Isobaric Thermal Expansivities of Toluene Measured by Scanning Transitiometry at Temperatures from (243 to 423) K and Pressures up to 200 MPa[†]

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Isobaric thermal expansivities of toluene were determined over the temperature range from (243.15 to 423.15) K at pressures up to 200 MPa using scanning transitiometry. The results have been critically evaluated and compared to the existing literature data. From the experimental results, the isobaric specific heat capacities and isothermal compressibilities have been derived over a wide pressure and temperature range.

Introduction

Toluene is a solvent or intermediate product in many chemical reactions of practical importance, for example, in syntheses of pharmaceuticals, herbicides, pesticides, etc. The amount of experimental data available in the literature for toluene is important. From a practical point of view, toluene can then be considered as a reference substance. However, the data have been obtained with various techniques, very often not direct, and important discrepancies exist between them. The aim of the present contribution is to determine experimentally the thermal expansivities of toluene over a wide pressure and temperature range and on this basis to derive its other thermophysical properties such as heat capacities and compressibilities. Isobaric thermal expansivities have been determined over the temperature range from (243.15 to 423.15) K at pressures up to 200 MPa using scanning transitiometry, actually the most direct technique of their determination. The results have been critically evaluated with respect to the existing literature data, most of them obtained from speed of sound measurements,[1,2] density measurements,[3−7] or correlations[8−10] and by piezothermal techniques[11] or similar pressure scanning techniques.[12,13]

Experimental Section

Chemicals. Toluene (99.9 %) from J.T. Baker was used without further purification. The mass fraction of water, determined by the Karl Fisher method, was less than $3 \cdot 10^{-5}$. Prior to the measurement, the toluene was degassed in an ultrasonic stream. To check the purity of toluene, its densities with a vibrating-tube densimeter (Anton Paar) were determined within the temperature range from (273.15 to 363.15) K. In Table 1, the measured density of the toluene at 298.15 K is compared with literature values. Our experimental result is in good agreement with the literature values. Small differences in densities may result from differences in the purity of the chemicals.

Table 1. Comparison of the Densities for Toluene at $T = 298.15$ K Obtained in the Present Study with Those Reported in the Literature at Atmospheric Pressure

	$\rho/(\mathrm{kg \cdot m^{-3}})$	
T/K	this work	literature
298.15	862.22	862.3,[3] 862.5,[4] 862.5,[9] 862.29,[14] 862.2,[15] 862.1[16]

Apparatus and Procedure. The transitiometer was from BGR TECH Ltd., Warsaw, Poland. The transitiometric technique has already been described in the literature,[17−20] thus only a short description is given here. Figure 1 presents a schematic diagram of the transitiometer adapted to measurements of thermal expansion of liquids. It consists of a calorimeter containing high-pressure vessels, a *pVT*-controlled system, and LabView virtual instrument (VI) software. Two cylindrical calorimetric detectors (ø = 17 mm, l = 80 mm), made from 622 thermocouples (chromel-alumel) each, are mounted differentially and connected to a nanovolt amplifier. The calorimetric detectors are placed in a metallic block, the temperature of which is directly controlled with a 22 bit digital feedback loop [$\approx(10^{-4} \pm 10^{-5})$ K], which is part of the transitiometer software. The calorimeter block is surrounded by a heating−cooling shield. The temperature difference between the block and the shield is set at a constant value and is controlled by another controller. The temperature measurements, both absolute and differential, are made with calibrated Pt 100 sensors. The heaters are embedded in the outer surfaces of both the calorimeter block and the shield. The whole assembly is thermally insulated and enclosed in a stainless steel body fixed on a mobile stand, which allows the calorimeter to be moved up and down over the calorimetric vessels. When performing measurements near 273 K or below, dry air is pumped through the apparatus to prevent water condensation.

The calorimetric vessels were made from 0.47 cm internal diameter 316 stainless steel tubing and have been fixed on a mounting table attached to the mobile stand. Only the measuring vessel was connected to the high-pressure line. The reference vessel acts only as a thermal reference. The tubing of both measuring and reference vessels was connected to reducers, which have been positioned inside the calorimeter when it is in the lowered (measuring) position. The connections from the reducers to the manifold were made with thin stainless steel capillaries to reduce heat losses to the environment. The plunger pump (total displaced volume is 9 cm^3) has been driven by a stepping motor controlled by the transitiometer software (manual control is possible during preparatory operations). The pressure detector is a Viatran 245 transducer with uncertainty of 0.15 % and repeatability of 0.1 % full scale deflection.

The pressure detector, the output of the calorimetric amplifier, and the stepping motor were connected to a NI PCI-MIO-16XE-

