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Thermodynamic Equilibria in Xylene Isomerization. 5. Xylene Isomerization Equilibria from Thermodynamic Studies and Reconciliation of Calculated and Experimental Product Distributions[†]

Robert D. Chirico* and William V. Steele

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

Thermodynamic equilibria calculations based upon new calorimetric and physical-property measurements published in the first four papers of this series corroborate the assertion by Amelse (1993) that the existing thermodynamic data are in error. The largest errors are associated with the entropy of *o*-xylene in the liquid and gas states. New equilibria calculations described here are in excellent accord (within 0.7%) with product distributions determined experimentally by Amelse (1993). Deviations derived with previously available thermodynamic property compilations are three to four times larger. Statistical analysis shows that the uncertainties in the product distribution percentages derived from the thermodynamic measurements are approximately $2._5$% for *m*-xylene, $2._0$% for *p*-xylene, and $1._5$% for *o*-xylene under typical processing conditions. Equations are provided for the calculation of equilibrium product distributions for xylene isomerization for all temperatures above $T = 250$ K. Claims in the scientific and patent literature of isomerizations to *p*-xylene concentrations in excess of equilibrium are shown to be the result of errors in the thermodynamic literature and overstatement of the precision of the thermodynamic calculations. Literature compilations of thermodynamic functions for the xylenes and ethylbenzene are compared with those of this research. Origins of differences are discussed.

Introduction

Demand for *p*-xylene as a raw material for polyester fibers and films continues to grow and drive the search for improved xylene isomerization catalysts. In 1994, worldwide production of *p*-xylene was near 8×10^9 kg per year (approximately 260 $\text{kg}\cdot\text{s}^{-1}$) with an anticipated increase of 5 to 6% per year into the late 1990s (Tomasula, 1994). Recently, it was estimated that global capacity for the production of *p*-xylene will double by the year 2000, as companies position themselves to meet expected increases in demand, which grew 7% in 1996 (Thayer, 1997). Domestic production of *p*-xylene grew through 1995 with 3×10^9 kg produced in the United States (*Chem. Eng. News*, 1996). Domestic production will continue to grow as planned expansions by major oil companies are completed (Thayer, 1997).

The discovery of the shape-selective zeolite catalyst ZSM-5 has led to the development of new conversion processes yielding a distribution of aromatics, particularly methylbenzenes (Chen and Garwood, 1986). The term PATE (percent *p*-xylene approach-to-equilibrium) is often used to characterize the isomerization activity of a catalyst. As discussed by Amelse (1993), this quantity is very sensitive to errors in an assumed equilibrium xylene distribution, which has led to claims in the scientific and patent literature that isomerization to a *p*-xylene concentration in excess of equilibrium is possible (Seddon, 1986). Amelse (1993) exploited the shape-selectivity of ZSM-5 to experimentally determine the equilibrium xylene distribution with high precision at the temperatures $T = 623$ K and 673 K. Comparison with calculated equilibria based upon available standard thermodynamic properties for the xylenes (specifically, Stull et al., 1987) led Amelse (1993) to conclude that the existing thermodynamic data for the xylenes are in error. The present research was undertaken to investigate the sources of the observed discrepancies.

This is the fifth in a series of papers concerning thermodynamic studies related to xylene isomerization. In the four previous papers, standard Gibbs free energies of formation $\Delta_f G^\circ_m$ were derived for temperatures between 250 K and 550 K on the basis of experimental calorimetric and physical-property information for *p*-xylene (Chirico et al., 1997a), *m*-xylene (Chirico et al., 1997b), *o*-xylene (Chirico et al., 1997c), and ethylbenzene (Chirico et al., 1997d). The standard state is defined as the ideal gas at the pressure $p = p^\circ = 101.325$ kPa.

In the present paper, thermodynamic equilibrium product distributions are calculated for xylene isomerization and compared with published reaction equilibria results (Amelse, 1993; Bhattacharya and Rao, 1975; Pitzer and Scott, 1943; Norris and Vaala, 1939). Determination of uncertainties for the calculated product distributions is an important aspect of this research. Comparisons with product distributions calculated with literature $\Delta_f G^\circ_m$ compilations are discussed. Product distributions for the xylenes plus ethylbenzene are calculated also. The origins of discrepancies between literature $\Delta_f G^\circ_m$ compilations and those of this research (Chirico et al., 1997a−d) are discussed in the Appendix.

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 and ethylbenzene provide the basis for structure−property

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* To whom correspondence should be addressed.

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Table 1. Equilibrium Product Distributions (in mol %) for Xylene Isomerization Calculated from the Calorimetric Studies of This Research

T/K	m-xylene	o-xylene	p-xylene
250	63.$_0$	13.$_4$	23.$_6$
300	61.$_3$	14.$_8$	23.$_9$
350	59.$_5$	16.$_1$	24.$_4$
400	58.$_2$	17.$_2$	24.$_6$
450	56.$_8$	18.$_4$	24.$_8$
500	55.$_9$	19.$_2$	24.$_9$
550	55.$_0$	20.$_1$	24.$_9$
600[a]	54.$_2$	21.$_0$	24.$_8$
650[a]	53.$_4$	21.$_8$	24.$_8$
700[a]	52.$_8$	22.$_5$	24.$_7$
800[a]	51.$_6$	23.$_9$	24.$_5$
1000[a]	50	26	24
1500[a]	47	30	23
∞	40	40	20

[a] Values at this temperature were calculated by extrapolation of the calorimetric results, as described in the text.

