

Reference Correlation of the Thermal Conductivity of Toluene from the Triple Point to 1000 K and up to 1000 MPa

M. J. Assael^{a)} and S. K. Mylona

Laboratory of Thermophysical Properties and Environmental Processes, Chemical Engineering Department, Aristotle University, Thessaloniki 54124, Greece

M. L. Huber and R. A. Perkins

Thermophysical Properties Division, National Institute of Standards and Technology, 325 Broadway, Boulder, Colorado 80305, USA

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This paper contains new, representative equations for the thermal conductivity of toluene. The equations are based in part upon a body of experimental data that has been critically assessed for internal consistency and for agreement with theory whenever possible. Although there are a sufficiently large number of data at normal temperatures, data at very low and very high temperatures as well as near the critical region are scarce. In the case of the dilute-gas thermal conductivity, a theoretically based correlation was adopted in order to extend the temperature range of the experimental data. Moreover, in the critical region, the experimentally observed enhancement of the thermal conductivity is well represented by theoretically based equations containing just one adjustable parameter. The correlations are applicable for the temperature range from the triple point to 1000 K and pressures up to 1000 MPa. The overall uncertainty (considered to be estimates of a combined expanded uncertainty with a coverage factor of two) of the proposed correlation is estimated, for pressures less than 700 MPa and temperatures less than 550 K, to be less than 3% for the liquid, while for the region $550 \text{ K} \leq T \leq 700 \text{ K}$ the uncertainty is estimated to be 4%. For the region $T > 700 \text{ K}$ and $500 \text{ MPa} \leq p \leq 1000 \text{ MPa}$, the equations can safely be used with an uncertainty of the order of 10%. Finally, the uncertainty along the saturation line is estimated to be 2% with a coverage factor of two. © 2012 by the U.S. Secretary of Commerce on behalf of the United States. All rights reserved. [<http://dx.doi.org/10.1063/1.3700155>]

Key words: correlation; critical phenomena; thermal conductivity; toluene; transport properties.

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^{a)}Author to whom correspondence should be addressed; electronic mail: assael@auth.gr.
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1. Introduction

Toluene is an important industrial fluid that is used as a solvent, a chemical intermediate for explosives production, and a valuable blending component in high-octane gasolines.¹ It can easily be obtained in high purity, is a liquid over a wide range of temperatures, and is noncorrosive with respect to standard engineering materials, making it potentially of interest as a reference fluid for thermophysical properties such as thermal conductivity.² Jamieson *et al.*³ provided a data survey of liquid thermal conductivity to 1973. Liley⁴ surveyed the gas-phase data to 1968. Touloukian⁵ surveyed both the gas and liquid phases to 1970 and provided recommended values. More recently, reference correlations for the thermal conductivity at the saturation boundary have been published.^{6,7} In 1986, Nieto de Castro *et al.*⁷ reviewed and analyzed the available liquid-phase thermal conductivity data for water, toluene, and *n*-heptane and provided two correlations for the thermal conductivity of liquid toluene along the saturation boundary: one for a limited temperature range $230 \text{ K} \leq T \leq 360 \text{ K}$ where the experimental data are of the lowest uncertainty, and a second, wider-range correlation valid for the range $189 \text{ K} \leq T \leq 360 \text{ K}$ that has slightly larger uncertainties. In 2000, Ramirez *et al.*⁶ provided new reference-quality experimental measurements and proposed a new reference correlation for the saturation

boundary valid over the range $189 \text{ K} \leq T \leq 553 \text{ K}$, which significantly increased the upper temperature range. Vargaftik *et al.*⁸ provided tables of recommended values of the thermal conductivity of toluene not only for the liquid at saturation, but also for the gas, liquid, and supercritical regions over a range of pressures up to 150 MPa. It is the goal of this work to review the experimental data, and propose a wide-ranging correlation for the thermal conductivity surface of toluene that is valid over gas, liquid, and supercritical states.

2. Methodology

The thermal conductivity λ is expressed as the sum of three independent contributions, as

$$\lambda(\rho, T) = \lambda_o(T) + \Delta\lambda(\rho, T) + \Delta\lambda_c(\rho, T), \quad (1)$$

where ρ is the density, T is the temperature, and the first term, $\lambda_o(T) = \lambda(0, T)$, is the contribution to the thermal conductivity in the dilute-gas limit, where only two-body molecular interactions occur. The last term, $\Delta\lambda_c(\rho, T)$, for the critical enhancement, arises from the long-range density fluctuations that occur in a fluid near its critical point, and that contribute to a divergence of the thermal conductivity at that singular point. The remaining term, $\Delta\lambda(\rho, T)$, for the residual thermal conductivity, represents the contribution of all other effects to the thermal conductivity of the fluid at elevated densities, including many-body collisions, molecular-velocity correlations, and collisional transfer.

The identification of these three separate contributions to the thermal conductivity and to a transport property in general is useful because it is possible, to some extent, to treat both $\lambda_o(T)$ and $\Delta\lambda_c(\rho, T)$ theoretically. In addition, it is possible to derive information about $\lambda_o(T)$ from experiment. In contrast, there is almost no theoretical guidance concerning the residual contribution, $\Delta\lambda(\rho, T)$, so that its evaluation is based entirely on experimentally obtained data.

It is obvious that the analysis described above must be applied to the best available experimental data for the thermal conductivity. Thus, a prerequisite to the analysis is a critical assessment of the experimental data. For this purpose, two categories of experimental data are defined: primary data employed in the development of the correlation, and secondary data used simply for comparison purposes. According to the recommendation adopted by the Subcommittee of Transport Properties [now known as The International Association for Transport Properties (IATP)] of the International Union of Pure and Applied Chemistry, the primary data are identified by the following criteria:⁹

- Measurements must have been made with a primary experimental apparatus, i.e., one for which a complete working equation is available.
- The form of the working equation should be such that sensitivity of the property measured to the principal variables does not magnify the random errors of measurement.

- (iii) All principal variables should be measurable to a high degree of precision.
- (iv) The published work should include some description of purification methods and a guarantee of the purity of the sample.
- (v) The data reported must be unsmoothed data. While graphs and fitted equations are useful summaries for the reader, they are not sufficient for standardization purposes.
- (vi) The lack of accepted values of the thermal conductivity of standard reference materials implies that only absolute, and not relative, measurement results can be considered.
- (vii) Explicit quantitative estimates of the uncertainty of reported values should be given, taking into account the precision of experimental measurements and possible systematic errors.
- (viii) Owing to the desire to produce reference values of low uncertainty, limits must be imposed on the uncertainty of the primary data sets. These limits are determined after critical evaluation of the existing data sets.

These criteria have been successfully employed to establish standard reference values for the viscosity and thermal conductivity of fluids over wide ranges of conditions, with uncertainties in the range of 1%. However, in many cases in practice, such a narrow definition would limit the range of

the data representation unacceptably. Consequently, within the primary data set, it is also necessary to include results that extend over a wide range of conditions, albeit with a higher uncertainty, provided they are consistent with other more accurate data or with theory. In all cases, the accuracy claimed for the final recommended data must reflect the estimated uncertainty in the primary information.

In the following sections, the individual contributions to the thermal conductivity of toluene are treated separately, in each case subjecting all of the relevant available experimental data to a critical scrutiny in order to compile the primary data set and derive a global correlation of $\lambda(\rho, T)$.

3. The Correlation

Table 1 summarizes, to the best of our knowledge, experimental measurements of the thermal conductivity of toluene reported in the literature. Over 90 sets are included in the table, representing 2539 thermal conductivity measurements. References that present only graphical results or a correlating equation are not included in this summary. Also, references that employed toluene in order to calibrate thermal-conductivity instruments are not included. In addition, two theses or reports that have been mentioned in the literature, but that we were unable to obtain,^{105,106} are also not included in Table 1. From the aforementioned sets, 25 were considered as primary data.

TABLE 1. Thermal conductivity measurements of toluene

1 st author	Year Publ.	Technique employed ^a	Purity ^a (%)	Uncertainty (%)	No of data	Temperature range (K)	Pressure range (MPa)
Primary data							
Wu ¹⁰	2009	THW-Abs	99.5	2.0	38	274–375	0–0.08
Wu ¹¹	2005	THW-Abs	99.9	2.0	8	234–373	0–0.08
Sun ¹²	2002	THW-Abs	99.95	0.5	24	297–423	3–35
Watanabe ¹³	2002	THW-Abs	99.0	0.5	21	260–330	0–0.01
Assael ¹⁴	2001	THW-Abs	99.9	0.5	50	234–336	0.1–18
Perkins ¹⁵	2000	THW-Abs	PurSpect	0.5–1.5	184	300–550	0–3
Lei ¹⁶	1997	THW-Abs	na	0.7	6	253–303	0.1
Watanabe ¹⁷	1997	THW-Abs	99.0	0.5	84	295–319	0–0.008
Ramires ¹⁸	1993	THW-Abs	99.99	0.5	37	299–367	0–0.06
Yamada ¹⁹	1993	THW-Abs	99.7	0.5	70	193–452	0.1–20
Assael ²⁰	1992	TWH-Abs	99.9	0.5	48	253–335	0.1–27.8
Perkins ²¹	1991	THW-Abs	PurSpect	1.0	105	301–554	0.09–19
Ramires ²²	1989	THW-Abs	99.99	0.3	11	299–366	0–0.06
Taxis ²³	1988	THW-Abs	99.9	0.3	28	308–347	0–67
Charitidou ²⁴	1987	THW-Abs	99.9	0.5	12	307–347	0.1
Shulga ²⁵	1986	ACHW-Abs	99.5	1.0	87	255–401	0–1000
Nieto de Castro ²⁶	1983	THW-Abs	99.95	0.3	104	308–360	0.9–585
Kashiwagi ²⁷	1982	THW-Abs	99.5	1.0	94	273–373	0.1–250
Nagasaka ^{28,29}	1981	THW-Abs	99.0	0.5	5	274–354	0.1
Zaitseva ³⁰	1976	CC	na	3.0	17	370–683	0.1
Geller ³¹	1974	SSHW	na	1.2	32	183–313	0–60
Kandiyoti ³²	1973	THW-Abs	na	3.5	17	303–364	0.1–633
Mani ³³	1973	THW-Abs	AR	1.0–2.0	81	317–581	0.09–14
McLaughlin ³⁴	1971	THW-Abs	Analar	0.7–1.5	23	180–400	0–0.15
Akhundov ³⁵	1970	THW-Abs	99.9	2.0	163	299–673	0.006–30