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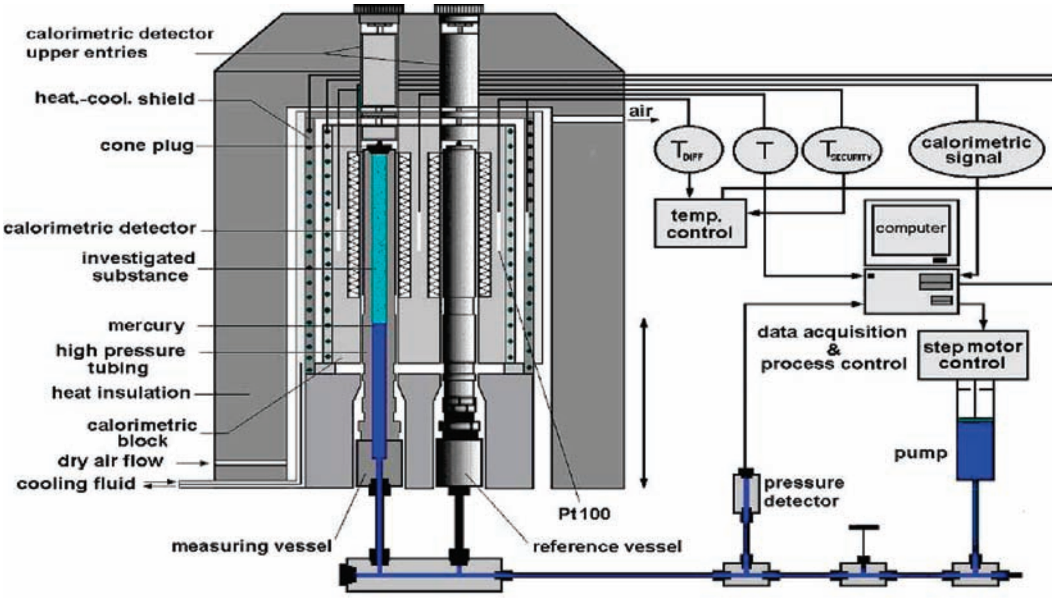

Figure 1. Schematic diagram of a scanning transitiometer.

50 multifunction board through a NI SCB-68 shielded connector block. The temperature measurements and digital control of the calorimetric block were performed through a serial port. The software, elaborated with the use of LabView language, performs as a Virtual Instrument (VI). It consists of 90 subVIs, each responsible for a particular function: pressure measurements, temperature measurements, counting the motor steps for recording the volume variations, measuring the calorimetric signal, etc., and each performs independently. However, all the subVIs form a hierarchical structure with a top window, where the experimenter can see simultaneously all four variables (pressure, p, volume variations, V, temperature, T, and the heat flux, q, associated with the process under investigation) and the current status of the temperature and pressure control loops.

The hydraulic part of the system was filled with mercury. The mercury level in the measuring vessel can be moved up and down by displacing the pump plunger. On the top of the mercury level, the investigated liquid sample was placed, and the vessel was closed with a cone plug in such a way as to avoid any air space. The lower level of the sample was near 2 cm below the calorimetric detector limit. In such a way the pressure to the vessel was transmitted directly by the sample. The mass of the sample contained in the calorimetric detector changed during the course of the experiment and was equal to $V_E/V(p,T)$, where V_E is the internal volume of the calorimetric vessel directly exchanging heat with the calorimetric detector and $V(p,T)$ is the molar volume of the investigated liquid. In such a configuration when pressure is varied under isothermal conditions as a stepwise function of time the volume coefficient of thermal expansion α/K^{-1} can be derived from the measured variables with the use of the following relation[21]

$$\langle \alpha_p \rangle = \alpha_{SS} - \frac{kI_n}{T\Delta P_n} \qquad (1)$$

where k is a temperature-dependent calibration constant; I_n is the integral of the calorimetric signal that is the response to the pressure change ΔP_n at temperature T; and α_{SS} is the volume coefficient of thermal expansion of the stainless steel ($5.1 \cdot 10^{-5}$ K^{-1}), practically independent of both pressure and temperature. The transitiometer was calibrated with a hexane at six temperatures [(245.1, 274.5, 304.1, 323.4, 372.3, and 422.2) K] because reliable data exist for that substance proposed as a model of a simple liquid.[22] The results of calibration are presented in Table 2. Pressure values given in Table 2 are the mean values between the beginning and end of pressure step ΔP_n. The end values were measured at the end of the thermogram, after the thermal and mechanical equilibria were established. Each ending pressure became the beginning pressure for the next change. After initial pressurization to the highest pressure, the transitiometer was allowed to equilibrate thermally and mechanically for a few hours before measurements began.

The uncertainty of the calibration constants was about 1 % at each temperature. The uncertainty of determination of integral I_n never exceeded 0.2 %. However, taking into account the uncertainties made on determination of all parameters of eq 1, the global uncertainty of determination of thermal expansivities was found to be 2 %, while the repeatability of the present measurements is estimated to be ± 0.5 %.

Densities ρ at atmospheric pressure were measured with a vibrating-tube densimeter (Anton Paar, model DMA 5000) operated in the static mode with an uncertainty of $5 \cdot 10^{-2}$ $\mathrm{kg \cdot m^{-3}}$, as estimated from results of measurements on standard materials for density determinations, such as highly purified and degassed water, aqueous solutions of sodium chloride, and selected organic liquids.

The reference volume isotherm $V(p,T_R)$ was determined in the transitiometer as follows. A sample of known mass (near 1.5 g) was placed in the measuring vessel, and a compression at a very low rate was performed at ambient temperature T_R. From the recorded data, the total compressibility bdN_t/dp was then determined (b is the calibration constant of the pump, and N_t is the number of motor steps). In a separate experiment, the compression of the hydraulic liquid was performed, without any investigated sample, and its compressibility bdN_h/dp was determined (N_h is the number of motor steps). From the difference, the compressibility of the investigated sample i was determined as follows