Table 2. Equilibrium Product Distributions (in mol %) for the Xylenes Plus Ethylbenzene Calculated from the Calorimetric Studies of This Research

T/K	m-xylene	o-xylene	p-xylene	ethylbenzene
250	62.$_9$	13.$_3$	23.$_6$	0.$_2$
300	60.$_9$	14.$_7$	23.$_8$	0.$_5$
350	58.$_9$	15.$_9$	24.$_2$	1.$_1$
400	57.$_1$	16.$_9$	24.$_2$	1.$_8$
450	55.$_3$	17.$_9$	24.$_1$	2.$_8$
500	53.$_8$	18.$_5$	23.$_9$	3.$_8$
550	52.$_3$	19.$_1$	23.$_7$	4.$_9$
600[a]	50.$_9$	19.$_5$	23.$_4$	6.$_1$
650[a]	49.$_6$	19.$_9$	23.$_2$	7.$_3$
700[a]	48.$_2$	20.$_6$	22.$_5$	8.$_8$
800[a]	46	21	22	11
1000[a]	42	22	20	16
1500[a]	35	22	17	26
∞	18.2	18.2	9.1	54.5

[a] Values at this temperature were calculated by extrapolation of the calorimetric results, as described in the text.

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

Calculation of Thermodynamic Equilibria from Calorimetric Studies

Thermodynamic equilibrium product distributions for the xylenes and for the xylenes plus ethylbenzene in the standard state (ideal gas at $p = p° = 101.325$ kPa) were calculated between the temperatures $T = 250$ K and $T = 550$ K. Tables of the $\Delta_f G^\circ_m$ values used in the calculations and complete descriptions of their derivation were provided in the four previous papers of this series (Chirico et al., 1997a−d).

Product distributions were calculated by linear combination of the following equations:

$$\{p(o\text{-xylene})/p(m\text{-xylene})\} = K_1 = \exp(-\Delta_{r1}G^\circ_m/RT) \quad (1)$$

$$\{p(m\text{-xylene})/p(p\text{-xylene})\} = K_2 = \exp(-\Delta_{r2}G^\circ_m/RT) \quad (2)$$

$$\{p(p\text{-xylene})/p(o\text{-xylene})\} = K_3 = \exp(-\Delta_{r3}G^\circ_m/RT) \quad (3)$$

$$\{p(\text{ethylbenzene})/p(m\text{-xylene})\} = K_4 = \exp(-\Delta_{r4}G^\circ_m/RT) \quad (4)$$

where $\Delta_r G^\circ_m$ is the molar standard free energy of isomerization and K is the equilibrium constant for the indicated isomer pair. The partial pressure p is assumed equal to the mole fraction x such that

$$x_{(o-\text{xylene})} + x_{(m-\text{xylene})} + x_{(p-\text{xylene})} + x_{(\text{ethylbenzene})} = 1 \quad (5)$$

Calculated equilibrium percentages (i.e., $100x$) as a function of temperature are listed in Tables 1 and 2 and shown in Figures 1 and 2. Results reported in Table 1 and Figure 1 are for xylene isomerization only, while those reported in Table 2 and Figure 2 include ethylbenzene.

Product distributions calculated above the highest temperature of the calorimetric results (i.e., $T = 550$ K) were obtained with extrapolated K values for eqs 1−4. Plots of ln(K) against $1/T$ were used, as shown in Figure 3. Extrapolated values were calculated from fits of third-order polynomials to the values between $T = 250$ K and $T = 550$ K. The fitted polynomials were forced through the K values at $T \to \infty$. The K values at $T \to \infty$ are defined by the symmetry numbers σ of the isomers. The σ values for p-xylene, m-xylene, o-xylene, and ethylbenzene are 36, 18, 18, and 6, respectively. The polynomials used to represent the equilibrium constants as a function of temperature were

$$K_1 = \exp\{-791.8(T/\text{K})^{-1} + (1575 \times 10^2)(T/\text{K})^{-2} - (1417 \times 10^4)(T/\text{K})^{-3}\} \quad (6)$$

$$K_2 = \exp\{0.693 + 4.792(T/\text{K})^{-1} + 37\,070(T/\text{K})^{-2} - (5099 \times 10^3)(T/\text{K})^{-3}\} \quad (7)$$

$$K_3 = \exp\{-0.693 + 787.1(T/\text{K})^{-1} - (1946 \times 10^2)(T/\text{K})^{-2} + (1927 \times 10^4)(T/\text{K})^{-3}\} \quad (8)$$

$$K_4 = \exp\{1.0986 - 2248(T/\text{K})^{-1} + (2357 \times 10^2)(T/\text{K})^{-2} - (2490 \times 10^4)(T/\text{K})^{-3}\} \quad (9)$$

The temperatures 623 K and 673 K at which Amelse (1993) determined high-precision isomerization equilibria are indicated in Figure 3. The extrapolation of the calorimetric results to these temperatures is seen to be short.

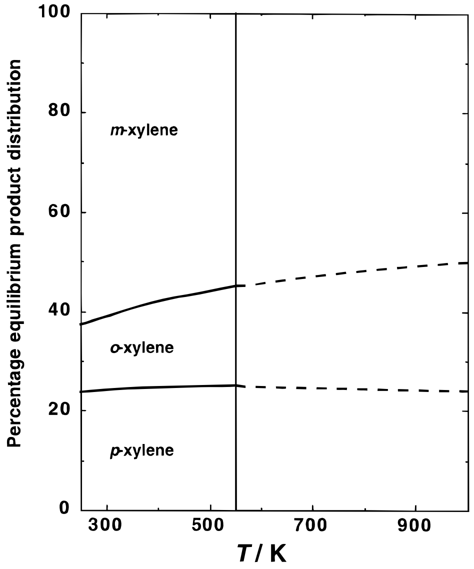

Figure 1. Percentage equilibrium product distribution for xylene isomerization calculated with standard Gibbs free energies of formation derived from calorimetric and physical-property studies (Chirico et al., 1997a−c). The dashed portion of the curves are based upon extrapolations described in the text.

