Reference Correlations of the Thermal Conductivity of *o*-Xylene, *m*-Xylene, *p*-Xylene, and Ethylbenzene from the Triple Point to 700 K and Moderate Pressures

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This paper contains new, representative reference equations for the thermal conductivity of *o*-xylene, *m*-xylene, *p*-xylene, and ethylbenzene. 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. 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. All four correlations are applicable for the temperature range from the triple point of each fluid to 700 K, and an upper pressure limit determined by the maximum density limit for the equation of state used to provide density. At the upper temperature limit of 700 K, the maximum pressure was 200 MPa for *m*-xylene and *p*-xylene, but 60 and 70 MPa for ethylbenzene and *o*-xylene, respectively. At lower temperatures, the maximum pressure is lower. The overall uncertainty (at the 95% confidence level) of the correlations of the thermal conductivity of *o*-, *m*-, *p*-xylene, and ethylbenzene, over their range of applicability, varies for each fluid. For *o*-xylene, we estimate the uncertainty for liquid and supercritical densities for temperatures from the triple point to 400 K to be 2.6%, and 4% at higher temperatures, and in the dilute-gas region we estimate the uncertainty to be 2%. For *m*-xylene, the estimated uncertainty for liquid and supercritical densities at temperatures from the triple point to 375 K is 3.6%, and 5% at higher temperatures, and 6% for the dilute gas. For *p*-xylene, the estimated uncertainty for liquid and supercritical densities at temperatures from the triple point to 700 K is 3.6%, and 2.5% for the dilute gas. Finally, for ethylbenzene the estimated uncertainty for liquid and supercritical densities at temperatures from the triple point to 400 K is 2.8%, and 2.5% in the dilute-gas region. Uncertainties in the critical region for all four fluids are much larger, since the thermal conductivity approaches infinity at the critical point and is very sensitive to small changes in density. © *2014 by the U.S. Secretary of Commerce on behalf of the United States. All rights reserved.* [http://dx.doi.org/10.1063/1.4901166]

Key words: critical phenomena; ethylbenzene; reference correlations; thermal conductivity; transport properties; xylene.

CONTENTS

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List of Tables

List of Figures

1. Introduction

In a series of recent papers, new reference correlations for the thermal conductivity of normal and parahydrogen,[1] water,[2] SF$_6$,[3] toluene,[4] benzene,[5] *n*-hexane,[6] *n*-heptane,[7] methanol,[8] and ethanol,[9] covering a wide range of conditions of temperature and pressure, were reported. In this paper, the work is extended to the thermal conductivity of *ortho*-xylene, *meta*-xylene, *para*-xylene, and ethylbenzene.

The goal of this work is to critically assess the available literature data, and provide wide-ranging correlations for the thermal conductivity of *o*-, *m*-, *p*-xylene, and ethylbenzene, that are valid over gas, liquid, and supercritical states, and incorporate densities provided by the recent equations of state of Zhou *et al.*[10] It was decided to treat the four compounds in one paper, since they are quite similar in their thermophysical properties, and are usually found together.

2. Methodology

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

$$\lambda(\rho, T) = \lambda_{\mathrm{o}}(T) + \Delta\lambda(\rho, T) + \Delta\lambda_{\mathrm{c}}(\rho, T), \qquad (1)$$

where ρ is the density, T is the temperature, and the first term, $\lambda_{\mathrm{o}}(T) = \lambda(0, T)$, is the contribution to the thermal conductivity in the dilute-gas limit, where only two-body molecular interactions occur. The final term, $\Delta\lambda_{\mathrm{c}}(\rho, T)$, 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 the critical 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 $\lambda_{\mathrm{o}}(T)$ and $\Delta\lambda_{\mathrm{c}}(\rho, T)$ theoretically. In addition, it is possible to derive information about $\lambda_{\mathrm{o}}(T)$ 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 a well-established set of criteria.[11] 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

TABLE 1. Coefficients and exponents of Eq. (4)[10]

i	v_i	u_i (K)	v_i	u_i (K)	v_i	u_i (K)	v_i	u_i (K)
	o-Xylene		*m*-Xylene		*p*-Xylene		Ethylbenzene	
0	3.748798	0.0	2.169909	0.0	5.2430504	0.0	5.2557889	0.0
1	4.754892	225	4.443120	160	5.2291378	414	9.7329909	585
2	6.915052	627	2.862794	190	19.549862	1256	11.201832	4420
3	25.84813	1726	24.83298	1333	16.656178	2649	25.440749	1673
4	10.93886	4941	16.26077	3496	5.9390291	6681		

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.

