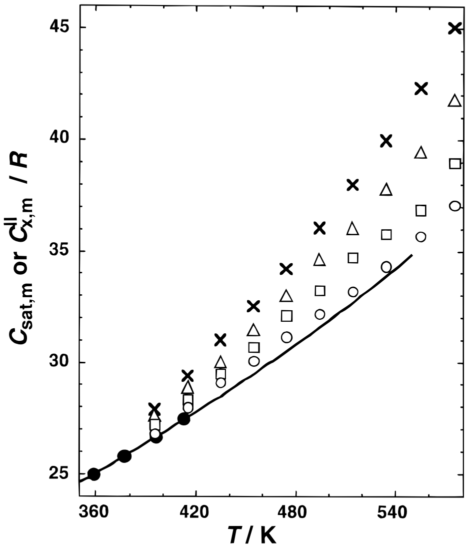

Figure 3. Curve of heat capacity against temperature for ethylbenzene. $C^{II}_{x,m}$ by DSC for four cell fillings: (○) 21.19 mg; (□) 15.49 mg; (△) 11.19 mg; (×) 8.26 mg of sample. (●) $C_{sat,m}$ determined by adiabatic calorimetry in this research. The curve represents the saturation heat capacities derived in this research and listed in Table 8.

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 fillings, vapor pressures, and reliable liquid-density values are required.

Table 6 lists molar two-phase heat capacities $C^{II}_{x,m}$ for ethylbenzene obtained for four cell fillings with the DSC. Heat capacities were determined at 20-K intervals with a heating rate of 0.083 K·s^{-1} and a 120-s equilibration period between heats. Figure 3 shows the $C^{II}_{x,m}$ values determined by DSC and $C_{sat,m}$ values determined by adiabatic

Table 6. Measured Two-Phase (Liquid + Vapor) Heat Capacities $C^{II}_{x,m}$ for Ethylbenzene[a]

T/K	$C^{II}_{x,m}/R$ for V(cell) = 0.052 17 cm^3 m = 0.021 19 g	$C^{II}_{x,m}/R$ for V(cell) = 0.052 19 cm^3 m = 0.015 49 g	$C^{II}_{x,m}/R$ for V(cell) = 0.052 17 cm^3 m = 0.011 19 g	$C^{II}_{x,m}/R$ for V(cell) = 0.052 19 cm^3 m = 0.008 26 g
395.0	26.80	27.21	27.61	27.89
415.0	27.96	28.33	28.87	29.37
435.0	29.10	29.45	30.00	31.02
455.0	30.04	30.71	31.46	32.51
475.0	31.12	32.08	33.00	34.18
495.0	32.18	33.23	34.62	36.02
515.0	33.17	34.71	36.03	37.96
535.0	34.33	35.76	37.79	39.96
555.0	35.67	36.85	39.48	42.33
575.0	37.06	38.95	41.84	45.02

[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}).

calorimetry. The effect of vaporization of the sample into the free space of the DSC 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 1 and the $C^{\mathrm{II}}_{\mathrm{x,m}}$ values given in Table 6 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 in this research for the temperature range $358 < (T/\mathrm{K}) < 412$ 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 T_{c} value selected by Tsonopoulos and Ambrose (1995), 617.15 K, was used in the fits. The designation (2,4) refers to the exponents of the last two terms in the equation. Recently, Wagner and co-workers (Duschek et al., 1990) used the (2,4) form to represent the vapor pressures of carbon dioxide from T_{tp} to the critical temperature. Subsequently, the (2,4) form was used to represent successfully the vapor pressures of pyridine from T_{tp} to T_{c} (Chirico et al., 1996), as well as those of the three xylenes from approximately 250 K to T_{c} (Chirico et al., 1997a−c).

The critical pressure was included initially as a variable in the fits. The derived p_{c} value (3630 ± 40) kPa was found to be in accord with the more precise value recommended by Tsonopoulos and Ambrose (1995), (3609 ± 10) kPa, and with that measured recently by Wilson et al. (1995), (3616 ± 5) kPa. The value reported by Wilson et al. (1995) was published after the review by Tsonopoulos and Ambrose (1995) and was not considered in their analysis. The value $p_{\mathrm{c}} = 3610$ kPa was used in all calculations of the present research. The small difference between this value and that recommended by Tsonopoulos and Ambrose or measured by Wilson et al., does not have a significant effect on the properties derived here.

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

$$C^{\mathrm{II}}_{\mathrm{x,m}} = C^{\mathrm{II}}_{\mathrm{x,m}} - T/n\ \{(\partial V_x/\partial T)_x(\partial p/\partial T)_{\mathrm{sat}}\} \quad (3)$$

where n is the number of moles of ethylbenzene used for the particular cell filling, as listed in Table 6. The equation for the variation of the cell volume with temperature $(\partial V_x/\partial T)_x$ has been published (Steele, 1995). The vapor-pressure fit was used for calculation of $(\partial p/\partial T)_{\mathrm{sat}}$. The values of $C^{\mathrm{II}}_{\mathrm{x,m}}$ and the vapor pressures were used in a weighted nonlinear least-squares fit to derive required 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

