

Reference Correlation of the Thermal Conductivity of Benzene from the Triple Point to 725 K and up to 500 MPa

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Reference Correlation of the Thermal Conductivity of Benzene from the Triple Point to 725 K and up to 500 MPa

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This paper contains new, representative reference equations for the thermal conductivity of benzene. The equations are based in part upon a body of experimental data that have been critically assessed for internal consistency and for agreement with theory whenever possible. 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 725 K and pressures up to 500 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 350 MPa and temperatures less than 725 K, to be less than 4.4%. © 2012 by the U.S. Secretary of Commerce on behalf of the United States. All rights reserved. [<http://dx.doi.org/10.1063/1.4755781>]

Key words: benzene; critical phenomena; thermal conductivity; transport properties.

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1. Introduction

In a series of recent papers, new reference correlations for the thermal conductivity of normal and parahydrogen,¹ toluene,² and SF₆,³ covering a wide range of conditions of temperature and pressure, were reported. In this paper, the work is extended to the thermal conductivity of benzene. In 1990, the Subcommittee on Transport Properties (now International Association for Transport Properties) of the International Union of Pure and Applied Chemistry published a reference correlation for the thermal conductivity of benzene at atmospheric pressure, covering only the liquid range from 295 to 350 K.⁴ The present work extends this range from the triple point to 725 K and pressures up to 500 MPa.

The goal of this work is to critically assess the available literature data, and provide a wide-ranging correlation for the thermal conductivity of benzene that is valid over gas, liquid, and supercritical states, and that incorporates densities provided by the recent equation of state of Thol *et al.*⁵ It should further be noted that, although there are some alternative approaches today for developing such correlations (e.g., neural networks), we preferred to follow a procedure based upon kinetic theory and our previous work, as will be discussed in Secs. 2 and 3.

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 final term, $\Delta\lambda_c(\rho, T)$, the critical enhancement, arises from the long-range density fluctuations that occur in a fluid near its critical point, which contribute to divergence of the thermal conductivity at that point. Finally, the term $\Delta\lambda(\rho, T)$, the residual property, 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 transport properties 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.

The analysis described above should 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 on Transport Properties (now known as The International Association for Transport Properties) of the International Union of Pure and Applied Chemistry, the primary data are identified by the following criteria:⁴

- (i) Measurements must have been made with a primary experimental apparatus, i.e., one for which a complete working equation is available.
- (ii) 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 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 low-uncertainty reference values, limits must be imposed on the uncertainties 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, such a narrow definition unacceptably limits the range of the data representation. Consequently, within the primary data set, it is also necessary to include results that extend over a wide range of conditions, albeit with a poorer accuracy, 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.

3. The Correlation

Table 1 summarizes, to the best of our knowledge, the experimental measurements^{6–58} of the thermal conductivity of benzene reported in the literature. Fifty-three sets are included in the table. From these sets, 13 were considered as primary data.

The data of Mensah-Brown and Wakeham,⁹ Ramires *et al.*,¹⁰ Charitidou *et al.*,¹¹ and Li *et al.*¹² were measured in an absolute transient hot-wire instrument with an uncertainty of 0.5%, and these sets were considered as primary data. The older measurements of Horrocks and McLaughlin,¹⁸ performed in an absolute transient hot-wire instrument, were also included in the primary data set. The measurements of Watanabe and Kato⁶ and Kashiwagi *et al.*,¹³ performed in a relative way in a transient hot-wire instrument, were also considered as primary data, together with the absolute pulsed hot-wire measurements of Tarzimanov *et al.*⁷ Tong and Tianxiang⁸ performed thermal conductivity measurements employing a thermal resistor in a relative way, which were included in the primary data set as they extend to higher pressures, with the exception of their 473 K isotherm which appeared inconsistent with their other measurements. Four more investigators were included in the primary data set: Zaitseva *et al.*¹⁴ who employed a concentric-cylinder instrument, Akhundov¹⁵ and Kostrovskii and Prostov¹⁶ who employed a hot-wire instrument, and finally Rastorguev and Pugash¹⁷ who employed an absolute hot-filament instrument for measurements at very high pressures.

Figure 1 shows the temperature and pressure range of the primary measurements outlined in Table 1. Temperatures for all data were converted to the ITS-90 temperature scale. The development of the correlation requires densities; recently, Thol *et al.*⁵ reviewed the thermodynamic properties of benzene and developed an accurate, wide-ranging equation of state up to 725 K and 500 MPa – limits that hence also restrict the present thermal conductivity correlation. The approximate uncertainties of the density (at a coverage factor of 2) calculated with this equation are 0.1% below 350 K and 0.2% above 350 K for liquid densities, 1% for saturated vapor densities, 0.1% for densities up to 350 K and 100 MPa, and 0.1%–0.5% in density above 350 K. The isobaric and saturated heat capacities are obtained with an uncertainty of 1%. Uncertainties in the critical region are higher for the above properties. We also adopt the values for the critical point and triple point from their equation of state; the critical temperature, T_c , and the critical density, ρ_c , were taken to be equal to 562.02 K and 304.792 kg m^{−3}, respectively. The triple-point temperature is 278.674 K.⁵

