Thermodynamic Properties of Liquid Toluene and *n*-Butane Determined from Speed of Sound Data

Ahmed El Hawary¹ · Karsten Meier¹

Received: 31 October 2021 / Accepted: 1 December 2021 / Published online: 4 March 2022
© The Author(s) 2022

Abstract

The method of thermodynamic integration is applied to calculate accurate data for the density and isobaric and isochoric heat capacity of toluene and *n*-butane from speed of sound data sets measured previously in our laboratory. Values for the density and isobaric heat capacity on the initial isobar for the integration are derived from very accurate density and speed of sound data sets using well-known thermodynamic relations. The relative expanded uncertainties (at the 0.95 confidence level) in the derived values for the density and isobaric and isochoric heat capacities are estimated to be 0.011 %, 0.3 %, and 0.4 % for toluene and 0.02 %, 0.5 %, and 0.7 % for *n*-butane, respectively. Comparisons with experimental data, values of other authors derived by the thermodynamic integration, and equations of state show that our values for both fluids are more accurate than most data available in the literature. Moreover, the domain of the thermodynamic integration for toluene extends down to 240 K and covers lower temperatures than recently considered by other authors. The derived values for the isobaric heat capacity of *n*-butane fill a gap as this property has hitherto only been measured at ambient pressure. Because of their low uncertainty, the values of the derived properties reported in this work in combination with recent data of other authors are useful for developing new and improved equations of state for both fluids.

Keywords Density · Isobaric heat capacity · Isochoric heat capacity · *n*-Butane · Speed of sound · Thermodynamic integration · Toluene

---

This article is part of the Special Issue in Memory of Professor Talgat Khasanshin.

✉ Karsten Meier
karsten.meier@hsu-hh.de

Ahmed El Hawary
a.elhawary@gmx.net

¹ Institut für Thermodynamik, Helmut-Schmidt-Universität/Universität der Bundeswehr Hamburg, Holstenhofweg 85, 22043 Hamburg, Germany

1 Introduction

When the speed of sound of a fluid in a certain domain of temperature and pressure is known and combined with data for the density and isobaric heat capacity along one isobar at a low pressure in this domain, the density and isobaric heat capacity at high pressures can be obtained from it by numerical integration of the differential relations between the thermodynamic properties with little computational effort [1].

We have recently applied the method of thermodynamic integration to determine the density and isobaric and isochoric heat capacity of isobutane from an accurate speed of sound data set, which was measured with a double-path-length pulse-echo apparatus in our laboratory [2]. In that work, it was shown that initial values of the isobaric heat capacity, which are often not available, can be derived from very accurate density data sets, which cover the temperature range of the speed of sound measurements at moderate pressures.

Here, we apply this method to toluene and *n*-butane, for which extensive and accurate speed of sound data sets were measured in our laboratory with the same apparatus. Meier and Kabelac [3] measured the speed of sound in liquid toluene between 240 K and 420 K up to 100 MPa with a relative uncertainty of 0.03 %. In this work, uncertainties are always given as expanded uncertainties (at the 0.95 confidence level), but simply referred to as uncertainties to retain conciseness. El Hawary and Meier [4] measured the speed of sound in liquid *n*-butane in the temperature range between 200 K and 420 K with pressures up to 100 MPa with a relative uncertainty of 0.016 %. McLinden and Splett [5] published accurate data for the density of toluene in the temperature range between 213.15 K and 473.15 K with pressures up to 35 MPa with a relative uncertainty of 0.01 %, and Glos *et al.* [6] provided an accurate data set for the density of *n*-butane with a relative uncertainty of 0.02 % in the temperature range between 95 K and 340 K with pressures up to 14 MPa. These data can be used in combination with the experimental speeds of sound for toluene and *n*-butane to derive values for the density and isobaric heat capacity on the initial isobar of the thermodynamic integration.

During the course of this work, three further experimental data sets for the speed of sound and derived properties of liquid toluene were published. Shchamialiou *et al.* [7] measured the speed of sound between 298.15 K and 433.15 K with pressures up to 100 MPa and a relative uncertainty of 0.05 %. In the work of Dhakal *et al.* [8], two data sets are reported. One was measured at the University of Western Australia in the temperature range from 306 K to 423 K at pressures up to 65 MPa with a relative uncertainty of 0.04 % to 0.08 %. The second was measured at Imperial College London and covers the temperature range between 283.15 K and 473.15 K with pressures up to 350 MPa and has a relative uncertainty of 0.12 %. Since our speed of sound data extend down to 240 K and are more accurate than these three data sets, it is worthwhile to explore the thermodynamic integration with our data as well.

This article is organized as follows. Section 2 describes the fundamentals of the thermodynamic integration, Sect. 3 presents correlations of our speed

of sound data for toluene and *n*-butane, and Sect. 4 presents the results for the derived properties of toluene and *n*-butane. Our results are compared with experimental data and derived values of other authors from the literature in Sect. 5. Conclusions are presented in Sect. 6.

2 Method of Thermodynamic Integration

By numerical integration of the partial differential equations

$$\left(\frac{\partial \rho}{\partial p}\right)_T = \frac{1}{c^2} + \frac{T}{\rho^2 c_p} \left(\frac{\partial \rho}{\partial T}\right)_p^2 \quad (1)$$

$$\left(\frac{\partial c_p}{\partial p}\right)_T = -\frac{T}{\rho^3} \left[2 \left(\frac{\partial \rho}{\partial T}\right)_p^2 - \rho \left(\frac{\partial^2 \rho}{\partial T^2}\right)_p \right] \quad (2)$$

for the unknown functions $\rho(T, p)$ and $c_p(T, p)$, values for the density ρ and isobaric heat capacity c_p in the domain of the speed of sound measurements can be derived from the speed of sound data. In Eqs. 1 and 2, T denotes the temperature, p the pressure, and c the speed of sound. A well-posed initial value problem is obtained when Eqs. 1 and 2 are supplemented with values for the density and isobaric heat capacity at a low pressure isobar in the domain of the speed of sound measurements. The numerical integration of Eqs. 1 and 2 is performed on a regular grid in the pressure-temperature diagram. For the calculation of the speed of sound at the grid points, the speed of sound data are correlated as a function of temperature and pressure.

For the numerical integration of Eqs. 1 and 2, we apply the predictor-corrector method devised by Dávila and Trusler [9]. Starting on the initial isobar p_0 , intermediate values for the density and isobaric heat capacity at the next pressure on the grid p_1 are calculated by the predictor step

$$\rho(p_1) = \rho(p_0) + \Delta p \left(\frac{\partial \rho}{\partial p}\right)_{T, p_0} \quad (3)$$

$$c_p(p_1) = c_p(p_0) + \Delta p \left(\frac{\partial c_p}{\partial p}\right)_{T, p_0}, \quad (4)$$

in which Δp denotes the pressure step size of the integration. The partial derivatives $(\partial \rho / \partial p)_{T, p_0}$ and $(\partial c_p / \partial p)_{T, p_0}$ on the initial isobar are calculated with Eqs. 1 and 2, which requires values for the derivatives $(\partial \rho / \partial T)_p$ and $(\partial^2 \rho / \partial T^2)_p$ on the initial isobar. These values are obtained using the analytical derivatives of a polynomial fit to the initial values of the density as a function of temperature. The chosen order of the polynomial depends on the fluid and the temperature range, in which the thermodynamic integration is carried out.

The equations for the corrector step

$$\rho(p_1) = \rho(p_0) + \frac{1}{2} \Delta p \left[\left(\frac{\partial \rho}{\partial p} \right)_{T, p_0} + \left(\frac{\partial \rho}{\partial p} \right)_{T, p_1} \right] \quad (5)$$

$$c_p(p_1) = c_p(p_0) + \frac{1}{2} \Delta p \left[\left(\frac{\partial c_p}{\partial p} \right)_{T, p_0} + \left(\frac{\partial c_p}{\partial p} \right)_{T, p_1} \right] \quad (6)$$

contain the derivatives $(\partial \rho / \partial p)_T$ and $(\partial c_p / \partial p)_T$ at both isobars p_0 and p_1 and yield the final values for the density and isobaric heat capacity at the pressure p_1 . The partial derivatives $(\partial \rho / \partial p)_T$ and $(\partial c_p / \partial p)_T$ at p_1 are calculated by Eqs. 1 and 2 using the speed of sound correlation and values for the density and isobaric heat capacity calculated by Eqs. 3 and 4 in the predictor step. Moreover, a polynomial of the same order as in the predictor step is fitted to the predicted values for the density at p_1 as a function of temperature. Values for the derivatives $(\partial \rho / \partial T)_p$ and $(\partial^2 \rho / \partial T^2)_p$ at p_1 are then again calculated using the analytical derivatives of the polynomial. After an integration step has been completed, the corrected densities and isobaric heat capacities at the isobar p_1 serve as initial values for the next integration step. This procedure is repeated until the final pressure p_F is reached.

With a speed of sound correlation and the results of the thermodynamic integration for the density and its derivatives, further properties, such as the isochoric heat capacity, the thermal expansivity, or the isothermal and isentropic compressibility, can be calculated using well-known thermodynamic relations. In this work, we provide values for the isochoric heat capacity in addition to the density and isobaric heat capacity, which are calculated with the relation

$$c_v = c_p - \frac{T}{\rho^2} \left(\frac{\partial \rho}{\partial T} \right)_p^2 \left(\frac{\partial \rho}{\partial p} \right)_T^{-1}. \quad (7)$$

3 Speed of Sound Correlations

As an input for the thermodynamic integration, correlations of the speed of sound data for toluene and *n*-butane as a function of temperature and pressure in the domain of the integration are required. The functional form of the speed of sound correlations for toluene and *n*-butane was established by the linear structural optimization technique devised by Wagner [10]. The structural optimization is a statistical method that determines a functional representation of a given data set with a small number of terms, which represents the data set with the smallest sum of squared deviations, from a large initial set of terms, the so-called bank of terms. An implementation of the structural optimization technique, which was developed by Bischoff [11] at the University of Hannover in 1988, was translated into modern Fortran 90 code, and quadruple-precision 128-bit arithmetic was used throughout. The bank of terms consisted of 1281 polynomial terms of the reduced pressure p/p_c , the reduced temperature T/T_c , and products of both with integer and rational

exponents between 0 and 15 in steps of 0.25 for temperature and between 0 and 4 in steps of 0.2 for pressure. The symbol p_c denotes the critical pressure and T_c the critical temperature of the fluid. It was observed that correlating the square of the speed of sound instead of the speed of sound yielded a somewhat more accurate representation of the experimental speeds of sound. Therefore, the square of the speed of sound was correlated as a double polynomial in reduced temperature and reduced pressure given by

$$[c(p, T)]^2 = \sum_{i=1}^N a_i \left(\frac{p}{p_c} \right)^{m_i} \left(\frac{T}{T_c} \right)^{n_i}, \quad (8)$$

where N is the number of terms in the polynomial. The coefficients a_i and exponents m_i and n_i of the correlations for toluene and n -butane are reported in Table 1. The correlation for toluene covers the complete temperature range of our measurements from 240 K to 420 K, whereas for n -butane the temperature range of the speed of sound correlation was chosen as large as the range, in which our speed of sound data and the density data of Glos *et al.* [6], which were used to determine the initial values for the thermodynamic integration, overlap, that is from 200 K to 340 K.

Relative deviations of the experimental data from the correlations are depicted in Fig. 1. Both correlations represent the data within 50 parts per million (ppm) or better with the exception of one state point for toluene at the lowest pressures on the highest isotherm, which deviates by 93 ppm from the correlation. At high pressures, the deviations decrease to 20 ppm. The uncertainty of the correlations is estimated by the sum of the uncertainty of the experimental data and their largest deviation from the correlation. It amounts to 0.04 % for toluene and 0.02 % for n -butane.

4 Results for Derived Properties

4.1 Toluene

The thermodynamic integration for toluene was carried out in the temperature range between 238.15 K and 423.15 K, which is moderately larger than the range of the speed of sound measurements. At temperatures below 240 K and above 420 K, the speed of sound correlation was extrapolated beyond its range of validity. Since the extrapolation extends only modestly over the limits of the range of validity, it was assumed that the correlation predicts the speed of sound at 238.15 K and 423.15 K still within its uncertainty. The initial pressure for the thermodynamic integration was chosen as 1 MPa. With this choice, it is larger than the vapor pressure at the highest considered temperature of 423.15 K, so that the whole temperature range between 238.15 K and 423.15 K can be covered with the same initial pressure. Initial values for the density and isobaric heat capacity were derived in the range of the thermodynamic integration in steps of 5 K. This rather small step size was necessary to stabilize the polynomial fit at each pressure step of the integration.