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

Table 7. Parameters for Eqs 2 and 4, Critical Constants, and Acentric Factor for Ethylbenzene

$A = -7.350\,768$	$b_0 = -0.432\,04$
$B = \ \ 1.252\,545$	$b_1 = -0.433\,96$
$C = -0.737\,422$	$b_2 = \ \ 0.513\,07$
$D = -4.311\,384$	$b_3 = -0.708\,84$

$T_{\mathrm{c}} = 617.15$ K $\quad p_{\mathrm{c}} = 3610$ kPa $\quad \rho_{\mathrm{c}} = 285\ \mathrm{kg{\cdot}m^{-3}}$ $\quad \omega = 0.3033$

Table 8. Molar Thermodynamic Functions at Vapor-Saturation Pressure for Ethylbenzene[a] (R = 8.31451 J·K^{-1}·mol^{-1})

T/K	$C_{\mathrm{sat,m}}/R$	$\Delta_0^T S_{\mathrm{m}}/R$	$\Delta_0^T H_{\mathrm{m}}/RT$	T/K	$C_{\mathrm{sat,m}}/R$	$\Delta_0^T S_{\mathrm{m}}/R$	$\Delta_0^T H_{\mathrm{m}}/RT$
			Crystals				
5.00	0.024	0.008	0.006	90.00	7.962	7.171	4.160
10.00	0.220	0.069	0.053	100.00	8.537	8.040	4.569
15.00	0.695	0.239	0.180	110.00	9.091	8.880	4.955
20.00	1.354	0.527	0.389	120.00	9.631	9.694	5.323
30.00	2.789	1.349	0.951	130.00	10.173	10.486	5.675
40.00	4.055	2.330	1.574	140.00	10.720	11.260	6.016
50.00	5.092	3.350	2.177	150.00	11.279	12.019	6.348
60.00	5.955	4.357	2.737	160.00	11.847	12.765	6.674
70.00	6.694	5.332	3.251	170.00	12.419	13.500	6.995
80.00	7.352	6.269	3.723	178.20	12.891	14.096	7.255
			Liquid				
178.20	18.877	20.287	13.446	360.00	25.038	35.133	17.499
180.00	18.903	20.477	13.501	380.00	25.957	36.511	17.920
200.00	19.246	22.486	14.058	400.00	26.886	37.866	18.345
220.00	19.694	24.340	14.549	420.00	27.861	39.201	18.774
240.00	20.252	26.077	15.000	440.0[b]	28.83	40.52	19.21
260.00	20.902	27.723	15.428	460.0[b]	29.81	41.82	19.65
280.00	21.633	29.298	15.845	480.0[b]	30.82	43.11	20.09
298.15	22.350	30.679	16.219	500.0[b]	31.87	44.39	20.54
300.00	22.425	30.817	16.257	520.0[b]	32.99	45.66	21.00
320.00	23.263	32.291	16.668	540.0[b]	34.23	46.93	21.47
340.00	24.135	33.728	17.082	550.0[b]	34.93	47.56	21.71

[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.

Four terms were used in this research, i.e., expansion to $n = 3$. Table 7 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 1.

Molar saturation heat capacities $C_{\mathrm{sat,m}}$ for ethylbenzene were derived with the equation

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

Temperature derivatives of the pressure were calculated with the Wagner-equation parameters listed in Table 7. Molar volumes of the liquid $V_{\mathrm{m}}(\mathrm{l})$ were calculated with densities obtained with a form of the corresponding-states equation of Riedel (1954):

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

Values of $(\partial^2\mu/\partial T^2)_{\mathrm{sat}}$ were determined with the derived coefficients for eq 4, as listed in Table 7. The derived $C_{\mathrm{sat,m}}$ values are included in Table 8. The estimated uncertainty in these values is 1%. Derived $C_{\mathrm{sat,m}}$ values for ethylbenzene are included in Figures 1 and 3.

Critical Density. Tsonopoulos and Ambrose (1995) recommended the value $\rho_{\mathrm{c}} = (283 \pm 4)\ \mathrm{kg{\cdot}m^{-3}}$ for the critical density of ethylbenzene on the basis of the mea-

Table 9. Enthalpies of Vaporization $\Delta_l^g H_m$ for Ethylbenzene 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]	45.23 ± 0.08	340.00	39.83 ± 0.06	460.00[a]	32.03 ± 0.17
260.00[a]	44.61 ± 0.08	360.00	38.65 ± 0.06	480.00[a]	30.41 ± 0.22
280.00[a]	43.38 ± 0.07	380.00	37.45 ± 0.07	500.00[a]	28.65 ± 0.26
298.15[a]	42.28 ± 0.07	400.00	36.21 ± 0.08	520.00[a]	26.69 ± 0.32
300.00[a]	42.17 ± 0.07	420.00	34.90 ± 0.10	540.00[a]	24.51 ± 0.37
320.00	40.99 ± 0.07	440.00	33.52 ± 0.13	550.00[a]	23.31 ± 0.41

[a] Values at this temperature were calculated with extrapolated vapor pressures determined from the fitted Wagner coefficients listed in Table 7.