TABLE 1. Thermal conductivity measurements of toluene—Continued

1 st author	Year Publ.	Technique employed ^a	Purity ^a (%)	Uncertainty (%)	No of data	Temperature range (K)	Pressure range (MPa)
Secondary data							
Garnier ³⁶	2008	THW	99.9	5.0	2	273, 298	0.1
Tomida ³⁷	2007	THW-Rel	na	2.0	9	294–334	0.1–20
Pan ³⁸	2004	THW	99.9	2.0	8	234–373	0–0.07
Ould-Lahoucine ³⁹	2003	ThPr	99.5	3.0	1	298	0.1
Tarzimanov ⁴⁰	2002	PHW	na	1.0	5	293–493	0–1.05
Zhang ⁴¹	2001	Cal-Rel	na	3.0	8	292–363	0.1
Will ⁴²	1998	DLS	99.9	na	65	298–590	0–4
Fujii ⁴³	1997	THW-Rel	na	2.0	2	295–299	0.1
Frezzotti ⁴⁴	1995	CC-Rel	99.9	3.0	10	302–392	0–0.12
Kraft ⁴⁵	1995	PCS	99.9	2.5	24	290–520	0–1.6
Tong ⁴⁶	1995	SSHW	na	1.0	19	323–523	5–18
Wang ⁴⁷	1995	Cal-Rel	na	1.0	1	298	0.1
Kim ⁴⁸	1993	THW-Abs	98.0	2.0	3	293–333	0.1
DiGuilio ⁴⁹	1992	THW-Rel	na	2.0	7	298–356	0.003–0.04
Gross ⁵⁰	1992	THW-Abs	na	2.0	1	293	0.1
Naziev ⁵¹	1991	CC	99.98	2.0	80	197–473	0.1–50
DiGuilio ⁵²	1990	THW-Rel	HPLC	2.0	4	298–354	0.1
Huang ⁵³	1989	THW-Rel	na	3.0	3	273–301	0.0008–0.004
Richard ⁵⁴	1989	THW-Abs	na	na	4	311–343	0.1
Rowley ⁵⁵	1988	THW-Rel	99.99	1.0	3	313	0.1
Knibbe ⁵⁶	1987	THW	na	1.0	9	288–445	0–0.4
Rowley ⁵⁷	1987	THW-Rel	99.99	1.0	3	293–308	0.1
Ogiwara ⁵⁸	1985	PP-Rel	na	2.0	2	298–313	0.1
Baroncini ⁵⁹	1984	SSHW-Rel	na	na	2	298–323	0–0.01
Yata ⁶⁰	1984	THW	99.90	1.5	5	289–364	0–0.05
Atalla ⁶¹	1981	ACHS	na	2.2	7	283–313	0–0.01
Kitazawa ⁶²	1981	THW-Abs	99.5	1.6	18	213–352	0.1–25
Nefedov ⁶³	1980	ACHW	na	2.0	80	300–640	0–30
Ogiwara ⁶⁴	1980	SSPP-Rel	na	2.0	6	293–343	0.003–0.03
Spirin ⁶⁵	1980	THW-Rel	na	1.5	9	293–453	0–0.5
Leidenfrost ⁶⁶	1979	SSHW	na	na	48	253–473	0.5–2.7
Tada ⁶⁷	1978	LasFl	99.7	2.6	4	293–303	0.101
Julia ⁶⁸	1977	THW-Rel	na	0.3	6	273–353	0–0.04
Trump ⁶⁹	1977	THW	na	1.0	3	273–313	0–0.007
Il'in ⁷⁰	1976	THW-Rel	na	3.0	8	293–363	0–0.05
Kostrovskii ⁷¹	1974	SSHW	99.96	2.0	30	396–642	0.1–3
Davis ⁷²	1971	THW-Abs	na	1.0	9	297–403	0–0.17
Venart ⁷³	1971	THW-Abs	99.96	1.0	22	180–373	0–0.08
Brykov ⁷⁴	1970	SSHW-Abs	na	2.0	16	183–333	0–0.01
Rastorguev ⁷⁵	1970	SSHF-Abs	HighPur	1.5	70	293–453	0.09–150
Stupak ⁷⁶	1970	CC	na	na	4	298–350	0.101
Rastorguev ⁷⁷	1969	SSHF-Abs	HighPur	1.3	173	276–453	0.09–49
Rastorguev ⁷⁸	1969	SSHF-Abs	HighPur	1.5	74	270–405	0.001–0.98
Trec ⁷⁹	1969	CC	99.97	0.8	40	277–368	0.2–2.5
Ganiev ⁸⁰	1968	CC	na	1.0	15	299–438	0.4
Geller ⁸¹	1968	SSHW	na	1.2	24	300–473	0.1–0.9
Pittman ⁸²	1968	THW	Analar	1.0	65	181–396	0.1
Vargaftik ⁸³	1968	SSHW	na	1.5	13	309–702	0.000001
Poltz ⁸⁴	1967	GPP	na	0.5	3	298–328	0.1
Rastorguev ⁸⁵	1967	THW-Abs	HighPur	1.0	27	297–428	0.003–0.3
Arrigoni ⁸⁶	1966	THW	na	5.0	1	294	0.1
Tufeu ⁸⁷	1966	CC	na	1.0	10	273–363	0.1
Tsvetkov ⁸⁸	1965	CC	na	na	8	193–363	0–0.05
Venart ⁸⁹	1965	RHF-Abs	na	2.0	9	273–353	0–0.04
Horrocks ⁹⁰	1963	THW	99.95	0.3	4	298–334	0.1
Ziebland ²	1961	CC	na	2.0	26	258–384	0.1–4
Frontasev ⁹¹	1959	GHP	na	1.0	1	293	0.1

TABLE 1. Thermal conductivity measurements of toluene—Continued

1 st author	Year Publ.	Technique employed ^a	Purity ^a (%)	Uncertainty (%)	No of data	Temperature range (K)	Pressure range (MPa)
Schrock ⁹²	1958	CS	na	2.0	6	207–288	0–0.002
Briggs ⁹³	1957	CC	na	3.0	8	293–363	0.1
Challoner ⁹⁴	1956	GHP-Abs	na	1.0	5	273–353	0.1
Schmidt ⁹⁵	1954	PP	na	na	7	294–352	0.003–0.03
Filippov ⁹⁶	1953	CC	na	3.0	9	300–514	0.004–1.4
Riedel ⁹⁷	1951	CC	na	na	3	193–353	0.1
Abas-Zade ⁹⁸	1949	HW	na	na	26	273–593	0–4.3
Shiba ⁹⁹	1931	PB	na	na	1	300	0.1
Smith ¹⁰⁰	1930	CC	na	na	2	303–348	0–0.03
Davis ¹⁰¹	1924	HTHW	na	5.0	2	292–342	0.1
Bridgman ¹⁰²	1923	CC	na	0.8	20	303–348	0.1–882
Goldschmidt ¹⁰³	1911	HW	na	na	2	273–293	0.1
Weber ¹⁰⁴	1886	na	na	na	1	293	0.1

^aAbs, absolute; ACHS, alternating current hot strip; ACHW, alternating current hot wire; Cal, calorimetry; CC, coaxial cylinder; CS, concentric spheres; DLS, dynamic light scattering; GHP, guarded hot plate; GPP, guarded parallel plate; LasFl, laser flash; na, not available; PCS, photon correlation spectroscopy; PHW, pulse-heated wire; PB, piezometer bulb; PP, parallel plate; RHF, radial heat flow; SSSH, steady-state hot filament; SSSH, steady-state hot wire; ThPr, thermistor probe; THW, transient hot wire; Analar, AR, HighPur, HPLC, PurSpect, type of purity quoted.

The data of Sun *et al.*,¹² Watanabe and Seong,¹³ Watanabe,¹⁷ Assael and Dalaouti,¹⁴ Assael *et al.*,²⁰ Perkins *et al.*,^{15,21} Lei *et al.*,¹⁶ Ramires *et al.*,^{18,22} Yamada *et al.*,¹⁹ Taxis *et al.*,²³ Charitidou *et al.*,²⁴ Nieto de Castro *et al.*,²⁶ and Nagasaka and Nagashima,²⁸ were all performed in transient hot-wire instruments in an absolute way, exhibited very low uncertainty (typically $\pm 0.5\%$), and fulfill the aforementioned criteria for primary data. The data of Wu *et al.*^{10,11} and Kashiwagi *et al.*,²⁷ performed also in transient hot-wire instruments but of slightly higher uncertainty, were also included in the primary data sets. In addition to these sets, some more sets were included; while they only partially fulfill the aforementioned criteria, they extend the temperature and pressure ranges of application. Thus the measurements of Shulga *et al.*,²⁵ performed in an AC transient hot-wire instrument, and of Kandiyoti *et al.*,³² performed in a transient hot-wire instrument, were also included, as they extended the pressure range of application. To extend the temperature range, the measurements of Zaitseva *et al.*,³⁰ Geller and Zaporozhan,³¹ Mani and Venart,³³ McLaughlin and Pittman,³⁴ and Akhundov and Gasanova³⁵ were also included, but with a lower statistical weight. The remaining measurements in Table 1 did not fulfill the criteria for primary data, nor did they contribute to extending the experimental coverage, and hence they were considered as secondary data.