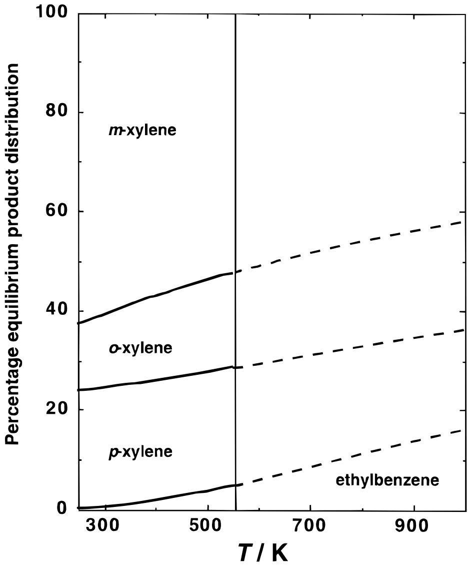

Figure 2. Percentage equilibrium product distribution for isomerization of the xylenes and ethylbenzene calculated with standard Gibbs free energies of formation derived from calorimetric and physical-property studies (Chirico et al., 1997a−d). The dashed portion of the curves are based upon extrapolations described in the text.

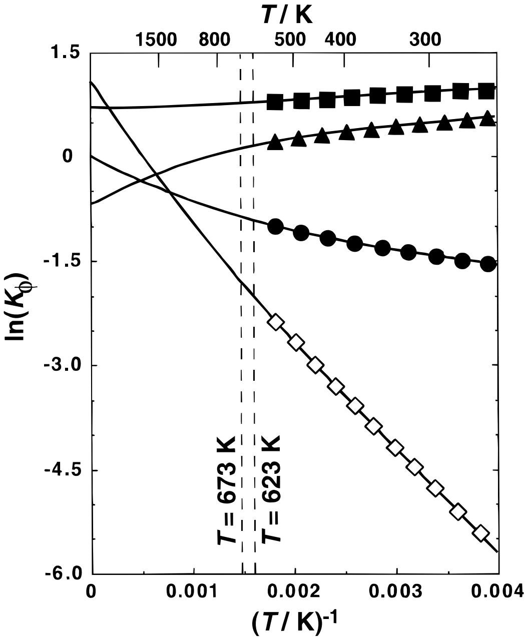

Figure 3. Natural logarithm of the equilibrium constants K_ϕ, defined in eqs 1−4, plotted as a function of inverse temperature. (●) $\phi = 1$ (*m*-xylene $\leftrightarrows$ *o*-xylene); (■) $\phi = 2$ (*p*-xylene $\leftrightarrows$ *m*-xylene); (▲) $\phi = 3$ (*o*-xylene $\leftrightarrows$ *p*-xylene); (◇) $\phi = 4$ (*m*-xylene $\leftrightarrows$ ethylbenzene). Extrapolations of results from $T = 550$ K to $T \rightarrow \infty$ are described in the text. The vertical dashed lines indicate the temperatures $T = 623$ K and $T = 673$ K of the equilibrium distributions determined by Amelse et al. (1993).

Table 3. Enthalpies of Formation in the Liquid Phase at $T = 298.15$ K[a]

compound	$\Delta_f H^\circ_m(l)$[b]	original ±[c]	revised ±[d]
o-xylene	−24.38	1.02	0.4
m-xylene	−25.38	0.62	0.37
p-xylene	−24.39	0.91	0.63
ethylbenzene	−12.39	0.72	0.52

[a] All units are kJ·mol^{-1}. [b] Calculated from the combustion calorimetric measurements by Prosen et al. (1945). [c] The uncertainty interval published by Prosen et al. (1945). [d] The uncertainty interval derived in this research for xylene isomerization. See text.

Uncertainties Associated with Calculation of Thermodynamic Equilibria from the Calorimetric Studies

Calculation of standard Gibbs free energies of formation for the xylenes from the calorimetric measurements, including the propagation of errors, was described in the previous papers of this series (Chirico et al., 1997a−d). In the calculations reported here, uncertainties associated with the enthalpies of formation of the liquids determined by combustion calorimetry (Prosen et al., 1945) were reduced to include only the uncertainties in the energies of combustion. Uncertainties associated with the energy equivalent of the combustion calorimeter and the enthalpies of formation of CO_2(g) and H_2O(l) were not included here because these cancel in the Gibbs free energy of isomerization calculations. This approach is justified because the compounds were all burned in a single series of experiments in the same experimental apparatus.

Preliminary measurements of the enthalpy of combustion for *o*-xylene (Chirico et al., 1997c) were in excellent agreement (within 0.2 kJ·mol^{-1}) with the results of Prosen et al. (1945). The uncertainty in the enthalpy of combustion calculated from the results of Prosen et al. is 0.77 kJ·mol^{-1}. This uncertainty was reduced to 0.4 kJ·mol^{-1} here to reflect the corroboration provided by our experiments.

The enthalpies of formation for the liquid xylenes and ethylbenzene at $T = 298.15$ K (Prosen et al., 1945) together with the published and revised uncertainties are listed in Table 3. Representative standard $\Delta_f H^\circ_m$ and $\Delta_f G^\circ_m$ values calculated with the revised uncertainties are listed in Table 4. It is important to note that the revised uncertainties are only valid for the isomerization reactions. For other reactions involving the xylenes and ethylbenzene, the uncertainties published previously (Chirico et al., 1997a−d) should be used.