$$dV_i/dp = b(dN_t/dp - dN_h/dp) \qquad (2)$$

Table 2. Results of Calibration Experiments Using Hexane as a Calibrating Liquid

α_p(hexane)[a]$\cdot 10^3$ K^{-1}	$\langle p \rangle$ MPa	Δp MPa	I V$\cdot$s	$kV^{-1}\cdot 10^3$ [b] W$\cdot$V$^{-1}\cdot$cm^{-3}
T = 245.1 K				
0.669	170.0	21.15	−51.4944	62.26
0.700	148.8	19.85	−51.9885	60.74
0.733	129.0	19.83	−54.9828	60.28
0.771	109.2	19.96	−57.8157	60.91
0.815	89.2	19.96	−62.1574	60.17
0.869	69.2	14.85	−48.6485	61.19
0.916	54.4	15.00	−53.9659	58.97
	39.4			
mean and standard deviation				60.65 ± 1.01
T = 274.5 K				
0.658	170.0	21.05	−58.3891	60.05
0.691	148.9	19.87	−57.4106	60.82
0.727	129.1	19.89	−61.3795	60.15
0.770	109.2	19.97	−65.6862	59.98
0.821	89.2	19.94	−70.4283	59.87
0.884	69.3	14.84	−56.4861	60.10
0.942	54.4	14.99	−62.0493	59.09
	39.4			
mean and standard deviation				60.01 ± 0.51
T = 304.1 K				
0.642	169.9	20.97	−63.1372	59.69
0.677	149.0	19.82	−62.9066	59.93
0.715	129.1	19.93	−67.1695	59.93
0.762	109.2	19.96	−72.3295	59.63
0.819	89.3	19.89	−78.2336	59.35
0.890	69.4	14.86	−63.2560	59.93
0.958	54.5	14.99	−69.7063	59.31
	39.5			
mean and standard deviation				59.68 ± 0.27
T = 323.4 K				
0.630	169.9	20.92	−65.5192	59.78
0.666	148.9	19.81	−65.4748	60.14
0.705	129.1	19.95	−70.3183	60.02
0.754	109.2	19.88	−75.6291	59.74
0.813	89.3	19.90	−82.4152	59.52
0.890	69.4	14.84	−66.8455	60.23
0.964	54.6	15.01	−73.8738	59.95
	39.6			
mean and standard deviation				59.91 ± 0.25
T = 372.3 K				
0.599	169.9	20.82	−68.9843	61.55
0.635	149.1	19.90	−69.7428	62.07
0.677	129.2	19.89	−74.5530	62.19
0.728	109.3	19.90	−81.1774	61.82
0.793	89.4	19.88	−89.3004	61.53
0.880	69.5	14.88	−74.5669	61.56
0.966	54.7	14.93	−82.4691	61.71
	39.7			
mean and standard deviation				61.78 ± 0.27
T = 422.2 K				
0.572	169.9	20.71	−68.3081	66.76
0.609	149.2	19.86	−70.0944	66.75
0.652	129.3	19.93	−76.0124	66.50
0.705	109.4	19.91	−82.6682	66.51
0.774	89.5	19.82	−92.2415	65.62
0.868	69.7	14.93	−77.7848	66.22
0.967	54.7	14.96	−88.4206	65.38
	39.8			
mean and standard deviation				66.25 ± 0.55

[a] Values calculated from ref 22. [b] Values calculated by use of eq 1.

The compressibility of the investigated sample i was then correlated with a derivative form of the Tait equation

$$\frac{dV_{\mathrm{i}}}{dp} = -\frac{V_{\mathrm{i}}(p_0)C}{B + p} \tag{3}$$

and the Tait constants B and C were determined. The initial volume $V_{\mathrm{i}}(p_0)$ was found from the mass of the sample and its density measured separately. The constants B and C were then used to derive the reference volume isotherm of the investigated substance

$$V(p, T_{\mathrm{R}}) = V_0(T_{\mathrm{R}}, p_0)\left[1 - C\ln\left(\frac{B + p}{B + p_0}\right)\right] \tag{4}$$

where $V(T_{\mathrm{R}}, p_0)$ is the specific volume of the investigated substance under atmospheric pressure and reference temperature conditions.

Results and Discussion

Isobaric Thermal Expansion. Isobaric thermal expansivities of toluene determined at (245.1, 274.5, 304.1, 323.4, 372.3, and 422.2) K at various pressures are presented in Table 3.

The experimental results in Table 3 were correlated as a function of both temperature and pressure with the following equation

$$\alpha_p(p, T) = \frac{a_0 + a_1T + a_2T^2}{[(b_0 + b_1T + b_2T^2) + p]^{-0.5}} \tag{5}$$

where α_p is the isobaric expansion; T is the absolute temperature; and p is pressure.

Adjustable parameters a_i and b_i have been estimated by a nonlinear regression procedure using the Levenberg−Marquardt (StatSoft 2007) algorithm in double precision. The set of the a_i and b_i coefficients for toluene is given in Table 4.

Isobaric thermal expansivities of toluene derived with eq 5 at (243.15, 273.15, 303.15, 323.15, 373.15, and 423.15) K are presented in Figure 2, which shows that the values of the thermal expansion decrease with increasing pressure and also that the influence of temperature on the α_p decreases with increasing pressure. The present data clearly exhibit a single crossing point of the thermal expansion isotherms, which appear in the vicinity of 60 MPa, similarly to the previous observations for simple liquids, like hexane.[22] It is worth noting that for unknown reasons the results of Ter Minassian et al.[11] do not exhibit such a single crossing point over a wide temperature range. Below 60 MPa, the coefficient of thermal expansion for toluene increases with temperature, while above 60 MPa the change is opposite and the coefficient of thermal expansion decreases with temperature.