Table 10. Standard Molar Thermodynamic Properties in the Ideal-Gas State for Ethylbenzene at $p = p° = 101.325$ kPa ($R = 8.314\ 51$ J·K^{-1}·mol^{-1})

T/K	$\Delta_0^T H°_m/RT$	$\Delta_{imp} H°_m/RT$[a]	$\Delta_0^T S°_m/R$	$\Delta_{imp} S°_m/R$[b]	$\Delta_f H°_m/RT$	$\Delta_f S°_m/R$	$\Delta_f G°_m/RT$
250.00[c]	36.98 ± 0.04	0.00	40.89 ± 0.05	0.00	16.42 ± 0.18	−38.83 ± 0.05	55.24 ± 0.18
260.00[c]	36.06 ± 0.04	0.00	41.41 ± 0.05	0.00	15.38 ± 0.17	−39.24 ± 0.05	54.62 ± 0.17
280.00[c]	34.48 ± 0.04	0.00	42.44 ± 0.04	0.00	13.53 ± 0.16	−40.02 ± 0.04	53.55 ± 0.16
298.15[c]	33.28 ± 0.03	0.01	43.37 ± 0.04	0.01	12.07 ± 0.15	−40.67 ± 0.04	52.74 ± 0.15
300.00[c]	33.17 ± 0.03	0.01	43.46 ± 0.04	0.01	11.93 ± 0.15	−40.74 ± 0.04	52.67 ± 0.15
320.00	32.09 ± 0.03	0.02	44.49 ± 0.04	0.01	10.56 ± 0.14	−41.39 ± 0.04	51.94 ± 0.14
340.00	31.20 ± 0.03	0.03	45.52 ± 0.04	0.03	9.37 ± 0.13	−41.98 ± 0.04	51.34 ± 0.13
360.00	30.47 ± 0.03	0.06	46.55 ± 0.04	0.04	8.32 ± 0.12	−42.51 ± 0.04	50.83 ± 0.13
380.00	29.86 ± 0.03	0.09	47.57 ± 0.04	0.07	7.41 ± 0.12	−43.00 ± 0.04	50.41 ± 0.12
400.00	29.36 ± 0.03	0.13	48.59 ± 0.05	0.10	6.60 ± 0.11	−43.45 ± 0.05	50.05 ± 0.12
420.00	28.96 ± 0.04	0.19	49.61 ± 0.05	0.14	5.89 ± 0.11	−43.85 ± 0.05	49.74 ± 0.11
440.00	28.63 ± 0.05	0.26	50.63 ± 0.06	0.19	5.26 ± 0.11	−44.22 ± 0.06	49.48 ± 0.11
460.00[c]	28.37 ± 0.06	0.34	51.64 ± 0.07	0.25	4.69 ± 0.11	−44.56 ± 0.07	49.25 ± 0.11
480.00[c]	28.16 ± 0.07	0.45	52.64 ± 0.08	0.33	4.18 ± 0.12	−44.87 ± 0.08	49.06 ± 0.11
500.00[c]	28.00 ± 0.09	0.57	53.64 ± 0.09	0.41	3.73 ± 0.12	−45.16 ± 0.09	48.89 ± 0.11
520.00[c]	27.88 ± 0.11	0.70	54.62 ± 0.11	0.52	3.31 ± 0.14	−45.43 ± 0.11	48.74 ± 0.12
540.00[c]	27.78 ± 0.13	0.86	55.59 ± 0.13	0.63	2.93 ± 0.15	−45.68 ± 0.13	48.60 ± 0.14
550.00[c]	27.75 ± 0.14	0.95	56.08 ± 0.14	0.70	2.75 ± 0.16	−45.79 ± 0.14	48.54 ± 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 $T \rightarrow 0$ K. [b] Gas imperfection correction included in the ideal-gas entropy. [c] Values at this temperature were calculated with extrapolated vapor pressures calculated from the fitted Wagner-equation parameters listed in Table 7.

surements of Simon (1957). Subsequent to the review by Tsonopoulos and Ambrose, Wilson et al. (1995) measured $\rho_c = (285.4 \pm 0.8)$ kg·m^{-3} for ethylbenzene with a static method. In the present research, the value $\rho_c = 285$ kg·m^{-3} was used with eq 6. Comparisons of literature densities with values calculated with eq 6 will be described separately (Chirico and Steele, 1997b). Systematic deviations exist but do not exceed ±1%. Propagated errors due to a 1% uncertainty in densities calculated with eq 7 are negligible for all properties derived here.

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

$$dp/dT = \Delta_l^g H_m/(T\Delta_l^g V_m) \tag{7}$$

$\Delta_l^g V_m$ is the difference in molar volume between the liquid and the real vapor. Estimates of liquid-phase volumes were made with eq 6. Vapor-phase volumes were calculated with the virial equation of state truncated at the third virial coefficient. Second virial coefficients were estimated with the corresponding-states equation of Pitzer and Curl (1957), and third virial coefficients were estimated with the corresponding-states method of Orbey and Vera (1983). This formulation for third virial coefficients was applied successfully in analyses of the thermodynamic properties of pyridine (Chirico et al., 1996), benzene and toluene (Chirico and Steele, 1994), 2-methylaniline (Steele et al., 1994), and the xylenes (Chirico et al., 1997a−c). Uncertainties in the virial coefficients were assumed to be 5%. Derived enthalpies of vaporization are reported in Table 9. 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 $T \rightarrow 0$ K for the solid and liquid phases of ethylbenzene are listed in Table 8. The tabulated values were derived by integration of the smoothed heat capacities corrected for premelting, together with the entropies and enthalpies of fusion. The integration procedure has been described (Chirico et al., 1997b,c). Premelting corrections were made by means of published methods (Westrum et al., 1968) for solid-insoluble impurities with the mole-fraction impurity value 0.0001.