3.1. The dilute-gas limit

From the primary measurements shown in Table 1, only three investigators^{14–16} performed measurements near the dilute-gas limit. To increase the number of data sets, four more investigators that performed thermal-conductivity measurements near the dilute-gas limit^{35,49,50,52} from the secondary data were also included. As only two of the seven sets

extend to over 600 K,^{15,16} a theoretically based scheme was preferred in order to correlate the dilute-gas limit thermal conductivity, $\lambda_o(T)$, over a wide temperature range. The same scheme was successfully adopted in the case of the dilute-gas limit thermal conductivity correlation of toluene² and SF₆.³

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 ideal-gas heat capacity at constant volume, C_{vo} , through the modified Eucken correlation,⁵⁹

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

In the above equation, M represents the molar mass of benzene⁵ (78.1118 g/mol), and R the universal gas constant⁶⁰ (8.314 462 J mol^{−1} K^{−1}). To employ the above equation, the dilute-gas viscosity and the ideal-gas heat capacity at constant volume are required. The dilute-gas viscosity can be written as a function of the reduced collision integral, $\Omega^*(T^*)$, as

$$\begin{aligned} \eta_o(T) &= \frac{5}{16} \left[\frac{MRT}{\pi} \right]^{1/2} \frac{1}{\sigma^2 \Omega^*(T^*)} \\ &= 0.0266957 \frac{\sqrt{MT}}{\sigma^2 \Omega^*(T^*)}, \end{aligned} \quad (3)$$

where the viscosity is expressed in $\mu\text{Pa s}$, the temperature is in kelvins, and the Lennard-Jones length parameter, σ , is in nm. The reduced collision integral can be calculated⁶¹ as a function of the reduced temperature, $T^* = T(k_B/\epsilon)$, where ϵ/k_B (K) is the Lennard-Jones temperature parameter (and k_B is Boltzmann's constant), and for the range $0.3 < T^* < 100$, as

$$\begin{aligned} \Omega^*(T^*) &= 1.16145(T^*)^{-0.14874} + 0.52487 e^{-0.7732T^*} \\ &\quad + 2.16178 e^{-2.43787T^*} - 6.435 \times 10^{-4} (T^*)^{0.14874} \\ &\quad \times \sin[18.0323(T^*)^{-0.7683} - 7.27371] \end{aligned} \quad (4)$$

and the ideal-gas heat capacity at constant volume, C_{vo} , can be obtained from the heat capacity at constant pressure, C_{po} (J mol^{−1} K^{−1}), (as $C_{po} - C_{vo} = R$), as this is given by⁵

$$\frac{C_{po}}{R} = 3.94645 + \sum_{k=3}^5 v_k \left(\frac{u_k}{T} \right)^2 \frac{\exp(u_k/T)}{[\exp(u_k/T) - 1]^2}, \quad (5)$$

where $v_3 = 7.36374$, $v_4 = 18.649$, $v_5 = 4.01834$, $u_3 = 4116$ K, $u_4 = 1511$ K, and $u_5 = 630$ K. Equations (2)–(5) form a consistent scheme for the calculation of the dilute-limit thermal conductivity. It should be noted that the above equations assume that benzene 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 *et al.*⁶²). Furthermore, the use of fixed numerical values in the modified Eucken correlation, Eq. (2), was preferred to the various more sophisticated theories employing quantities that are not easily accessible such the rotational collision number and the diffusion of the internal energy in the gas. The approximation in Eq. (2) is simpler and at the same time produced very good