2.1. The dilute-gas limit

In order to be able to extrapolate the temperature range of the measurements, 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 traditional kinetic approach for thermal conductivity results in an expression involving three generalized cross sections.[12,13] However, it is possible to derive an equivalent kinetic theory expression for thermal conductivity by making use of the approach of Thijsse *et al.*[14,15] where one considers expansion in terms of total energy, rather than separating translational from internal energy as is done traditionally. In this case, the dilute-gas limit thermal conductivity, $\lambda_o(T)$ (mW m^{-1} K^{-1}), of a polyatomic gas can be shown to be inversely proportional to a single generalized cross section,[12–15] $S(10E)$, as

$$\lambda_o(T) = 1000 \frac{5k_B^2(1 + r^2)T}{2m\langle v \rangle_o S(10E)} f_\lambda, \tag{2}$$

where k_B is the Boltzmann constant, T (K) is the absolute temperature, f_λ (−) is the dimensionless higher-order correction factor, m (kg) is the molecular mass of *o*-, *m*-, *p*-xylene, and ethylbenzene [(0.106165/6.02214 × 10^{23}) kg], and $\langle v \rangle_o = 4\sqrt{k_B T/\pi m}$ (m/s) is the average relative thermal speed. The quantity r^2 is defined by $r^2 = 2C_{int}^o/5k_B$, where C_{int}^o is the contribution of both the rotational, C_{rot}^o, and the vibrational, C_{vib}^o, degrees of freedom to the isochoric ideal-gas heat capacity C_v^o.

Recent classical trajectory calculations[16–18] confirm that, for most molecules studied, the higher-order thermal conductivity correction factor is near unity. One can take advantage of this finding to define the effective generalized cross section S_λ ($=S(10E)/f_\lambda$) (nm^2), and rewrite Eq. (2) for the dilute-gas limit thermal conductivity of the xylene isomers and ethylbenzene, $\lambda_o(T)$ (mW m^{-1} K^{-1}), as

$$\lambda_o(T) = 0.0541409 \frac{(C_p^o/k_B)\sqrt{T}}{S_\lambda}. \tag{3}$$

The ideal-gas isobaric heat capacity for the xylene isomers and ethylbenzene, C_p^o ($=C_{int}^o + 2.5 k_B$) can be obtained from Zhou

et al.[10] as

$$\frac{C_p^o}{k_B} = v_0 + \sum_{i=1}^{I_{Ideal}} v_i \left(\frac{u_i}{T}\right)^2 \frac{\exp(u_i/T)}{[\exp(u_i/T) - 1]^2}, \tag{4}$$

where I_{Ideal} is 3 for ethylbenzene and 4 for *o*-, *m*-, and *p*-xylene. The coefficients and exponents of the ideal-gas heat capacity equations are given in Table 1.

It has been previously noted[15] and recently confirmed[13] for smaller molecules, that the cross section $S(10E)$ exhibits a nearly linear dependence on the inverse temperature. Hence, experimental data will be employed to obtain coefficients a_0 and a_1 in

$$S_\lambda = a_0 + a_1/T. \tag{5}$$

Equations (3)–(5) form a consistent set of equations for the calculation of the dilute-gas limit thermal conductivity.

2.2. 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.[19–21] 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, 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. 22) to fit all the primary data simultaneously to the residual thermal conductivity and the critical enhancement, while maintaining the values of the dilute-gas thermal-conductivity data already obtained. The density values employed were obtained by the equations of state of Zhou *et al.*[10] The primary data were weighted inversely proportional to the square of their uncertainty.

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

$$\Delta\lambda(\rho, T) = \sum_{i=1}^{5} (B_{1,i} + B_{2,i}(T/T_c))(\rho/\rho_c)^i. \tag{6}$$

Coefficients $B_{1,i}$ and $B_{2,i}$ are obtained for each fluid separately employing the corresponding primary data.

2.3. The critical enhancement

The theoretically based crossover model proposed by Olchowy and Sengers[19–21] 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.[23] The critical enhancement of the thermal conductivity from this simplified model is given by

$$\Delta\lambda_c = \frac{\rho C_p R_D k_B T}{6\pi\overline{\eta}\xi}(\overline{\boldsymbol{\Omega}} - \overline{\boldsymbol{\Omega}}_0), \tag{7}$$

with

$$\overline{\boldsymbol{\Omega}} = \frac{2}{\pi}\left[\left(\frac{C_p - C_v}{C_p}\right)\arctan(\overline{q}_D\xi) + \frac{C_v}{C_p}\overline{q}_D\xi\right] \tag{8}$$

and

$$\overline{\boldsymbol{\Omega}}_0 = \frac{2}{\pi}\left[1 - \exp\left(-\frac{1}{(\overline{q}_D\xi)^{-1} + (\overline{q}_D\xi\rho_c/\rho)^2/3}\right)\right]. \tag{9}$$