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 ethylbenzene using values in Tables 8 and 9 and are listed in columns 2 and 4 of Table 10. Entropies and enthalpies of compression to 101.325 kPa were calculated on the basis of the virial equation truncated after the third virial coefficient:

$$pV_m = RT + Bp + C'p^2 \tag{8}$$

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 10. 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 ethylbenzene were combined with the enthalpy of formation of the liquid phase $-(12.39 \pm 0.72)$ 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 10. The uncertainty in the enthalpy of formation of the liquid phase is the "uncertainty interval" defined by Rossini (1956). The enthalpies of formation of CO_2(g) and H_2O(l) were taken as $-(393.51 \pm 0.13)$ kJ·mol^{-1} and $-(285.830 \pm 0.420)$ kJ·mol^{-1}, respectively, as assigned by CODATA (Cox et al., 1989). 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 10 represent 1 standard deviation and do not include uncertainties in the properties of the elements.

Comparisons with Literature Values

The thermophysical and thermochemical properties of ethylbenzene 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 energy of combustion of ethylbenzene was measured by Coops et al. (1953), Prosen et al. (1945), Richards and Barry (1915) and Jesse (1912). Values reported by Richards and Barry (1915) and Jesse (1912) are of historical interest only. The enthalpy of combustion for the liquid phase of ethylbenzene reported by Coops et al. (1953) is 2.5 kJ·mol^{-1} more positive than that reported by Prosen et al. Similar differences between the results of these research groups are observed for the xylenes. A preliminary energy of combustion for *o*-xylene was measured in this laboratory as part of research on the xylenes and was found to be in excellent agreement with the value reported by Prosen et al. (1945). Consequently, the values reported by Prosen et al. for the xylenes and ethylbenzene were used in all calculations of this research.

Vapor Pressures. Previously reported ebulliometric studies (Forziati et al., 1949; Willingham et al., 1945; Osborn and Scott, 1980) are in excellent accord with the results of this research as shown in Figure 4. The values are shown relative to vapor pressures calculated with eq 2 and the parameters listed in Table 7. The value at the lowest temperature reported by Forziati et al., $T = 329.8$ K, is 0.22% high and is not shown in the figure.

Vapor pressures for ethylbenzene between 430 K and T_c (617.15 K) have been measured by Akhundov (1973), Ambrose et al. (1967), and Newitt and Burgoyne (1936). Deviations from values calculated with eq 2 and the parameters listed in Table 7 are shown in Figure 5. Deviations for the results of Newitt and Burgoyne (1936) range from 8% high near 460 K to 6% low between 540 K and 608 K and are not shown in the figure. Deviations for the values listed by Ambrose et al. (1967) and Akhundov (1973) do not exceed 0.8%.

Ambrose et al. (1967) and Akhundov and co-workers also measured high-temperature vapor pressures for the three xylenes. Deviations similar to those shown in Figure 5 were observed between these literature values and those calculated with the (2,4)-form of the Wagner equation fitted to our ebulliometric results for the xylenes (Chirico et al., 1997a−c). Values reported by Ambrose et al. (1967) were shown to be consistently lower than those of this research by several tenths of 1% for the temperature range $430 < (T/\mathrm{K}) < 600$ for all of the xylenes. This result is also obtained in the present research. Deviations in the region of overlap between the values measured by Ambrose et al. (1967) and those of this research, $430 < (T/\mathrm{K}) < 450$, indicate that several tenths of 1% is near the accuracy limits of the values reported by Ambrose et al. (1967).

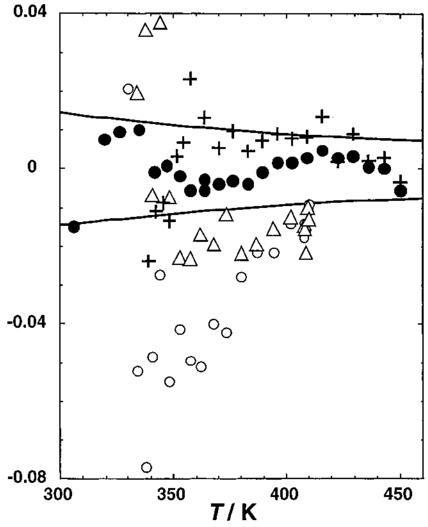

Figure 4. Deviation plot for ethylbenzene vapor pressures; *p*(calc) represents the values calculated with eq 2 and the parameters listed in Table 7. Values of *p*(expt): (●) Fitted values of this research (Table 1); (+) Osborn and Scott (1980); (△) Forziati et al. (1949); (○) Willingham et al. (1945). The curved lines indicate the estimated experimental uncertainties (1 standard deviation) for the values of this research (eq 1).