TABLE 1. Thermal conductivity measurements of benzene

First author	Year publ.	Technique employed ^a	Purity (%)	Uncertainty (%)	No. of data	Temperature range (K)	Pressure range (MPa)
Primary Data							
Watanabe ⁶	2004	THW-Rel	99.0	0.4	12	301–320	0.101
Tarzmanov ⁷	2002	PHW-Abs	na	2	5	293–493	0.01–1.94
Tong ⁸	1995	ThRes.-Rel	na	1	19	323–524	5–18
Mensah-Brown ⁹	1993	THW-Abs	99.7	0.3	27	320–345	0.1–261.2
Ramires ¹⁰	1989	THW-Abs	99.999	0.3	11	298–332	0.008–0.05
Charitidou ¹¹	1988	THW-Abs	99.8	0.5	11	298–335	0.101
Li ¹²	1984	THW-Abs	99.8	0.3	59	310–360	1.6–332
Kashiwagi ¹³	1982	THW-Rel	99.0	2	5	303–348	0.101
Zaitseva ^{14,b}	1976	CC	na	3	9	304–511	0.01–0.1
Akhundov ^{15,b}	1974	HW	99.98	2	121	293–682	0.01–30
Kostrovski ^{16,b}	1974	HW	na	2	29	364–628	0.1–4.0
Rastorguev ¹⁷	1970	HF-Abs	na	1.5	58	293–453	0.098–152
Horrocks ¹⁸	1963	THW-Abs	99.95	0.25	11	295–346	0.101
Secondary Data							
Salavera ¹⁹	2010	CC-Rel	99.8	2	4	302–392	1
Lamvik ²⁰	1995	PP-Rel	99.5	6	1	278	0.101
Rowley ²¹	1988	THW-Rel	na	1	1	313	0.101
Rowley ²²	1987	THW-Rel	na	1	1	298	0.101
Fischer ²³	1985	PP	99	8	20	281–473	0.005–1.39
Atalla ²⁴	1981	HW	na	2.2	1	293	0.101
Ogiwara ²⁵	1980	PP-Rel	99.85	2	4	293–323	0.101
Spirin ²⁶	1978	THW-Rel	na	1.5	12	293–444	0.01–0.86
Takizawa ²⁷	1978	THW-Rel	na	1.5	5	283–324	0.101
Corti ²⁸	1974	RS	na	4	1	298	0.101
Gulari ²⁹	1973	QELS	na	5	1	292.65	0.101
Mallan ³⁰	1972	THW-Rel	na	1.3	6	303–399	0.016–0.345
Kerimov ³¹	1970	ACHW	na	1	3	299–353	0.101
Bachmann ³²	1969	THW	na	1.0	8	279–343	0.101
Poltz ³³	1967	GPP	na	0.5	3	283–313	0.101
Geller ³⁴	1966	HW	na	1.2	1	313.15	0.101
Reiter ^{35,b}	1966	HW-Abs	na	2	10	323–527	0.03–2.98
Tufeu ³⁶	1966	CC	na	1	7	290–350	0.101
Yamamoto ³⁷	1966	HW	na	na	1	291	0.101
Filippov ³⁸	1965	ACHF	na	1.9	7	288–343	0.101
Geller ³⁹	1965	HW	na	1.2	5	299–334	0.101
Venart ⁴⁰	1965	CC	na	2	7	283–344	0.101
Jamieson ⁴¹	1963	HW	na	5	5	298	0.101
Powell ⁴²	1963	ThComp	na	5	1	298	0.101
Scheffy ⁴³	1961	TF	na	15	6	341–442	0.06–0.84
Eldarov ⁴⁴	1960	ACHW	na	1	4	298–353	0.101
Frontasev ⁴⁵	1959	GPP	na	0.5	1	293	0.101
Tsedebereg ⁴⁶	1958	HF	na	1.5	5	279–349	0.004–0.09
Briggs ⁴⁷	1957	CC	na	3.0	1	293	0.101
Schmidt ⁴⁸	1954	PP	na	na	5	295–334	0.101
Vines ^{49,b}	1953	HW-Abs	na	1	2	348–384	0
Vines ^{50,b}	1954	HW-Abs	na	1	5	352–436	0.098–0.74
Riedel ⁵¹	1951	CC	na	na	2	293–323	0.101
Lambert ^{52,b}	1950	HW-Rel	na	1	2	339,359	0
van der Held ⁵³	1949	THW	na	2	1	295	0.101
Vargaftik ⁵⁴	1949	SSHW	na	2	1	295	0.101
Abas-Zade ⁵⁵	1949	HW	na	na	22	313–561	0.02–4.86
Shiba ⁵⁶	1931	PB	na	na	1	303.15	0.101
Goldschmidt ⁵⁷	1911	HW	na	na	2	289–306	0.101
Weber ⁵⁸	1886	na	na	na	1	298	0.101

^aAbs, absolute; ACHF, AC hot filament; ACHW, AC hot wire; CC, coaxial cylinder; DLS, dynamic light scattering; GPP, guarded parallel plate; HF, hot filament; HW, hot wire; na, not available; PB, piezometer bulb; PHW, pulsed hot wire; PP, parallel plate; QELS, quasi-elastic light scattering; RS, Rayleigh scattering of laser light; RHF, radial heat flow; Rel, relative; SSHW, steady-state hot wire; TF, thin film; ThComp, thermal comparator; ThRes, thermal resistor; THW, transient hot wire.

^bIncludes vapor data employed to derive the dilute-gas thermal-conductivity correlation.

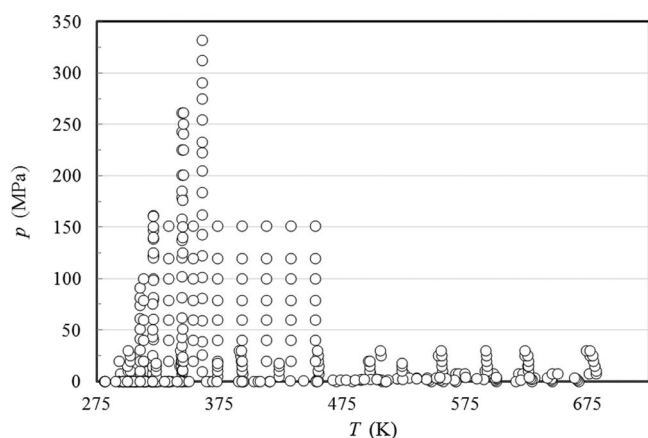


FIG. 1. Temperature and pressure ranges of the experimental thermal-conductivity data for benzene

results. This has also been successfully employed in a similar correlation for toluene.²

In the above scheme, the only unknowns are the Lennard-Jones parameters, σ and ϵ/k_B . The seven sets of thermal conductivity measurements in the dilute limit were used to optimize these two parameters. The values thus obtained were $\sigma = 0.540$ nm and $\epsilon/k_B = 412$ K. These values also predict the viscosity values of Vogel *et al.*⁶² within 1.8%. The experimental dilute-limit thermal-conductivity values as well as the values predicted by the scheme of Eqs. (2)–(5) are shown in Fig. 2, while Fig. 3 presents the percentage deviations of the dilute-gas experimental data from the values calculated by this scheme.