The initial values for the density were derived from the data of McLinden and Splett [5]. In the range of the thermodynamic integration, the relative uncertainty

Table 1 Coefficients a_i and exponents m_i and n_i , range of validity, and relative uncertainty $U_{r,cor}$ of the speed of sound correlations for toluene and *n*-butane

Fluid	Toluene			<i>n</i> -Butane		
$U_{r,cor} / \%$	0.04			0.02		
T / K	240 – 420			200–340		
p / MPa	0.1 – 100			0.1–100		
N	18			24		
i	a_i	m_i	n_i	a_i	m_i	n_i
1	7.346568859×10^6	0.0	0.00	1.526691289×10^7	0.0	0.00
2	-1.006333550×10^8	0.0	1.50	-1.584335498×10^7	0.0	0.25
3	2.058285415×10^8	0.0	2.25	-2.448176482×10^7	0.0	4.25
4	-2.196537400×10^8	0.0	3.50	8.203950115×10^7	0.0	4.75
5	1.245672651×10^8	0.0	4.75	-5.722257018×10^7	0.0	5.00
6	3.840633815×10^7	1.0	1.00	-3.319575702×10^5	0.2	0.50
7	-7.721252816×10^7	1.0	1.25	3.307498468×10^5	0.2	15.00
8	4.243289708×10^7	1.0	1.50	7.274464181×10^5	0.4	0.50
9	6.528954478×10^6	1.0	5.00	1.052971594×10^5	0.4	2.00
10	-3.678603287×10^6	2.0	1.75	-8.273271755×10^5	0.6	0.50
11	2.205968755×10^7	2.0	3.25	-2.954336476×10^5	0.6	3.50
12	-6.321457583×10^7	2.0	4.25	4.551657014×10^5	0.8	0.50
13	3.914401469×10^5	3.0	1.50	2.916030873×10^5	0.8	4.50
14	1.011497550×10^8	3.0	5.00	-4.553659639×10^4	1.0	10.00
15	-8.834938446×10^7	4.0	4.75	-2.109373749×10^4	1.2	3.00
16	-5.695920201×10^5	5.0	3.00	3.897464962×10^4	1.4	0.50
17	3.495907226×10^7	5.0	4.25	-1.374951150×10^5	1.4	1.00
18	-5.305286744×10^6	6.0	3.75	1.160847105×10^5	1.4	1.50
19				-8.104495304×10^4	1.8	5.00
20				4.601134908×10^4	2.0	5.50
21				-4.805077871×10^2	3.2	7.00
22				9.008971896×10^1	3.6	7.00
23				4.056885202×10^0	4.0	9.00
24				-1.317359886×10^0	4.4	7.50

of these data is between 60 ppm and 114 ppm. Since McLinden and Splett did not measure the density exactly at 1 MPa, but at slightly different pressures, values for the density at 1 MPa were interpolated from the experimental data with third- to sixth-order polynomials, which were fitted to the data at each measured isotherm. In the next step, a fifth-order polynomial in temperature was fitted to the interpolated values, from which the final initial values were calculated.

The isobaric heat capacity of liquid toluene at high pressures was measured by Akhundov and Eksaev [12, 13], Akhundov *et al.* [14], San José *et al.* [15], Nefedov and Filippov [16], Shulga *et al.* [17], and Segovia *et al.* [18]. Since only

Fig. 1 Relative deviations of the experimental speeds of sound in toluene of Meier and Kabelac [3] and in *n*-butane of El Hawary and Meier [4] from values calculated with the speed of sound correlations as a function of pressure and temperature. Experimental data: ○, 200 K; ○, 220 K; ○, 240 K; ○, 260 K; ○, 280 K; ○, 300 K; ○, 320 K; ○, 340 K; ○, 360 K; ○, 380 K; ○, 400 K; ○, 420 K

a few data of these seven data sets lie in the temperature range of the thermodynamic integration near or at the 1 MPa isobar and there are systematic differences between them, as will be shown in Sect. 5.1.2, the initial values for the isobaric heat capacity were derived from the density data of McLinden and Splett [5] and the speed of sound correlation for toluene by applying the procedure developed in our previous work on isobutane [2]. In this procedure, Eq. 1 is solved for the isobaric heat capacity to yield

$$c_p = \frac{T \left(\frac{\partial \rho}{\partial T} \right)_p^2}{\rho^2 \left[\left(\frac{\partial \rho}{\partial p} \right)_T - \frac{1}{c^2} \right]} \quad (9)$$

and applied to calculate values for the isobaric heat capacity on the initial isobar from initial values for the density, speed of sound, and the derivatives $(\partial \rho / \partial T)_p$ and $(\partial \rho / \partial p)_T$. The speed of sound on the initial isobar was obtained from the speed of sound correlation, Eq. 8, and the derivative $(\partial \rho / \partial T)_p$ at the initial pressure from the polynomial representation of the density. Initial values for $(\partial \rho / \partial p)_T$ on each isotherm were calculated with fifth-order polynomial fits to the isothermal density data of McLinden and Splett. Initial values for the derivative $(\partial^2 \rho / \partial T^2)_p$, which are required in Eq. 2 to calculate the initial values for the derivative $(\partial c_p / \partial p)_T$, were also obtained from the polynomial representation of the density on the initial isobar.

With the calculated initial values, the thermodynamic integration was tentatively performed. First, the numerical stability of the algorithm was assessed by applying different pressure step sizes of 0.01 MPa, 0.1 MPa, and 1 MPa. Since

the maximum differences in density and isobaric heat capacity between integrations with 0.01 MPa and 0.1 MPa were less than 0.1 ppm and 2 ppm, respectively, the pressure step size was chosen as 0.1 MPa. Second, the results for the derivatives of the density and $(\partial c_p / \partial p)_T$ were visually inspected after each run to check them for correct physical behavior. When the integration was performed with the initial values for the derivative $(\partial \rho / \partial p)_T$, it resulted in crossing isotherms of the derivative $(\partial c_p / \partial p)_T$, and the spacings between the isotherms were irregular and physically unreasonable. Moreover, the derived densities showed small deviations from the data of McLinden and Splett at high pressures. To improve the agreement, the initial values for the derivative $(\partial \rho / \partial p)_T$ were manually adjusted by a combination of trial and error and physical intuition until the data of McLinden and Splett were optimally matched, no intersections of the isotherms of the derivatives were observed, and the spacings between the isotherms of the derivatives were reasonable.

The results for the derivatives after this optimization process are depicted in Fig. 2. Due to the low degree of the polynomial representation of the initial densities, the derivatives $(\partial \rho / \partial T)_p$ and $(\partial^2 \rho / \partial T^2)_p$ are very stable and show reasonable behavior. The spacings between the isotherms of the derivative $(\partial^2 \rho / \partial T^2)_p$ decrease with increasing temperature and do not intersect nor touch each other. Even during the optimization process of the initial values for $(\partial \rho / \partial p)_T$, the isotherms of this derivative always remained physically correct. Therefore, the optimization focused on establishing the correct behavior of the derivative $(\partial c_p / \partial p)_T$. Since this derivative is mostly influenced by changes in $(\partial \rho / \partial p)_T$, the initial values for $(\partial \rho / \partial p)_T$ were adjusted until the behavior of $(\partial c_p / \partial p)_T$ was physically correct. The spacings between the lowest and highest isotherms 238.15 K and 423.15 K and their neighboring isotherms 243.15 K and 418.15 K are a little bit smaller than the spacings between the other isotherms. This is probably due to the application of the speed of sound correlation outside the range in which it was fitted to experimental data.

Figure 3 depicts relative deviations of the results for the initial values from the short fundamental equation of state (EOS) of Lemmon and Span [19] for toluene. The uncertainty of the EOS in density is 0.01 % in the vicinity of 300 K at ambient pressure and 0.05 % in the domain of the thermodynamic integration, and the uncertainty in the isobaric and isochoric heat capacity is 0.5 % in the domain of the thermodynamic integration. The initial values for the density agree with the EOS within 0.015 %, which is well within its uncertainty. The largest deviation of -0.015 % is observed at 423.15 K. The deviations of the isobaric heat capacity at low temperatures are larger than the uncertainty of the EOS. Between 238.15 K and 298.15 K, they amount to between 0.78 % and 0.52 %. Above 298.15 K, they agree with the EOS within its uncertainty. The derivative $(\partial \rho / \partial p)_T$ deviates between -0.71 % and 1.5 % from the EOS, while the deviations of the derivative $(\partial \rho / \partial T)_p$ change from -0.18 % at 238.15 K to 0.1 % at 393.15 K and decrease to -0.06 % at 423.15 K.

The results for the derived values are reported in Table 2. It is noted that the tabulated values for the density at pressures below 30 MPa resemble the experimental data of McLinden and Splett [5] and do not provide new information, but are

Fig. 2 Derivatives $(\partial\rho/\partial T)_p$, $(\partial^2\rho/\partial T^2)_p$, $(\partial\rho/\partial p)_T$, and $(\partial c_p/\partial p)_T$ for toluene along isotherms between 238.15 K and 423.15 K in steps of 5 K as a function of pressure. The plots in the right column are enlargements of the grey-shaded areas in the plots in the left column

Fig. 3 Relative deviations in the optimized initial values for the density, isobaric heat capacity, and derivatives $(\partial \rho / \partial T)_p$ and $(\partial \rho / \partial p)_T$ of toluene from values calculated with the EOS of Lemmon and Span [19] as a function of temperature at the isobar 1 MPa. The error bars represent relative uncertainties in the initial values

included for the sake of completeness. The uncertainties in the derived values for the density and isobaric heat capacity were estimated by applying the Gaussian error-propagation law on each step of the predictor-corrector method using the uncertainties of the initial values as input. The relative uncertainties in density and isobaric heat capacity are plotted for all calculated isotherms as a function of pressure in Fig. 4. The relative uncertainty in the density decreases with pressure on each isotherm from 114 ppm at the initial isobar to 100 ppm at 423.15 K and 100 MPa and 109 ppm at 238.15 K and 100 MPa. This unexpected behavior is due to the fact that the absolute uncertainty increases less with pressure than the value of the density. The relative uncertainty in isobaric heat capacity increases with pressure on all isotherms because each integration step adds a larger contribution to its uncertainty than to the uncertainty in density. It varies from 0.28 % at 423.15 K and 1 MPa to

Fig. 4 Relative uncertainties in the derived densities and isobaric heat capacities of toluene as a function of pressure for all calculated isotherms

Table 2 Derived values for the density ρ , the isobaric heat capacity c_p , and the isochoric heat capacity c_v of toluene determined by thermodynamic integration as a function of temperature T and pressure p

p MPa	ρ $\text{kg}\cdot\text{m}^{-3}$	c_p $\text{kJ}(\text{kg}^{-1}\cdot\text{K}^{-1})$	c_v $\text{kJ}(\text{kg}^{-1}\cdot\text{K}^{-1})$	p MPa	ρ $\text{kg}\cdot\text{m}^{-3}$	c_p $\text{kJ}(\text{kg}^{-1}\cdot\text{K}^{-1})$	c_v $\text{kJ}(\text{kg}^{-1}\cdot\text{K}^{-1})$
$T = 238.15 \text{ K}$							
1	918.204	1.5493	1.1148	55	944.472	1.5357	1.1408
5	920.396	1.5476	1.1169	60	946.609	1.5351	1.1430
10	923.071	1.5457	1.1194	65	948.707	1.5346	1.1452
15	925.676	1.5441	1.1219	70	950.767	1.5342	1.1474
20	928.216	1.5425	1.1244	75	952.790	1.5338	1.1495
25	930.695	1.5412	1.1268	80	954.779	1.5335	1.1516
30	933.117	1.5400	1.1292	85	956.735	1.5333	1.1537
35	935.485	1.5389	1.1316	90	958.659	1.5330	1.1558
40	937.802	1.5380	1.1339	95	960.552	1.5329	1.1579
45	940.071	1.5371	1.1362	100	962.416	1.5327	1.1599
50	942.293	1.5364	1.1385				
$T = 243.15 \text{ K}$							
1	913.591	1.5598	1.1253	55	940.488	1.5452	1.1510
5	915.844	1.5580	1.1273	60	942.668	1.5446	1.1532
10	918.590	1.5559	1.1298	65	944.807	1.5440	1.1554
15	921.263	1.5541	1.1323	70	946.907	1.5435	1.1576
20	923.867	1.5525	1.1347	75	948.969	1.5431	1.1597
25	926.407	1.5511	1.1371	80	950.995	1.5428	1.1618
30	928.886	1.5498	1.1395	85	952.986	1.5425	1.1639
35	931.308	1.5486	1.1419	90	954.944	1.5423	1.1659
40	933.677	1.5476	1.1442	95	956.871	1.5421	1.1680
45	935.994	1.5467	1.1465	100	958.767	1.5419	1.1700
50	938.264	1.5459	1.1488				
$T = 253.15 \text{ K}$							
1	904.382	1.5830	1.1482	55	932.583	1.5662	1.1736
5	906.763	1.5809	1.1502	60	934.851	1.5655	1.1758
10	909.660	1.5785	1.1526	65	937.075	1.5649	1.1779
15	912.473	1.5765	1.1551	70	939.256	1.5643	1.1801
20	915.210	1.5746	1.1575	75	941.395	1.5638	1.1822
25	917.874	1.5730	1.1599	80	943.496	1.5634	1.1843
30	920.472	1.5715	1.1622	85	945.559	1.5631	1.1863
35	923.006	1.5702	1.1646	90	947.587	1.5628	1.1884
40	925.481	1.5690	1.1669	95	949.580	1.5626	1.1904
45	927.900	1.5679	1.1691	100	951.541	1.5624	1.1924
50	930.267	1.5670	1.1714				
$T = 263.15 \text{ K}$							
1	895.185	1.6084	1.1731	55	924.757	1.5893	1.1983
5	897.703	1.6060	1.1750	60	927.117	1.5885	1.2004
10	900.759	1.6034	1.1775	65	929.427	1.5878	1.2026
15	903.722	1.6010	1.1799	70	931.691	1.5871	1.2047
20	906.599	1.5989	1.1823	75	933.911	1.5866	1.2068