Figure 1 shows the temperature and pressure ranges of the primary measurements outlined in Table 1. Temperatures for all data were converted to the ITS-90 temperature scale.¹⁰⁷ The development of the correlation requires densities; the equation of state (EOS) of Lemmon and Span,¹⁰⁸ valid from 178 K to 700 K and pressures up to 500 MPa, was used to provide the density for each experimental state point from the experimental temperature and pressure. Some of the primary data sets (Shulga *et al.*,²⁵ Nieto de Castro *et al.*,²⁶ and Kandiyoti *et al.*³²) exceed the upper pressure limit of the

EOS, but we believe the extrapolation behavior of this EOS is reasonable and used it to provide densities at pressures above 500 MPa. We also adopted the values for the critical point and triple point from this EOS; the critical temperature, T_c , the critical pressure, p_c , and the critical density, ρ_c , were taken to be equal to 591.75 K, 4.1263 MPa, and 291.992 kg m⁻³, respectively.¹⁰⁸ The triple-point temperature is 178 K.¹⁰⁸ It should be noted that, for this EOS, the uncertainty in density from an input of temperature and pressure was reported to be 0.05% in the liquid phase up to 540 K, 0.5% from 540 K up to the critical temperature, 1% at temperatures above 540 K, 0.5% at pressures from 100 MPa to 500 MPa, and 0.2% in the vapor phase. The uncertainty for the saturated liquid density (and densities near atmospheric pressure) approaches 0.01% around 300 K. We also note that the estimated uncertainty in heat capacities is 0.5% and increases to 3% in the critical region.¹⁰⁸

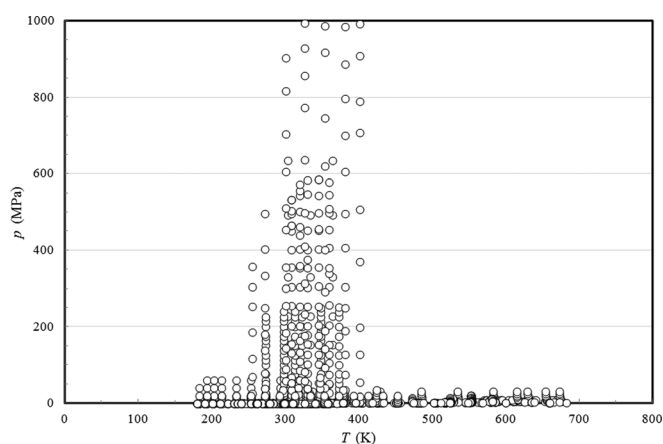


Fig. 1. Temperature and pressure ranges of the experimental thermal conductivity data for toluene.

3.1. The dilute-gas limit

In addition to the data of Zaitseva *et al.*³⁰ and Akhundov and Gasanova,³⁵ two other investigators (Nefedov and Filippov⁶³ in 1980, and Kostrovski and Prostov⁷¹ in 1974) performed measurements near the dilute-gas limit. As these four sets are restricted to the temperature range from 350 K to 700 K, a theoretical based scheme was preferred in order to correlate the dilute-gas limit thermal conductivity, $\lambda_o(T)$, over a much wider temperature range.

A reasonable estimate of the thermal conductivity, $\lambda_o(T)$, of a pure dilute gas may be obtained from the viscosity, $\eta_o(T)$, and perfect-gas heat capacity at constant volume, C_{Vo} , through the modified Eucken correlation,¹⁰⁹

$$f_{Eu} = \frac{\lambda_o(T) M}{\eta_o(T) C_{Vo}} = 1.32 + 1.77 \left(\frac{R}{C_{Vo}} \right) \quad (2)$$

In the above equation, M represents the molar mass of toluene ($92.140 \text{ g mol}^{-1}$), and R the universal gas constant¹¹⁰ ($8.3144621 \text{ J mol}^{-1} \text{ K}^{-1}$). To employ the above equation, the dilute-gas viscosity and the perfect-gas heat capacity at constant volume are required. The dilute-gas viscosity can easily be obtained as a function of the reduced collision integral $\Omega^*(T^*)$, as

$$\eta_o(T) = \frac{5}{16} \left[\frac{MRT}{\pi} \right]^{1/2} \frac{1}{\sigma^2 \Omega^*(T^*)}, \quad (3)$$

where the collision integral can be calculated¹¹¹ as a function of the reduced temperature, $T^* = T(k_B/\varepsilon)$, for the range $0.3 < T^* < 100$, as

$$\begin{aligned} \Omega^*(T^*) = & 1.16145(T^*)^{-0.14874} + 0.52487e^{-0.7732T^*} \\ & + 2.16178e^{-2.43787T^*} - 6.435 \times 10^{-4}(T^*)^{0.14874} \\ & \times \sin \left[18.0323(T^*)^{-0.7683} - 7.2371 \right], \end{aligned} \quad (4)$$

and the perfect-gas heat capacity at constant volume, C_{Vo} , can be obtained from the heat capacity at constant pressure, C_{po} ($\text{J mol}^{-1} \text{ K}^{-1}$), since $C_{po} - C_{vo} = R$. C_{po} is calculated according to Lemmon and Span,¹⁰⁸

$$\frac{C_{po}}{R} = c_0 + \sum_{k=1}^5 v_k \left(\frac{u_k}{T} \right)^2 \frac{\exp(u_k/T)}{[\exp(u_k/T) - 1]^2}. \quad (5)$$

The coefficients c_0 , v_k , and u_k for Eq. (5) are provided in Table 2. Equations (2)–(5) form a consistent scheme for the calculation of the dilute-gas limit thermal conductivity. It should be noted that the above equations assume that toluene vapor, although not spherical in shape, behaves like a Lennard–Jones gas, an assumption that has been employed successfully in the prediction and correlation of its viscosity (see for example Vogel and Hendl¹¹²). Furthermore, the fixed numerical value employed in the modified Eucken correlation, Eq. (2), was preferred, as it was simpler and at the same time produced very good results.

TABLE 2. Coefficients of Eq. (5) for the dilute-gas thermal conductivity of toluene

K	1	2	3	4	5
v_k (–)	1.6994	8.0577	17.059	8.4567	8.6423
u_k (K)	190.0	797.0	1619.0	3072.0	7915.0
c_0 (–)	4.0				

In the above equations, the only unknowns are the Lennard–Jones parameters, σ (m) and ε/k_B (K). Since only four sets of thermal conductivity measurements exist near the dilute limit, these data were employed in order to optimize these two parameters. The values obtained were $\sigma = 0.524 \times 10^{-10} \text{ m}$ and $\varepsilon/k_B = 595 \text{ K}$. It should be noted that these values predict the viscosity values of Vogel and Hendl¹¹² within $\pm 5\%$. The deviations of the present experimental dilute-limit thermal conductivity values from those calculated by the scheme of Eqs. (2)–(5) are shown in Fig. 2.

The values of the dilute-gas limit thermal conductivity, $\lambda_o(T)$, in $\text{mW m}^{-1} \text{ K}^{-1}$, obtained by the scheme of Eqs. (2)–(5), were fitted for ease of use to a fifth-order polynomial as

$$\begin{aligned} \lambda_o(T) = & 5.8808 - 6.1693 \times 10^{-2}T + 3.4151 \times 10^{-4}T^2 \\ & - 3.0420 \times 10^{-7}T^3 + 1.2868 \times 10^{-10}T^4 \\ & - 2.1303 \times 10^{-14}T^5. \end{aligned} \quad (6)$$

Values calculated by Eq. (6) do not deviate from the values calculated by the scheme of Eqs. (2)–(5) by more than 1% over the temperature range 175–2000 K (with the largest deviations at the high end). In the same figure, the dilute-gas limit thermal-conductivity values proposed by Vargaftik *et al.*,⁸ which are valid between 400 K and 650 K, are also shown. The agreement is excellent. However, due to the uncertainties in the limited data available, we estimate the uncertainty of Eqs. (2)–(5) as well as Eq. (6) to be

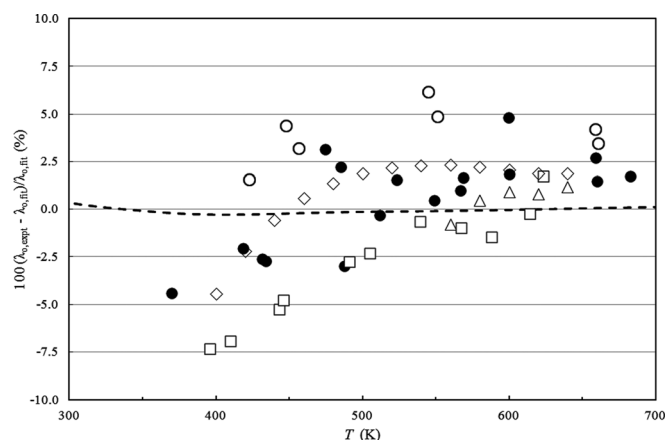


Fig. 2. Percentage deviations of experimental data for dilute-gas toluene from the values calculated by Eqs. (2)–(5). Nefedov and Filippov⁶³ (Δ), Zaitseva *et al.*³⁰ (\bullet), Kostrovskii and Prostov⁷¹ (\square), Akhundov and Gasanova³⁵ (\circ), Vargaftik *et al.*⁸ (\diamond), Values calculated by Eq. (6) (–).

approximately 5% above 400 K, and larger below 400 K, possibly reaching 10% at the triple point.

Finally it should be added that Abas-Zade⁹⁸ also proposed some dilute-gas limit thermal conductivity values in 1948, and these were the basis for some of the earliest compilations of recommended values such as those of Touloukian⁵ and of Liley.⁴ However, these values are much higher than any other set (by 14%–25%), and hence are not considered further.

3.2. The residual thermal conductivity

The thermal conductivities of pure fluids exhibit an enhancement over a large range of densities and temperatures around the critical point and become infinite at the critical point. This behavior can be described by models that produce a smooth crossover from the singular behavior of the thermal conductivity asymptotically close to the critical point to the non-singular residual values far away from the critical point.^{113–115} The density-dependent terms for thermal conductivity can be grouped according to Eq. (1) as $[\Delta\lambda(\rho, T) + \Delta\lambda_c(\rho, T)]$. To assess the critical enhancement either theoretically or empirically, we need to evaluate, in addition to the dilute-gas thermal conductivity, the residual thermal-conductivity contribution. The procedure adopted during this analysis used ODRPACK (Ref. 116) to fit all the primary data simultaneously to the residual thermal conductivity and the critical enhancement, while maintaining the parameters already obtained from the fit of the dilute-gas thermal-conductivity data. The density values employed were obtained by the Helmholtz EOS of Lemmon and Span.¹⁰⁸

The residual thermal conductivity was represented with a polynomial in temperature and density,

$$\Delta\lambda(\rho, T) = \sum_{i=1}^6 (B_{1,i} + B_{2,i}(T/T_c))(\rho/\rho_c)^i. \quad (7)$$

The coefficients $B_{1,i}$ and $B_{2,i}$ are shown in Table 3.