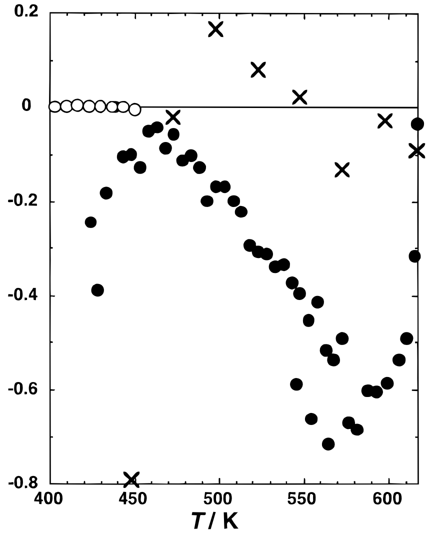

Figure 5. Deviation plot for ethylbenzene vapor pressures at high temperatures; *p*(calc) represents the values calculated with eq 2 and the parameters listed in Table 7. Values of *p*(expt): (○) fitted values of this research (Table 2); (●) Ambrose et al. (1967); (×) Akhundov (1973).

Comparisons with other literature values are shown in Figure 6. The vertical axis in Figure 6 is expanded by a factor of approximately 20 relative to that of Figure 4. Values reported by Rintelen et al. (1937) for temperatures between 283 K and 323 K range from 25% to 2% lower than

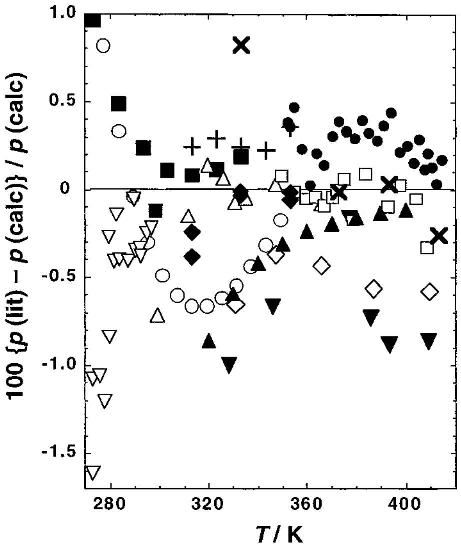

Figure 6. Low-resolution deviation plot for ethylbenzene vapor pressures; p(calc) represents the values calculated with eq 2 and the parameters listed in Table 7. Values of p(expt): (×) Sühnel and Wittig (1983); (◆) Funk et al. (1972); (□) Kraus and Linek (1971); (+) Kind et al. (1968); (△) Chaiyavech and Van Winkle (1959); (▼) Dreyer et al. (1955); (◇) Yang and Van Winkle (1955); (▽) Scott and Brickwedde (1945); (●) Young and Fortey (1903). The following results were provided in equation form only: (▲) Paul et al. (1986); (■) Guttman and Westrum (1943); (○) Stuckey and Saylor (1940).

the calculated values and are not shown in the figure. Values reported by Woringer (1900) for temperatures between 273 K and 408 K show very large deviations from the values of this research, particularly at the lower temperatures. The relatively crude measurements by Buck et al. (1949) are in good accord with those of this research but show large scatter (±2%) and are not shown. Also, values measured by Linder (1931) show large deviations and are not shown in the figure.

Vapor pressure values obtained at one or two temperatures as part of vapor−liquid equilibria (VLE) studies were not included in the comparisons. These are typically of low precision and are often performed on materials of relatively low purity.

Densities. Densities for ethylbenzene have been reported in the literature from near T_{tp} to near T_c. This extensive literature will be reviewed in a separate paper concerning the densities of the xylenes and ethylbenzene (Chirico and Steele, 1997b). The Riedel equation (eq 6) will be shown to provide values in good accord with the experimental values (within ±1%); however, the deviations far exceed the experimental uncertainties for the best available density values. Alternative density representations such as those suggested by Campbell and Thodos (1985) and Spencer and Danner (1972) will also be discussed in the separate paper (Chirico and Steele, 1997b). The correlation of Riedel (1954) provides values of adequate precision for the calculations of the present research.

Enthalpies of Vaporization. Enthalpies of vaporization for ethylbenzene for a range of temperatures were reported by Svoboda et al. (1982), Hossenlopp and Scott (1981), and Bittrich and Kind (1969). Al-Dhahir and Swan (1982) reported a single value at $T = 408$ K with a gas-chromatographic technique. Calorimetrically determined single values were reported by Osborne and Ginnings (1947) and Scott and Brickwedde (1945) of the National Bureau of Standards, Saito and Kusano (1973), Kolossowsky and Megénine (1931), and Mathews (1926). The literature values are compared in Figure 7 with those calculated in this research with the fitted Wagner equation (eq 2) and the Clapeyron equation (eq 7), as described earlier. The values reported by Scott and Brickwedde (1945), Osborne and Ginnings (1947), and Hossenlopp and Scott (1981) are in excellent accord with those derived in the present research; the others are not. This excellent accord supports the validity of the corresponding-states methods (Pitzer and Curl, 1957; Orbey and Vera, 1983) used to estimate the required virial coefficients.