Uncertainties in the xylene isomerization product distributions calculated here were estimated with the following procedure. Product distributions were calculated with the six permutations of the $\Delta_f G^\circ_m$ values with the uncertainties set at the extremes listed in Table 4. One standard deviation was assumed to be ≈0.67 of the maximum distribution span for each isomer. The calculated uncertainties in the product distribution percentages were $\pm 2._5$% for *m*-xylene, $2._0$% for *p*-xylene, and $1._5$% for *o*-xylene. These uncertainties do not increase significantly when the results are extrapolated to the temperatures investigated by Amelse (1993) because of the short extrapolations involved and the slow variation of the product distribution with temperature. The uncertainty in the product distribution percentages for ethylbenzene are more dependent on temperature. The percentage uncertainty for ethylbenzene is 0.2% near 400 K and 0.5% near 500 K.

Most of the uncertainty remaining in the calculated product distributions arises from uncertainties in the enthalpies of formation of the liquids, $\Delta_f H^\circ_m$(l). Accurate vibrational assignments for the xylenes could improve the quality of the extrapolation of results to temperatures above 550 K, particularly for long extrapolations. Nonetheless, the comparisons with experimental equilibria discussed in the following section indicate that the third-order fits shown in Figure 3 provide adequate representations of the equilibrium constants as a function of temperature. It is important to note that statistically calculated thermodynamic properties are not used in the present research. Consequently, uncertainties associated with the

Table 4. Standard Molar Enthalpies of Formation $\Delta_f H_m^\circ$ and Gibbs Free Energies of Formation $\Delta_f G_m^\circ$ in the Ideal-Gas State Calculated with Revised Uncertainties for the Calculation of Xylene Isomerization Equilibria

$p = p^\circ = 101.325$ kPa $(R = 8.314\ 51\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}})$

T/K	$\Delta_f H_m^\circ/RT$	$\Delta_f G_m^\circ/RT$
	o-Xylene	
250.00	11.10 ± 0.10	51.08 ± 0.10
300.00	7.60 ± 0.08	49.38 ± 0.09
350.00	5.18 ± 0.07	48.40 ± 0.08
400.00	3.44 ± 0.07	47.83 ± 0.07
450.00	2.18 ± 0.07	47.49 ± 0.07
500.00	1.23 ± 0.10	47.30 ± 0.09
550.00	0.52 ± 0.14	47.18 ± 0.12
	m-Xylene	
250.00	10.40 ± 0.10	49.53 ± 0.09
300.00	6.89 ± 0.08	47.96 ± 0.08
350.00	4.47 ± 0.07	47.09 ± 0.07
400.00	2.76 ± 0.06	46.61 ± 0.07
450.00	1.51 ± 0.07	46.36 ± 0.07
500.00	0.57 ± 0.10	46.23 ± 0.09
550.00	-0.14 ± 0.15	46.17 ± 0.13
	p-Xylene	
250.00	10.69 ± 0.16	50.51 ± 0.15
300.00	7.15 ± 0.13	48.90 ± 0.13
350.00	4.72 ± 0.11	47.98 ± 0.11
400.00	2.99 ± 0.10	47.47 ± 0.10
450.00	1.73 ± 0.10	47.19 ± 0.10
500.00	0.79 ± 0.12	47.04 ± 0.12
550.00	0.05 ± 0.17	46.96 ± 0.15
	Ethylbenzene	
250.00	16.41 ± 0.13	55.24 ± 0.13
300.00	11.93 ± 0.11	52.67 ± 0.11
350.00	8.82 ± 0.09	51.07 ± 0.10
400.00	6.60 ± 0.08	50.05 ± 0.09
450.00	4.96 ± 0.09	49.36 ± 0.08
500.00	3.72 ± 0.11	48.88 ± 0.10
550.00	2.74 ± 0.15	48.54 ± 0.13

statistical treatment of hindered rotors have no influence on the results.

Comparisons with Isomerization Equilibria Measured by Amelse (1993)

Amelse (1993) exploited the shape-selectivity of the zeolite catalyst ZSM-5 to experimentally determine the equilibrium xylene distribution with high precision at T = 623 K and T = 673 K. Amelse (1993) monitored the approach to equilibrium for xylene isomerization using both a non-shape-selective molecular sieve and the shape-selective ZSM-5. The differing approaches to the equilibrium distribution were used to extrapolate with high precision to the equilibrium values.

Uncertainties associated with the extrapolation to the equilibrium values were estimated by Amelse to be ±0.04 mol %. These uncertainties did not include those associated with the analyses or with temperature measurement. Errors resulting from uncertainties in temperature measurement are expected to be very small because the product distribution is a slowly varying function of temperature. Amelse analyzed the product distribution by capillary gas chromatography using a column “capable of giving baseline separation of the xylenes”. The combined temperature and analysis errors should not exceed a few tenths of 1%, which is well within the uncertainties of the thermodynamic calculations.

The experimental equilibrium distributions reported by Amelse (1993) are listed in Table 5 and are compared in Table 6 with those calculated with $\Delta_f G_m^\circ$ values of this research and calculated with $\Delta_f G_m^\circ$ values from the literature (Draeger, 1985; Chao et al., 1984; Taylor et al., 1946). Agreement between the calculations of this research and the experimental results of Amelse (1993) is excellent. Deviations do not exceed 0.7%, which is well within the combined uncertainties of the calculated and experimental results. Product distributions based upon the literature $\Delta_f G_m^\circ$ values (Draeger, 1985; Chao et al., 1984; Taylor et al., 1946) show deviations which are three to four times larger, particularly for the ortho isomer. Origins of differences between standard thermodynamic functions of this research and those of the literature are discussed in the Appendix.