3.3. The critical enhancement

3.3.1. Simplified crossover model

The theoretical based crossover model proposed by Olchowy and Sengers^{113–115} is complex and requires solution of a quartic system of equations in terms of complex variables. A simplified crossover model has also been proposed by Olchowy and Sengers.¹¹⁷ The critical enhancement of the thermal conductivity is given by

$$\Delta\lambda_c = \frac{\rho C_p R_D k_B T}{6\pi\bar{\eta}\xi} (\bar{\Omega} - \bar{\Omega}_0), \quad (8)$$

with

$$\bar{\Omega} = \frac{2}{\pi} \left[\left(\frac{C_p - C_V}{C_p} \right) \arctan(\bar{q}_D \xi) + \frac{C_V}{C_p} \bar{q}_D \xi \right] \quad (9)$$

and

$$\bar{\Omega}_0 = \frac{2}{\pi} \left[1 - \exp \left(- \frac{1}{(\bar{q}_D \xi)^{-1} + (\bar{q}_D \xi \rho_c / \rho)^2 / 3} \right) \right]. \quad (10)$$

In Eqs. (8)–(10), k_B is Boltzmann's constant and $\bar{\eta}$ is the viscosity that we obtained from a preliminary correlation¹¹⁸ currently implemented in the REFPROP database¹¹⁹ that uses the empirical form given by Lemmon and Jacobsen.¹²⁰ The method is not tied to any particular viscosity model; other formulations may be used as well. C_p and C_V are the isobaric and isochoric specific heat obtained from the EOS.¹⁰⁸ The effective wavenumber cutoff \bar{q}_D can be determined by fitting thermal conductivity data in the critical region; however, the only data that were perhaps close enough to critical to show an enhancement were six points on the 3.5 MPa isobar of Akhundov *et al.*,³⁵ which proved insufficient for the regression. We instead used a predictive correlation¹²¹ to obtain the value $\bar{q}_D^{-1} = 6.2 \times 10^{-10}$ m. The correlation length ξ is given by

$$\xi = \xi_0 \left(\frac{p_c \rho}{\Gamma \rho_c^2} \right)^{\nu/\gamma} \left[\left. \frac{\partial \rho(T, \rho)}{\partial p} \right|_T - \left(\frac{T_{\text{ref}}}{T} \right) \left. \frac{\partial \rho(T_{\text{ref}}, \rho)}{\partial p} \right|_T \right]^{\nu/\gamma}. \quad (11)$$

As already mentioned, the coefficients $B_{1,i}$ and $B_{2,i}$ in Eq. (7) were fitted with ODRPACK (Ref. 116) to the primary data for the thermal conductivity of toluene. This crossover model requires the universal constants¹¹⁷ $R_D = 1.02$, $\nu = 0.63$, and $\gamma = 1.239$, and system-dependent amplitudes Γ and ξ_0 . For this work, we adopted the values $\Gamma = 0.05$ and estimated $\xi_0 = 2.2 \times 10^{-10}$ m, using the method that will be presented in Ref 121. The reference temperature T_{ref} , far above the critical temperature where the critical enhancement is negligible, was calculated by $T_{\text{ref}} = (\sqrt[3]{2}) T_c$,¹²² which for toluene is 887.625 K. In other works, T_{ref} has been set at $2T_c$ (Ref. 113) or even $2.5T_c$ (Ref. 123). The optimal value of the parameter \bar{q}_D will change slightly due to the selection of a different cutoff; we have selected $1.5T_c$ due to the fact that the upper limit of the EOS is 700 K and we want to minimize extrapolations of the EOS.

Table 4 summarizes comparisons of the primary data with the correlation. Here we define the percent deviation as $\text{PCTDEV} = 100 * (\lambda_{\text{exp}} - \lambda_{\text{fit}}) / \lambda_{\text{fit}}$, where λ_{exp} is the experimental value of the thermal conductivity and λ_{fit} is the value

TABLE 3. Coefficients of Eq. (7) for the residual thermal conductivity of toluene

i	$B_{1,i}$ (W m ⁻¹ K ⁻¹)	$B_{2,i}$ (W m ⁻¹ K ⁻¹)
1	-5.18530×10^{-2}	5.17449×10^{-2}
2	1.33846×10^{-1}	-1.21902×10^{-1}
3	-1.20446×10^{-1}	1.37748×10^{-1}
4	5.30211×10^{-2}	-7.32792×10^{-2}
5	-1.00604×10^{-2}	1.72914×10^{-2}
6	6.33457×10^{-4}	-1.38585×10^{-3}

TABLE 4. Evaluation of the toluene correlation for the primary data

1st author	Year Publ.	AAD (%)	BIAS (%)	STDEV (%)
Wu ¹⁰	2009	0.55	0.26	0.60
Wu ¹¹	2005	0.71	0.45	0.64
Sun ¹²	2002	0.87	-0.87	0.54
Watanabe ¹³	2002	0.16	0.16	0.17
Assael ¹⁴	2001	0.17	0.12	0.17
Perkins ¹⁵	2000	1.48	1.03	1.30
Lei ¹⁶	1997	0.54	0.49	0.41
Watanabe ¹⁷	1997	0.49	0.38	0.45
Ramires ¹⁸	1993	0.32	-0.14	0.40
Yamada ¹⁹	1993	0.98	0.18	1.15
Assael ²⁰	1992	0.44	0.43	0.27
Perkins ²¹	1991	0.42	0.01	0.47
Ramires ²²	1989	0.49	-0.28	0.53
Taxis ²³	1988	0.47	-0.46	0.23
Charitidou ²⁴	1987	0.54	0.51	0.30
Shulga ²⁵	1986	1.75	-0.79	1.92
Nieto de Castro ²⁶	1983	0.86	0.23	1.05
Kashiwagi ²⁷	1982	0.79	-0.06	0.98
Nagasaka ^{28,29}	1981	0.33	-0.13	0.39
Zaitseva ³⁰	1976	1.70	0.30	2.00
Geller ³¹	1974	1.03	0.93	0.64
Kandiyoti ³²	1973	1.45	0.47	1.58
Mani ³³	1973	0.79	-0.72	0.83
McLaughlin ³⁴	1971	1.36	1.36	0.89
Akhundov ³⁵	1970	2.21	-0.64	3.84
Entire data set		1.13	0.25	1.81

calculated from the correlation. The average absolute percent deviation (AAD) is found with the expression $AAD = (\sum |PCTDEV|)/n$, where the summation is over all n points, the bias percent is found with the expression $BIAS = (\sum PCTDEV)/n$, and the standard deviation is $STDEV = ([n \sum PCTDEV^2 - (\sum PCTDEV)^2]/n^2)^{1/2}$.

Figure 3 shows the percentage deviations of all primary thermal conductivity data from the values calculated by Eqs. (1)–(11) as a function of the density, while Figs. 4 and 5 show the same deviations but as a function of the temperature and pressure. The primary data for toluene listed in Table 1 cover a wide range of conditions and extend to 1000 MPa. Based on comparisons with the primary data, we estimate the uncertainty (considered to be estimates of a combined expanded uncertainty with a coverage factor of two) for pressures less than 700 MPa and temperatures less than 550 K to be less than 3%; for the region $550 \text{ K} \leq T \leq 700 \text{ K}$ the uncertainty is estimated to be 4%. The region near the saturation boundary (within 0.5 MPa of the saturation pressure) has lower uncertainties and will be treated separately in Sec. 3.4. Uncertainties in the critical region are much larger, since the thermal conductivity approaches infinity at the critical point. The Olchow–Senegers critical-enhancement model gives the correct behavior, but due to lack of accurate data in the critical region we were unable to provide a detailed assessment of the performance

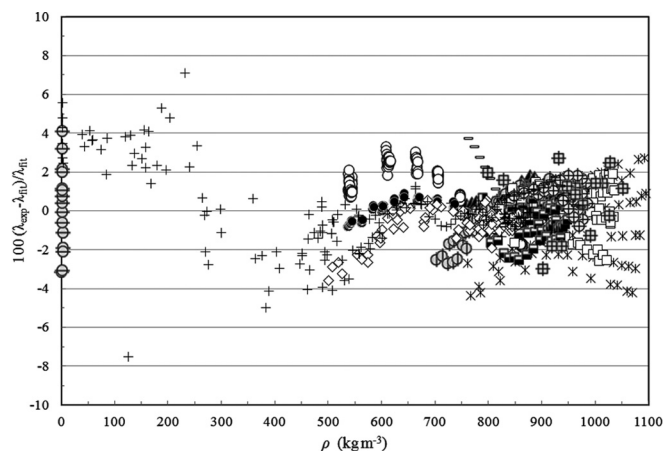


Fig. 3. Percentage deviations of primary experimental data of toluene from the values calculated by the present model as a function of the density. Wu *et al.*¹⁰ (□), Wu *et al.*¹¹ (■), Sun *et al.*¹² (▲), Watanabe and Seong¹³ (⊞), Assael and Dalaouti¹⁴ (△), Perkins *et al.*¹⁵ (○), Lei *et al.*¹⁶ (◇), Watanabe¹⁷ (⊠), Ramires *et al.*¹⁸ (◆), Yamada *et al.*¹⁹ (⊕), Assael *et al.*²⁰ (▲), Perkins and Roder²¹ (●), Ramires *et al.*²² (◇), Taxis *et al.*²³ (◆), Charitidou *et al.*²⁴ (△), Shulga *et al.*²⁵ (✱), Nieto de Castro *et al.*²⁶ (□), Kashiwagi *et al.*²⁷ (■), Nagasaka and Nagashima^{28,29} (■), Zaitseva *et al.*³⁰ (⊖), Geller and Zaporozhan³¹ (⊕), Kandiyoti *et al.*³² (⊞), Mani and Venart³³ (◇), McLaughlin and Pittman³⁴ (-), Akhundov and Gasanova³⁵ (+).

in this region. Finally, we believe the equations may safely be used for extrapolation in the region $T > 700 \text{ K}$ and $500 \text{ MPa} \leq p \leq 1000 \text{ MPa}$ with an uncertainty on the order of 10%.