The results of α_p derived with eq 5 were compared with available literature data, most of them obtained from density measurements[3−7] or density correlations.[8,9] Apart from the Cibulka and Takagi[8] and Assael et al.[9] density correlations for toluene, Lemmon and Span[10] have recently developed an equation of state for this compound. Data were compared also with the ones calculated by Sun et al.[2] using Davis and Gordon's method based on speed of sound measurements. For this purpose, based on a literature data source,[1,2] to calculate thermal expansivities of toluene in rounded temperatures our program[23] has been used. Additionally, toluene data were compared with those obtained by Ter Minassian et al.[11] with piezothermal analysis and by Navia et al.[13] and Verdier and Andersen[12] with the calorimetric method. In Figures 3, 4, and 5, the isobaric expansivities at (243.15, 303.15, and 373.15) K have been compared with literature data, respectively.

The statistical information in Table 5, concerning each data set at (243.15, 303.15, and 373.15) K, consists of the Absolute

Table 3. Results of Measurements for Toluene

$\langle p \rangle$ / MPa	Δp / MPa	I / V·s	$\alpha_p \cdot 10^3$ / K^{-1}
	$T = 245.1$ K		
194.85	25.64	−61.0009	0.640
169.21	20.30	−49.7637	0.658
148.92	19.95	−50.3555	0.675
128.96	19.97	−53.0261	0.708
108.99	19.99	−54.9182	0.730
89.00	19.90	−57.7590	0.769
69.09	14.93	−45.9525	0.812
54.16	14.98	−48.2519	0.848
39.18	15.07	−50.4131	0.879
24.11	15.46	−54.7708	0.928
8.65	6.67	−25.0639	0.981
	$T = 274.5$ K		
194.96	25.23	−66.2969	0.625
169.73	20.57	−55.9444	0.646
149.17	19.95	−56.4629	0.670
129.21	19.98	−59.6128	0.703
109.23	20.01	−62.4967	0.734
89.22	19.99	−65.9013	0.772
69.23	14.86	−51.5800	0.810
54.37	14.97	−55.0095	0.854
39.41	15.08	−58.8151	0.904
24.33	15.27	−63.3821	0.958
9.06	7.06	−31.1557	1.015
	$T = 304.1$ K		
194.99	25.66	−73.5556	0.614
169.33	20.23	−59.6032	0.629
149.10	19.87	−61.4072	0.658
129.23	20.15	−65.0964	0.685
109.08	19.76	−67.9626	0.726
89.32	20.13	−73.8633	0.771
69.19	14.68	−57.1421	0.815
54.51	15.09	−62.8006	0.868
39.42	14.93	−66.4713	0.925
24.49	15.22	−73.2177	0.995
9.27	7.27	−37.1482	1.054
	$T = 323.4$ K		
194.97	25.51	−76.5283	0.607
169.46	20.12	−63.3186	0.634
149.34	19.79	−65.8406	0.667
129.55	20.17	−70.0183	0.694
109.38	20.03	−73.3106	0.729
89.35	19.96	−77.7902	0.773
69.39	14.92	−62.4211	0.826
54.47	15.01	−66.8037	0.876
39.46	15.04	−71.6984	0.934
24.42	15.13	−78.6927	1.015
9.29	7.31	−41.2090	1.096
	$T = 372.3$ K		
194.98	25.52	−77.3083	0.554
169.46	20.18	−63.1062	0.570
149.28	19.92	−66.5826	0.606
129.36	20.03	−71.1527	0.640
109.33	20.01	−76.6278	0.686
89.31	19.74	−81.5078	0.736
69.57	14.87	−66.1287	0.789
54.70	14.96	−73.1171	0.862
39.74	15.16	−80.9138	0.937
24.59	14.78	−88.6720	1.046
9.81	7.83	−53.1891	1.178
	$T = 422.2$ K		
194.89	25.47	−74.6457	0.511
169.43	20.04	−62.4071	0.540
149.39	20.04	−67.3386	0.578
129.35	19.97	−72.1632	0.618
109.38	19.92	−78.5580	0.670
89.47	19.86	−85.4731	0.726
69.61	14.93	−69.7577	0.784
54.68	14.91	−76.7364	0.858
39.76	14.93	−88.4096	0.980
24.83	14.91	−101.4517	1.118
9.92	7.92	−63.0588	1.300

Table 4. Coefficients of Equation 5 for Toluene in the Temperature Limits (243.15 to 423.15) K at Pressures up to 200 MPa, Together with the Mean (δ) and Maximum (Δ) Deviations from the Regression Line

i	a_i / MPa$^{-0.5}$·K^{-i-1}	b_i / MPa·K^{-i}
0	$1.586717 \cdot 10^{-2}$	372.897
1	$-1.858937 \cdot 10^{-5}$	−1.316465
2	$-2.298217 \cdot 10^{-9}$	$1.158079 \cdot 10^{-3}$
δ/K^{-1}	0.000008	
Δ/K^{-1}	0.000024	