Table 5. Experimental Isomerization Equilibria Results from the Literature

ref	T/K	*m*-xylene	*o*-xylene	*p*-xylene
Amelse (1993)[a]	623	54.0_0	21.6_1	24.3_9
Amelse (1993)[a]	673	52.2_1	22.8_0	23.9_9
Bhattacharya and Rao (1975)[b]	823	53.0	23.1	23.9
Pitzer and Scott (1943)[c]	323	(71 ± 5)	(12 ± 3)	(17 ± 2)
Norris and Vaala (1939)[d]	323	(65 ± 10)	(16 ± 10)	(19 ± 5)

[a] Uncertainties in the distribution percentages are probably less than ±0.5%. Products were in the gaseous phase. See text. [b] Normalized to 100% xylenes. Uncertainties in the distribution percentages are near ±1%. [c] Products were in the liquid phase. [d] Uncertainties estimated by Taylor et al. (1946). All products were in the liquid phase.

A Comment Concerning Available $\Delta_f G_m^\circ$ Compilations

In spite of the numerous compilations of standard Gibbs free energies of formation available for the xylenes, there are only four distinguishable sources: our present series of papers (Chirico et al., 1997a−d), Draeger (1985), Chao et al. (1984), and Taylor et al. (1946). All other published $\Delta_f G_m^\circ$ compilations use the results of Chao et al. (1984) or Taylor et al. (1946) as their source. For example, values listed by Stull et al. (1987, 1969) are those of Taylor et al. (1946), while those listed by TRC (1996), Daubert et al. (1996) for the Design Institute for Physical Property Data (DIPPR), Laesecke (1993) of NIST, and Frenkel et al. (1994) are those produced by Chao et al. (1984).

Comparisons with Other Experimental Isomerization Equilibria

Bhattacharya and Rao (1975) studied isomerization of xylenes over a silica−alumina catalyst and reported the product distribution at 823 K listed in Table 5. Analyses were accomplished with infrared and NMR spectroscopic measurements. Scatter in their graphical results indicates analysis uncertainties near 1%. In spite of the analysis uncertainties and long extrapolation of the calorimetric results (from 550 K to 823 K), the agreement with the results of Bhattacharya and Rao (1975) is good. Deviations do not exceed 1.6%, as listed in Table 6. Product distributions based upon the literature $\Delta_f G_m^\circ$ values (Draeger, 1985; Chao et al., 1984; Taylor et al., 1946) show larger deviations, again, particularly for the ortho isomer. All deviations are listed in Table 6.

Pitzer and Scott (1943) and Norris and Vaala (1939) reported isomerization equilibria in the liquid phase at T = 323 K. Their reported product distributions are listed in Table 5. Gibbs free energies of formation for the xylenes in the liquid phase (Chirico et al., 1997a−c) were used to calculate the isomerization product slate at T = 323 K: *m*-xylene, $(58._9 \pm 2._9)\%$; *o*-xylene, $(18._3 \pm 1._7)\%$; *p*-xylene, $(22._8 \pm 2._4)\%$. These values are within the broad uncertainty ranges reported by Norris and Vaala (1939). The

Table 6. Comparison of Calculated Equilibrium Isomerization Distributions with Experimental Reaction Equilibria in the Gas Phase

		% deviation from Amelse (1993)			% deviation from Bhattacharya and Rao (1975)
source of $\Delta_f G^\circ_m$	compound	623 K	673 K	% rmsd[a]	823 K
this research	*o*-xylene	−0.2	−0.7	0.2	1.1
	m-xylene	−0.2	−0.1		−1.6
	p-xylene	0.4	0.7		0.5
Draeger (1985)	*o*-xylene	2.7	2.3	0.8	3.9
	m-xylene	−0.3	−0.2		−1.7
	p-xylene	−2.4	−2.1		−2.3
Chao et al. (1984)	*o*-xylene	2.7	2.1	0.7	3.5
	m-xylene	−0.6	−0.5		−2.2
	p-xylene	−2.1	−1.6		−1.3
Taylor et al. (1946)	*o*-xylene	2.5	2.5	0.7	2.9
	m-xylene	−1.6	−1.6		−2.0
	p-xylene	−0.9	−0.8		−0.9

[a] % rmsd is the root-mean-square deviation of the percentage deviations for the three isomers.

large uncertainties listed by Norris and Vaala are associated with analysis difficulties. Modern analytical techniques were not available in 1939. The results of Pitzer and Scott (1943) are not in accord with the present calculations. Undetected analysis errors are probably the source of the discrepancies.

Claims in the scientific and patent literature of xylene isomerizations to *p*-xylene concentrations in excess of equilibrium, discussed by Amelse (1993), resulted from comparisons of experimental product distributions with values derived with $\Delta_f G^\circ_m$ values, which included experimental and calculational errors. Claims of enhanced *p*-xylene formation are not supported by the thermodynamic calculations of the present research. For example, Seddon (1986) claimed an isomerization pathway for *m*-xylene at $T = 723$ K that produced a *p*-xylene level, “well in excess of thermodynamic equilibrium (e.g., 26% *p*-xylene versus an equilibrium value of 23.4%)”. The *p*-xylene concentration at 723 K derived with the thermodynamic information of the present research is $24._6 \pm 2$. Similar claims are often based upon an unrealistic expectation of the precision of the thermodynamic calculations. For example, Amelse (1993) reported product distributions to the nearest 0.01% calculated from thermodynamic information. The present research shows this calculation to be overly optimistic by a factor of more than 100.

Conclusions

Thermodynamic equilibria calculations based upon new calorimetric and physical-property studies published in the first four papers of this series (Chirico et al., 1997a−d) corroborate the assertion by Amelse (1993) that the existing thermodynamic data are in error. The largest errors were shown to be associated with the entropy of *o*-xylene in the liquid and gas states. Equations are provided for the calculation of equilibrium product distributions for xylene isomerization for all temperatures above $T = 250$ K. The Gibbs free energies of formation $\Delta_f G^\circ_m$ used in the derivation of these equations were published in the earlier papers of this series (Chirico et al., 1997a−d).