It can be seen in Fig. 3 that the calculated values from Eqs. (2)–(5) are more or less within the uncertainty of the measurements of each investigator, with the exception of Vines⁴⁹ and Vines and Bennett,⁵⁰ whose measurements show a maximum deviation of 4.5% although they both quote 1% uncertainty. In the same figure, the older polynomial correlation of Touloukian *et al.*⁶³ is also included. The Touloukian

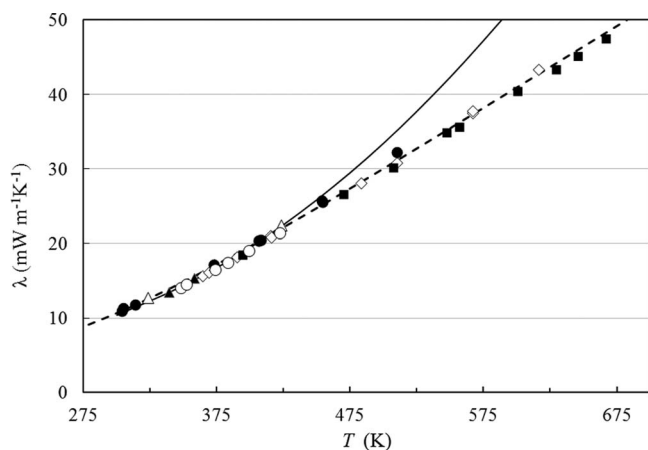


FIG. 2. Dilute-gas limit thermal conductivity as a function of temperature. Kostrovskii and Prostov¹⁶ ($\diamond$), Lambert *et al.*⁵² ($\blacktriangle$), Reiter³⁵ (Δ), Zaitseva *et al.*¹⁴ ($\bullet$), Touloukian *et al.*⁶³ (—), Akhundov¹⁵ ($\blacksquare$), Vines⁴⁹ and Vines and Bennett⁵⁰ ($\circ$), (—) Eqs. (2)–(5)

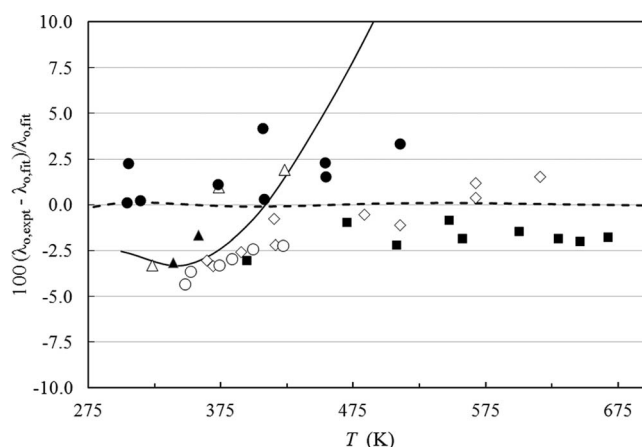


FIG. 3. Percentage deviations of primary experimental data for dilute-gas benzene from the values calculated by Eqs. (2)–(5). Kostrovskii and Prostov¹⁶ ($\diamond$), Lambert *et al.*⁵² ($\blacktriangle$), Reiter³⁵ (Δ), Zaitseva *et al.*¹⁴ ($\bullet$), Touloukian *et al.*⁶³ (—), Akhundov¹⁵ ($\blacksquare$), Vines⁴⁹ and Vines and Bennett⁵⁰ ($\circ$), (—) Eq. (6)

correlation provides recommended values up to 600 K, with an estimated uncertainty of 5% for the region from 280 K to 490 K. The correlation agrees well with the present correlation up to 470 K, and then it deviates as can be seen from Figs. 2 and 3.

Based upon the aforementioned discussion, Eqs. (2)–(5) represent the dilute-gas limit thermal conductivity to within 4% at the 95% confidence level.

For ease of use, the values of the dilute-gas limit thermal conductivity, $\lambda_o(T)$ ($\text{mW m}^{-1} \text{K}^{-1}$), obtained by the scheme of Eqs. (2)–(5), were fitted, which resulted in the equation

$$\lambda_o(T) = \frac{101.404 - 521.440(T/T_c) + 868.266(T/T_c)^2}{1 + 9.714(T/T_c) + 1.467(T/T_c)^2}. \quad (6)$$

Values calculated by this equation do not deviate from the values calculated by the scheme of Eqs. (2)–(5) by more than 0.1% over the temperature range 279 K–725 K (the upper temperature limit imposed by the use of the equation of state of Thol *et al.*⁵ in the remaining contributions), and hence Eq. (6) was used for the dilute-gas limit thermal conductivity for the work described in all of the following sections.