Table 2 (continued)

p MPa	ρ $\text{kg}\cdot\text{m}^{-3}$	c_p $\text{kJ}(\text{kg}^{-1}\cdot\text{K}^{-1})$	c_v $\text{kJ}(\text{kg}^{-1}\cdot\text{K}^{-1})$	p MPa	ρ $\text{kg}\cdot\text{m}^{-3}$	c_p $\text{kJ}(\text{kg}^{-1}\cdot\text{K}^{-1})$	c_v $\text{kJ}(\text{kg}^{-1}\cdot\text{K}^{-1})$
25	909.395	1.5970	1.1847	80	936.088	1.5861	1.2088
30	912.117	1.5953	1.1870	85	938.225	1.5857	1.2109
35	914.769	1.5938	1.1893	90	940.323	1.5854	1.2129
40	917.355	1.5925	1.1916	95	942.385	1.5851	1.2149
45	919.879	1.5913	1.1938	100	944.411	1.5849	1.2169
50	922.345	1.5903	1.1961				
$T = 273.15 \text{ K}$							
1	885.986	1.6355	1.1994	55	917.006	1.6139	1.2244
5	888.651	1.6328	1.2013	60	919.460	1.6129	1.2265
10	891.879	1.6298	1.2038	65	921.860	1.6121	1.2286
15	895.001	1.6271	1.2062	70	924.210	1.6114	1.2307
20	898.026	1.6247	1.2085	75	926.511	1.6108	1.2328
25	900.962	1.6226	1.2109	80	928.767	1.6102	1.2349
30	903.814	1.6207	1.2132	85	930.980	1.6098	1.2369
35	906.588	1.6190	1.2155	90	933.150	1.6094	1.2389
40	909.291	1.6175	1.2177	95	935.282	1.6090	1.2409
45	911.925	1.6161	1.2200	100	937.375	1.6088	1.2428
50	914.495	1.6149	1.2222				
$T = 283.15 \text{ K}$							
1	876.774	1.6639	1.2267	55	909.324	1.6395	1.2515
5	879.596	1.6608	1.2286	60	911.876	1.6384	1.2537
10	883.008	1.6574	1.2311	65	914.369	1.6375	1.2558
15	886.300	1.6543	1.2335	70	916.807	1.6367	1.2579
20	889.483	1.6516	1.2358	75	919.193	1.6360	1.2599
25	892.566	1.6492	1.2381	80	921.530	1.6354	1.2620
30	895.556	1.6471	1.2404	85	923.820	1.6348	1.2640
35	898.459	1.6452	1.2427	90	926.065	1.6344	1.2660
40	901.283	1.6435	1.2450	95	928.267	1.6340	1.2679
45	904.032	1.6420	1.2472	100	930.429	1.6336	1.2699
50	906.711	1.6407	1.2494				
$T = 293.15 \text{ K}$							
1	867.535	1.6934	1.2549	55	901.707	1.6660	1.2795
5	870.528	1.6899	1.2568	60	904.360	1.6648	1.2816
10	874.137	1.6860	1.2592	65	906.949	1.6637	1.2837
15	877.611	1.6826	1.2616	70	909.479	1.6628	1.2858
20	880.962	1.6795	1.2639	75	911.952	1.6620	1.2879
25	884.200	1.6769	1.2662	80	914.372	1.6613	1.2899
30	887.335	1.6745	1.2685	85	916.741	1.6607	1.2919
35	890.375	1.6723	1.2708	90	919.062	1.6602	1.2939
40	893.326	1.6705	1.2730	95	921.337	1.6597	1.2958
45	896.195	1.6688	1.2752	100	923.569	1.6593	1.2978
50	898.987	1.6673	1.2774				

Table 2 (continued)

p MPa	ρ $\text{kg}\cdot\text{m}^{-3}$	c_p $\text{kJ}(\text{kg}^{-1}\cdot\text{K}^{-1})$	c_v $\text{kJ}(\text{kg}^{-1}\cdot\text{K}^{-1})$	p MPa	ρ $\text{kg}\cdot\text{m}^{-3}$	c_p $\text{kJ}(\text{kg}^{-1}\cdot\text{K}^{-1})$	c_v $\text{kJ}(\text{kg}^{-1}\cdot\text{K}^{-1})$
$T = 303.15 \text{ K}$							
1	858.257	1.7238	1.2838	55	894.149	1.6932	1.3082
5	861.436	1.7199	1.2857	60	896.907	1.6919	1.3103
10	865.257	1.7155	1.2881	65	899.595	1.6907	1.3124
15	868.925	1.7117	1.2904	70	902.219	1.6897	1.3145
20	872.454	1.7083	1.2927	75	904.782	1.6888	1.3165
25	875.858	1.7053	1.2950	80	907.288	1.6880	1.3185
30	879.146	1.7026	1.2973	85	909.739	1.6873	1.3205
35	882.329	1.7003	1.2995	90	912.138	1.6867	1.3225
40	885.414	1.6982	1.3017	95	914.488	1.6862	1.3244
45	888.408	1.6963	1.3039	100	916.791	1.6857	1.3263
50	891.317	1.6947	1.3061				
$T = 313.15 \text{ K}$							
1	848.928	1.7553	1.3134	55	886.644	1.7211	1.3375
5	852.307	1.7508	1.3152	60	889.511	1.7196	1.3396
10	856.357	1.7459	1.3176	65	892.303	1.7184	1.3417
15	860.233	1.7416	1.3199	70	895.024	1.7172	1.3438
20	863.953	1.7378	1.3222	75	897.680	1.7162	1.3458
25	867.532	1.7345	1.3244	80	900.273	1.7153	1.3478
30	870.982	1.7315	1.3267	85	902.807	1.7145	1.3498
35	874.315	1.7289	1.3289	90	905.286	1.7139	1.3517
40	877.540	1.7266	1.3311	95	907.713	1.7133	1.3537
45	880.665	1.7246	1.3333	100	910.089	1.7128	1.3556
50	883.698	1.7227	1.3354				
$T = 323.15 \text{ K}$							
1	839.534	1.7877	1.3436	55	879.188	1.7497	1.3675
5	843.131	1.7826	1.3454	60	882.168	1.7481	1.3696
10	847.428	1.7771	1.3477	65	885.066	1.7467	1.3716
15	851.528	1.7723	1.3500	70	887.888	1.7454	1.3737
20	855.451	1.7681	1.3522	75	890.639	1.7443	1.3757
25	859.216	1.7644	1.3545	80	893.323	1.7433	1.3777
30	862.837	1.7612	1.3567	85	895.943	1.7424	1.3796
35	866.328	1.7583	1.3589	90	898.504	1.7417	1.3816
40	869.699	1.7557	1.3611	95	901.009	1.7410	1.3835
45	872.961	1.7535	1.3632	100	903.460	1.7404	1.3854
50	876.122	1.7515	1.3654				
$T = 333.15 \text{ K}$							
1	830.061	1.8210	1.3744	55	871.777	1.7789	1.3979
5	833.896	1.8153	1.3762	60	874.873	1.7771	1.4000
10	838.460	1.8091	1.3784	65	877.882	1.7756	1.4020
15	842.799	1.8038	1.3806	70	880.807	1.7742	1.4041
20	846.940	1.7991	1.3828	75	883.656	1.7730	1.4061
25	850.902	1.7950	1.3851	80	886.433	1.7719	1.4080

Table 2 (continued)

p MPa	ρ $\text{kg}\cdot\text{m}^{-3}$	c_p $\text{kJ}(\text{kg}^{-1}\cdot\text{K}^{-1})$	c_v $\text{kJ}(\text{kg}^{-1}\cdot\text{K}^{-1})$	p MPa	ρ $\text{kg}\cdot\text{m}^{-3}$	c_p $\text{kJ}(\text{kg}^{-1}\cdot\text{K}^{-1})$	c_v $\text{kJ}(\text{kg}^{-1}\cdot\text{K}^{-1})$
30	854.704	1.7915	1.3873	85	889.142	1.7709	1.4100
35	858.361	1.7883	1.3894	90	891.787	1.7701	1.4119
40	861.887	1.7855	1.3916	95	894.371	1.7693	1.4138
45	865.292	1.7830	1.3937	100	896.898	1.7687	1.4157
50	868.586	1.7808	1.3958				
$T = 343.15 \text{ K}$							
1	820.493	1.8552	1.4056	55	864.405	1.8085	1.4288
5	824.588	1.8487	1.4073	60	867.623	1.8066	1.4308
10	829.443	1.8418	1.4095	65	870.745	1.8049	1.4329
15	834.040	1.8359	1.4117	70	873.778	1.8034	1.4349
20	838.412	1.8307	1.4139	75	876.728	1.8021	1.4368
25	842.584	1.8262	1.4160	80	879.600	1.8009	1.4388
30	846.578	1.8223	1.4182	85	882.399	1.7998	1.4407
35	850.411	1.8188	1.4204	90	885.130	1.7989	1.4427
40	854.098	1.8158	1.4225	95	887.796	1.7981	1.4445
45	857.652	1.8131	1.4246	100	890.402	1.7974	1.4464
50	861.085	1.8107	1.4267				
$T = 353.15 \text{ K}$							
1	810.815	1.8900	1.4371	55	857.071	1.8385	1.4599
5	815.195	1.8828	1.4388	60	860.414	1.8364	1.4619
10	820.365	1.8750	1.4408	65	863.654	1.8346	1.4639
15	825.241	1.8684	1.4430	70	866.797	1.8330	1.4659
20	829.861	1.8627	1.4451	75	869.851	1.8315	1.4679
25	834.257	1.8578	1.4473	80	872.821	1.8302	1.4698
30	838.453	1.8535	1.4494	85	875.713	1.8291	1.4717
35	842.471	1.8497	1.4515	90	878.532	1.8280	1.4736
40	846.327	1.8463	1.4536	95	881.282	1.8272	1.4755
45	850.038	1.8434	1.4557	100	883.967	1.8264	1.4774
50	853.615	1.8408	1.4578				
$T = 363.15 \text{ K}$							
1	801.009	1.9254	1.4687	55	849.770	1.8685	1.4910
5	805.703	1.9172	1.4702	60	853.243	1.8663	1.4930
10	811.218	1.9085	1.4722	65	856.605	1.8643	1.4950
15	816.394	1.9012	1.4743	70	859.862	1.8626	1.4969
20	821.281	1.8949	1.4764	75	863.023	1.8610	1.4989
25	825.914	1.8895	1.4785	80	866.094	1.8596	1.5008
30	830.325	1.8848	1.4806	85	869.082	1.8583	1.5027
35	834.537	1.8806	1.4827	90	871.991	1.8572	1.5046
40	838.572	1.8770	1.4848	95	874.826	1.8563	1.5065
45	842.446	1.8738	1.4869	100	877.592	1.8554	1.5083
50	846.174	1.8710	1.4889				

Table 2 (continued)

p MPa	ρ $\text{kg}\cdot\text{m}^{-3}$	c_p $\text{kJ}(\text{kg}^{-1}\cdot\text{K}^{-1})$	c_v $\text{kJ}(\text{kg}^{-1}\cdot\text{K}^{-1})$	p MPa	ρ $\text{kg}\cdot\text{m}^{-3}$	c_p $\text{kJ}(\text{kg}^{-1}\cdot\text{K}^{-1})$	c_v $\text{kJ}(\text{kg}^{-1}\cdot\text{K}^{-1})$
$T = 373.15 \text{ K}$							
1	791.056	1.9612	1.5000	55	842.501	1.8984	1.5219
5	796.098	1.9519	1.5015	60	846.109	1.8960	1.5238
10	801.989	1.9421	1.5034	65	849.596	1.8939	1.5258
15	807.491	1.9339	1.5055	70	852.971	1.8920	1.5278
20	812.664	1.9270	1.5075	75	856.243	1.8903	1.5297
25	817.551	1.9211	1.5096	80	859.418	1.8888	1.5316
30	822.189	1.9159	1.5116	85	862.503	1.8875	1.5335
35	826.607	1.9115	1.5137	90	865.504	1.8863	1.5354
40	830.829	1.9076	1.5158	95	868.427	1.8852	1.5372
45	834.874	1.9041	1.5178	100	871.276	1.8843	1.5391
50	838.760	1.9011	1.5198				
$T = 383.15 \text{ K}$							
1	780.935	1.9971	1.5310	55	835.262	1.9279	1.5523
5	786.364	1.9865	1.5324	60	839.010	1.9253	1.5543
10	792.668	1.9756	1.5343	65	842.627	1.9230	1.5563
15	798.524	1.9665	1.5362	70	846.123	1.9210	1.5582
20	804.004	1.9589	1.5382	75	849.508	1.9192	1.5601
25	809.163	1.9524	1.5402	80	852.790	1.9176	1.5620
30	814.042	1.9468	1.5423	85	855.975	1.9162	1.5639
35	818.677	1.9419	1.5443	90	859.071	1.9149	1.5657
40	823.095	1.9377	1.5463	95	862.084	1.9138	1.5676
45	827.319	1.9340	1.5483	100	865.017	1.9128	1.5694
50	831.369	1.9308	1.5504				
$T = 393.15 \text{ K}$							
1	770.625	2.0331	1.5615	55	828.050	1.9569	1.5823
5	776.484	2.0211	1.5628	60	831.944	1.9541	1.5843
10	783.243	2.0088	1.5646	65	835.696	1.9517	1.5862
15	789.484	1.9988	1.5664	70	839.317	1.9496	1.5882
20	795.296	1.9904	1.5684	75	842.819	1.9477	1.5901
25	800.744	1.9833	1.5704	80	846.210	1.9460	1.5919
30	805.880	1.9772	1.5724	85	849.498	1.9445	1.5938
35	810.744	1.9720	1.5744	90	852.691	1.9431	1.5956
40	815.368	1.9674	1.5764	95	855.794	1.9419	1.5974
45	819.780	1.9634	1.5784	100	858.815	1.9408	1.5992
50	824.001	1.9599	1.5804				
$T = 403.15 \text{ K}$							
1	760.099	2.0695	1.5917	55	820.865	1.9855	1.6120
5	766.442	2.0559	1.5929	60	824.908	1.9826	1.6139
10	773.703	2.0420	1.5945	65	828.799	1.9800	1.6158
15	780.363	2.0308	1.5963	70	832.549	1.9778	1.6177
20	786.532	2.0216	1.5982	75	836.171	1.9758	1.6196
25	792.291	2.0139	1.6001	80	839.674	1.9740	1.6215