The new equilibria calculations presented here are in excellent accord (within 0.7%) with the reaction equilibria studies by Amelse (1993). Previously available compilations yield deviations which are three to four times larger. Statistical analysis shows that the uncertainties in the product distribution percentages derived from the thermodynamic measurements are approximately $2._5$%, $2._0$%, and $1._5$% for *m*-xylene, *p*-xylene, and *o*-xylene, respectively, under typical processing conditions in the gas phase. Further reductions in the product distribution uncertainties will require more precise determination of the enthalpy-of-formation for each compound.

Appendix. Comparisons of Standard Thermodynamic Functions of This Research for the Xylenes and Ethylbenzene with Values from the Literature

All sources of $\Delta_f G^\circ_m$ values for the xylenes (this research; Draeger, 1985; Chao et al., 1984; Taylor et al., 1946) base the value of the enthalpy of formation in the liquid phase on the combustion calorimetric measurements by Prosen et al. (1945). Consequently, differences between the sources arise primarily from alternative methods of calculation for standard heat capacities and standard entropies for the particular compound. Additional small differences (i.e., ≤ 0.03 in the values of $\Delta_f S^\circ_m/R$, $\Delta_f H^\circ_m/RT$ and $\Delta_f G^\circ_m/RT$) arise from differences in the thermodynamic functions used by each research group for H_2(g) and C(graphite) in their respective reference states. Of these, differences originating from alternative reference state functions for graphite predominate. Consequently, it is important to use care when $\Delta_f G^\circ_m$values from different sources are used for thermodynamic calculations, particularly for reactions involving many carbon atoms.

For the comparisons shown here, the formation properties from the literature were recalculated using a common reference state (Chase et al., 1985) for C(graphite) and H_2(g). The reference state pressure for H_2(g) listed in the JANAF Tables (Chase et al., 1985) is 100 kPa. The thermodynamic functions were adjusted to a reference pressure $p = p^\circ = 101.325$ kPa in all publications of this research (Chirico et al., 1997a−d). The reference pressure $p = 101.325$ kPa was used also by Draeger (1985), Chao et al. (1984), and Taylor et al. (1946).

Figure 4 shows deviations of the literature values (Draeger, 1985; Chao et al., 1984; Taylor et al., 1946) from those of this research for standard enthalpies of formation $\Delta_f H^\circ_m$, standard entropies $\Delta_0^T S^\circ_m$, and standard Gibbs free energies of formation $\Delta_f G^\circ_m$ for the xylenes. The signs of the entropy differences are reversed relative to those for the enthalpies of formation to ease comparisons with the Gibbs free energy differences. It is apparent from Figure 4 that the deviations of the literature $\Delta_f G^\circ_m$ values from those of this research originate predominantly from the $\Delta_0^T S^\circ_m$ differences.

The standard entropy differences for *o*-xylene for Draeger (1985) and Taylor et al. (1946) arise because their results

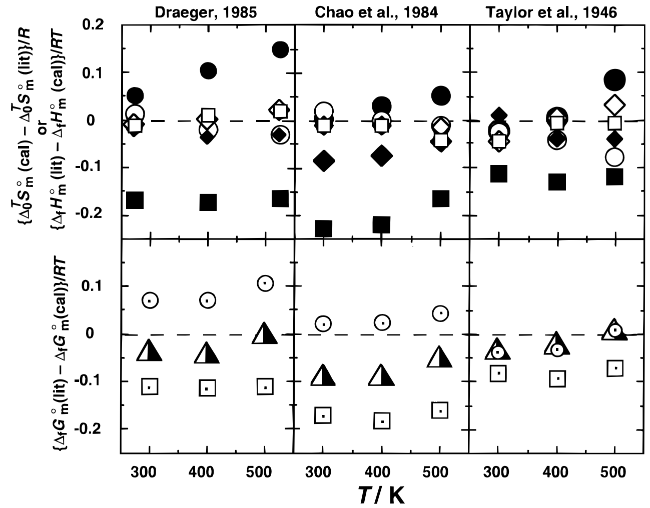

Figure 4. Comparison of standard thermodynamic functions for the xylenes from the literature (lit) with those derived from the thermodynamic measurements and calculations of this research (cal). The values from the literature are those of Draeger (1985), Chao et al. (1984), and Taylor et al. (1946), as indicated at the top of the three sections of the figure. The values of this research are those listed in Chirico et al. (1997a−c). $\{\Delta_0^T S^\circ_m(\text{cal}) - \Delta_0^T S^\circ_m(\text{lit})\}/R$ values are: (■) *o*-xylene; (◆) *m*-xylene; (●) *p*-xylene. $\{\Delta_f H^\circ_m(\text{lit}) - \Delta_f H^\circ_m(\text{cal})\}/RT$ values are: (□) *o*-xylene; (◇) *m*-xylene; (○) *p*-xylene. $\{\Delta_f G^\circ_m(\text{lit}) - \Delta_f G^\circ_m(\text{cal})\}/RT$ values are: (⊡) *o*-xylene; (◭) *m*-xylene; (⊙) *p*-xylene.

were based in large part upon a standard entropy value at $T = 298.15$ K derived from an entropy for the liquid phase derived from the heat-capacity study by Pitzer and Scott (1943) and a calorimetrically determined enthalpy of vaporization (Osborne and Ginnings, 1947). It was shown in the third paper of this series (Chirico et al., 1997) that the entropy of the liquid phase at $T = 298.15$ K reported by Pitzer and Scott (1943) is $\approx 0.08R$ (i.e., 0.3%) high.

Chao et al. (1984) erroneously used a standard entropy value $T = 298.15$ K reported by Pitzer and Scott (1943) for *o*-xylene, which included an enthalpy of vaporization derived from low-resolution vapor-pressure studies. Consequently, Chao et al. (1984) ignored the high-precision enthalpy of vaporization reported by (Osborne and Ginnings, 1947). This error remains uncorrected in those compilations using the results published by Chao et al. (Daubert et al., 1996; TRC, 1996; Frenkel et al., 1994; Laesecke, 1993).