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 residual values far away from the critical point.^{64–66} 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

TABLE 2. Coefficients of Eq. (7) for the residual thermal conductivity of benzene

i	$B_{1,i}$ (W m ⁻¹ K ⁻¹)	$B_{2,i}$ (W m ⁻¹ K ⁻¹)
1	$2.824\ 89 \times 10^{-2}$	$-1.192\ 68 \times 10^{-2}$
2	$-7.734\ 15 \times 10^{-2}$	$8.333\ 89 \times 10^{-2}$
3	$7.140\ 01 \times 10^{-2}$	$-8.981\ 76 \times 10^{-2}$
4	$-2.367\ 98 \times 10^{-2}$	$3.630\ 25 \times 10^{-2}$
5	$3.008\ 75 \times 10^{-3}$	$-4.900\ 52 \times 10^{-3}$

procedure adopted during this analysis used ODRPACK (Ref. 67) to fit all the primary data simultaneously to the residual thermal conductivity and the critical enhancement, while maintaining the parameters in Eq. (6) already obtained from the fit of the dilute-gas thermal-conductivity data. The density values employed were obtained by the equation of state of Thol *et al.*⁵

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

$$\Delta\lambda(\rho, T) = \sum_{i=1}^5 (B_{1,i} + B_{2,i}(T/T_c))(\rho/\rho_c)^i. \quad (7)$$

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

3.3. The critical enhancement

3.3.1. Simplified crossover model

The theoretically based crossover model proposed by Olchoway and Sengers^{64–66} 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 Olchoway and Sengers.⁶⁸ The critical enhancement of the thermal conductivity from this simplified model 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, $\bar{\eta}$ is the viscosity, and C_p and C_v are the isobaric and isochoric specific heat obtained from the Thol *et al.*⁵ equation of state. Since a wide-ranging reference correlation for the viscosity of benzene is presently unavailable, we used the generalized method of Chung *et al.*⁶⁹ to estimate the viscosity. To improve the representation of the viscosity specific to benzene, we fit the parameters in the Chung model (σ , ε/k_B , ω , μ_r , and κ) to the data of Assael *et al.*,⁷⁰ Vieira dos Santos and Nieto de Castro,⁷¹ and

TABLE 3. Evaluation of the benzene thermal-conductivity correlation for the primary data

First author	Year Publ.	AAD (%)	BIAS (%)	STDEV (%)
Watanabe ⁶	2004	0.29	0.29	0.14
Tarzmanov ⁷	2002	0.84	-0.19	1.08
Tong ⁸	1995	2.57	2.14	1.98
Mensah-Brown ⁹	1993	0.30	0.09	0.39
Ramires ¹⁰	1989	0.29	0.16	0.29
Charitidou ¹¹	1988	0.58	-0.57	0.16
Li ¹²	1984	0.28	0.25	0.32
Kashiwagi ¹³	1982	1.97	1.97	0.20
Zaitseva ¹⁴	1976	0.96	-0.72	1.12
Akhundov ¹⁵	1974	2.22	-0.31	2.95
Kostrovski ¹⁶	1974	2.64	-0.55	3.06
Rastorguev ¹⁷	1970	3.08	-3.08	1.04
Horrocks ¹⁸	1963	0.72	-0.69	0.41
Entire data set		1.67	-0.50	2.33

Vogel *et al.*⁶² to obtain the values 0.5023 nm, 444.37 K, 0.5693, 0.3209, and 0.0642, respectively. The correlation length ξ is given by

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

As already mentioned, the coefficients $B_{1,i}$ and $B_{2,i}$ in Eq. (7) and $\bar{q}_D$ in Eqs. (8)–(11) were fitted with ODRPACK (Ref. 67) to the primary data for the thermal conductivity of benzene. This crossover model requires the universal constants⁶⁸ $R_D = 1.02$, $v = 0.63$, and $\gamma = 1.239$, and system-dependent amplitudes Γ and ξ_0 . For this work, we adopted the values $\Gamma = 0.0569$ and estimated $\xi_0 = 2.16 \times 10^{-10}$ m, using the method presented in Ref. 72. The effective wavenumber cutoff $\bar{q}_D$ was found to be equal to 6.2×10^{-10} m. The reference temperature T_{ref} , far above the critical temperature where the critical enhancement is negligible, was calculated by $T_{\text{ref}} = (3/2) T_c$,⁷³ which for benzene is 843.0 K.

Table 3 summarizes comparisons of the primary data with the correlation. We have defined 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 calculated from the correlation. Thus, the average absolute percent deviation (AAD) is found with the expression $\text{AAD} = (\sum |\text{PCTDEV}|) / n$, where the summation is over all n points, the bias percent is found with the expression $\text{BIAS} = (\sum \text{PCTDEV}) / n$, and the standard deviation is $\text{STDEV} = ([n \sum \text{PCTDEV}^2 - (\sum \text{PCTDEV})^2 / n^2])^{1/2}$.