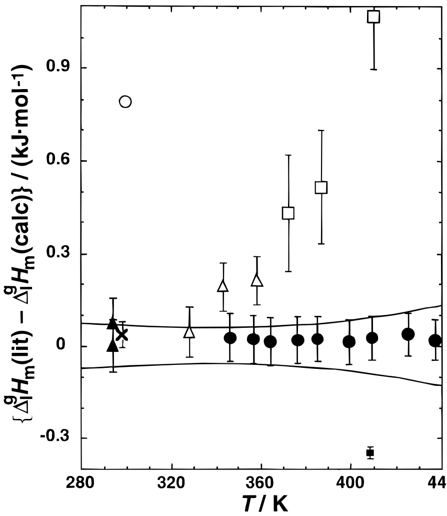

Figure 7. Deviation plot for ethylbenzene enthalpies of vaporization $\Delta_l^g H_m$. $\Delta_l^g H_m$(calc) represents values derived with the Clapeyron equation in this research and listed in Table 6. —, Error limits (1 standard deviation) assigned to the calculated $\Delta_l^g H_m$ values. Values of $\Delta_l^g H_m$(lit): (△) Svoboda et al. (1982); (●) Hossenlopp and Scott (1981); (□) Bittrich and Kind (1969); (×) Osborne and Ginnings (1947); (▲) Scott and Brickwedde (1945); (○) Kolossowsky and Megénine (1931); (■) Mathews (1926).

Condensed-Phase Heat Capacities and Entropies. Heat capacities for ethylbenzene by adiabatic calorimetry were first reported by Huffman et al. (1930) for temperatures between 93 K and 305 K. Subsequently, measurements between 15 K and 300 K were completed by Scott and Brickwedde (1945) of the National Bureau of Standards and Guthrie et al. (1944) of this laboratory. Both of these later studies are in good accord with the results of the present research, as shown in Figure 8. Heat capacity values published by Huffman et al. (1930) are low by approximately 0.5 to 2.5% and are not shown in the figure for clarity. The literature heat-capacity values were not adjusted for changes in temperature scale. Such adjustments rarely exceed 0.1% and were not justified.

The enthalpies of fusion reported by Scott and Brickwedde (1945) and Guthrie et al. (1944) are in excellent accord (within ±0.1%) with the value obtained in the present research. The triple-point temperatures reported by Guthrie et al., (178.20 ± 0.03) K, and Scott and Brickwedde, (178.18 ± 0.01) K, are also in accord with that of this research, (178.20 ± 0.01) K. The uncertainty assigned to the value of this research includes uncertainties associated with calibration of the thermometer.

Johnson et al. (1990) measured enthalpies for the liquid phase of ethylbenzene (349 K to 551 K, 1.5 bar to 200 bar) with a flow calorimeter and reported heat capacities as a function of pressure for pressures between 20 bar and 200 bar. $C_{sat,m}$ values were calculated in the present research by extrapolation of the $C_{p,m}$ values to the saturation pressure. The extrapolated values are shown in Figure 8 to be in good accord with those of the present research. Johnson et al. (1990) claimed uncertainties of ±2% for their

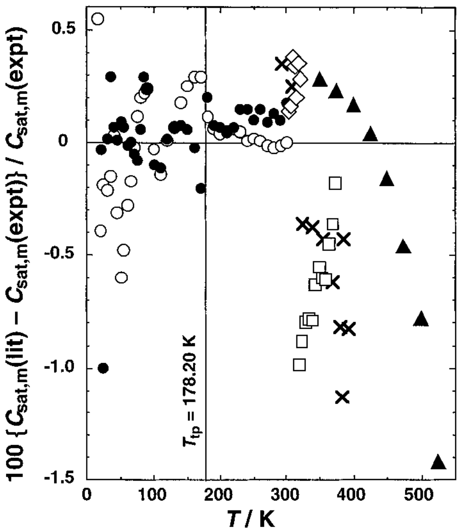

Figure 8. Deviation plot for ethylbenzene condensed-phase heat capacities. $C_{sat,m}$(expt) are the results of the present research (Table 8). Values of $C_{sat,m}$(lit): (□) Garg et al. (1993); (◇) Jain et al. (1992); (▲) Johnson et al. (1990); (×) Andolenko and Grigorév (1979); (●) Scott and Brickwedde (1945), smoothed values; (○) Guthrie et al. (1944), smoothed values. Additional citations are provided in the text. The vertical line indicates the triple-point temperature.

heat-capacity values. The largest deviation shown in Figure 8 is 1.4%.

Kurbatov (1947) reported heat capacities for ethylbenzene in the liquid phase between 288 K and 463 K derived from enthalpy-increment measurements. Deviations of values calculated with the linear equation provided by Kurbatov from the values of this research range from 1% low near 288 K to 7% high near 463 K. Similar large deviations were found for the xylenes (Chirico et al., 1997a−c).