The work of Chao et al. (1984) and Draeger (1985) include errors for *o*-xylene which increase further the deviations of their results from those of this research. Chao et al. (1984) mistakenly assumed that the band observed by Pardoe et al. (1970) at (162 ± 5) cm^{-1} in the far infrared spectrum was associated with the $0 \rightarrow 1$ torsional transition. This resulted in the use of an inappropriately high barrier to methyl-group rotation in their calculations, as was described previously (Chirico et al., 1997c). The band observed by Pardoe et al. (1970) is the lowest vibrational fundamental for *o*-xylene in the vapor phase, as reported by Draeger (1985b) near 163 cm^{-1}. This error is also propagated in the compilations using the results of Chao et al. (Daubert et al., 1996; Frenkel et al., 1994; Laesecke, 1993; TRC, 1996).

Draeger (1985) erroneously substituted a fundamental wavenumber value of 157 cm^{-1} for the correct value at 163 cm^{-1} in his calculations. Consequently, the values listed by Draeger (1985) differ from those of the present research by more than the $\approx 0.08R$ arising from the bias in the early liquid phase entropy value at $T = 298.15$ K reported by Pitzer and Scott (1943).

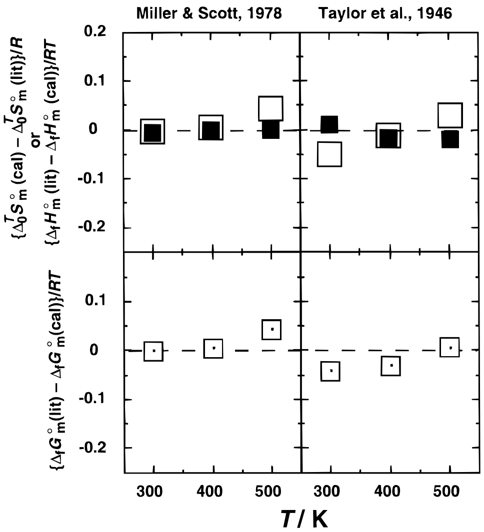

Figure 5. Comparison of standard thermodynamic functions for ethylbenzene from the literature (lit) with those derived from the thermodynamic measurements and calculations of this research (cal). The values from the literature are those of Miller and Scott (1978) and Taylor et al. (1946), as indicated at the top of the two sections of the figure. The values of this research are listed in Chirico et al. (1997d). (■) $\{\Delta_0^T S^\circ_m(\text{cal}) - \Delta_0^T S^\circ_m(\text{lit})\}/R$; (□) $\{\Delta_f H^\circ_m(\text{lit}) - \Delta_f H^\circ_m(\text{cal})\}/RT$; (⊡) $\{\Delta_f G^\circ_m(\text{lit}) - \Delta_f G^\circ_m(\text{cal})\}/RT$.

Standard thermodynamic functions for ethylbenzene have been tabulated by Miller and Scott (1978), Taylor et al. (1946), and Brickwedde et al. (1945). The origin of subsequent compilations (Stull et al., 1969, 1987; Frenkel, 1994; TRC, 1996) can be traced to either Miller and Scott (1978) or Taylor et al. (1946). Brickwedde et al. (1945) adjusted their results based in part upon literature hydrogenation studies (Dolliver et al., 1937). Their results show relatively large differences from the present research and were not used in any subsequent compilations. The results of Brickwedde et al. (1945) are not considered further here.

Figure 5 shows deviations of the literature $\Delta_f H^\circ_m$, $\Delta_0^T S^\circ_m$, and $\Delta_f G^\circ_m$values from those of this research for ethylbenzene (Miller and Scott, 1978; Taylor et al., 1946), in analogy with Figure 4. In contrast to the results for the xylenes, it is apparent from Figure 5 that the standard thermodynamic properties for ethylbenzene are well established. Miller and Scott (1978) and Taylor et al. (1946) used approximate vibrational assignments and adjusted internal rotational barriers to force agreement between their statistically calculated values and those derived from calorimetric studies. Those efforts were successful because the original property measurements from the 1940s (Guthrie et al., 1944; Scott and Brickwedde, 1945; Osborne and Ginnings, 1947) were of high quality (see Chirico et al., 1997d). Similar approaches for the xylenes used by Draeger (1985), Chao et al. (1984), and Taylor et al. (1946) were not successful, particularly for *o*-xylene, because the standard entropies with which agreement was forced were incorrect (Chirico et al., 1997c).

The fact that the available standard entropies calculated with the methods of statistical mechanics (Chao et al., 1984; Taylor et al., 1946) were adjusted to agree with the available calorimetric studies is rarely recognized. For example, Everdell (1967) believed that the available standard entropies were “probably of great accuracy” based upon “very good agreement having been obtained between the calorimetric values and those obtained as the result of spectroscopic measurements and the formulas of statistical mechanics”. Similarly, Amelse (1993) stated, “Entropy is calculated based on statistical thermodynamics, using vibrational band positions from Infra-red and Raman spectra". The thermodynamic properties used by Amelse (1993) were those listed by Stull et al. (1987), who in turn used those listed by Taylor et al. (1946), which were adjusted to match the calorimetric results of Pitzer and Scott (1943). It is difficult to fault Everdell (1967) and Amelse (1993) for these misunderstandings. The origins of the compiled values are seldom well documented by the compilers. It is common for one compilation to simply cite another (cf., Daubert et al., 1996; TRC, 1996; Frenkel et al., 1994; Laesecke, 1993; Stull et al., 1987).

Literature Cited

Amelse, J. A. The influence of diffusion limitations on xylene isomerization. *Proc. 9th Int. Zeolite Conf. (Montreal 1992)* **1993**, *2*, 457−465.