Figure 4 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. 5 and 6 show the same deviations but as a function of the temperature and pressure. The primary data for benzene listed in Table 1 cover a wide range of conditions and extend to 350 MPa. Based on comparisons with the primary data, we calculate the uncertainty (considered to be estimates of a combined expanded uncertainty with a coverage factor of 2) for pressures less than 500 MPa and temperatures less than 725 K to be less

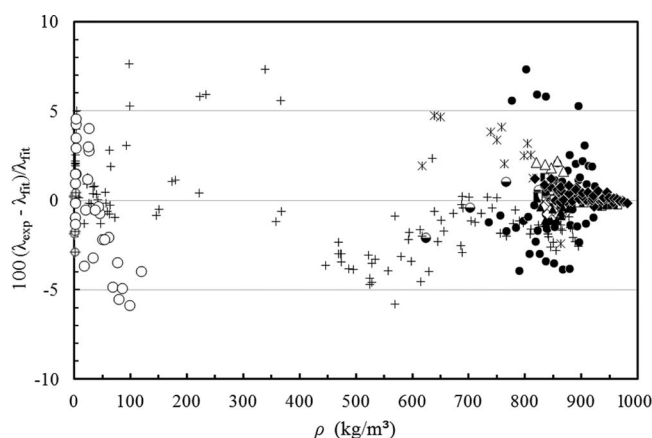


FIG. 4. Percentage deviations of primary experimental data of benzene from the values calculated by the present model as a function of density. Watanabe and Kato⁶ (●), Tarzimanov *et al.*⁷ (⊖), Ramires *et al.*¹⁰ (⊞), Akhundov¹⁵ (+), Charitidou *et al.*¹¹ (◇), Kashiwagi *et al.*¹³ (Δ), Zaitseva *et al.*¹⁴ (⊕), Tong and Tianxiang⁸ (×), Rastorguev and Pugash¹⁷ (●), Mensah-Brown and Wakeham⁹ (■), Li *et al.*¹² (◆), Horrocks and McLaughlin¹⁸ (▲), Kostrovskii and Prostov¹⁶ (○)

than 4.4%. Uncertainties in the critical region are much larger, since the thermal conductivity approaches infinity at the critical point and the properties become very sensitive to small differences in the state variables.

The standard correlation proposed by Assael *et al.*,⁴ for the thermal conductivity of benzene along the saturation line covering a temperature range from 290 to 350 K, is also shown in Fig. 5. Its deviations from the present correlation are less than 0.4%, which is considered excellent.

Figures 7 and 8 show the percentage deviations of the secondary data from the values calculated by the proposed scheme. The majority of the deviations are well within 10% of the present correlation.

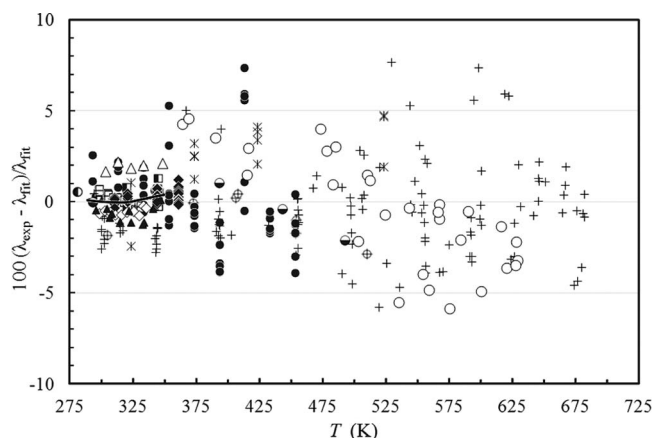


FIG. 5. Percentage deviations of primary experimental data of benzene from the values calculated by the present model as a function of temperature. Watanabe and Kato⁶ (●), Tarzimanov *et al.*⁷ (⊖), Ramires *et al.*¹⁰ (⊞), Akhundov¹⁵ (+), Charitidou *et al.*¹¹ (◇), Kashiwagi *et al.*¹³ (Δ), Zaitseva *et al.*¹⁴ (⊕), Tong and Tianxiang⁸ (×), Rastorguev and Pugash¹⁷ (●), Mensah-Brown and Wakeham⁹ (■), Li *et al.*¹² (◆), Horrocks and McLaughlin¹⁸ (▲), Kostrovskii and Prostov¹⁶ (○), Reference correlation of Assael *et al.*⁴ (—)