In Eqs. (7)–(9), k_B is Boltzmann's constant, $\overline{\eta}$ is the viscosity, and C_p and C_v are the isobaric and isochoric specific heat obtained from Zhou et al.[10] The correlation length ξ is given by

$$\xi = \xi_0\left(\frac{p_c\rho}{\Gamma\rho_c^2}\right)^{\nu/\gamma}\left[\frac{\partial\rho(T,\rho)}{\partial p}\bigg|_T - \left(\frac{T_{ref}}{T}\right)\frac{\partial\rho(T_{ref},\rho)}{\partial p}\bigg|_T\right]^{\nu/\gamma}. \tag{10}$$

In the above equations for the four fluids studied, values for the universal constants $R_D = 1.02$, $\nu = 0.63$, and $\gamma = 1.239$ were employed using a universal representation of the critical enhancement of the thermal conductivity (based on a simplified solution of mode-coupling theory with fluid specific parameters

determined by a corresponding states method) by Perkins et al.[24] Furthermore, since for these particular fluids very few data exist in the critical region, it was preferred to employ the same method presented by Perkins et al.[24] to predict the effective cutoff wavelength $\overline{q}_D^{-1}$. The system-dependent amplitude Γ and ξ_o, as well as the reference temperature T_{ref}, will be discussed separately for each fluid.

3. Thermal Conductivity Correlations

3.1. The correlation for *o*-xylene

Table 2 summarizes, to the best of our knowledge, the experimental measurements of the thermal conductivity of *o*-xylene reported in the literature. Sixteen sets are included in the table. From these sets, eight were considered as primary data.

The atmospheric-pressure data of Assael et al.[25] and the high-pressure data of Taxis et al.[26] were obtained in absolute transient hot-wire instruments employing two anodized Ta wires, with uncertainties 0.5% and 0.3%, respectively. The operation of both instruments is based on a full theoretical model and it is proven to operate with an uncertainty of less than 0.5%. Measurements performed by the group of Assael have already been successfully employed in many thermal-conductivity reference correlations.[1,2,4–9] Similarly, measurements performed by the second group headed by Wakeham have also been successfully employed in many thermal-conductivity reference correlations.[2,4–7] Hence, these two sets were considered as primary data.

The measurements of Watanabe and Kato[27] were also performed in an absolute transient hot-wire instrument, with an uncertainty of 0.4%. Measurements of these investigators have been employed in previous thermal conductivity

TABLE 2. Thermal conductivity measurements of *o*-xylene

1st author	Year Publ.	Technique employed[a]	Purity (%)	Uncertainty (%)	No. of data	Temperature range (K)	Pressure range (MPa)
			Primary data				
Watanabe[27]	2004	THW	98	0.4	15	257–328	0.1
Assael[25]	1988	THW	99	0.5	12	295–357	0.1
Taxis[26]	1988	THW	99	0.3	27	308–360	0.3–70[b]
Naziev[28]	1987	CC	na	0.5	60	273–473	0.1–50
Kashiwagi[29]	1982	THW	99	2	6	298–358	0.1
Mustafaev[30]	1977	CC	na	2	113	306–673	0.1–70[b]
Rastorguev[31]	1970	SSHF	High Purity[c]	1.5	42	293–453	0.1–70[b]
Akhundov[32,d]	1970	THW	99	2	139	302–698	0.002–30
			Secondary data				
Tarzimanov[33]	2002	THW	na	1	5	293–493	0.001–0.53
Briggs[34]	1977	CC	95	3	8	293–363	0.1
Kerimov[35]	1970	HW	na	na	3	298–353	0.1
Bachmann[36]	1969	THW	na	2	11	253–353	0.1
Filippov[37]	1965	CC	na	3	6	293–343	0.1
Gudzinowicz[38]	1964	HW	na	na	1	290	0.1
Frontasev[39]	1959	HW	na	0.5	1	293	0.1
Linder[40]	1956	PP	99	3.5	5	310–345	0.1

[a]CC, coaxial cylinder; HW, hot wire; na, not available; PP, parallel plate; SSHF, steady-state hot filament; THW, transient hot wire.
[b]Measurements restricted to 918 kg m^{-3} (restriction imposed by the density limit of the equation of state[10]).
[c]'High Purity' grade was quoted in the paper.
[d]Includes vapor data employed to derive the dilute-gas thermal-conductivity correlation.