Average Deviation (AAD), the Maximum Deviation (Dmax), and the Average Deviation (bias) defined as follows

$$\mathrm{AAD}/\% = \frac{100}{N}\sum_{i=1}^{N}\left|\frac{\alpha_i^{\mathrm{results}} - \alpha_i^{\mathrm{lit}}}{\alpha_i^{\mathrm{results}}}\right| \tag{6}$$

$$\mathrm{Dmax}/\% = \mathrm{Max}\left(100\left|\frac{\alpha_i^{\mathrm{results}} - \alpha_i^{\mathrm{lit}}}{\alpha_i^{\mathrm{results}}}\right|\right) \tag{7}$$

$$\mathrm{bias}/\% = \frac{100}{N}\sum_{i=1}^{N}\frac{\alpha_i^{\mathrm{results}} - \alpha_i^{\mathrm{lit}}}{\alpha_i^{\mathrm{results}}} \tag{8}$$

where N is the number of points of the data set considered and superscripts results and lit denote experimental and literature values, respectively. Valencia et al.[3] and Verdier and Andersen[12] mentioned that the overestimations and underestimations appear, where comparison was done using the data correlations of Cibulka and Takagi.[8] For this reasons, in Figures 3, 4, and 5 and in Table 5 were omitted the comparisons of our results with those of Cibulka and Takagi.[8] Additionally, some authors[14,24−26] mention that the estimated isobaric thermal expansivity depends on the form of functions of adjustable parameters of the Tamman−Tait equation. Verdier and Andersen[12] found that data of thermal expansivities obtained from the Tamman−Tait equation are not more relevant than experimental ones because that equation implies uncertainties as well. Moreover, toluene is considered as a reference liquid for viscosities by the International Association of Transport Properties.[9] Therefore,

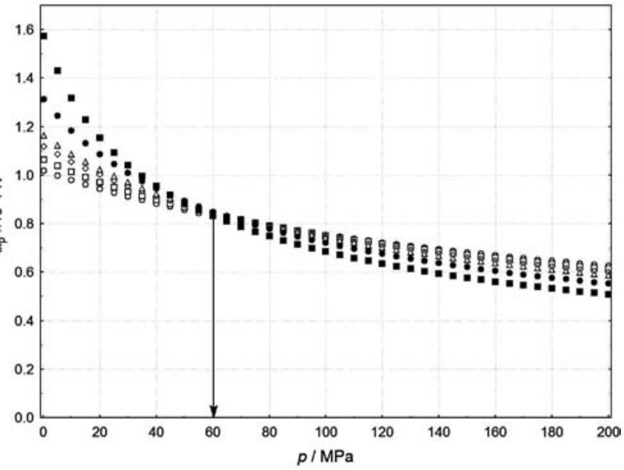

Figure 2. Isobaric thermal expansivity of toluene calculated from eq 5 vs pressure at different temperatures: ○, T = 243.15 K; □, T = 273.15 K; ◊, T = 303.15 K; Δ, T = 323.15 K; ●, T = 373.15 K; ■, T = 423.15 K.

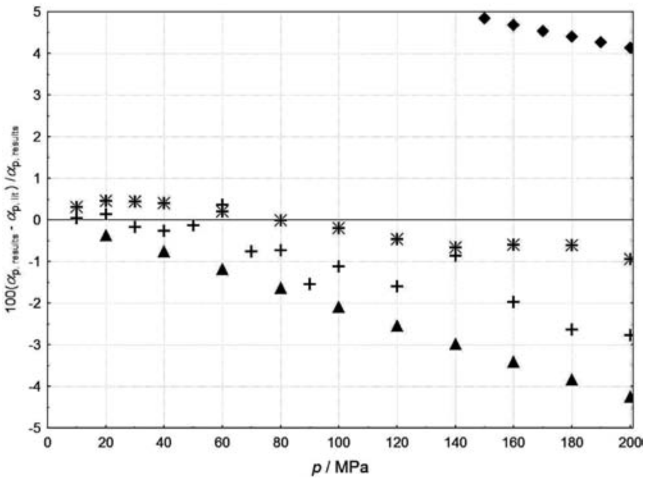

Figure 3. Relative deviations of the experimental values of isobaric expansivities of toluene from the literature data at 243.15 K. ◆, ref 11; ▲, ref 2; +, ref 9; ∗, ref 10.

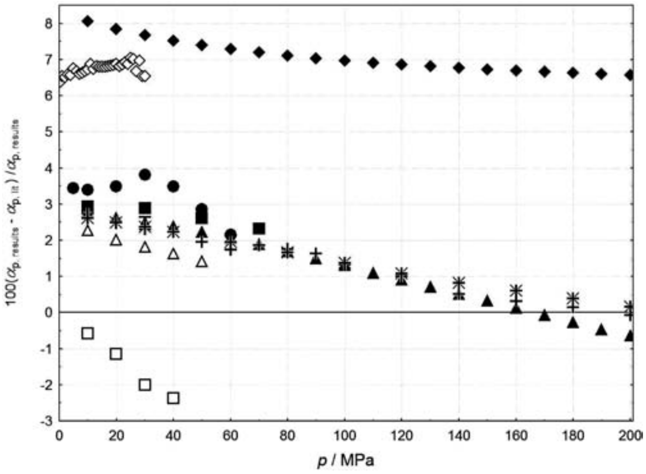

Figure 4. Relative deviations of the experimental values of isobaric expansivities of toluene from the literature data at 303.15 K. □, ref 7; ◇, ref 12; Δ, ref 13; ●, ref 3; ■, ref 4; ◆, ref 11; ▲, ref 2; +, ref 9; −, ref 5; ∗, ref 10.