Bhattacharya, R. N.; Rao, H. S. Isomerization of Xylenes over a Silica-Alumina Catalyst. *J. Appl. Chem. Biotechnol.* **1975**, *25*, 183−194.

C&E News: Facts and Figures for the Chemical Industry. *Chem. Eng. News* **1996**, *74* (26), 38−79.

Chao, J.; Hall, K. R.; Yao, J. Chemical thermodynamic properties of toluene, *o*-, *m*-, and *p*-xylenes. *Thermochim. Acta* **1984**, *72*, 323−334.

Chen, N. Y.; Garwood, W. E. Industrial Applications of Shape-Selective Catalysts. *Catal. Rev.-Sci. Eng.* **1986**, *28*, 185−264.

Chirico, R. D.; Knipmeyer, S. E.; Nguyen, A.; Steele W. V. Thermodynamic Equilibria in Xylene Isomerization. 1. The Thermodynamic Properties of *p*-Xylene. *J. Chem. Eng. Data* **1997a**, *42*, 248−261.

Chirico, R. D.; Knipmeyer, S. E.; Nguyen, A.; Reynolds, J. W.; Steele W. V. Thermodynamic Equilibria in Xylene Isomerization. 2. The Thermodynamic Properties of *m*-Xylene. *J. Chem. Eng. Data* **1997b**, *42*, 475−487.

Chirico, R. D.; Knipmeyer, S. E.; Nguyen, A.; Cowell, A. B.; Reynolds, J. W.; Steele W. V. Thermodynamic Equilibria in Xylene Isomerization. 3. The Thermodynamic Properties of *o*-Xylene. *J. Chem. Eng. Data* **1997c**, *42*, 758−771.

Chirico, R. D.; Knipmeyer, S. E.; Nguyen, A.; Steele W. V. Thermodynamic Equilibria in Xylene Isomerization. 4. The Thermodynamic Properties of Ethylbenzene. *J. Chem. Eng. Data* **1997d**, *42*, 772−783.

Daubert, T. E.; Danner, R. P.; Sibul, H. M.; Stebbins, C. C. *Physical and Thermodynamic Properties of Pure Chemicals: Data Compilation of the Design Institute for Physical Property Data*; Taylor and Francis Publishing: Bristol, PA, extant 1996.

Dolliver, M. A.; Gresham, T. L.; Kistiakowsky, G. B.; Vaughan, W. E. Heats of organic reactions. V. Heats of hydrogenation of various hydrocarbons. *J. Am. Chem. Soc.* **1937**, *59*, 831−841.

Draeger, J. A. The methylbenzenes II. Fundamental vibrational shifts, statistical thermodynamic functions, and properties of formation. *J. Chem. Thermodyn.* **1985**, *17*, 263−275.

Everdell, M. H. Some remarks on the thermodynamics of the xylenes. *J. Chem. Educ.* **1967**, *44*, 538−540.

Frenkel, M.; Marsh, K. N.; Wilhoit, R. C.; Kabo, G. J.; Roganov, G. N. *Thermodynamics of Organic Compounds in the Gas State*; Thermodynamics Research Center: College Station, TX, 1994; Vol. II.

Laesecke, A. Correlation of the ideal-gas properties of five aromatic hydrocarbons. *Ind. Eng. Chem. Res.* **1993**, *32*, 759−761.

Norris, J. F.; Vaala, G. T. The Rearrangement of the Xylenes by Aluminum Chloride. *J. Am. Chem. Soc.* **1939**, *61*, 2131−2134.

Osborne, N. S.; Ginnings, D. C. Measurements of heat of vaporization and heat capacities of a number of hydrocarbons. *J. Res. Natl. Bur. Stand.* **1947**, *39*, 453−477.

Pardoe, G. W. F.; Larson, S. J.; Gebbie, H. A.; Strickler, S. J.; Ingham, K. C.; Johnson, D. G. Far-infrared spectrum of ortho-xylene. *J. Chem. Phys.* **1970**, *52*, 6426−6427.

Pitzer, K. S.; Scott, D. W. The thermodynamics and molecular structure of benzene and its methyl derivatives. *J. Am. Chem. Soc.* **1943**, *65*, 803−829.

Prosen, E. J.; Gilmont, R.; Rossini, F. D. Heat of combustion of benzene, toluene, ethylbenzene, o-xylene, m-xylene, p-xylene, propylbenzene, and styrene. *J. Res. Natl. Bur. Stand.* **1945**, *34*, 65−71.

Seddon, D. Selectivity for para-Xylene in the isomerization of xylenes catalyzed by zeolites with ten-ring windows. *J. Catal.* **1986**, *98*, 1−6.

Stull, D. R.; Westrum, E. F., Jr.; Sinke, G. C. *The Chemical Thermodynamics of Organic Compounds*; Wiley: New York, 1969.

Stull, D. R.; Westrum, E. F., Jr.; Sinke, G. C. *The Chemical Thermodynamics of Organic Compounds*, 2nd ed.; Robert F. Krieger: Malabar, FL, 1987.

Taylor, W. J.; Wagman, D. D.; Williams, M. G.; Pitzer, K. S.; Rossini, F. D. Heats, Equilibrium Constants, and Free Energies of Formation of the Alkylbenzenes. *J. Res. Natl. Bur. Stand.* **1946**, *37*, 95−122.

Thayer, A. M. Petrochemicals *Chem. Eng. News* **1997**, *75* (12), 20−26.

Tomasula, D. Aromatics set for '95 rebound. *Chem. Mark. Rep.* **1994**, *245* (14), 7−11.

TRC Thermodynamic Tables-Hydrocarbons; Thermodynamics Research Center, Texas A&M University: College Station, TX, extant 1996.

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