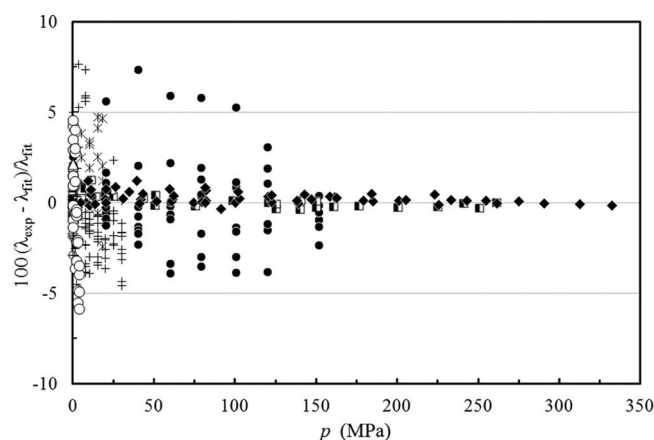


FIG. 6. Percentage deviations of primary experimental data of benzene from the values calculated by the present model as a function of pressure. Watanabe and Kato⁶ (●), Tarzimanov *et al.*⁷ (⊖), Ramires *et al.*¹⁰ (⊞), Akhundov¹⁵ (+), Charitidou *et al.*¹¹ (◇), Kashiwagi *et al.*¹³ (Δ), Zaitseva *et al.*¹⁴ (⊕), Tong and Tianxiang⁸ (×), Rastorguev and Pugash¹⁷ (●), Mensah-Brown and Wakeham⁹ (■), Li *et al.*¹² (◆), Horrocks and McLaughlin¹⁸ (▲), Kostrovskii and Prostov¹⁶ (○)

Finally, Fig. 9 shows a plot of the thermal conductivity of benzene 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:

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

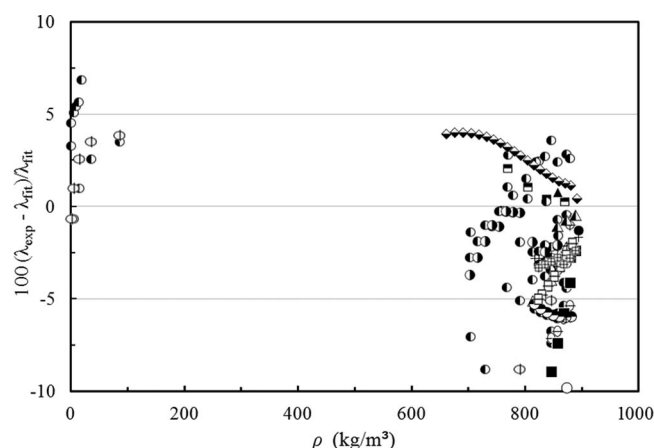


FIG. 7. Percentage deviations of secondary experimental data of benzene from the values calculated by the present model as a function of density (period 1965–2010). Salavera *et al.*¹⁹ (⊞), Lamvik and Zhou²⁰ (●), Goldschmidt⁵⁷ (●), Rowley and Gubler²¹ (▲), Rowley and White²² (×), Fischer and Obermeier²³ (◇), Atalla *et al.*²⁴ (◆), Ogiwara *et al.*²⁵ (⊞), Takizawa *et al.*²⁷ (■), Spirin²⁶ (○), Corti and Degiorgio²⁸ (○), Gulari *et al.*²⁹ (⊕), Kerimov *et al.*³¹ (Δ), Bachmann³² (+), Poltz and Jugel³³ (▲), Yamamoto and Akiyama³⁷ (■), Tufeu *et al.*³⁶ (●), Reiter³⁵ (⊞), Filipov³⁸ (⊞), Geller *et al.*³⁹ (×), Venart⁴⁰ (⊕)

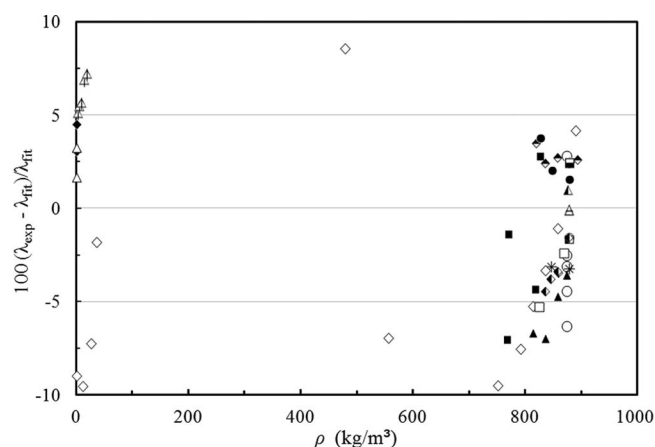


FIG. 8. Percentage deviations of secondary experimental data of benzene from the values calculated by the present model as a function of density (period 1886–1964). Jamieson and Tudhope⁴¹ (○), Powell and Tye⁴² (△), Scheffy and Johnson⁴³ (■), Eldarov⁴⁴ (▲), Frontasev and Gusakov⁴⁵ (●), Tseiderberg⁴⁶ (✱), Briggs⁴⁷ (▣), Vines and Bennett⁵⁰ (△), Vines⁴⁹ (◆), Schmidt and Leidenfrost⁴⁸ (◀), Riedel⁵¹ (*), Lambert *et al.*⁵² (Δ), Abas-Zade⁵⁵ (◊), Vargaftik⁵⁴ (□), van der Held and van Drunen⁵³ (▲), Shiba⁵⁶ (●), Weber⁵⁸ (■)

where $\Delta T_c = (T/T_c) - 1$ and $\Delta \rho_c = (\rho/\rho_c) - 1$. This equation does not require accurate information on the compressibility, specific heat, and viscosity of benzene in the critical region, as does the theory of Olchowy and Sengers.⁶⁸ 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 $C_1 = 1.1 \times 10^{-3} \text{ W m}^{-1} \text{ K}^{-1}$, $C_2 = 7.0 \times 10^{-2}$, and $C_3 = 1.8$. Figure 10 shows the percentage deviations between the primary data and the values calculated by Eqs. (6), (7), and (12) as a function of the temperature. By comparing Figs. 5 and 10, it can be seen that employing Eq. (12) results in little deterioration in the representation of the data.