reference correlations,[4–7] and hence are also included in the present primary set. Two more investigators have employed transient hot-wire instruments of slightly inferior uncertainty: Kashiwagi *et al.*[29] and Akhundov and Gasanova.[32] Although their quoted uncertainty is 2%, measurements of these investigators have successfully been employed in the past in many thermal conductivity reference correlations, and hence are also considered as primary data. Naziev *et al.*[28] and Mustafaev and Gabulov[30] employed concentric-cylinder instruments for the measurement of the thermal conductivity with a 2% uncertainty, up to high pressures. The measurements of Naziev *et al.*[28] have been successfully employed in previous thermal conductivity reference correlations,[6–8] and thus are included in the primary dataset. The measurements of Mustafaev andGabulov[30] seem to agree very well with the other measurements, and as they extend to higher temperatures, have also been included. The last set to be included in the primary dataset is the steady-state hot-filament measurements of Rastorguev.[31] These are characterized by a 1.5% uncertainty, and measurements of this investigator have successfully been included in other thermal conductivity reference correlations.[3,5] The remaining datasets were considered as secondary data.

Figures 1 and 2 show the ranges of the primary measurements outlined in Table 2, and the saturation curve may be seen in Fig. 2. Temperatures for all data were converted to the ITS-90 temperature scale.[41] The development of the correlation requires densities; Zhou *et al.*[10] in 2012 reviewed the thermodynamic properties of *o*-xylene and developed an accurate, wide-ranging equation of state valid for single-phase and saturation states from the triple point to 700 K at pressures up to 70 MPa and a maximum density of 918 kg m^{-3}, with an uncertainty in density of 0.1%, and up to 1% in the critical region. It should be noted that the maximum density of the correlation imposes a pressure limit in the present measurements shown in Table 2 (e.g., at 250 K the maximum pressure is only 3 MPa, while over 300 K it is near 70 MPa). We also
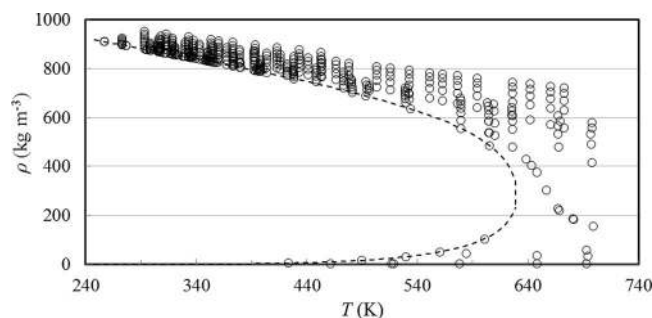
FIG. 2. Temperature-density ranges of the primary experimental thermal conductivity data for *o*-xylene. (- -) saturation line.

adopt their values for the critical temperature, T_c, the critical density, ρ_c, and the triple-point temperature, as 630.259 K, 285.00 kg m^{-3}, and 247.985 K, respectively. Finally, as already discussed, the isobaric ideal-gas heat capacity proposed by Zhou *et al.*[10] (estimated by a group contribution method) was also employed.

3.1.1. The dilute-gas limit of *o*-xylene

From the primary measurements shown in Table 2, only Akhundov and Gasanova[32] performed measurements near the dilute-gas limit. These measurements were employed together with Eqs. (3)–(5) in order to obtain the coefficients a_0 and a_1 of Eq. (5), as

$$S_\lambda = 0.7288 + 107.9/T. \tag{11}$$

Equations (3)–(5) and (11) represent the dilute-gas thermal conductivity to within 1% at the 95% confidence level.

The values of the dilute-gas limit thermal conductivity, $\lambda_0(T)$ in mW m^{-1} K^{-1}, obtained by the scheme of Eqs. (3)–(5) and (11), were fitted as a function of the reduced temperature $T_r = T/T_c$ for ease of use to the following equation:

$$\lambda_0(T) = \frac{-0.837488 + 12.7856T_r - 37.1925T_r^2 + 63.9548T_r^3 - 4.43443T_r^4}{0.262226 - 0.490519T_r + T_r^2}. \tag{12}$$
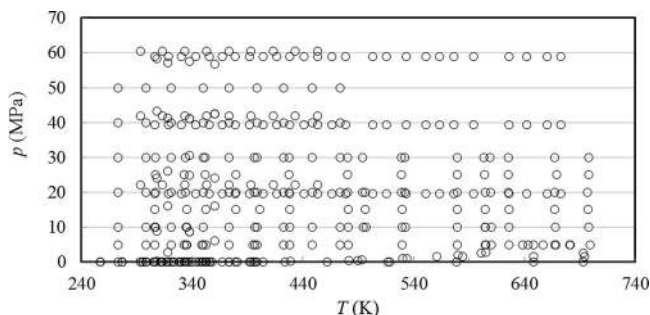
Values calculated by Eq. (12) do not deviate from the values calculated by the scheme of Eqs. (3)–(5) and (11) by more than 0.05% over the temperature range from 248 to 2000 K. Equation (12) is hence employed in the calculations that will follow.