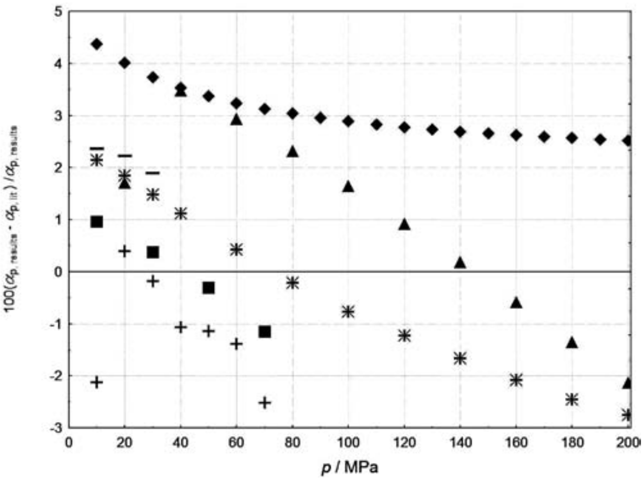

Figure 5. Relative deviations of the experimental values of isobaric expansivities of toluene from the literature data at 373.15 K. ■, ref 4; ◆, ref 11; ▲, ref 6; +, ref 9; −, ref 5; ∗, ref 10.

Assael et al.[9] have also proposed a correlation for the densities of toluene in a wide range of temperature and pressure. As can be observed, the relative differences between our data and Assael et al.[9] correlations are in agreement within the range of 0.1 % to −2.8 %, 2.7 % to −0.1 %, and 0.4 % to −2.5 % at (243.15, 303.15, and 373.15) K, respectively.

As can be seen from Figures 3, 4, and 5 and Table 5, the values of α_p determined in this work and those obtained from the equation of state proposed by Lemmon and Span[10] are in agreement within the range of 0.5 % to −0.9 %, 0.2 % to 2.6 %, and 2.1 % to −2.8 % at (243.15, 303.15, and 373.15) K, respectively. The relative difference between our results and the ones calculated by Sun et al.[2] is between −0.4 % and −4.3 % at 243.15 K and is between −0.6 % and 2.8 % at 303.15 K. Toluene data were compared also with those obtained from calorimetric measurements by Navia et al.[13] ($T = 303.15$ K). The relative difference varies between 1.4 % and 2.3 %. The relative deviation with Valencia et al.[3] ($T = 303.15$ K) varies between 2.1 % and 3.8%. As can also be seen, the relative differences between our data and Segovia et al.[4] are in agreement within the range of 2.3 % to 2.9 % ($T = 303.15$ K) and 1.0 % to −1.2 % ($T = 373.15$ K).

In conclusion, it should be noted that the smallest relative deviations between the present thermal expansivities and those obtained from literature data were observed for values recently provided by the Lemmon and Span[10] equation of state.

Derived Properties. Specific Volume. Values of the specific volume isotherm $V(p, T_R)$ of liquid toluene measured at ambient temperature ($T_R = 292.95$ K) are given in Table 6, column 4. These data were derived from densitometric measurements at atmospheric pressure and compressibility measurements as a function of pressure with the use of eq 4. The compressibilty measurements were performed at a low compression rate of $4 \cdot 10^{-5}$ cm$^3 \cdot$s^{-1}, and the pump calibration constant determined in a separate experiment was $b = 5.11 \cdot 10^{-6}$ cm$^3 \cdot$step^{-1}. The Tait constants obtained with eq 3 were as follows: $B = 95.5771$ MPa, $C = 0.0845307$, the specific volume $V(T_R, p_0) = 1.1533$ cm$^3 \cdot$g^{-1} was determined from density measurements, $p_0 = 0.1013$ MPa. The standard deviation of the differences between the experimental data points and values calculated from eq 4 is $6.7 \cdot 10^{-6}$ cm$^3 \cdot$g^{-1}.

The specific volumes of liquid toluene from atmospheric p_0 or saturation p_s pressure up to 200 MPa and from (243.15 to 423.15) K were obtained from eq 9 with thermal expansivities from eq 5

$$V(T, p) = V(T_R, p)\exp\left[\int_{T_R}^{T} \alpha_p \mathrm{d}T\right] \qquad (9)$$

The saturation vapor pressures, p_s, were taken from Goodwin.[27] The results of calculations of the specific volumes with eq 9 for pressures up to 200 MPa at temperatures from (243.15 to 423.15) K are given in Table 6. Remarkably, our values of specific volumes agree very well with the ones obtained from the Lemmon−Span[10] equation of state, and the average deviation between the two sets of values is 0.2 % with a maximum relative deviation of 0.7 % within the temperature range from (243.15 to 423.15) K and pressures up to 200 MPa.

Coefficient of Isothermal Compressibility. The isothermal compressibilities were derived from the volumes in Table 6 using eq 10

$$\kappa_T(p) = \frac{C}{(B + p)\left[1 - C\ln\left(\frac{B + p}{B + p_s}\right)\right]} \qquad (10)$$

Table 5. Absolute Average Deviation (AAD), Maximum Deviation (Dmax), and Average Deviation (bias) for α_p of Toluene at (243.15, 303.15, and 373.15) K