4. Computer-Program Verification

Table 4 is provided to assist the user in computer-program verification. The thermal-conductivity calculations are based

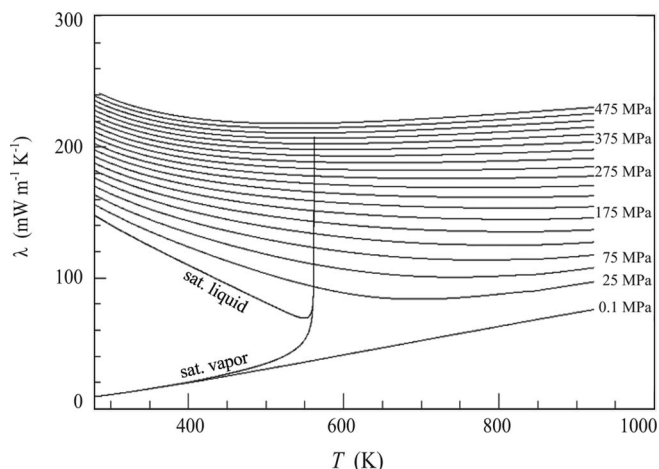


FIG. 9. Thermal conductivity of benzene as a function of temperature for different pressures

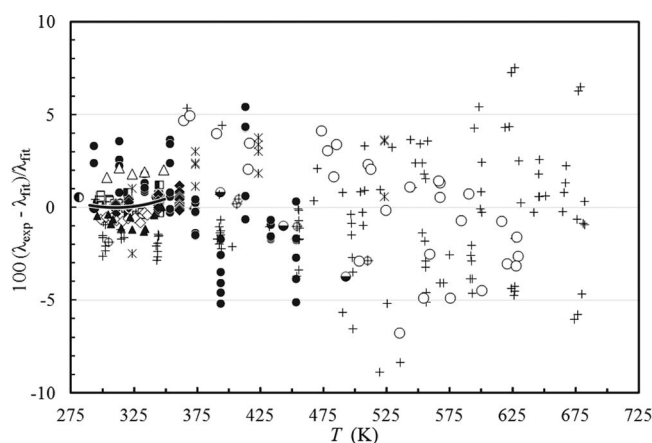


FIG. 10. Percentage deviations of primary experimental data of benzene from the values calculated by Eqs. (1), (6), (7), and (12) as a function of temperature. Watanabe and Kato⁶ (●), Tarzimanov *et al.*⁷ (●), Ramirez *et al.*¹⁰ (□), Akhundov¹⁵ (+), Charitidou *et al.*¹¹ (◊), Kashiwagi *et al.*¹³ (Δ), Zaitseva *et al.*¹⁴ (✱), Tong and Tianxiang⁸ (✱), Rastorguev and Pugash¹⁷ (●), Mensah-Brown and Wakeham⁹ (■), Li *et al.*¹² (◆), Horrocks and McLaughlin¹⁸ (▲), Kostrovskii and Prostov¹⁶ (◊), Reference correlation of Assael *et al.*⁴ (—)

on the tabulated temperatures and densities. Note that Eq. (6) was employed for the dilute-gas correlation.

5. Conclusion

New wide-ranging correlations for the thermal conductivity of benzene were developed based on critically evaluated experimental data. The correlations are valid from the triple point to 725 K, and at pressures up to 500 MPa. The correlations are expressed in terms of temperature and density, and the densities were obtained from the equation of state of Thol *et al.*⁵ The overall uncertainty (considered to be estimates of a combined expanded uncertainty with a coverage factor of 2) of the proposed correlation is calculated, for pressures less than 350 MPa and temperatures less than 725 K, to be less than 4.4%.

TABLE 4. Sample points for computer verification of the correlating equations

T (K)	ρ (kg m ⁻³)	λ (mW m ⁻¹ K ⁻¹)
290.00	890.00	147.66
500.00	2.00	30.174
500.00	32.00	32.175
500.00	800.00	141.24
570.00	1.70	37.763 ^a
570.00	1.70	38.290 ^b

^aComputed with modified Olchowy-Sengers critical enhancement; the viscosity at this point for use in Eq. (8) was taken as $\eta = 14.429 \text{ } \mu\text{Pa s}$ (see Sec. 3.3.1), and all other properties required for the enhancement term are from Thol *et al.*⁵

^bComputed with empirical critical enhancement Eq. (12).

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