Heat capacity values for the liquid phase for short temperature ranges between 300 K and 380 K were reported by Garg et al. (1993), Jain et al. (1992), Blacet et al. (1931), and Williams and Daniels (1924). Garg et al. (1993) and Jain et al. (1992) claimed accuracies of 0.1% or better for their measured values. These assessments are overly optimistic, as shown in Figure 8. Heat capacities reported by Blacet et al. (1931) range from 4% low near 285 K to 7% high near 370 K and are not shown in the figure. Values reported by Williams and Daniels (1924) and Smith and Andrews (1931) are 1 to 3% low and also are not shown in the figure. The results of Williams and Daniels (1924) for the xylenes showed similar large deviations. Heat capacities reported before 1900 or for single temperatures were not considered in the comparisons here.

Comparisons of Standard Entropies and Heat Capacities from Calorimetric Studies with Values from Spectroscopic Studies and Statistical Thermodynamics. The calculation of standard entropies $\Delta_0^T S^\circ_m$ and standard heat capacities $C^\circ_{p,m}$ for ethylbenzene with assigned vibrational spectra and statistical thermodynamics is complicated by the presence of two internal rotations with significant hindering potentials; rotation of the phenyl group with respect to the ethyl group and rotation of the methyl group. Miller and Scott (1978), Taylor et al. (1946), and Brickwedde et al. (1945) calculated standard thermodynamic properties for ethylbenzene with wavenumbers from vibrational spectra and selected rotational barriers. The rotational barriers were adjusted to force agreement between the statistical and calorimetric $\Delta_0^T S^\circ_m$ values near 300 K and $C^\circ_{p,m}$ values at higher temperatures. Taylor et al. (1946) and Brickwedde et al. (1945) used a $C^\circ_{p,m}$ value measured by Scott and Mellors (1945) near 373 K. Miller and Scott (1978) used $C^\circ_{p,m}$values between $T = 386$ K and $T = 523$ K determined with vapor-flow calorimetry by Hossenlopp and Scott (1981). Calorimetrically derived $\Delta_0^T S^\circ_m$ values near $T = 300$ K were based on the adiabatic calorimetry results of Guthrie et al. (1944) and Scott and Brickwedde (1945) combined with the enthalpy of vaporization measured by Osborne and Ginnings (1947).

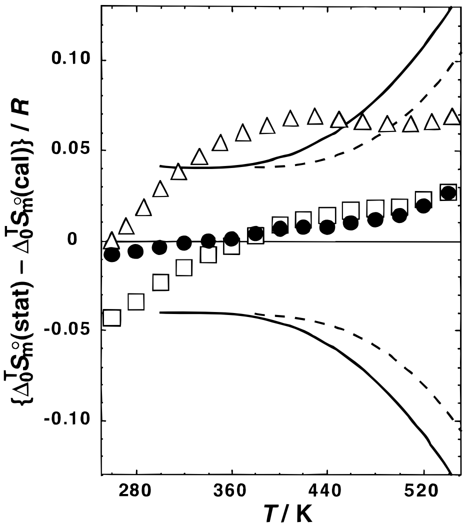

Figure 9. Deviation plot for ethylbenzene standard entropies. —, Error limits (1 standard deviation) assigned to the calorimetric values $\Delta_0^T S^\circ_m$(cal) (Table 10); - - -, error limits without uncertainty in the virial coefficients. $\Delta_0^T S^\circ_m$(stat) was calculated with the wavenumber values and rotational barriers listed by: (●) Miller and Scott (1978); (□) Taylor et al. (1946); (△) Brickwedde et al. (1945).

Standard entropies calculated by Miller and Scott (1978), Taylor et al. (1946), and Brickwedde et al. (1945) are shown in Figure 9 relative to the calorimetrically derived values of this research (Table 10) between $T = 250$ K and $T = 550$ K. Deviations are small, particularly for the values listed by Miller and Scott (1978). Deviations for the values of Miller and Scott (1978) do not exceed 0.03R (i.e., less than 0.05% of $\Delta_0^T S^\circ_m$) for the entire temperature range.

The wavenumber values not involving the internal rotations (i.e., 46 fundamental vibrations) used by Miller and Scott (1978), Taylor et al. (1946), and Brickwedde et al. (1945) differ significantly. Contributions to $\Delta_0^T S^\circ_m$ calculated with the different wavenumber values differ from each other by up to 0.23R, which is much larger than the uncertainties in the $\Delta_0^T S^\circ_m$ values derived in the present research (see Table 10 and Figure 9). In all cases adjustment of the rotational barrier heights by Miller and Scott (1978), Taylor et al. (1946), and Brickwedde et al. (1945) compensated for the differences in the vibrational assignments.

Miller and Scott (1978) reported 17.15 kJ·mol^{-1} and 4.85 kJ·mol^{-1} for the methyl group and phenyl group rotation barriers, respectively, while Taylor et al. (1946) listed 14.2 kJ·mol^{-1} and 4.5 kJ·mol^{-1}, and Brickwedde et al. (1945) listed 11.3 kJ·mol^{-1} and 5.4 kJ·mol^{-1} for the analogous values. Until a definitive vibrational assignment for ethylbenzene in the vapor phase is determined, rotational barriers derived in this manner have little physical significance. Miller and Scott (1978), Taylor et al. (1946), and Brickwedde et al. (1945) all recognized this fact, but this is not often recognized by other researchers using their work.