Table 2 (continued)

p MPa	ρ $\text{kg}\cdot\text{m}^{-3}$	c_p $\text{kJ}(\text{kg}^{-1}\cdot\text{K}^{-1})$	c_v $\text{kJ}(\text{kg}^{-1}\cdot\text{K}^{-1})$	p MPa	ρ $\text{kg}\cdot\text{m}^{-3}$	c_p $\text{kJ}(\text{kg}^{-1}\cdot\text{K}^{-1})$	c_v $\text{kJ}(\text{kg}^{-1}\cdot\text{K}^{-1})$
30	797.699	2.0073	1.6021	85	843.067	1.9724	1.6233
35	802.804	2.0016	1.6041	90	846.359	1.9709	1.6252
40	807.645	1.9967	1.6060	95	849.556	1.9697	1.6270
45	812.253	1.9925	1.6080	100	852.664	1.9685	1.6288
50	816.652	1.9888	1.6100				
$T = 413.15 \text{ K}$							
1	749.329	2.1068	1.6222	55	813.700	2.0142	1.6416
5	756.216	2.0912	1.6231	60	817.898	2.0111	1.6436
10	764.033	2.0757	1.6246	65	821.932	2.0085	1.6455
15	771.151	2.0632	1.6262	70	825.814	2.0061	1.6474
20	777.706	2.0530	1.6280	75	829.559	2.0040	1.6493
25	783.796	2.0446	1.6299	80	833.176	2.0021	1.6511
30	789.492	2.0375	1.6318	85	836.677	2.0004	1.6530
35	794.853	2.0314	1.6338	90	840.070	1.9989	1.6548
40	799.922	2.0261	1.6358	95	843.362	1.9976	1.6566
45	804.734	2.0216	1.6377	100	846.560	1.9964	1.6584
50	809.318	2.0177	1.6397				
$T = 423.15 \text{ K}$							
1	738.283	2.1461	1.6539	55	806.546	2.0440	1.6724
5	745.785	2.1283	1.6545	60	810.904	2.0408	1.6743
10	754.220	2.1107	1.6556	65	815.084	2.0379	1.6762
15	761.837	2.0969	1.6571	70	819.102	2.0354	1.6781
20	768.808	2.0857	1.6588	75	822.972	2.0332	1.6800
25	775.251	2.0765	1.6607	80	826.707	2.0313	1.6819
30	781.254	2.0688	1.6626	85	830.317	2.0295	1.6837
35	786.882	2.0622	1.6645	90	833.812	2.0280	1.6855
40	792.189	2.0566	1.6665	95	837.200	2.0266	1.6873
45	797.214	2.0518	1.6684	100	840.488	2.0254	1.6891
50	801.990	2.0476	1.6704				

Relative expanded uncertainties (at the 0.95 confidence level): $U_r(\rho) = 0.011\%$; $U_r(c_p) = 0.32\%$ at 238.15 K to $U_r(c_p) = 0.30\%$ at 423.15 K; $U_r(c_v) = 0.44\%$ at 200 K to $U_r(c_v) = 0.37\%$ at 340 K

0.32 % at 238.15 K and 100 MPa. Since both uncertainties change only modestly with temperature and pressure, the relative uncertainties are generally estimated by their largest values to be 0.011 % in density and 0.32 % in isobaric heat capacity.

4.2 *n*-Butane

The temperature range of the density measurements of Glos *et al.* [6] overlaps with the range of the speed of sound measurements of El Hawary and Meier [4] between 200 K and 340 K. Since there are no further accurate density data available at higher temperatures in the liquid region, the thermodynamic integration was applied in this temperature range only. The initial isobar was chosen at 2 MPa. The initial values for the density and isobaric heat capacity were derived in the same way as described in Sect. 4.1 for toluene from the density data of Glos *et al.* and the speed of sound correlation for *n*-butane. This includes interpolation of densities at the initial isobar, the interpolation of density values at the isotherms 220 K and 240 K, which were not measured by Glos *et al.*, and the determination of initial values for the isobaric heat capacity at 2 MPa by the procedure described in Sect. 4.1 for toluene and Ref. [2] for isobutane. Since the *n*-butane data of Glos *et al.* scatter somewhat more than their data for isobutane [6], it was more difficult to determine accurate initial values for the derivatives $(\partial\rho/\partial T)_p$, $(\partial^2\rho/\partial T^2)_p$, and $(\partial\rho/\partial p)_T$. At 260 K, the density data at the lowest pressures scatter, so that a reliable initial value for the density could not be estimated at first instance. Furthermore, they published a wrong value for the pressure for the measurement at 280 K and 4 MPa, which made it more difficult to derive an accurate initial value for the derivative $(\partial\rho/\partial p)_T$ at 2 MPa at this isotherm. Since the isotherms 260 K and 280 K are in the center of the temperature range of the thermodynamic integration, inconsistent initial values have a large influence on the results for the density and heat capacities. Therefore, the measurements of Glos *et al.* [6] at the other isotherms were assigned a higher weight than the data at 260 K and 280 K.

As for toluene, the pressure step size was chosen as 0.1 MPa. In order to ensure correct physical behavior of the derivatives $(\partial\rho/\partial T)_p$, $(\partial^2\rho/\partial T^2)_p$, $(\partial\rho/\partial p)_T$, and $(\partial c_p/\partial p)_T$, the thermodynamic integration was tentatively performed with slightly different initial values for the derivative $(\partial\rho/\partial p)_T$, and the results for the derivatives were visually inspected for each run of the integration. The initial values for the derivative $(\partial\rho/\partial p)_T$ were manually adjusted until the Glos *et al.* data were optimally matched, no crossings of the isotherms of the derivatives $(\partial\rho/\partial T)_p$, $(\partial\rho/\partial p)_T$, and $(\partial c_p/\partial p)_T$ were observed, and the spacings between them were reasonable. Figure 5 depicts the results for the four derivatives. The isotherms of the derivatives $(\partial\rho/\partial T)_p$ and $(\partial\rho/\partial p)_T$ show the expected characteristic behavior and are well spaced. The isotherms of the derivative $(\partial^2\rho/\partial T^2)_p$ generally also show the correct physical behavior, but between 275 K and 340 K they are too close to each other. Moreover, the 200 K isotherm is too close to the 205 K isotherm. However, the influence of these deficiencies on the results for the isobaric heat capacity is small since the absolute values of the second derivative are small, especially at high pressures. The isotherms of the derivative $(\partial c_p/\partial p)_T$ do not

Fig. 5 Derivatives $(\partial\rho/\partial T)_p$, $(\partial^2\rho/\partial T^2)_p$, $(\partial\rho/\partial p)_T$, and $(\partial c_p/\partial p)_T$ for *n*-butane along isotherms between 200 K and 340 K in steps of 5 K as a function of pressure. The plots in the right column are enlargements of the grey-shaded areas in the plots in the left column

cross each other and are overall reasonably spaced, except at the lower and upper limits of the temperature range of the integration. The two isotherms at 200 K and 340 K are a little bit too close to the 205 K and 335 K isotherms. The optimization of the initial values of the derivative $(\partial\rho/\partial p)_T$ is important because they have a large influence on the results for the isobaric heat capacity. In order to improve the behavior of the derivative $(\partial^2\rho/\partial T^2)_p$ further, even more accurate density data would be required.

Figure 6 shows relative deviations of the optimized initial values for the density, isobaric heat capacity, and the derivatives $(\partial\rho/\partial p)_T$ and $(\partial\rho/\partial T)_p$ from the EOS of Bückner and Wagner [20]. The initial values for the density agree with the EOS within 60 ppm, whereas higher deviations of up to 1.3 % are observed for the isobaric heat capacity. The derivatives $(\partial\rho/\partial p)_T$ and $(\partial\rho/\partial T)_p$ deviate by up to 0.8 % and 0.16 %, respectively, from the EOS. The relative uncertainties in the initial values are estimated to be 0.02 % in density, between 0.50 % at 200 K and 0.27 % at 340 K in isobaric heat capacity, 0.05 % in the derivative $(\partial\rho/\partial p)_T$, and between 0.22 % at 200 K and 0.08 % at 340 K in $(\partial\rho/\partial T)_p$. As the density data of Glos *et al.* for *n*-butane scatter more than their data for isobutane, the maximum uncertainty of 0.02 % reported by Glos *et al.* was used as an estimate for the uncertainty of the initial values for the density. The initial values for the density and isobaric heat capacity agree with the EOS of Bückner and Wagner well within its uncertainty in both properties of 0.02 % and 1 % to 3 %, respectively.

The derived values for the density and isobaric and isochoric heat capacities are reported in Table 3. As for toluene, the uncertainties in the derived properties were estimated by applying the Gaussian error-propagation law on the predictor-corrector method with the uncertainty in the initial values for density, the isobaric heat capacity, the derivatives $(\partial\rho/\partial p)_T$ and $(\partial\rho/\partial T)_p$, and the speed of sound correlation as inputs. Relative uncertainties in the derived values for the density and isobaric heat

Fig. 6 Relative deviations of the initial values for the density, isobaric heat capacity, and derivatives $(\partial\rho/\partial p)_T$ and $(\partial\rho/\partial T)_p$ of *n*-butane from values calculated with the EOS of Bückner and Wagner [20] as a function of temperature along the initial isobar 2 MPa. The error bars represent relative uncertainties in the initial values

capacity are shown in Fig. 7 as a function of pressure for all calculated isotherms. The uncertainties in both properties exhibit a similar behavior as for toluene. The relative uncertainties in the derived properties are conservatively estimated by the largest value on each isotherm to be 0.02 % for the density and between 0.52 % at 200 K and 0.30 % at 340 K for the isobaric heat capacity.

5 Comparison of Derived Properties with Data from the Literature

In this section, our derived properties are compared to the fundamental EOSs of Lemmon and Span for toluene [19] and Bückner and Wagner for *n*-butane [20] and data of other authors from the literature. The literature search for experimental data sets for the properties of toluene and *n*-butane was carried out with the NIST TDE database [21].

5.1 Toluene

5.1.1 Density

More than 750 data sets for the density are available in the NIST TDE database [21]. These data sets were filtered with regard to accuracy and extensiveness. Only data sets with data at pressures above ambient pressure, at temperatures in the region of thermodynamic integration, and which agree with the EOS of Lemmon and Span [19] within its uncertainty of less than 0.05 % were selected for the comparison. Especially single data were not considered. Table 4 summarizes details of the selected data sets for the density of toluene from the literature. Although many measurements of the density of toluene were carried out in the past, only the ten data sets of Akhundov and Abdullaev [22], Avelino *et al.* [23], Zéberg-Mikkelsen *et al.* [24], Moravkova *et al.* [25], Watson *et al.* [26], Segovia *et al.* [27], Valencia *et al.* [28], Rowane *et al.* [29], Tay and Trusler [30], and Shchamialiou *et al.* [7] extend into the high pressure liquid region above 35 MPa. The data of Rowane *et al.* have

Fig. 7 Relative uncertainties in derived densities and isobaric heat capacities of *n*-butane as a function of pressure for all calculated isotherms