Figures 6 and 7 show the deviations of the secondary data from the values calculated by the proposed scheme. It can be seen that the majority of the secondary data are within 4% of the proposed correlation. Most of the larger deviations refer

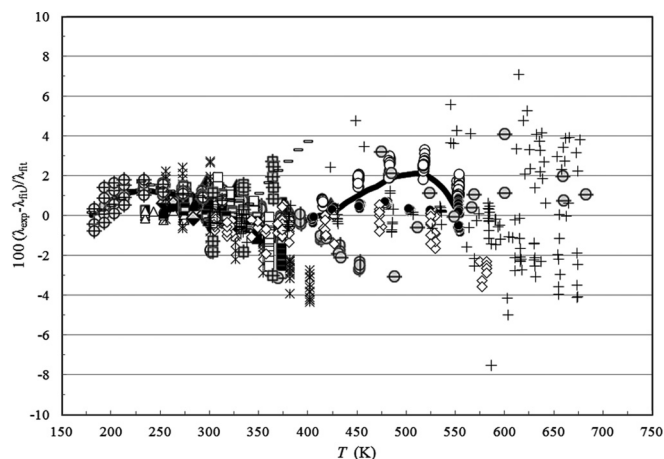


Fig. 4. Percentage deviations of primary experimental data of toluene from the values calculated by the present model as a function of the temperature. Wu *et al.*¹⁰ (□), Wu *et al.*¹¹ (■), Sun *et al.*¹² (▲), Watanabe and Seong¹³ (⊞), Assael and Dalaouti¹⁴ (△), Perkins *et al.*¹⁵ (○), Lei *et al.*¹⁶ (◇), Watanabe¹⁷ (⊠), Ramires *et al.*¹⁸ (◆), Yamada *et al.*¹⁹ (⊕), Assael *et al.*²⁰ (▲), Perkins and Roder²¹ (●), Ramires *et al.*²² (◇), Taxis *et al.*²³ (◆), Charitidou *et al.*²⁴ (△), Shulga *et al.*²⁵ (✱), Nieto de Castro *et al.*²⁶ (□), Kashiwagi *et al.*²⁷ (■), Nagasaka and Nagashima^{28,29} (■), Zaitseva *et al.*³⁰ (⊖), Geller and Zaporozhan³¹ (⊕), Kandiyoti *et al.*³² (⊞), Mani and Venart³³ (◇), McLaughlin and Pittman³⁴ (-), Akhundov and Gasanova³⁵ (+), Reference correlation of Ramires *et al.*⁶ (—).

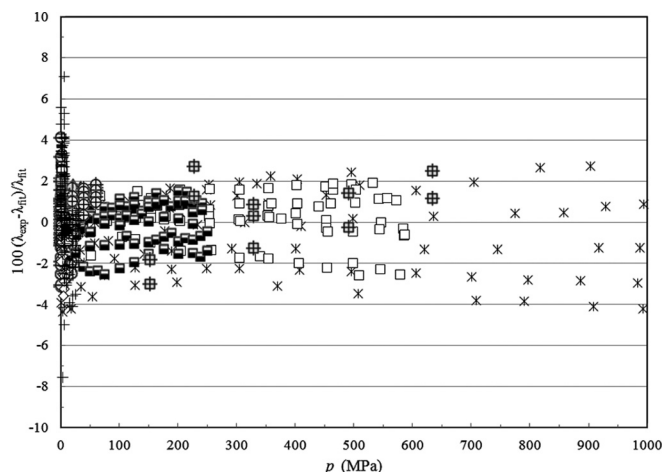


Fig. 5. Percentage deviations of primary experimental data of toluene from the values calculated by the present model as a function of the pressure. Wu *et al.*¹⁰ (■), Wu *et al.*¹¹ (□), Sun *et al.*¹² (▲), Watanabe and Seong¹³ (⊖), Assael and Dalaouti¹⁴ (△), Perkins *et al.*¹⁵ (○), Lei *et al.*¹⁶ (◇), Watanabe¹⁷ (⊞), Ramires *et al.*¹⁸ (⊠), Yamada *et al.*¹⁹ (⊕), Assael *et al.*²⁰ (▲), Perkins and Roder²¹ (●), Ramires *et al.*²² (◇), Taxis *et al.*²³ (◆), Charitidou *et al.*²⁴ (△), Shulga *et al.*²⁵ (✱), Nieto de Castro *et al.*²⁶ (□), Kashiwagi *et al.*²⁷ (■), Nagasaka and Nagashima^{28,29} (⊞), Zaitseva *et al.*³⁰ (⊕), Geller and Zaporozhan³¹ (⊞), Kandiyoti *et al.*³² (⊞), Mani and Venart³³ (◇), McLaughlin and Pittman³⁴ (-), Akhundov and Gasanova³⁵ (+).

to data in the vicinity of the critical point. In particular, the light-scattering photon correlation spectroscopy (PCS) data of Will *et al.*⁴⁷ provide thermal diffusivity data that were converted to thermal conductivity with ρ and C_p calculated from the EOS.³⁹ This conversion process introduces additional uncertainty in the critical region, where the uncertainty

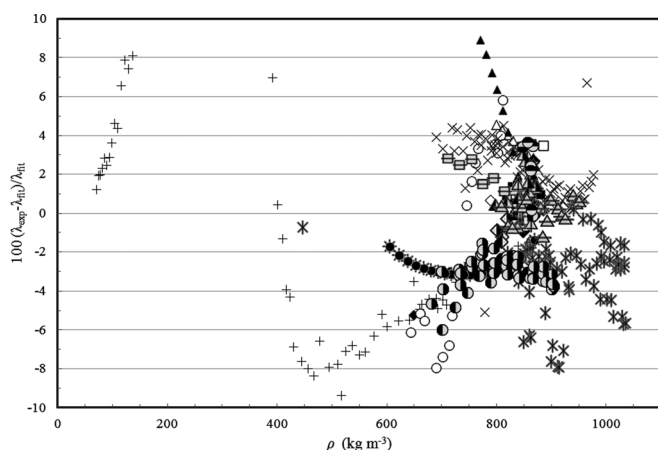


Fig. 6. Percentage deviations of secondary experimental data of toluene from the values calculated by the present model as a function of the density (period 1978–2008). Garnier *et al.*³⁶ (□), Tomida *et al.*³⁷ (■), Pan *et al.*³⁸ (◇), Ould-Lahoucine *et al.*³⁹ (⊕), Tarzimanov *et al.*⁴⁰ (◆), Zhang and Xu⁴¹ (△), Will *et al.*⁴² (+), Fujii *et al.*⁴³ (⊖), Frezzotti *et al.*⁴⁴ (▲), Kraft *et al.*⁴⁵ (●), Tong and Li⁴⁶ (○), Wang and Yang⁴⁷ (⊕), Kim *et al.*⁴⁸ (◆), DiGiulio *et al.*⁴⁹ (◇), Gross *et al.*⁵⁰ (◇), Naziev *et al.*⁵¹ (X), DiGiulio and Teja⁵² (◇), Huang *et al.*⁵³ (■), Richard and Shankland⁵⁴ (■), Rowley and Gubler⁵⁵ (■), Knibbe and Raal⁵⁶ (⊖), Rowley and White⁵⁷ (■), Ogiwara *et al.*⁵⁸ (⊞), Baroncini *et al.*⁵⁹ (△), Yata *et al.*⁶⁰ (▲), Atalla *et al.*⁶¹ (▲), Kitazawa and Nagashima⁶² (△), Nefedov and Filippov⁶³ (✱), Ogiwara *et al.*⁶⁴ (●), Spirin⁶⁵ (●), Leidenfrost⁶⁶ (●), Tada *et al.*⁶⁷ (●).

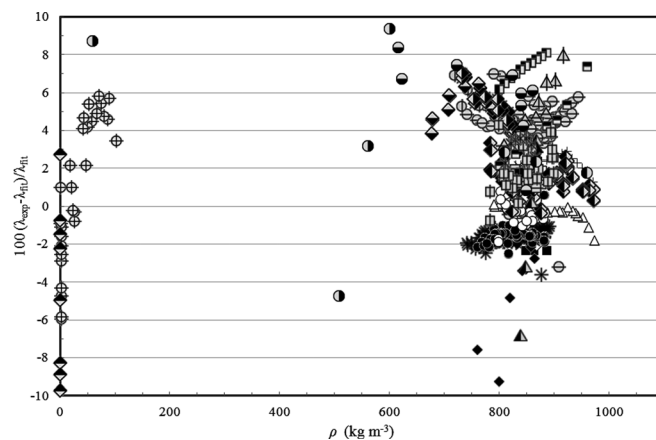


Fig. 7. Percentage deviations of secondary experimental data of toluene from the values calculated by the present model as a function of the density (period 1930–1977). Julia *et al.*⁶⁸ (□), Trump *et al.*⁶⁹ (■), Il'in⁷⁰ (◇), Kostrovskii and Prosov⁷¹ (⊕), Davis *et al.*⁷² (◆), Venart and Mani⁷³ (△), Brykov *et al.*⁷⁴ (+), Rastorguev and Pugash⁷⁵ (⊖), Stupak *et al.*⁷⁶ (▲), Rastorguev *et al.*⁷⁷ (✱), Rastorguev *et al.*⁷⁸ (●), Tree and Leidenfrost⁷⁹ (○), Ganiev and Rastorguev⁸⁰ (⊕), Geller and Rastorguev⁸¹ (◆), Pittman⁸² (◇), Vargaftik *et al.*⁸³ (◆), Poltz and Jugel⁸⁴ (X), Rastorguev and Geller⁸⁵ (◇), Arrigoni⁸⁶ (■), Tufeu⁸⁷ (⊞), Tsvetkov⁸⁸ (■), Venart⁸⁹ (⊖), Horrocks and McLaughlin⁹⁰ (■), Ziebland² (⊞), Schrock and Starkman⁹² (△), Briggs⁹³ (▲), Frontasev and Gusakov⁹¹ (▲), Challoner and Powell⁹⁴ (△), Schmidt and Leidenfrost⁹⁵ (✱), Filippov⁹⁶ (●), Riedel⁹⁷ (●), Abas-Zade⁹⁸ (●), Shiba⁹⁹ (●), Smith¹⁰⁰ (-).

in the calculated C_p increases. Finally, Fig. 8 shows a plot of the thermal conductivity of toluene as a function of the temperature for different pressures.