The approaches used by Miller and Scott (1978), Taylor et al. (1946), and to a lesser extent, Brickwedde et al. (1945) were successful for ethylbenzene because the original thermodynamic-property measurements from the 1940s (Guthrie et al., 1944; Scott and Brickwedde, 1945; Osborne and Ginnings, 1947) were of high quality. Miller and Scott (1978) further benefited from the availability of the vapor-flow calorimetric results of Hossenlopp and Scott (1981). By an analogous method, Draeger (1985) and Chao et al. (1984) attempted to force accord between calorimetric and statistically derived $\Delta_0^T S_m^\circ$ and $C_{p,m}^\circ$ values for the xylenes. They were not successful, particularly for *m*-xylene (Chirico et al., 1997b) and *o*-xylene (Chirico et al., 1997c) because the standard entropies with which they attempted to force agreement were incorrect.

Colgate et al. (1990) determined $C_{p,m}^\circ$ values at four temperatures between 298.15 K and 408.15 K with an acoustical method. The authors claimed an overall uncertainty of 0.1%. The value listed by Colgate et al. (1990) at $T = 298.15$ K is 2% lower than that calculated by Miller and Scott (1978), while those between $T = 323$ K and $T = 408$ K are scattered within ±0.3%. As described earlier, Miller and Scott based their calculations in part upon a forced agreement between their calculated $C_{p,m}^\circ$ values and those derived by Hossenlopp and Scott (1981) from vapor-flow calorimetry for temperatures between 386 K and 523 K. The uncertainty claimed by Colgate et al. (1990) appears optimistic, particularly at the lowest temperature. It is highly improbable that the statistical calculations of Miller and Scott (1978) would provide values within 0.3% between 323 K and 523 K and yet be in error by 2% at $T = 298$ K.

Mamedov et al. (1976) measured isobaric heat capacities for ethylbenzene vapors with an adiabatic flow calorimeter. They reported heat capacities of the vapor at the saturation pressure $C_{p,m}$ for temperatures from $T = 480$ K to $T = 602$ K. The corresponding pressures were 0.5 MPa to 3.0 MPa. An attempt was made in the present research to convert the $C_{p,m}$ values to standard heat capacities $C_{p,m}^\circ$ with the equation:

$$(C_{p,m} - C_{p,m}^\circ) = -T\,[(d^2B/dT^2) + (d^2C'/dT^2) + ...] \qquad (9)$$

truncated after the third virial coefficient. After conversion to $C_{p,m}^\circ$, the value near $T = 480$ K (at $p = 0.5$ MPa) reported by Mamedov et al. (1976) was only 0.8% higher than the value determined calorimetrically by Hossenlopp and Scott (1981) and calculated by Miller and Scott (1978). The difference $(C_{p,m} - C_{p,m}^\circ)$ was 6% of the measured $C_{p,m}$ value at $T = 480$ K. Mamedov et al. (1976) claimed uncertainties of 1% to 1.2% for their $C_{p,m}$ values near the saturation line. At higher pressures (i.e., $p \geq 1$ MPa), the adjustments of the $C_{p,m}$ values with eq 9 were inadequate, and it was apparent that virial coefficients beyond the third were required.

Miller and Scott (1978) based their wavenumber values primarily upon vapor-phase far-infrared and Raman spectra at low wavenumbers together with liquid-phase spectra for some high wavenumbers. Wavenumbers were reported as a list and were not assigned to specific molecular vibrations. Recently, Gruner and Brumer (1991) calculated wavenumbers for the vibrational modes of ethylbenzene with a semi-empirical "consistent force field" technique. Their results show large differences from those of Miller and Scott (1978) even for low wavenumber values. It is apparent that a definitive vibrational assignment for ethylbenzene in the vapor phase is yet to be established. Once it is established, it will then be possible to test proposed restricting potentials with the calorimetric results provided here in Table 10.

Attempts to determine rotational barriers for the methyl and ethyl groups of ethylbenzene by experiment and calculations continue to appear in the literature (cf. Schaefer et al., 1994; Caminati et al., 1991; Reynolds, 1988; Schaefer et al., 1987; Camail et al., 1975). Values derived to date agree qualitatively with those suggested by Miller and Scott (1978) but are not of sufficient precision to provide a check on the validity of the vibrational assignment.

Conclusions

Standard thermodynamic properties for ethylbenzene based on calorimetric and physical-property studies are reported for temperatures between 250 K and 550 K. Thermodynamic consistency was demonstrated for heat capacities of condensed and vapor phases, vapor pressures, enthalpies of vaporization, virial coefficients, densities, and critical properties. The calorimetrically derived thermodynamic property values of this research will be used to calculate aromatic C_8H_{10} isomerization equilibria over a broad temperature range. These results will be published separately (Chirico and Steele, 1997a). The standard thermodynamic properties for ethylbenzene derived by Miller and Scott (1978) are in excellent accord with the present research but do not provide an independent check because they are based on a forced agreement between calorimetric and statistically derived values.

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