Table 3 Derived values for the density ρ , the isobaric heat capacity c_p , and the isochoric heat capacity c_v of *n*-butane determined by thermodynamic integration as a function of temperature T and pressure p

p MPa	ρ kg·m ⁻³	c_p kJ (kg K)	c_v kJ (kg ⁻¹ ·K) ⁻¹	p MPa	ρ kg·m ⁻³	c_p kJ (kg ⁻¹ ·K ⁻¹)	c_v kJ (kg ⁻¹ ·K) ⁻¹
$T = 200$ K							
2	675.321	2.0632	1.4773	55	704.221	2.0194	1.5171
5	677.279	2.0589	1.4798	60	706.489	2.0174	1.5204
10	680.431	2.0526	1.4838	65	708.699	2.0155	1.5237
15	683.455	2.0469	1.4878	70	710.855	2.0139	1.5270
20	686.364	2.0420	1.4917	75	712.961	2.0124	1.5302
25	689.168	2.0376	1.4956	80	715.019	2.0110	1.5333
30	691.876	2.0336	1.4993	85	717.032	2.0098	1.5364
35	694.497	2.0301	1.5030	90	719.001	2.0087	1.5394
40	697.036	2.0270	1.5066	95	720.930	2.0078	1.5424
45	699.499	2.0242	1.5102	100	722.821	2.0069	1.5454
50	701.893	2.0217	1.5137				
$T = 220$ K							
2	656.343	2.1050	1.5016	55	689.198	2.0484	1.5413
5	658.640	2.0992	1.5041	60	691.704	2.0459	1.5447
10	662.309	2.0907	1.5081	65	694.139	2.0436	1.5480
15	665.802	2.0833	1.5121	70	696.508	2.0416	1.5512
20	669.138	2.0768	1.5160	75	698.815	2.0398	1.5544
25	672.332	2.0711	1.5198	80	701.064	2.0382	1.5576
30	675.400	2.0661	1.5236	85	703.259	2.0368	1.5607
35	678.353	2.0617	1.5272	90	705.403	2.0355	1.5637
40	681.201	2.0578	1.5309	95	707.498	2.0343	1.5667
45	683.953	2.0543	1.5344	100	709.546	2.0333	1.5697
50	686.617	2.0512	1.5379				
$T = 230$ K							
2	646.692	2.1306	1.5180	55	681.760	2.0663	1.5573
5	649.188	2.1238	1.5204	60	684.392	2.0635	1.5607
10	653.158	2.1140	1.5244	65	686.946	2.0610	1.5640
15	656.918	2.1055	1.5283	70	689.428	2.0588	1.5672
20	660.494	2.0982	1.5322	75	691.841	2.0568	1.5704
25	663.907	2.0918	1.5360	80	694.190	2.0550	1.5735
30	667.174	2.0861	1.5397	85	696.480	2.0534	1.5766
35	670.310	2.0812	1.5434	90	698.714	2.0520	1.5796
40	673.326	2.0768	1.5470	95	700.895	2.0507	1.5826
45	676.234	2.0729	1.5505	100	703.026	2.0496	1.5855
50	679.043	2.0694	1.5539				
$T = 240$ K							
2	636.906	2.1597	1.5374	55	674.364	2.0869	1.5762
5	639.624	2.1519	1.5397	60	677.129	2.0838	1.5795
10	643.927	2.1405	1.5436	65	679.807	2.0811	1.5827

Table 3 (continued)

p MPa	ρ $\text{kg}\cdot\text{m}^{-3}$	c_p $\text{kJ}(\text{kg K})$	c_v $\text{kJ}(\text{kg}^{-1}\cdot\text{K})^{-1}$	p MPa	ρ $\text{kg}\cdot\text{m}^{-3}$	c_p $\text{kJ}(\text{kg}^{-1}\cdot\text{K}^{-1})$	c_v $\text{kJ}(\text{kg}^{-1}\cdot\text{K})^{-1}$
15	647.980	2.1308	1.5475	70	682.405	2.0786	1.5859
20	651.818	2.1225	1.5513	75	684.928	2.0764	1.5891
25	655.466	2.1153	1.5551	80	687.381	2.0744	1.5922
30	658.947	2.1089	1.5587	85	689.769	2.0727	1.5952
35	662.277	2.1034	1.5624	90	692.096	2.0711	1.5982
40	665.472	2.0985	1.5659	95	694.365	2.0697	1.6011
45	668.544	2.0942	1.5694	100	696.580	2.0684	1.6041
50	671.505	2.0903	1.5728				
$T = 260 \text{ K}$							
2	616.823	2.2296	1.5855	55	659.685	2.1365	1.6226
5	620.076	2.2189	1.5877	60	662.732	2.1329	1.6258
10	625.164	2.2036	1.5913	65	665.672	2.1296	1.6290
15	629.897	2.1910	1.5950	70	668.516	2.1266	1.6321
20	634.331	2.1803	1.5986	75	671.269	2.1240	1.6351
25	638.508	2.1712	1.6022	80	673.939	2.1216	1.6381
30	642.462	2.1633	1.6057	85	676.531	2.1195	1.6411
35	646.220	2.1565	1.6092	90	679.051	2.1176	1.6440
40	649.805	2.1506	1.6127	95	681.504	2.1159	1.6469
45	653.234	2.1453	1.6160	100	683.892	2.1143	1.6497
50	656.523	2.1407	1.6194				
$T = 280 \text{ K}$							
2	595.858	2.3148	1.6445	55	645.134	2.1960	1.6796
5	599.809	2.2997	1.6463	60	648.485	2.1918	1.6827
10	605.891	2.2791	1.6496	65	651.708	2.1880	1.6857
15	611.457	2.2625	1.6529	70	654.814	2.1846	1.6888
20	616.603	2.2489	1.6564	75	657.812	2.1816	1.6917
25	621.400	2.2375	1.6598	80	660.712	2.1789	1.6947
30	625.900	2.2279	1.6632	85	663.519	2.1764	1.6975
35	630.145	2.2196	1.6666	90	666.242	2.1742	1.7003
40	634.166	2.2125	1.6699	95	668.886	2.1723	1.7031
45	637.991	2.2063	1.6732	100	671.456	2.1705	1.7059
50	641.641	2.2008	1.6764				
$T = 300 \text{ K}$							
2	573.687	2.4148	1.7115	55	630.697	2.2620	1.7439
5	578.581	2.3932	1.7128	60	634.378	2.2572	1.7470
10	585.952	2.3648	1.7154	65	637.903	2.2529	1.7500
15	592.556	2.3429	1.7184	70	641.288	2.2491	1.7529
20	598.565	2.3255	1.7216	75	644.546	2.2457	1.7559
25	604.093	2.3113	1.7248	80	647.687	2.2427	1.7587
30	609.225	2.2995	1.7280	85	650.720	2.2400	1.7615
35	614.023	2.2896	1.7313	90	653.655	2.2376	1.7643

Table 3 (continued)

p MPa	ρ kg·m ⁻³	c_p kJ (kg K)	c_v kJ (kg ⁻¹ ·K) ⁻¹	p MPa	ρ kg·m ⁻³	c_p kJ (kg ⁻¹ ·K ⁻¹)	c_v kJ (kg ⁻¹ ·K) ⁻¹
40	618.535	2.2811	1.7345	95	656.498	2.2355	1.7670
45	622.798	2.2739	1.7377	100	659.255	2.2335	1.7697
50	626.844	2.2675	1.7408				
$T = 320$ K							
2	549.836	2.5327	1.7852	55	616.368	2.3326	1.8136
5	556.064	2.5001	1.7856	60	620.403	2.3271	1.8166
10	565.158	2.4600	1.7873	65	624.252	2.3223	1.8195
15	573.081	2.4309	1.7897	70	627.934	2.3180	1.8224
20	580.142	2.4086	1.7925	75	631.465	2.3143	1.8252
25	586.539	2.3909	1.7954	80	634.860	2.3109	1.8280
30	592.404	2.3766	1.7984	85	638.129	2.3080	1.8308
35	597.833	2.3647	1.8015	90	641.284	2.3053	1.8335
40	602.895	2.3547	1.8045	95	644.333	2.3030	1.8362
45	607.645	2.3462	1.8076	100	647.284	2.3009	1.8388
50	612.125	2.3389	1.8106				
$T = 340$ K							
2	523.544	2.6741	1.8635	10	543.273	2.5638	1.8631
5	531.786	2.6221	1.8625	15	552.899	2.5246	1.8648
20	561.260	2.4962	1.8672	65	610.751	2.3952	1.8932
25	568.692	2.4744	1.8698	70	614.747	2.3906	1.8961
30	575.409	2.4572	1.8727	75	618.566	2.3865	1.8989
35	581.556	2.4433	1.8756	80	622.226	2.3828	1.9016
40	587.235	2.4317	1.8786	85	625.742	2.3796	1.9043
45	592.522	2.4220	1.8815	90	629.125	2.3768	1.9070
50	597.476	2.4138	1.8845	95	632.388	2.3742	1.9096
55	602.143	2.4067	1.8874	100	635.539	2.3719	1.9122
60	606.558	2.4006	1.8903				

Relative expanded uncertainties (at the 0.95 confidence level): $U_r(\rho) = 0.02$ %; $U_r(c_p) = 0.52$ % at 200 K to $U_r(c_p) = 0.30$ % at 340 K; $U_r(c_v) = 0.73$ % at 200 K to $U_r(c_v) = 0.40$ % at 340 K

a rather large relative uncertainty of 0.8 % and are therefore not considered in the following discussion. Accurate data below 35 MPa were published by Sommer *et al.* [31], Glen and Johns [32], Zéberg-Mikkelsen and Andersen [33], Masui [34], Ihmels and Gmehling [35], Comuñas *et al.* [36], Magee and Bruno [37], Chyliński and Gregorowicz [38], and McGregor [39]. Besides these experimental data sets, Muringer *et al.* [40] and Dhakal *et al.* [8] obtained densities from speed of sound measurements by the method of thermodynamic integration in large parts of the liquid region. Shchamaliou *et al.* [7] applied a method of thermodynamic integration, which can be viewed as inverse to our method, to derive speeds of sound, isobaric and isochoric heat capacities and further properties from experimental density data.

Table 4 Summary of selected data sets for the density and isobaric as well as isochoric heat capacity of toluene from the literature

Author	Year	Method	Purity (%)	Data	T K	p MPa	$U_r(\rho)$ (%)
<i>Density</i>							
Shchamialiou [7]	2020	VT	99.7	112	274–473	0.1–140.1	0.018
Tay [30]	2018	VT	99.96	140	283–473	1–65	0.09
Rowane [29]	2017	RBVD	99.9	222	295–535	3.2–300	0.8
Sommer [31]	2011	SSD	99.9	247	233–473	0.1–30.1	0.015
Valencia [28]	2009	VT	99.8	72	283–323	0.1–60	0.036
Segovia [27]	2009	VT	99.0	48	283–398	0.1–70	0.09
Glen [32]	2009	SSD	99.9	74	293–373	0.6–30.1	0.01
McLinden [5]	2008	TSD	99.92	975	213–473	0.01–35.6	0.007
Watson [26]	2006	VT	99.8	98	293–353	0.1–65	0.062
Zéberg-Mikkelsen [33]	2005	VT	99.9	28	303–333	0.1–30	0.05
Zéberg-Mikkelsen [24]	2005	VT	99.8	80	283–353	0.1–45	0.012
Morávková [25]	2005	VT	99.9	92	298–328	0.1–39.6	0.012
Avelino [23]	2003	VW	99.8	80	223–348	0.1–80.6	0.15
Masui [34]	2002	SSD	99.92	65	298–423	0.04–30.2	0.025
Ihmels [35]	2001	VT	99.99	497	273–623	0.5–30	0.03
Comuñas [36]	2000	VT	99.8	65	283–323	0.5–12.2	0.024
Magee [37]	1996	GDS	99.974	311	180–400	0.5–35.1	0.05
Chylinski [38]	1991	CVP	99.9	19	298–333	0.1–4.9	0.018
McGregor [39]	1989	VT	N/A	54	350–600	0.8–14	N/A
Akhundov [22]	1970	CVP	99.98	278	298–673	0.5–57.3	0.1
<i>Isobaric heat capacity</i>							
Segovia [18]	2008	FC	99.7	20	273–333	0.1–20	0.5
Shulga [17]	1986	ACHW	99.5	86	255–400	0.1–994	3.0
Nefedov [16]	1980	PHW	N/A	80	300–620	SL–30	N/A
San José [15]	1976	CLFC	N/A	30	393–503	1–2.5	1.0
Holzhauser [41]	1975	AC	99.76	36	162–312	0.1	0.2
Akhundov [12]	1973	CLFC	99.98	199	303–573	0.5–25	0.55
Akhundov [13]	1973	CLFC	99.98	104	573–673	2.5–25	0.6
Akhundov [14]	1973	CLFC	99.98	774	298–673	0.5–20	1.0
<i>Isochoric heat capacity</i>							
Abdulagatov [42]	2008	AC	99.99	52	380–590	isochoric	2.0
Polikhronidi [43]	2001	AC	99.82	120	411–620	isochoric	3.0

AC adiabatic calorimeter, ACHW ac-heated wire, CLFC closed-loop flow calorimetry, CVP constant-volume piezometer, FC flow calorimeter, GDS gravimetric determination of amount of substance, N/A information not available, PHW periodic hot wire, RBVD rolling-ball viscometer/densimeter, SSD single-sinker densimeter, SL saturated liquid, TSD two-sinker densimeter, VT vibrating-tube densimeter, and VW vibrating-wire densimeter

This version of thermodynamic integration uses a correlation of experimental density data as a function of temperature and pressure and initial values for the isobaric heat capacity derived from experimental data at atmospheric pressure as input. The distribution of the experimental data from the literature and the range of the thermodynamic integrations of this work, of Muringer *et al.*, of Shchamialioui *et al.*, and of Dhakal *et al.* is shown in a pressure-temperature diagram in Fig. 8.