	AAD/%			Dmax/%			bias/%		
literature source and methods for the determination of α_p	$T =$ 243.15 K	$T =$ 303.15 K	$T =$ 373.15 K	$T =$ 243.15 K	$T =$ 303.15 K	$T =$ 373.15 K	$T =$ 243.15 K	$T =$ 303.15 K	$T =$ 373.15 K
density measurements									
Valencia et al.[3]		3.2			3.8			3.2	
Segovia et al.[4]		2.7	0.7		2.9	1.2		2.7	0.0
Glen and Johns[5]		2.6	2.2		2.6	2.4		2.6	2.2
Franck et al.[6]			1.7			3.5			0.9
Zéberg-Mikkelsen et al.[7]		1.5			2.4			−1.5	
density correlations									
Assael et al.[9]	1.0	1.5	1.3	2.8	2.7	2.5	−0.9	1.5	−1.1
Lemmon and Span[10]	0.4	1.5	1.5	0.9	2.6	2.8	−0.1	1.5	−0.3
calorimetric method									
Verdier and Andersen[12]		6.7			7			6.7	
Navia et al.[13]		1.8			2.3			1.8	
speed of sound									
Sun et al.[2]	2.3	1.3		4.3	2.8		−2.3	1.2	
piezothermal technique									
Ter Minassian et al.[11]	6.1	7.1	3.0	9.3	8.1	4.4	6.1	7.1	3.0

Table 6. Specific Volume of Liquid Toluene

	T/K						
p/MPa	243.15	273.15	292.95	303.15	323.15	373.15	423.15
	$\text{cm}^3 \cdot \text{g}^{-1}$						
p_0 or p_s	1.0942	1.1289	1.1533	1.1664	1.1933	1.2731	1.3673
10	1.0877	1.1207	1.1437	1.1560	1.1810	1.2538	1.3350
20	1.0816	1.1131	1.1349	1.1465	1.1699	1.2371	1.3089
30	1.0759	1.1060	1.1268	1.1378	1.1599	1.2226	1.2875
40	1.0705	1.0995	1.1193	1.1298	1.1507	1.2097	1.2693
50	1.0654	1.0934	1.1124	1.1224	1.1423	1.1982	1.2534
60	1.0607	1.0876	1.1059	1.1155	1.1346	1.1877	1.2393
70	1.0561	1.0822	1.0998	1.1090	1.1273	1.1781	1.2267
80	1.0518	1.0771	1.0941	1.1030	1.1206	1.1693	1.2153
90	1.0477	1.0722	1.0887	1.0973	1.1142	1.1611	1.2049
100	1.0438	1.0676	1.0836	1.0919	1.1083	1.1534	1.1953
110	1.0400	1.0632	1.0787	1.0868	1.1026	1.1463	1.1864
120	1.0364	1.0590	1.0741	1.0819	1.0973	1.1396	1.1781
130	1.0330	1.0550	1.0697	1.0773	1.0922	1.1332	1.1703
140	1.0296	1.0512	1.0655	1.0728	1.0873	1.1272	1.1630
150	1.0264	1.0475	1.0614	1.0686	1.0827	1.1215	1.1562
160	1.0233	1.0439	1.0575	1.0645	1.0783	1.1161	1.1497
170	1.0203	1.0405	1.0538	1.0606	1.0740	1.1110	1.1436
180	1.0174	1.0371	1.0502	1.0569	1.0700	1.1061	1.1377
190	1.0146	1.0339	1.0467	1.0532	1.0661	1.1013	1.1322
200	1.0119	1.0308	1.0433	1.0498	1.0623	1.0968	1.1269

Table 7. Coefficients of the Tait Equation 10 for Toluene, Together with the Mean (δ) and Maximum (Δ) Deviations from the Regression Line

T	B		δ	Δ
K	MPa	C	$10^3\text{m}^3 \cdot \text{kg}^{-1}$	$10^3\text{m}^3 \cdot \text{kg}^{-1}$
243.15	129.2185	0.0805099	0.0000	0.0000
273.15	108.0589	0.0829772	0.0000	0.0000
303.15	89.5016	0.0852778	0.0000	0.0000
323.15	78.0323	0.0865185	0.0000	0.0000
373.15	52.6421	0.0884305	0.0000	0.0001
423.15	31.6516	0.0887835	0.0000	0.0001

Table 7 presents the Tait constants B and C, which were estimated at each temperature by a nonlinear regression procedure using the Levenberg−Marquardt (StatSoft 2007) algorithm in double precision by fitting the specific volume data from Table 6. Figure 6 shows the variation of κ_T as a function of pressure of the liquid toluene at T = (243.15, 273.15, 303.15, 323.15, 373.15, and 423.15) K. The average relative deviation between our values of κ_T and the ones obtained from the Lemmon−Span[10] equation of state is 2.7 % within the temperature range from (243.15 to 423.15) K and pressures up to 200 MPa.

Specific Isobaric Heat Capacity. The effects of pressure on the isobaric heat capacity of liquid toluene at T = (243.15, 273.15, 303.15, 323.15, 373.15, and 423.15) K were calculated with eq 11

$$\Delta_{p_s}^{p} C_p(p) = -T \int_{p_s}^{p} V(p, T)\left[\alpha^2 + \left(\frac{\partial \alpha_p}{\partial T}\right)_p\right] \mathrm{d}p \qquad (11)$$

The isobaric heat capacity of liquid toluene as a function of pressure and temperature was derived with the thermodynamic relation in eq 12

$$C_p(p, T) = C_{p,p_s} + \Delta_{p_s}^{p} C_p(p, T) \qquad (12)$$

where C_{p,p_s} is the specific isobaric heat capacity of liquid toluene at the pressure of saturated vapor. Values of C_{p,p_s} were obtained from Zábranský et al.[28] The specific isobaric heat capacities