3.3.2. Empirical critical enhancement

For applications at state points that are relatively distant from the critical point (at least 10–15 K from the critical temperature), the critical enhancement is adequately represented by the following empirical expression,

$$\Delta\lambda_c(\rho, T) = \frac{C_1}{C_2 + |\Delta T_c|} \exp\left[-(C_3\Delta\rho_c)^2\right], \quad (12)$$

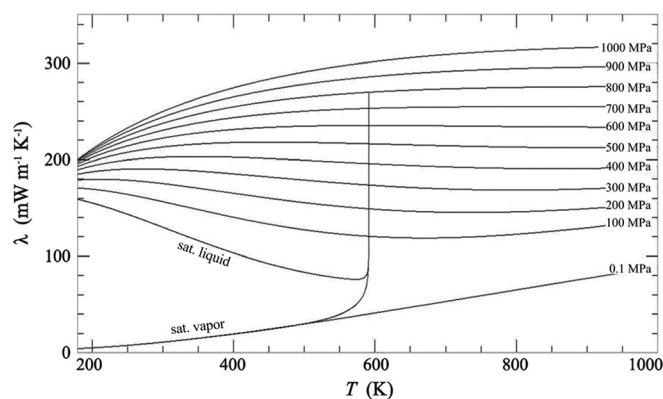


Fig. 8. Thermal conductivity of toluene as a function of the temperature for different pressures.

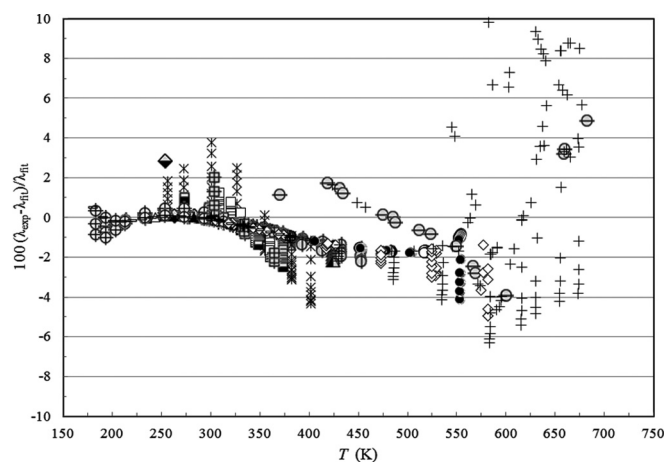


FIG. 9. Percentage deviations of primary experimental data of toluene from the values calculated by Eqs. (1), (6), (7), and (12) as a function of the temperature. Wu *et al.*¹⁰ (■), Wu *et al.*¹¹ (■), Sun *et al.*¹² (▲), Watanabe and Seong¹³ (⊕), Assael and Dalaouti¹⁴ (△), Perkins *et al.*¹⁵ (○), Lei *et al.*¹⁶ (◆), Watanabe¹⁷ (□), Ramires *et al.*¹⁸ (◆), Yamada *et al.*¹⁹ (⊕), Assael *et al.*²⁰ (▲), Perkins and Roder²¹ (●), Ramires *et al.*²² (◆), Taxis *et al.*²³ (◆), Charitidou *et al.*²⁴ (△), Shulga *et al.*²⁵ (✱), Nieto de Castro *et al.*²⁶ (□), Kashiwagi *et al.*²⁷ (■), Nagasaka and Nagashima^{28,29} (■), Zaitseva *et al.*³⁰ (⊕), Geller and Zaporozhan³¹ (⊕), Kandiyoti *et al.*³² (⊕), Mani and Venart³³ (◇), McLaughlin and Pittman³⁴ (-), Akhundov and Gasanova³⁵ (+).

where $\Delta T_c = (T/T_c) - 1$ and $\Delta \rho_c = (\rho/\rho_c) - 1$. This equation requires no accurate information on the compressibility, specific heat, and viscosity of toluene in the critical region, as does the theory of Olchowy and Sengers.^{113–115} The coefficients of Eqs. (6) and (7) were fixed, while the coefficients of Eq. (12) were fitted to the primary data. The values obtained were $C_1 = 0.20 \times 10^{-3} \text{ W m}^{-1} \text{ K}^{-1}$, $C_2 = 4.50 \times 10^{-2}$, and $C_3 = 0.090$. Figure 9 shows the percentage deviations between the primary data and the values calculated by Eqs. (1), (6), (7), and (12) as a function of the temperature. By comparing Figs. 4 and 10, it can be seen that employing Eq. (12) results in little deterioration in the representation of the data.

3.4. The liquid saturation line

Figure 10 shows the percentage deviations of all primary thermal conductivity data from the values calculated by Eqs. (1)–(11) as a function of the temperature along the liquid saturation line. It can be seen that the proposed correlation represents the data within 2% at a 95% confidence level. In addition to the deviations of the primary data, the deviations of the values calculated by the reference correlation proposed by Ramires *et al.*⁶ in 2000 are also shown. This correlation is characterized by uncertainties, at the 95% confidence level, of 1% for $189 \text{ K} < T < 440 \text{ K}$, 1.5% for $440 \text{ K} < T < 480 \text{ K}$, and 2% for $480 \text{ K} < T < 553 \text{ K}$, near the saturation line. The agreement between the two correlations is excellent.

In 1993, Vargaftik *et al.*⁸ published two correlations. The first correlation, A, considered a large number of experimental data sets and was characterized by an uncertainty of 1% for $180 \text{ K} < T < 400 \text{ K}$, 1.5% for $400 \text{ K} < T < 500 \text{ K}$, and

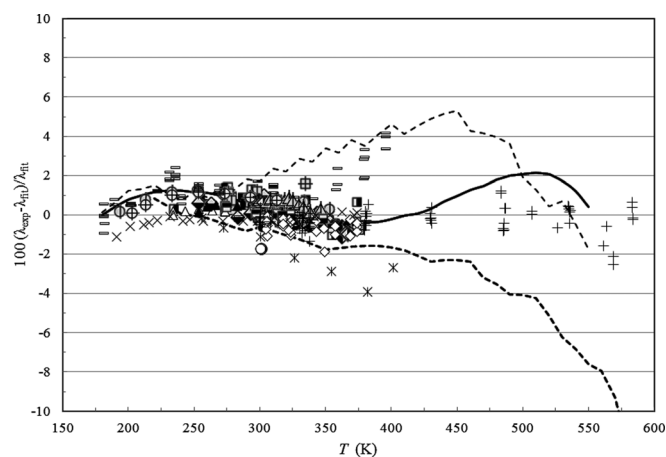


FIG. 10. Percentage deviations of primary experimental data of toluene from the values calculated by the present model as a function of the temperature along the liquid saturation line. Reference correlation of Ramires *et al.*⁶ (—); Correlation (A) of Vargaftik *et al.*⁸ (- - -); correlation (B) of Vargaftik *et al.*⁸ (- - -), and Wu *et al.*¹⁰ (■), Wu *et al.*¹¹ (■), Watanabe and Seong¹³ (⊕), Assael and Dalaouti¹⁴ (△), Perkins *et al.*¹⁵ (○), Lei *et al.*¹⁶ (◆), Watanabe¹⁷ (□), Ramires *et al.*¹⁸ (◆), Yamada *et al.*¹⁹ (⊕), Assael *et al.*²⁰ (▲), Perkins and Roder²¹ (●), Ramires *et al.*²² (◆), Taxis *et al.*²³ (◆), Charitidou *et al.*²⁴ (△), Shulga *et al.*²⁵ (✱), Nieto de Castro *et al.*²⁶ (□), Kashiwagi *et al.*²⁷ (■), Nagasaka and Nagashima^{28,29} (■), Geller and Zaporozhan³¹ (⊕), Kandiyoti *et al.*³² (⊕), Mani and Venart³³ (◇), McLaughlin and Pittman³⁴ (-), Venart and Mani⁷³ (X), Akhundov and Gasanova³⁵ (+).

2%–3% for $T > 500 \text{ K}$. Except in the region near 450 K, where the values calculated by that correlation deviate by up to 5% from the proposed one, in all other regions the agreement is considered satisfactory. In the same publication, Vargaftik *et al.*⁸ proposed an additional correlation based upon the previously employed data with the exception of the data of Gabulov,¹⁰⁵ Rastorguev and Pugash,⁷⁵ and Leidenfrost,⁶⁶ which he considered not to be obtained in “sophisticated instruments”; it should be noted that these sets were also not included in the primary data set of the present work. The resulting correlation, B, is also shown in Fig. 10. It can be seen that, at temperatures higher than 450 K, the deviations between the two correlations exceed their mutual uncertainties.

In Table 5, selected values of the thermal conductivity of toluene along the liquid saturation line calculated by the

TABLE 5. Selected values for the thermal conductivity of toluene along the liquid saturation line, calculated from the present scheme

T (K)	p (MPa)	ρ (kg m ⁻³)	λ (mW m ⁻¹ K ⁻¹)
180	0.00000055336	972.87	158.79
200	0.0000010833	953.54	155.09
250	0.00017649	906.74	143.35
300	0.0041774	860.44	129.81
350	0.034821	812.87	116.07
400	0.15731	762.19	103.22
450	0.48619	705.68	92.115
500	1.1766	638.14	83.384
550	2.4279	544.82	77.383
590	4.0385	366.89	85.764

TABLE 6. Sample points for computer-verification of the correlating equations

T (K)	ρ (kg m ⁻³)	λ (mW m ⁻¹ K ⁻¹)
298.15	0.000	10.749
298.15	862.948	130.66
298.15	876.804	136.70
595.00	0.000	40.538
595.00	46.512	41.549 ^a
595.00	46.512	44.851 ^b
185.00	0.000	4.3758
185.00	968.821	158.24

^aComputed with modified Olchow–Sengers critical enhancement; the viscosity at this point for use in Eq. (8) was taken as $\eta = 15.660 \mu\text{Pa s}$ (Ref. 119); all other properties required for the enhancement term are from Lemmon and Span (Ref. 108).