Relative deviations of the densities derived in this work, of the densities calculated by Muringer *et al.*, Shchamialioui *et al.*, and Dhakal *et al.*, and the selected experimental data from the literature from the EOS of Lemmon and Span [19] are depicted in Figs. 9 and 10. Since the initial values of the density for the thermodynamic integration were derived from the data of McLinden and Splett [5], our derived densities agree with them within 3 ppm on all isotherms except at 323.15 K, where the deviations increase to 5 ppm at 19 MPa. The agreement with the EOS is within 0.016 % between 243.15 K and 323.15 K and within 0.01 % between 333.15 K and 373.15 K. Above 373.15 K, the deviations increase up to 0.03 % at the highest pressures measured by McLinden and Splett. The largest deviations are observed at 423.15 K near 35 MPa. At higher pressures, our derived densities agree with the EOS within 0.02 % between 243.15 K and 353.15 K, within 0.01 % between 333.15 K and 373.15 K, and at higher temperatures the deviations increase up to 0.04 % at 423.15 K.

Sommer *et al.* [31] measured the density between 233.15 K and 473.15 K up to 30 MPa in steps of 20 K with a single-sinker hydrostatic balance densimeter with a

Fig. 8 Distribution of data from the literature for the density of toluene in the fluid region in a pressure-temperature diagram. The grey-shaded region denotes the region of thermodynamic integration. The dashed lines encircle the regions of thermodynamic integration of other authors: (red), Muringer *et al.* [40]; (blue), Shchamialioui *et al.* [7]; and (green), Dhakal *et al.* [8]. Experimental data: +, Akhundov and Abdullaev [22]; ×, Avelino *et al.* [23]; ▽, Chylinski and Gregorowicz [38]; □, Comuñas *et al.* [36]; ○, Glen and Johns [32]; △, Ihmels and Gmehling [35]; ▽, Magee and Bruno [37]; ◇, Masui [34]; □, McGregor [39]; □, McLinden and Splett [5]; ◇, Morávková *et al.* [25]; ○, Segovia *et al.* [27]; □, Shchamialioui *et al.* [7]; ○, Sommer *et al.* [31]; +, Tay and Trusler [30]; ○, Valencia *et al.* [28]; +, Watson *et al.* [26]; ○, Zéberg-Mikkelsen and Andersen [33]; and ×, Zéberg-Mikkelsen *et al.* [24]. - - -, Triple point temperature, critical pressure, and —, vapor pressure calculated with the EOS of Lemmon and Span [19]

Fig. 9 Relative deviations of derived densities for toluene and data from the literature at nearby temperatures ($T \pm 5$ K) from the EOS of Lemmon and Span [19] as a function of pressure. Derived values: —, this work (---, estimated uncertainty range); ○, Muringer *et al.* [40]; △, Shchamialioui *et al.* [7]; and ◇, Dhakal *et al.* [8]. Experimental data: +, Akhundov and Abdullaev [22]; ×, Avelino *et al.* [23]; ▽, Chylinski and Gregorowicz [38]; □, Comuñas *et al.* [36]; ○, Glen and Johns [32]; △, Ihmels and Gmehling [35]; ▽, Magee and Bruno [37]; ◇, Masui [34]; □, McLinden and Splett [5]; □, Shchamialioui *et al.* [7]; ○, Sommer *et al.* [31]; +, Tay and Trusler [30]; ○, Valencia *et al.* [28]; +, Watson *et al.* [26]; ○, Zéberg-Mikkelsen and Andersen [33]; and ×, Zéberg-Mikkelsen *et al.* [24]

Fig. 10 Relative deviations of derived densities for toluene and data from the literature at nearby temperatures ($T \pm 5$ K) from the EOS of Lemmon and Span [19] as a function of pressure. Derived values: —, this work (---, estimated uncertainty range); Δ , Shchamialiou *et al.* [7]; and $\diamond$, Dhakal *et al.* [8]. Experimental data: +, Akhundov and Abdullaev [22]; $\circ$, Glen and Johns [32]; Δ , Ihmels and Gmehling [35]; $\diamond$, Masui [34]; $\square$, McGregor [39]; $\square$, McLinden and Splett [5]; $\square$, Shchamialiou *et al.* [7]; $\circ$, Segovia *et al.* [27]; $\circ$, Sommer *et al.* [31]; and +, Tay and Trusler [30]

magnetic suspension coupling with a relative uncertainty of 0.015 %. Their results are very consistent and show the same pressure dependence as our derived densities and the McLinden and Splett data, but are systematically lower by up to 0.013 %. Unfortunately, Sommer *et al.* did not analyze the composition of their sample. However, at 293.15 K they carried out measurements with two further toluene samples in addition to the measurements with the sample with which all isotherms were measured to examine the influence of impurities. The measurements with the two additional samples agree better with the data of McLinden and Splett and our derived densities than the main body of measurements. Despite the systematic differences, the data of Sommer *et al.* agree with the data of McLinden and Splett and our derived densities within their uncertainty.

Except for the data of McLinden and Splett [5] and Sommer *et al.* [31], no other data set agrees with our derived densities completely within their uncertainty. However, in many cases mutual agreement within the uncertainties of our derived values and the data from the literature is found. Glen and Johns [32] also used a single-sinker densimeter for measurements of five isotherms between 293.14 K and 373.37 K in steps of 20 K up to 30 MPa and reported a relative uncertainty of 0.01 %. The deviations of their data from the data of McLinden and Splett and our values increase with temperature from +0.008 % at 293 K to +0.03 % at 373 K. Ihmels and Gmehling [35] measured the density between 273.15 K and 623.15 K up to 40 MPa with a vibrating-tube densimeter with an uncertainty of 0.03 %. Their data scatter somewhat more than the three single-sinker data sets, but also agree well with our derived densities and in large parts exhibit a similar pressure dependence as our derived densities. On some isotherms, for example at 373.15 K, 403.15 K, 413.15 K, and 423.15 K, they agree mostly with our values within their uncertainty. On the other isotherms, the deviations are larger and reach up to −0.04 % at 293.15 K. Shchamialiou *et al.* [7] also carried out measurements with a vibrating-tube densimeter. Their data cover the temperature range between 273.65 K and 473.15 K up to 140.1 MPa and have a relative uncertainty of 0.018 %. They show the same pressure dependence as our derived densities, the data of McLinden and Splett, and the data of Sommer *et al.*, but are between 0.015 % and 0.05 % lower than our derived values and the data of McLinden and Splett. The data of Akhundov and Abdullaev [22], Avelino *et al.* [23], Zéberg-Mikkelsen *et al.* [24], Watson *et al.* [26], Segovia *et al.* [27], Valencia *et al.* [28], Zéberg-Mikkelsen and Andersen [33], Masui [34], Comuñas *et al.* [36], Magee and Bruno [37], Chylinski and Gregorowicz [38], and McGregor [39] scatter more and show larger deviations from our derived densities than the data of McLinden and Splett, Sommer *et al.*, Glen and Johns, Shchamialiou *et al.*, and Ihmels and Gmehling.

The densities derived by Muringer [40] also exhibit a similar dependence on pressure as our derived densities. At 243.15 K, they are by 0.02 % and, at 273.15 K, by about 0.01 % higher than our values. At 293.15 K and 323.15 K, they almost coincide with our values. The derived density values reported by Shchamialiou *et al.* [7] were calculated from a correlation, which was fitted to experimental data sets. They also exhibit a similar pressure dependence as our data. In large parts, they agree well with the data of Sommer *et al.*, but at 313.15 K and 333.15 K they are systematically higher and coincide with the data of McLinden and Splett and our derived densities. The derived densities of Dhakal *et al.* [8] agree with our derived values and the data of McLinden and Splett near the initial isobars of thermodynamic integrations because their initial values for the density are also based on the data of McLinden and Splett. Between 283.15 K and 303.15 K, their data increase more strongly with pressure than our derived densities so that deviations up to 0.06 % are observed at 100 MPa. Nevertheless, the agreement of both data sets is within the uncertainty of 0.2 % of the densities derived by Dhakal *et al.* At higher temperatures, the derived densities of Dhakal *et al.* agree with our derived densities mostly within the uncertainty of our values.

5.1.2 Isobaric and Isochoric Heat Capacity

The NIST TDE database [21] contains 47 data sets for the isobaric heat capacity of toluene. Only Akhundov and Eksaev [12, 13], Akhundov *et al.* [14], Nefedov and Filippov [16], San José *et al.* [15], Segovia *et al.* [18], and Shulga *et al.* [17] reported data at pressures above ambient. Furthermore, Sun *et al.* [44], Shchamialiou *et al.* [7], and Dhakal *et al.* [8] derived values for the isobaric heat capacity by the method of thermodynamic integration from speed of sound data sets. The distribution of these eight data sets and the regions of thermodynamic integration of this work, Sun *et al.*, Shchamialiou *et al.*, and Dhakal *et al.* are shown in a pressure–temperature diagram in Fig. 11. The most comprehensive data set for the isobaric heat capacity was measured by Akhundov *et al.* [14]. They reported 774 data covering a large part of the liquid and supercritical regions between 298 K and 673 K with pressures up to 20 MPa. The two data sets of Akhundov and Eksaev [12, 13] cover a similar part of the liquid and superfluid regions from 310 K to 571 K and from 571 K to 672 K, respectively, up to 25 MPa. The data of Nefedov and Filippov [16] extend from 300 K to 620 K with pressures up to 30 MPa. Shulga *et al.* [17] performed measurements between 255 K and 402 K up to 993 MPa. San José *et al.* [15] reported data between 393 K and 503 K up to 2.5 MPa. Segovia *et al.* [18] measured four isotherms between 273.15 K and 333.15 K with pressures up to 20 MPa. Additionally, the data of Holzhauser and Ziegler [41] measured at ambient pressure between 162 K and 312 K are considered in the following discussion because there are only a few data at high pressures below 300 K for the isobaric heat capacity.

Fig. 11 Distribution of data from the literature for the isobaric and isochoric heat capacity of toluene in a pressure-temperature diagram. The grey-shaded region represents the region of thermodynamic integration. The dashed lines encircle the regions of thermodynamic integration of other authors: (red), Sun *et al.* [44], (blue), Shchamialiou *et al.* [7] and (green), Dhakal *et al.* [8]. Black symbols denote isobaric heat capacities, green symbols denote isochoric heat capacities. Experimental isobaric heat capacities: +, Akhundov and Eksaev [12, 13]; ×, Akhundov *et al.* [14]; ∇, Holzhauser and Ziegler [41]; ○, San José *et al.* [15]; □, Nefedov and Filippov [16]; △, Shulga *et al.* [17]; and ◇, Segovia *et al.* [18]. Experimental isochoric heat capacities: □, Abdulagatov *et al.* [42]. - - -, Triple point temperature, critical pressure, and —, vapor pressure calculated with the EOS of Lemmon and Span [19]

Fig. 12 Relative deviations of derived isobaric heat capacities of toluene and data from the literature at nearby temperatures ($T \pm 5$ K) from the EOS of Lemmon and Span [19] as a function of pressure. Derived values: —, this work (---, estimated uncertainty range); ○, Sun *et al.* [44]; and ◇, Dhakal *et al.* [8]. Experimental data: +, Akhundov and Eksaev [12, 13]; ×, Akhundov *et al.* [14]; ▽, Holzhauser and Ziegler [41]; □, Nefedov and Filippov [16]; and △, Shulga *et al.* [17]

Figure 12 depicts relative deviations of our derived isobaric heat capacities, the derived values of Dhakal *et al.* [8], and the selected data from the literature from the EOS of Lemmon and Span [19]. The experimental data of Segovia *et al.* [18] and the derived values of Shchamialioui *et al.* [7] are not included because they are only available at temperatures in the middle between the chosen isotherms in Fig. 12. The deviations of our derived values depend only little on pressure up to 303.15 K and

decrease with pressure at higher temperatures. Overall, they change from +0.8 % at 243.15 K to −0.38 % at 423.15 K. The deviations mainly result from the deviations of the initial values for the thermodynamic integration from the EOS. Above 303.15 K our values agree with the EOS within its uncertainty of 0.5 %, whereas at lower temperatures the deviations are somewhat larger than the uncertainty of the EOS, but the agreement is mostly within the mutual uncertainties.

The ambient pressure data of Holzhauser [41] agree with our derived values within the uncertainty of the derived values of about 0.32 % at 243.15 K and 263.15 K. At 283.15 K and 303.15 K, the deviations from our values are slightly larger than the uncertainty, but well within the mutual uncertainties. The extensive data of Akhundov *et al.* [14] agree well with our data at low pressure, but they exhibit a different dependence on pressure than our values, so that the deviations from our data increase with pressure. Up to 343.15 K, the deviations remain within the uncertainty of our values. On higher isotherms, the deviations from our values are larger than the uncertainty of our values, but they agree with them within their uncertainty of 0.8 %. The data of Akhundov and Eksaev [12, 13] show a similar dependence on pressure as the data of Akhundov *et al.* and agree with them within 0.3 %. The data of Nefedov and Filippov [16] and Shulga *et al.* [17] scatter more than the other data and agree only in parts with our values.

The values for the isobaric heat capacity derived by Dhakal *et al.* [8] agree with our derived values within the uncertainty of our values between 283.15 K and 343.15 K. At the higher isotherms, they are by up to 0.6 % lower than our derived values and lie moderately outside the uncertainty of our values, but well within the uncertainty of their data of 2.2 %. The derived values of Sun *et al.* [44] between 240 K and 300 K agree with our derived isobaric heat capacities with the uncertainty of our values with the exception of one value at 240 K and 100 MPa. Their values at 320 K are systematically lower than ours and lie moderately outside the uncertainty of our values.