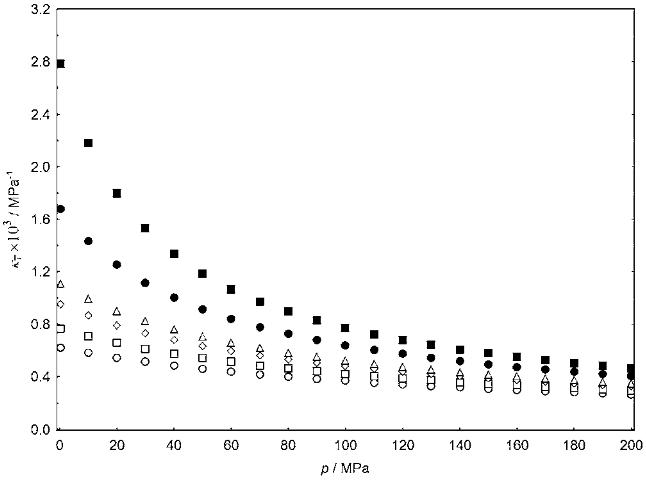

Figure 6. Isothermal compressibility of toluene calculated with eq 10. ○, T = 243.15 K; □, T = 273.15 K; ◇, T = 303.15 K; △, T = 323.15 K; ●, T = 373.15 K; ■, T = 423.15 K.

Table 8. Specific Isobaric Heat Capacity of Liquid Toluene

	T/K					
p/MPa	243.15	273.15	303.15	323.15	373.15	423.15
	C_p/kJ·K^{-1}·kg^{-1}					
p_0 or p_s	1.560	1.634	1.722	1.786	1.961	2.152
10	1.554	1.626	1.711	1.774	1.940	2.114
20	1.549	1.620	1.703	1.764	1.926	2.094
30	1.545	1.614	1.697	1.757	1.916	2.082
40	1.541	1.610	1.692	1.751	1.909	2.076
50	1.538	1.606	1.687	1.747	1.905	2.073
60	1.535	1.603	1.684	1.743	1.902	2.071
70	1.533	1.601	1.681	1.741	1.899	2.071
80	1.531	1.599	1.679	1.739	1.898	2.072
90	1.529	1.597	1.678	1.737	1.898	2.074
100	1.528	1.595	1.676	1.736	1.898	2.076
110	1.527	1.594	1.675	1.735	1.898	2.078
120	1.526	1.593	1.675	1.735	1.899	2.081
130	1.525	1.592	1.674	1.735	1.900	2.084
140	1.524	1.592	1.674	1.735	1.901	2.087
150	1.524	1.592	1.674	1.735	1.902	2.090
160	1.523	1.591	1.674	1.735	1.904	2.093
170	1.523	1.591	1.674	1.736	1.905	2.097
180	1.522	1.591	1.674	1.737	1.907	2.100
190	1.522	1.591	1.675	1.737	1.909	2.103
200	1.522	1.591	1.675	1.738	1.911	2.107

derived with eq 12 for pressures up to 200 MPa and at (243.15, 273.15, 303.15, 323.15, 373.15, and 423.15) K are given in Table 8. Figure 7 shows the variation of C_p as a function of pressure of the liquid toluene at T = (243.15, 273.15, 303.15, 323.15, 373.15, and 423.15) K. Satisfactorily, the minimum shown by C_p curves confirms the internal consistency of our experimental measurements and the derivations. The relative deviation between our values of C_p and the ones calculated by Sun et al.[2] is between −0.3 % and −2.3 % at 243.15 K and is between −0.1 % and −0.6 % at 303.15 K.

The estimation of the accuracy of the derived values of specific volume, coefficient of isothermal compressibility, and specific isobaric heat capacity is a nontrivial problem. A similar problem occurs in estimating the accuracy of derived thermodynamic quantities evaluated from speed of sound data as a function of pressure and temperature using the Davis and Gordon algorithm.[2,23] Thus, Sun et al.[2] proposed the introduction of perturbations on the input data and the tracing of their effects on the final values of derived quantities. Estimation of the accuracy of the computed values presented in this study is made difficult by the necessary sequences of fitting, integrating, and differentiating. Thus, an empirical approach has been taken by determining the effect on the derived values of shifting the input experimental data by a fixed percentage. The results show that the uncertainty in the calculated value is proportional to the uncertainty in the input data; i.e., there is no significant uncertainty amplification by the calculation procedures used in this study.[29] The estimated uncertainties in the data in Tables 6 and 8 are indicated by the number of significant digits listed.

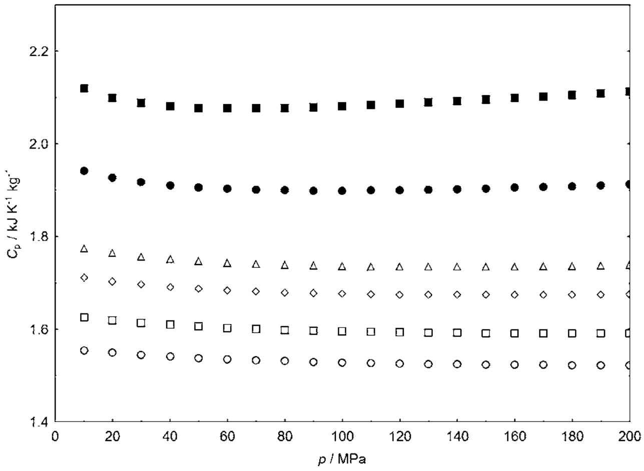

Figure 7. Isobaric specific heat capacity of toluene calculated with eq 12. ○, T = 243.15 K; □, T = 273.15 K; ◇, T = 303.15 K; △, T = 323.15 K; ●, T = 373.15 K; ■, T = 423.15 K.

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