^bComputed with empirical critical enhancement.

proposed scheme are shown. Values for the saturation pressure and density shown in the same table are obtained by the EOS of Lemmon and Span.¹⁰⁸

4. Computer-Program Verification

Table 6 is provided to assist the user in computer-program verification. The thermal conductivity calculations are based on the tabulated temperatures and densities.

5. Conclusions

New wide-ranging correlations for the thermal conductivity of toluene were developed based on critically evaluated experimental data. The correlations are valid from the triple point to 1000 K, and at pressures up to 1000 MPa. The correlations are expressed in terms of temperature and density, and the densities were obtained from the EOS of Lemmon and Span.¹⁰⁸

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6. References

- ¹Access Science Online Science Dictionary (McGraw-Hill, New York, NY), <http://www.accessscience.com/> (accessed March 12, 2012).
- ²H. Ziebland, *Int. J. Heat Mass Transfer* **2**, 273 (1961).
- ³D. T. Jamieson, J. B. Irving, and J. S. Tudhope, *Liquid Thermal Conductivity: A Data Survey to 1973* (National Engineering Laboratory (NEL), Crown Publishing, Edinburgh, Scotland, UK, 1975).
- ⁴P. E. Liley, in *Proceedings of 4th Symposium on Thermophysical Properties, Maryland, USA*, J. R. Mozyznski, ed., (American Society of Mechanical Engineers, New York, 1968), p. 323.
- ⁵Y. S. Touloukian, P. E. Liley, and S. C. Saxena, *Thermal Conductivity: Nonmetallic Liquids and Gases* (Plenum, New York, 1970).

- ⁶M. L. V. Ramires, C. A. Nieto de Castro, R. A. Perkins, Y. Nagasaka, A. Nagashima, M. J. Assael, and W. A. Wakeham, *J. Phys. Chem. Ref. Data* **29**, 133 (2000).
- ⁷C. A. Nieto de Castro, S. F. Y. Li, A. Nagashima, R. D. Trengove, and W. A. Wakeham, *J. Phys. Chem. Ref. Data* **15**, 1073 (1986).
- ⁸N. B. Vargaftik, L. P. Filippov, A. A. Tarzimanov, and E. E. Totksii, *Handbook of Thermal Conductivity of Liquids and Gases, 1st ed.* (CRC, Boca Raton, FL, USA, 1993).
- ⁹M. J. Assael, M. L. V. Ramires, C. A. Nieto de Castro, and W. A. Wakeham, *J. Phys. Chem. Ref. Data* **19**, 113 (1990).
- ¹⁰J. Wu, H. Zheng, X. Qian, X. Li, and M. J. Assael, *Int. J. Thermophys.* **30**, 385 (2009).
- ¹¹J. Wu, Z. Liu, X. Jin, and J. Pan, *J. Chem. Eng. Data* **50**, 102 (2005).
- ¹²L. Sun, J. E. S. Venart, and R. C. Prasad, *Int. J. Thermophys.* **23**, 1487 (2002).
- ¹³H. Watanabe and D. J. Seong, *Int. J. Thermophys.* **23**, 337 (2002).
- ¹⁴M. J. Assael and N. K. Dalaouti, *Int. J. Thermophys.* **22**, 659 (2001).
- ¹⁵R. A. Perkins, M. L. V. Ramires, and C. A. Nieto de Castro, *J. Res. Natl. Inst. Technol.* **105**, 255 (2000).
- ¹⁶Q.-F. Lei, R.-S. Lin, D.-Y. Ni, and Y.-C. Hou, *J. Chem. Eng. Data* **42**, 971 (1997).
- ¹⁷H. Watanabe, *Int. J. Thermophys.* **18**, 313 (1997).
- ¹⁸M. L. V. Ramires, J. M. N. A. Fareira, C. A. Nieto de Castro, M. Dix, and W. A. Wakeham, *Int. J. Thermophys.* **14**, 1119 (1993).
- ¹⁹T. Yamada, T. Yaguchi, Y. Nagasaka, and A. Nagashima, *High Temp.—High Press.* **25**, 513 (1993).
- ²⁰M. J. Assael, E. Karagiannidis, and W. A. Wakeham, *Int. J. Thermophys.* **13**, 735 (1992).
- ²¹R. A. Perkins and H. M. Roder, *J. Res. Natl. Inst. Technol.* **96**, 247 (1991).
- ²²M. L. V. Ramires, F. J. V. dos Santos, U. V. Mardolcar, and C. A. Nieto de Castro, *Int. J. Thermophys.* **10**, 1005 (1989).
- ²³B. Taxis, M. Zalaf, and W. A. Wakeham, *Int. J. Thermophys.* **9**, 21 (1988).
- ²⁴E. Charitidou, M. Dix, M. J. Assael, C. A. Nieto de Castro, and W. A. Wakeham, *Int. J. Thermophys.* **8**, 511 (1987).
- ²⁵V. M. Shulga, F. G. Eldarov, Y. A. Atanov, and A. A. Kuyumchev, *Int. J. Thermophys.* **7**, 1147 (1986).
- ²⁶C. A. Nieto de Castro, S. F. Y. Li, G. C. Maitland, and W. A. Wakeham, *Int. J. Thermophys.* **4**, 311 (1983).
- ²⁷H. Kashiwagi, T. Hashimoto, Y. Tanaka, H. Kubota, and T. Makita, *Int. J. Thermophys.* **3**, 201 (1982).
- ²⁸Y. Nagasaka and A. Nagashima, *Ind. Eng. Chem. Fundam.* **20**, 216 (1981).
- ²⁹Y. Nagasaka and A. Nagashima, *Rev. Sci. Instrum.* **52**, 229 (1981).
- ³⁰L. S. Zaitseva, L. V. Yakush, and N. A. Vanicheva, *J. Eng. Phys. Thermophys.* **31**, 1292 (1976).
- ³¹V. Geller and G. V. Zaporozhan, *Izv. Vyssh. Uchebn. Zaved., Neft Gaz.* **10**, 69 (1974).
- ³²R. Kandiyoti, E. McLaughlin, and J. F. T. Pittman, *J. Chem. Soc. Faraday Trans. 1* **69**, 1953 (1973).
- ³³N. Mani and J. E. S. Venart, in *Proceedings of the 6th Symposium Thermophysical Properties, Atlanta, USA*, P. E. Liley, ed., (American Society of Mechanical Engineers, New York, 1973), p. 1.
- ³⁴E. McLaughlin and J. F. T. Pittman, *Philos. Trans. R. Soc. London A* **270**, 579 (1971).
- ³⁵T. S. Akhundov and N. E. Gasanova, *Int. Chem. Eng.* **10**, 169 (1970).
- ³⁶J. P. Garnier, J. P. Maye, J. Saillard, G. Thevenot, A. Kadjo, and S. Martemianov, *Int. J. Thermophys.* **29**, 468 (2008).
- ³⁷D. Tomida, S. Kenmochi, T. Tsukada, K. Qiao, and C. Yokoyama, *Int. J. Thermophys.* **28**, 1147 (2007).
- ³⁸J. Pan, J. T. Wu, Z. G. Liu, and X. G. Jin, *Int. J. Thermophys.* **25**, 701 (2004).
- ³⁹C. Ould-Lahoucine, H. Sakashita, and T. Kumada, *Int. Commun. Heat Mass Transfer* **30**, 445 (2003).
- ⁴⁰A. A. Tarzimanov, F. D. Yuzmukhametov, F. R. Gabitov, R. A. Sharafutdinov, and N. Z. Shakirov, *High Temp.* **40**, 524 (2002).
- ⁴¹Z.-Y. Zhang and Y.-P. Xu, *Sol. Energy* **71**, 299 (2001).
- ⁴²S. Will, A. P. Froeba, and A. Leipertz, *Int. J. Thermophys.* **19**, 407 (1998).
- ⁴³M. Fujii, X. Zhang, N. Imaishi, S. Fujiwara, and T. Sakamoto, *Int. J. Thermophys.* **18**, 327 (1997).