Only two experimental data sets are available for the isochoric heat capacity of toluene. Their distribution in a pressure-temperature diagram is also shown in Fig. 11 using green symbols. Abdulagatov *et al.* [42] measured two isochors, but only one lies in the region of thermodynamic integration. The data of Polikhronidi *et al.* [43] are restricted to the vicinity of the critical point and, thus, lie outside the region of the thermodynamic integration. As for the isobaric heat capacity, Sun *et al.* [44], Shchamialiou *et al.* [7], and Dhakal *et al.* [8] provided values for the isobaric heat capacity, which were derived by the method of thermodynamic integration from speed of sound data sets.

Figure 13 depicts relative deviations of our derived isochoric heat capacities, the derived values of Sun *et al.* [44] and Dhakal *et al.* [8], and the experimental data of Abdulagatov *et al.* [42] from the EOS of Lemmon and Span. The uncertainty of the EOS in the isochoric heat capacity amounts to 0.5 %. The deviations of our values increase slightly with pressure and decrease with temperature. The largest deviations of about 1 % are found at 243.15 K and 100 MPa, while on the 423.15 K isotherm they agree with the EOS within 0.3 %. Only one datum of Abdulagatov *et al.* [42] is shown in the plot for 403.15 K at 10 MPa, which deviates by about 0.9 % from our result. The rest of the data lies outside the scale of the plots. The derived values for

Fig. 13 Relative deviations of derived isochoric heat capacities of toluene and data from the literature from the EOS of Lemmon and Span [19] as a function of pressure. Derived values: — this work (---, estimated uncertainty range); ○, Sun *et al.* [44]; and ◇, Dhakal *et al.* [8]. Experimental data: □, Abdulagatov *et al.* [42]

the isochoric heat capacity of Dhakal *et al.* [8] agree with our values mostly within the uncertainty of our values. Moderately larger deviations are observed at above 363.15 K. Overall, the agreement is well within the uncertainty of the derived values of Dhakal *et al.* of 2.6 %. The derived values of Sun *et al.* [44] show a similar behavior as for the isobaric heat capacity. Between 240 K and 300 K, they agree with our values within the uncertainty of our values. Their values at 320 K are systematically

lower than ours and lie somewhat outside the uncertainty of our values. We note that the deviations of the derived values of Dhakal *et al.* exhibit a shallow minimum at 10 MPa at the 283.15 K and 303.13 K isotherms. This effect is not observed for the derived values of Sun *et al.* and our derived values.

5.2 *n*-Butane

5.2.1 Density

Data for the density and isobaric and isochoric heat capacity for liquid *n*-butane of other authors from the literature that were published until 2006 and used in the development of the EOS of Bückner and Wagner were reviewed in Ref. [20]. Since then, six further data sets for the density were published by Kumagai *et al.* [45], Miyamoto and Uematsu [46–48], Ito *et al.* [49], and Herrmann and Vogel [50]. Furthermore, independent of this work Meschkat and Meier [51] measured the density of *n*-butane on the two isotherms 300 K and 320 K up to 100 MPa with a vibrating-tube densimeter in our laboratory. These data have a relative uncertainty of 90 ppm. Details of selected data sets for the three properties from the literature are summarized in Table 5. The distribution of data sets for the density of *n*-butane from the literature in a pressure-temperature diagram is shown in Fig. 14. Additionally, the domain of the thermodynamic integration is indicated by the grey-shaded region.

The relative deviations of the derived densities and data from the literature for the density from the EOS of Bückner and Wagner [20] are depicted in Figs. 15 and 16. The data of Glos *et al.* [6], Haynes [56], Ito *et al.* [49], Kayukawa *et al.* [52], Meschkat and Meier [51], Miyamoto and Uematsu [46], and Olds *et al.* [59] overlap with the region of the thermodynamic integration and were selected for the comparison. All other data from the literature either lie on the boiling line, in the temperature range below or above the domain of the thermodynamic integration, or their deviations from the EOS are mostly larger than the scale of the plots.

Our derived densities agree with the data of Glos *et al.* [6] within 10 ppm on all isotherms, except for the initial value for the density at 340 K and 2 MPa, which deviates by −15 ppm. The largest deviations are observed at 200 K, 260 K, 280 K, and 340 K. These deviations are related to the behavior of the derivative $(\partial^2 \rho / \partial T^2)_p$ at high pressure shown in Fig. 5, where the spacing of the isotherms is not as good as for toluene in Fig. 2. Up to 12 MPa, where the EOS was fitted to the data of Glos *et al.* [6], our derived densities and the Glos *et al.* data agree with the EOS within 60 ppm at 200 K, 40 ppm between 220 K and 320 K, and 0.013 % at 340 K. At higher pressures, the deviations of our derived densities increase up to −0.03 % between 200 K and 300 K and −0.06 % up to 340 K. Generally, the agreement is well within the uncertainty of the EOS, which is 0.02 % at pressures below 12 MPa and between 0.3 % and 0.5 % at higher pressures in the temperature range of the thermodynamic integration.

Arve *et al.* [55] performed measurements at pressures up to 1.13 MPa between 278.15 K and 338.15 K in steps of 20 K. Their data mostly agree with our derived values within the uncertainty of our derived values. Only their data at 338.15 K

Table 5 Summary of selected data sets for the density and isobaric and isochoric heat capacities of *n*-butane from the literature

Author	Year	Method	Purity %	Data	<i>T</i> K	<i>p</i> MPa	<i>U_i</i> (<i>p</i>) %
Density							
Meschkat [51]	2021	VT	99.99	31	300–320	1–100	0.009
Herrmann [50]	2015	SSD	99.99	295	298–444	0.6–30	0.2
Ito [49]	2014	VV	99.97	66	360–600	50–200	0.13–0.6
Miyamoto [48]	2008	VV	99.97	59	380–440	1–200	0.09
Miyamoto [46]	2007	VV	99.97	112	280–380	1–200	0.09
Miyamoto [47]	2007	PZ	99.97	46	280–424	<i>p</i> ^s –3.72	0.08
Kumagai [45]	2006	PZ	98	16	273–333	0.1–30	0.4
Kayukawa [52]	2005	VT	99.99	128	240–380	0.024–7	0.05
Glos [6]	2004	TSD	99.98	66	140–340	0.44–14	0.02
Gupta [53]	1997	BI	99.89	49	265–400	0.016–3.3	0.06–0.16
Kiran [54]	1992	FCVD	99.9	100	323–443	13–69	1.0
Arve [55]	1987	VT	N/A	16	278–338	0.44–1.13	0.02
Haynes [56]	1983	MSD	99.93	105	140–300	1.6–36	0.1
MacCallum [57]	1963	N/A	N/A	22	283–348	0.05–0.14	0.02
Petty [58]	1955	DVM	>99	64	322–411	0.1–3	0.2
Olds [59]	1944	DVM	99.7	217	311–511	0.069–69	0.2
Kay [60]	1940	DVM	N/A	453	311–589	0.19–8.3	0.15
Sage [61]	1937	DVM	99.7	48	294–344	1.72–20.7	0.1
Isobaric heat capacity							
Senftleben [62]	1964	N/A	N/A	5	298–473	0.1	2
Dailey [63]	1943	AFC	99	8	345–693	0.1	1
Dobratz [64]	1941	TC	–	4	294–444	0	5
Aston [65]	1940	AC	99.9	23	142–268	0.1	0.5
Sage [66]	1937	MTP	99.7	8	294–411	0.1	0.7
Beeck [67]	1936	TC	–	4	273–573	0, 0.1	1.0
Isochoric heat capacity							
Magee [68]	1998	AC	99.99	148	141–342	1.9–33	0.7

AC adiabatic calorimeter, AFC adiabatic flow calorimeter, BI Burnett-isochoric method, DVM determination of volume and mass of sample, FCVD falling-cylinder viscometer/densimeter, MSD magnetic suspension densimeter, MTP measurement of a change in temperature resulting a finite isentropic change in pressure, N/A information not available, *p*^s: vapor pressure, PZ Piezometer, TC theoretical calculation, VV metal-bellows variable volumometer, SSD single-sinker densimeter, TSD two-sinker densimeter, and VT vibrating tube densimeter

show somewhat larger deviations. Below 300 K, all other data sets show larger deviations from the EOS than our derived densities. The data of Miyamoto and Uematsu [46] have a similar pressure dependence as our derived values, but tend to scatter and are between 0.16 % and 0.18 % higher than our values. The data of Haynes [56] and Kayukawa et al. [52] agree with our derived values within 0.2 %, but exhibit a different pressure dependence. The data of Olds *et al.* [59] scatter more than the data

Fig. 14 Distribution of data from the literature for the density of *n*-butane in the fluid region in a pressure-temperature diagram. The critical point is at ($T = 425.13$ K; $p = 3.796$ MPa). The grey-shaded region represents the region of thermodynamic integration. Experimental data: Δ , Arve *et al.* [55]; $\square$, Glos *et al.* [6]; $\circ$, Gupta and Eubank [53]; $\times$, Haynes [56]; $\diamond$, Herrmann and Vogel [50]; $\diamond$, Ito *et al.* [49]; $+$, Kay [60]; $\diamond$, Kayukawa *et al.* [52]; $+$, Kiran and Sen [54]; $\square$, Kumagai *et al.* [45]; ∇ , MacCallum and McKetta [57]; $\square$, Meschkat and Meier [51]; $\circ$, Miyamoto and Uematsu [46]; $\square$, Miyamoto and Uematsu [48]; ∇ , Olds *et al.* [59]; $\triangle$, Petty and Smith [58]; and ∇ , Sage *et al.* [61]. - - -, Critical pressure, critical temperature, and —, vapor pressure calculated with the EOS of Bucker and Wagner [20]

of the other authors, but agree with the EOS within their uncertainty of 0.2 % and show the same pressure dependence as our derived densities and the data of Miyamoto and Uematsu. The data of Meschkat and Meier [51] agree with the derived densities and the data of Glos *et al.* [6] within 30 ppm at 300 K and within 60 ppm at 320 K, which confirms the high accuracy of our derived densities.

5.2.2 Isobaric and Isochoric Heat Capacity

For the isobaric heat capacity of *n*-butane, no data are available above ambient pressure. Aston and Messerly [65] published 23 data between 142 K and 268 K at ambient pressure, which can partly be compared with our derived isobaric heat capacities. The data of Beeck [67], Dailey and Felsing [63], Dobratz [64], Sage *et al.* [66], and Senftleben [62] lie in the gas region. Figure 17 depicts the distribution of these data sets and the region of thermodynamic integration in a pressure-temperature diagram.

Figure 18 shows relative deviations of our derived isobaric heat capacities and the data of Aston and Messerly [65] from the EOS of Bucker and Wagner [20]. Our derived values agree with the EOS within 0.9 %, which is within the uncertainty of the EOS of 1 % to 3 %. On all isotherms, the deviations are almost constant and change from +0.2 % at 200 K to −0.9 % at 340 K. The data of Aston and Messerly [65] agree with our derived values within their uncertainty except for a single value at 240 K.

Fig. 15 Relative deviations of derived densities for *n*-butane along isotherms and data from the literature at nearby temperatures ($T \pm 2$ K) from the EOS of Bucker and Wagner [20] as a function of pressure. Derived values: —, this work (---, estimated uncertainty range). Experimental data: Δ , Arve *et al.* [55]; $\square$, Glos *et al.* [6]; $\blacksquare$, Glos *et al.* [6] (interpolated); $\times$, Haynes [56]; $\diamond$, Kayukawa *et al.* [52]; $\circ$, Miyamoto and Uematsu [46]. - - -, Vapor pressure

Fig. 16 Relative deviations of derived densities for *n*-butane and data from the literature at nearby temperatures ($T \pm 5$ K) from the EOS of Bucker and Wagner [20] as a function of pressure. Derived values: —, this work (---, estimated uncertainty range). Experimental data: Δ , Arve *et al.* [55]; $\square$, Glos *et al.* [6]; $\times$, Haynes [56]; $\diamond$, Kayukawa *et al.* [52]; $\square$, Meschkat and Meier [51]; $\circ$, Miyamoto and Uematsu [46]; and ∇ , Olds *et al.* [59]. ---, Vapor pressure

Fig. 17 Distribution of data from the literature for the isobaric and isochoric heat capacities of *n*-butane in a pressure-temperature diagram. The critical point is at ($T = 425.13$ K; $p = 3.796$ MPa). The grey-shaded region denotes the region of the thermodynamic integration. Black symbols denote isobaric heat capacities, green symbols isochoric heat capacities. Experimental isobaric heat capacities: $\square$, Aston and Messerly [65]; $\times$, Beeck [67]; $\circ$, Dailey and Felsing [63]; $+$, Dobratz [64]; ∇ , Sage *et al.* [66]; and $\diamond$, Senteleben [62]. Experimental isochoric heat capacities: $\circ$, Magee and Lüddecke [68]. ---, Critical pressure, critical temperature; and —, vapor pressure calculated with the EOS of Bucker and Wagner [20]

Fig. 18 Relative deviations of derived isobaric heat capacities for *n*-butane along isotherms and data from the literature at nearby temperatures ($T \pm 7.5$ K) from the EOS of Bückner and Wagner [20] as a function of pressure. Derived values: —, this work (---, estimated uncertainty range). Experimental data: □, Aston and Messerly [65]. - - -, Vapor pressure calculated with the EOS of Bückner and Wagner [20]

Magee and Lüddecke [68] measured a comprehensive data set of the isochoric heat capacity of liquid *n*-butane between 150 K and 343 K up to 33.5 MPa with a relative uncertainty of 0.7 %. The distribution of these data in a pressure–temperature diagram is also shown in Fig. 17. Relative deviations of our derived isochoric heat capacities and the data of Magee and Lüddecke [68] from the EOS of Bückner and Wagner are shown in Fig. 19. Our derived isochoric heat capacities agree with the EOS within 1.1 % between 200 K and 240 K, within 1.5 % between 260 K and 280 K, and within 2.1 % between 300 K and 340 K. The uncertainty of the EOS in the isochoric heat capacity in the liquid region was estimated by Bückner and Wagner to be 1 % between 200 K and 300 K and 2 % to 3 % between 300 K and 340 K at pressures up to 33.5 MPa. At higher pressures, it amounts to 5 %. Thus, the agreement with the EOS is mostly within its uncertainty.

Fig. 19 Relative deviations of derived isochoric heat capacities for *n*-butane along isotherms and data from the literature at nearby temperatures ($T \pm 7.5$ K) from the EOS of Bückner and Wagner [20] as a function of pressure. Derived values: —, this work (---, estimated uncertainty range). Experimental data: ○, Magee and Lüddecke [68]. - - -, Vapor pressure calculated with the EOS of Bückner and Wagner [20]

The data of Magee and Lüddecke generally tend to scatter. At 200 K and 220 K, they agree with our derived values within the uncertainty of our derived values. At 240 K, they lie partly outside the uncertainty. At low pressures on the 260 K isotherm, they agree within the uncertainty of the derived values, but at high pressures they are systematically higher by 1.3 %. Between 280 K and 340 K, the data of Magee and Lüddecke [68] show a similar pressure dependence as our derived values, but at 280 K and 300 K they are about 0.8 % higher. At 320 K, the deviations decrease to 0.5 % and at the highest isotherm 340 K the derived values and the data of Magee and Lüddecke [68] agree mostly within the uncertainty in the derived values. Generally, the agreement is mostly within the mutual uncertainties of the two data sets.

6 Conclusions

Using the method of thermodynamic integration, accurate values for the density and isobaric and isochoric heat capacity of toluene and *n*-butane were derived from speed of sound data sets measured previously in our laboratory. Since no suitable data are available for the isobaric heat capacity on the initial isobars of the integration, a procedure developed by us in a previous work on isobutane, with which accurate values of the isobaric heat capacity can be derived from a speed of sound correlation and accurate experimental data for the density, has been applied to derive values for the isobaric heat capacity of toluene and *n*-butane on the initial isobar. Correlations of the experimental speeds of sound in toluene and *n*-butane as a function of temperature and pressure were developed using the method of structural optimization. Extensive comparisons of the derived properties with experimental data for the density and isobaric and isochoric heat capacity shows that our derived values are more accurate than most experimental data and values for these properties derived by other authors by the method of thermodynamic integration. Compared to recent works of other authors, our thermodynamic integration for toluene also covers the range of low temperatures between 240 K and 280 K. Especially valuable are the results for the isobaric heat capacity of *n*-butane at pressures above ambient because until now only data in the gas and liquid regions at ambient pressure have been published by other authors. Our derived values for the density and isobaric and isochoric heat capacity together with recent data from other authors can contribute to develop new improved EOSs for toluene and *n*-butane.

Funding Open Access funding enabled and organized by Projekt DEAL.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit <http://creativecommons.org/licenses/by/4.0/>.

References

1. J.P.M. Trusler, *Physical Acoustics and the Metrology of Fluids* (Adam Hilger, Bristol, 1991)
2. A. El Hawary, K. Meier, J. Chem. Eng. Data **63**, 3684 (2018)
3. K. Meier, S. Kabelac, J. Chem. Eng. Data **58**, 1398 (2013)
4. A. El Hawary, K. Meier, J. Chem. Eng. Data **61**, 3858 (2016)
5. M.O. McLinden, J.D. Splett, J. Res. Natl. Inst. Stand. Technol. **113**, 29 (2008)
6. S. Glos, R. Kleinrahm, W. Wagner, J. Chem. Thermodyn. **36**, 1037 (2004)
7. A.P. Shchamialioui, V.S. Samuilov, F.M. Mosbakh, N.V. Holubeva, A.G. Paddubski, D. Drăgoescu, F. Sîrbu, Fluid Phase Equilib. **507**, 112427 (2020)

8. S. Dhakal, W.J. Tay, S.Z.S. Al Ghafri, D. Rowland, S.P. Mullins, E.F. May, J.P.M. Trusler, P.L. Stanwix, Int. J. Thermophys. **42**, 169 (2021)
9. M.J. Dávila, J.P.M. Trusler, J. Chem. Thermodyn. **41**, 35 (2009)
10. W. Wagner, *A mathematical-statistical method for establishing thermodynamic equations – demonstrated using the vapor pressure curve of pure fluid substances as an example*, Fortschr.-Ber. VDI-Z. Reihe 3, Nr. 39 (1974)
11. M. Bischoff, *The calculation of a thermal equation of state for methanol by using Wagner's regression analysis*, Diploma thesis (Institut für Thermodynamik, Universität Hannover, Germany, 1988)
12. T.S. Akhundov, R.A. Eksaev, Izvestiya Vysshikh Uchebnykh Zavedenij, Neft' Gaz (2), 68 (1973)
13. T.S. Akhundov, R.A. Eksaev, Izvestiya Vysshikh Uchebnykh Zavedenij, Neft' Gaz (3), 66 (1973)
14. T.S. Akhundov, R.A. Eksaev, C.I. Sultanov, Teplofizicheskiye Svoystva Veshchestv i Materialov **7**, 84 (1973)
15. J.L. San José, G. Mellinger, R.C. Reid, J. Chem. Eng. Data **21**, 414 (1976)
16. S.N. Nefedov, L.P. Filippov, Izvestiya Vysshikh Uchebnykh Zavedenij, Neft' Gaz (2), 51 (1980)
17. V.M. Shulga, F.G. Eldarov, Y.A. Atanov, A.A. Kuyumchev, Int. J. Thermophys. **7**, 1147 (1986)
18. J.J. Segovia, D. Vega-Maza, C.R. Chamorro, M.C. Martín, J. Supercrit. Fluids **46**, 258 (2008)
19. E.W. Lemmon, R. Span, J. Chem. Eng. Data **51**, 785 (2006)
20. D. Bücker, W. Wagner, J. Phys. Chem. Ref. Data **35**, 929 (2006)
21. V. Diky, C.D. Muzny, A.Y. Smolyanitsky, A. Bazyleva, R.D. Chirico, J.W. Magee, E. Paulechka, A.F. Kazakov, S.A. Townsend, E.W. Lemmon, M. Frenkel, K.G. Kroenlein, NIST ThermoData Engine Version 10.0 (Pure compounds, binary mixtures, ternary mixtures, and chemical reactions): NIST Standard Reference Database 103b; National Institute of Standards and Technology, Standard Reference Data Program: Gaithersburg (2015)
22. T.S. Akhundov, F.G. Abdullaev, Izvestiya Vysshikh Uchebnykh Zavedenij, Neft' Gaz (5), 67 (1970)
23. H.M.T. Avelino, J.M.N.A. Fareleira, W.A. Wakeham, Int. J. Thermophys. **24**, 323 (2003)
24. C.K. Zéberg-Mikkelsen, L. Lugo, J. García, J. Fernández, Fluid Phase Equilibr. **235**, 139 (2005)
25. L. Morávková, Z. Wagner, J. Linek, J. Chem. Thermodyn. **37**, 658 (2005)
26. G. Watson, T. Lafitte, C.K. Zéberg-Mikkelsen, A. Baylaucq, D. Bessieres, C. Boned, Fluid Phase Equilibr. **247**, 121 (2006)
27. J.J. Segovia, O. Fandiño, E.R. López, L. Lugo, M.C. Martín, J. Fernández, J. Chem. Thermodyn. **41**, 632 (2009)
28. J.L. Valencia, D. González-Salgado, J. Troncoso, J. Peleteiro, E. Carballo, L. Román, J. Chem. Eng. Data **54**, 904 (2009)
29. A.J. Rowane, R.R. Mallepally, B.A. Bamgbade, M.S. Newkirk, H.O. Baled, W.A. Burgess, I.K. Gamwob, D. Tapriyal, R.M. Enick, M.A. McHugh, J. Chem. Thermodyn. **115**, 34 (2017)
30. W.J. Tay, J.P.M. Trusler, J. Chem. Thermodyn. **124**, 107 (2018)
31. D. Sommer, R. Kleinrahm, R. Span, W. Wagner, J. Chem. Thermodyn. **43**, 117 (2011)
32. N.F. Glen, A.I. Johns, J. Chem. Eng. Data **54**, 2538 (2009)
33. C.K. Zéberg-Mikkelsen, S.I. Andersen, J. Chem. Eng. Data **50**, 524 (2005)
34. R. Masui, Int. J. Thermophys. **23**, 921 (2002)
35. E.C. Ihmels, J. Gmehling, Ind. Eng. Chem. Res. **40**, 4470 (2001)
36. M.J.P. Comuñas, E.R. López, P. Pires, J. García, J. Fernández, Int. J. Thermophys. **21**, 831 (2000)
37. J.W. Magee, T.J. Bruno, J. Chem. Eng. Data **41**, 900 (1996)
38. K. Chyliński, J. Gregorowicz, Fluid Phase Equilibr. **64**, 237 (1991)
39. D.R. McGregor, A high pressure, high temperature vibrating tube densimeter: densities of toluene, ethylbenzene, and 2,2,4-trimethylpentane. Ph.D. Thesis, Texas A&M University, College Station, Texas, U.S.A. (1989)
40. M.J.P. Muringer, N.J. Trappeniers, S.N. Biswas, Phys. Chem. Liq. **14**, 273 (1985)
41. J.K. Holzhauser, W.T. Ziegler, J. Phys. Chem. **79**, 590 (1975)
42. I.M. Abdulagatov, N.G. Polikhronidi, T.J. Bruno, R.G. Batyrova, G.V. Stepanov, Fluid Phase Equilibr. **263**, 71 (2008)
43. N.G. Polikhronidi, I.M. Abdulagatov, J.W. Magee, R.G. Batyrova, J. Chem. Eng. Data **46**, 1064 (2001)
44. T.F. Sun, S.A.R.C. Bominaar, C.A. ten Seldam, S.N. Biswas, Ber. Bunsenges. Phys. Chem. **95**, 696 (1991)
45. A. Kumagai, D. Tomida, C. Yokoyama, Int. J. Thermophys. **27**, 376 (2006)
46. H. Miyamoto, M. Uematsu, J. Chem. Thermodyn. **39**, 588 (2007)
47. H. Miyamoto, M. Uematsu, J. Chem. Thermodyn. **39**, 827 (2007)

48. H. Miyamoto, M. Uematsu, *J. Chem. Thermodyn.* **40**, 240 (2008)
49. T. Ito, Y. Nagata, H. Miyamoto, *Int. J. Thermophys.* **35**, 1636 (2014)
50. S. Herrmann, E. Vogel, *J. Chem. Eng. Data* **60**, 3703 (2015)
51. M. Meschkat, K. Meier, unpublished, Institut für Thermodynamik, Helmut-Schmidt-Universität/Universität der Bundeswehr Hamburg (2021)
52. Y. Kayukawa, M. Hasumoto, Y. Kano, K. Watanabe, *J. Chem. Eng. Data* **50**, 556 (2005)
53. D. Gupta, P.T. Eubank, *J. Chem. Eng. Data* **42**, 961 (1997)
54. E. Kiran, Y.L. Sen, *Int. J. Thermophys.* **13**, 411 (1992)
55. D.S.C. Arve, D.B. Manley, B.E. Poling, *Fluid Phase Equilib.* **35**, 117 (1987)
56. W.M. Haynes, *J. Chem. Thermodyn.* **15**, 801 (1983)
57. R.N. MacCallum, J.J. McKetta, *Hydrocarbon Process. Petrol. Refinery* **42**, 191 (1963)
58. L.B. Petty, J.M. Smith, *Ind. Eng. Chem.* **47**, 1258 (1955)
59. R.H. Olds, H.H. Reamer, B.H. Sage, W.N. Lacey, *Ind. Eng. Chem.* **36**, 282 (1944)
60. W.B. Kay, *Ind. Eng. Chem.* **32**, 358 (1940)
61. B.H. Sage, D.C. Webster, W.N. Lacey, *Ind. Eng. Chem.* **29**, 1188 (1937)
62. H. Senftleben, *Z. Angew. Phys.* **17**, 86 (1964)
63. B.P. Dailey, W.A. Felsing, *J. Am. Chem. Soc.* **65**, 44 (1943)
64. C.J. Dobratz, *Ind. Eng. Chem.* **33**, 759 (1941)
65. J.G. Aston, G.H. Messerly, *J. Am. Chem. Soc.* **62**, 1917 (1940)
66. B.H. Sage, D.C. Webster, W.N. Lacey, *Ind. Eng. Chem.* **29**, 1309 (1937)
67. O. Beeck, *J. Chem. Phys.* **4**, 680 (1936)
68. J.W. Magee, T.O.D. Lüddecke, *Int. J. Thermophys.* **19**, 129 (1998)

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.