- ⁴⁴D. Frezzotti, G. Goffredi, and E. Bencini, *Thermochim. Acta* **265**, 119 (1995).
- ⁴⁵K. Kraft, M. M. Lopes, and A. Leipertz, *Int. J. Thermophys.* **16**, 423 (1995).
- ⁴⁶J. Tong and T. Li, *J. Eng. Thermophys.* **16**, 133 (1995).
- ⁴⁷C. Y. Wang and M. L. Yang, *Thermochim. Acta* **255**, 365 (1995).
- ⁴⁸S. H. Kim, D. S. Kim, M. S. Kim, and S. T. Ro, *Int. J. Thermophys.* **14**, 937 (1993).
- ⁴⁹R. M. DiGiulio, W. L. McGregor, and A. S. Teja, *J. Chem. Eng. Data* **37**, 242 (1992).
- ⁵⁰U. Gross, Y. W. Song, and E. Hahne, *Fluid Phase Equilib.* **76**, 273 (1992).
- ⁵¹Y. M. Naziev, A. N. Shakhverdiev, and A. S. Gasanov, *Thermophysical Properties of Substances and Materials* **30** (Standards Publishing, Moscow, 1991).
- ⁵²R. M. DiGiulio and A. S. Teja, *J. Chem. Eng. Data* **35**, 117 (1990).
- ⁵³S. Huang, Z. Jiang, J. Du, C. Lin, and D. Pan, *J. Chem. Eng. (China)* **17**, 62 (1989).
- ⁵⁴R. G. Richard and I. R. Shankland, *Int. J. Thermophys.* **10**, 673 (1989).
- ⁵⁵R. L. Rowley and V. Gubler, *J. Chem. Eng. Data* **33**, 5 (1988).
- ⁵⁶P. G. Knibbe and J. D. Raal, *Int. J. Thermophys.* **8**, 181 (1987).
- ⁵⁷R. L. Rowley and G. L. White, *J. Chem. Eng. Data* **32**, 63 (1987).
- ⁵⁸K. Ogiwara, Y. Arai, and S. Saito, *J. Chem. Eng. Jpn.* **18**, 273 (1985).
- ⁵⁹C. Baroncini, G. Latini, and P. Pierpaoli, *Int. J. Thermophys.* **5**, 387 (1984).
- ⁶⁰J. Yata, T. Minamiyama, and S. Tanaka, *Int. J. Thermophys.* **5**, 209 (1984).
- ⁶¹S. R. Atalla, A. A. El-Sharkawy, and F. A. Gasser, *Int. J. Thermophys.* **2**, 155 (1981).
- ⁶²N. Kitazawa and A. Nagashima, *Bull. JSME* **24**, 374 (1981).
- ⁶³S. N. Nefedov and L. P. Filippov, *Izv. Vyssh. Uchebn. Zaved., Neft Gaz.* **11**, 51 (1980).
- ⁶⁴K. Ogiwara, Y. Arai, and S. Salto, *Ind. Eng. Chem. Fundam.* **19**, 295 (1980).
- ⁶⁵G. G. Spirin, *J. Eng. Phys. Thermophys.* **38**, 390 (1980).
- ⁶⁶W. Leidenfrost, *High temp.—High Press.* **11**, 561 (1979).
- ⁶⁷Y. Tada, M. Harada, M. Tanigaki, and W. Eguchi, *Rev. Sci. Instrum.* **49**, 1305 (1978).
- ⁶⁸Y. H. Julia, J. F. Renaud, D. J. Ferrand, and P. F. Malbrunot, *Rev. Sci. Instrum.* **48**, 1654 (1977).
- ⁶⁹W. N. Trump, H. W. Luebke, L. Fowler, and E. M. Emery, *Rev. Sci. Instrum.* **48**, 47 (1977).
- ⁷⁰B. I. Il'in, V. F. Salokhin, and G. G. Spirin, *J. Eng. Phys. Thermophys.* **30**, 630 (1975).
- ⁷¹I. L. Kostrovskii and V. N. Prostov, *Ref. Zh. Khim.* **7**, 1 (1974).
- ⁷²P. S. Davis, F. Theeuwes, R. J. Bearman, and R. P. Gordon, *J. Chem. Phys.* **55**, 4776 (1971).
- ⁷³J. E. S. Venart and N. Mani, *Can. J. Chem.* **49**, 2468 (1971).
- ⁷⁴V. P. Brykov, G. K. Mukhamedzyanov, and A. G. Usmanov, *J. Eng. Phys. Thermophys.* **18**, 62 (1970).
- ⁷⁵Y. L. Rastorguev and V. V. Pugash, *Izv. Vyssh. Uchebn. Zaved., Neft Gaz.* **8**, 69 (1970).
- ⁷⁶P. M. Stupak, A. M. Aizen, and N. G. Yampol'skii, *J. Eng. Phys. Thermophys.* **19**, 853 (1970).
- ⁷⁷Y. L. Rastorguev, B. A. Grigor'ev, and G. F. Bogatov, *J. Eng. Phys. Thermophys.* **17**, 1370 (1969).
- ⁷⁸Y. L. Rastorguev, B. A. Grigor'ev, and G. F. Bogatov, *J. Eng. Phys. Thermophys.* **17**, 1107 (1969).
- ⁷⁹D. R. Tree and W. Leidenfrost, in *Proceedings of the Eighth Conference on Thermal Conductivity*, C. Y. Ho and R. E. Taylor, eds., (Plenum Press, 1969), p. 611.
- ⁸⁰Y. A. Ganiev and Y. L. Rastorguev, *J. Eng. Phys. Thermophys.* **15**, 880 (1968).
- ⁸¹V. Z. Geller and Y. L. Rastorguev, *Teplotenergetika* **7**, 80 (1968).
- ⁸²J. F. T. Pittman, Ph.D. Thesis, Imperial College of Science and Technology, London, 1968.
- ⁸³N. B. Vargaftik, L. S. Zaitseva, and L. V. Yakush, *J. Eng. Phys. Thermophys.* **14**, 466 (1968).
- ⁸⁴H. Poltz and R. Jugel, *Int. J. Heat Mass Transfer* **10**, 1075 (1967).
- ⁸⁵Y. L. Rastorguev and V. Z. Geller, *J. Eng. Phys. Thermophys.* **13**, 9 (1967).
- ⁸⁶V. Arrighoni, *Termotecnica* **20**, 197 (1966).
- ⁸⁷R. Tufeu, *C. R. Acad. Sci. Paris*, **B 262**, 229 (1966).
- ⁸⁸O. B. Tsvetkov, *Izv. Vyssh. Uchebn. Zaved. Priborostr.* **9**, 28 (1965).
- ⁸⁹J. E. S. Venart, *J. Chem. Eng. Data* **10**, 239 (1965).
- ⁹⁰J. K. Horrocks and E. McLaughlin, *Proc. R. Soc. London Ser. A, Math. Phys. Sci.* **273**, 259 (1963).
- ⁹¹V. P. Frontasev and M. Y. Gusakov, *Zh. Tekh. Fiz.* **29**, 1277 (1959).
- ⁹²V. E. Schrock and E. S. Starkman, *Rev. Sci. Instrum.* **29**, 625 (1958).
- ⁹³D. K. H. Briggs, *Ind. Eng. Chem.* **49**, 418 (1957).
- ⁹⁴A. R. Challoner and R. W. Powell, *Proc. R. Soc. London A* **238**, 90 (1956).
- ⁹⁵E. Schmidt and W. Leidenfrost, *Chem.-Ing.-Techn.* **26**, 35 (1954).
- ⁹⁶L. P. Filippov, *Trans. Moscow State Univ.* **9**, 2 (1953).
- ⁹⁷L. Riedel, *Chem.-Ing.-Techn.* **23**, 321 (1951).
- ⁹⁸A. K. Abas-Zade, *Dokl. Akad. Nauk. SSSR* **68**, 665 (1949).
- ⁹⁹H. Shiba, *Sci. Pap. Inst. Phys. Chem. Res. (Tokyo)* **16**, 205 (1931).
- ¹⁰⁰J. F. D. Smith, *Ind. Eng. Chem.* **22**, 1246 (1930).
- ¹⁰¹A. H. Davis, *Philos. Mag.* **47**, 972 (1924).
- ¹⁰²P. W. Bridgman, *Proc. Am. Acad. Arts Sci.* **59**, 141 (1923).
- ¹⁰³R. Goldschmidt, *Phys. Z.* **12**, 417 (1911).
- ¹⁰⁴H. F. Weber, *Rep. Phys.* **22**, 116 (1886).
- ¹⁰⁵D. M. Gabulov, Ph.D. Thesis, Grozny University, Grozny, Russia, 1978.
- ¹⁰⁶A. A. Tarzimanov, F. D. Yuzmukhametov, F. R. Gabitov, R. A. Sharafutdinov, and N. Z. Shakirov, *High Temp.* **40**, 524 (1985).
- ¹⁰⁷H. Preston-Thomas, *Metrologia* **27**, 3 (1990).
- ¹⁰⁸E. W. Lemmon and R. Span, *J. Chem. Eng. Data* **51**, 785 (2006).
- ¹⁰⁹R. C. Reid, J. M. Prausnitz, and B. E. Poling, *The Properties of Gases and Liquids*, 4th ed. (McGraw-Hill, New York, 1988).
- ¹¹⁰See <http://physics.nist.gov/cuu/Constants/index.html> for 2010 CODATA recommended values.
- ¹¹¹P. D. Neufeld, A. R. Janzen, and R. A. Aziz, *J. Chem. Phys.* **57**, 1100 (1972).
- ¹¹²E. Vogel and S. Hendl, *Fluid Phase Equilib.* **79**, 313 (1992).
- ¹¹³G. A. Olchowy and J. V. Sengers, *Phys. Rev. Lett.* **61**, 15 (1988).
- ¹¹⁴R. Mostert, H. R. van den Berg, and P. S. van der Gulik, *J. Chem. Phys.* **92**, 5454 (1990).
- ¹¹⁵R. A. Perkins, H. M. Roder, D. G. Friend, and C. A. Nieto de Castro, *Physica A* **173**, 332 (1991).
- ¹¹⁶P. T. Boggs, R. H. Byrd, J. E. Rogers, and R. B. Schnabel, ODRPACK, Software for Orthogonal Distance Regression, NISTIR 4834, v2.013 (National Institute of Standards and Technology, Gaithersburg, MD, 1992).
- ¹¹⁷G. A. Olchowy and J. V. Sengers, *Int. J. Thermophys.* **10**, 417 (1989).
- ¹¹⁸E. Lemmon, National Institute of Standards and Technology, Boulder, CO, personal communication (2012).
- ¹¹⁹E. W. Lemmon, M. L. Huber, and M. O. McLinden, NIST Reference Fluid Thermodynamic and Transport Properties Database (REFPROP), NIST Standard Reference Database 23, Version 9.0 (2010).
- ¹²⁰E. W. Lemmon and R. T. Jacobsen, *Int. J. Thermophys.* **25**, 21 (2004).
- ¹²¹R. A. Perkins, J. V. Sengers, I. M. Abdulagatov, and M. L. Huber, "A Universal Representation of the Critical Thermal-Conductivity Enhancement in Molecular Fluids" (Paper ID 2212), presented at the 18th Symposium on Thermophysical Properties, Boulder, CO, (June 24–29, 2012).
- ¹²²V. Vesovic, W. A. Wakeham, G. A. Olchowy, J. V. Sengers, J. T. R. Watson, and J. Millat, *J. Phys. Chem. Ref. Data* **19**, 763 (1990).
- ¹²³R. A. Perkins, H. M. Roder, D. G. Friend, and C. A. Nieto de Castro, *Physica A* **173**, 332 (1991).