Figure 3 shows the dilute-gas thermal conductivity values of Akhundov and Gasanova,[32] and the values calculated by Eq. (12), as a function of the temperature. In addition to these values, the values recommended by Vargaftik[43] and a more recent correlation proposed by Yaws[42] are also shown. In Fig. 4, percentage deviations of the dilute-gas thermal conductivity of *o*-xylene from the scheme of Eqs. (3)–(5) and (11) are also shown. They all agree with the present correlation
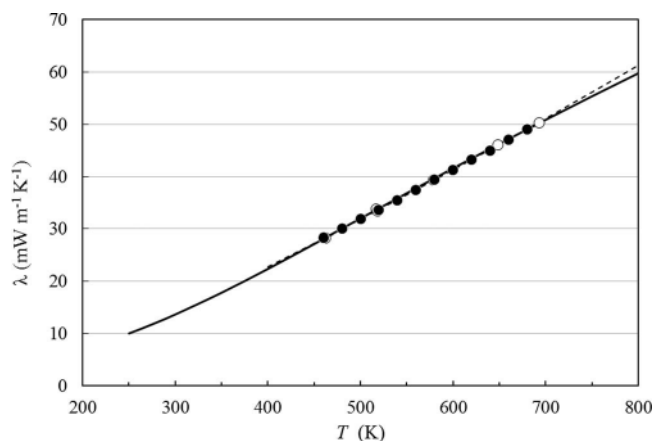

FIG. 1. Temperature-pressure ranges of the primary experimental thermal conductivity data for *o*-xylene.

FIG. 3. Dilute-gas thermal conductivity of *o*-xylene as a function of temperature. Akhundov and Gasanova[32] (○), Yaws[42] (- -), Vargaftik[43] (●), Eq. (12) (–).

within 1.5%. Based on the measurements of Akhundov and Gasanova[32] (whose uncertainty is 2%), the uncertainty of the correlation is believed also to be 2%. We note that sources employed by Yaws[42] are not known, while the sources employed by Vargaftik[43] include the measurements of Akhundov and Gasanova.[32]

3.1.2. The residual and the critical enhancement contributions of *o*-xylene

As already mentioned, the coefficients $B_{1,i}$ and $B_{2,i}$ in Eq. (6) were fitted with ODRPACK (Ref. 22) to the primary data for the thermal conductivity of *o*-xylene. The crossover model requires the system-dependent amplitudes Γ and ξ_0. For this work, we adopted the value $\Gamma = 0.058$ and estimated $\xi_0 = 2.36 \times 10^{-10}$ m, using a universal representation of the critical enhancement of the thermal conductivity (based on a simplified solution of mode-coupling theory with fluid-specific parameters determined by a corresponding states method) by Perkins *et al.*[24] Furthermore, since very few data exist in the critical region, it was preferred to employ the method of
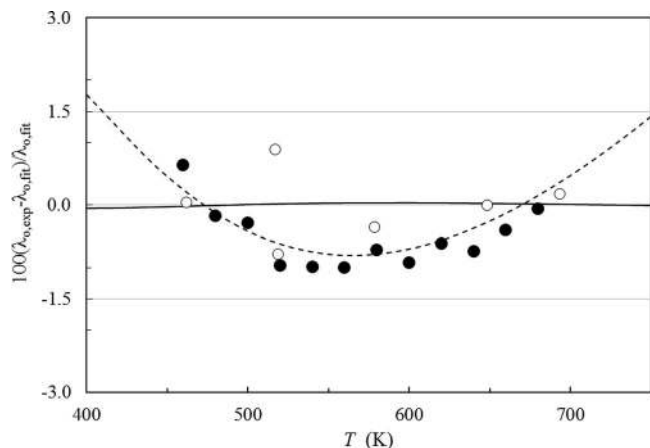
FIG. 4. Percentage deviations of the dilute-gas thermal conductivity of *o*-xylene from the scheme of Eqs. (3)–(5) and (11). Akhundov and Gasanova[32] (○), Yaws[42] (- -), Vargaftik[43] (●), Eq. (12) (–).

TABLE 3. Coefficients of Eq. (6) for the residual thermal conductivity of *o*-xylene

i	$B_{1,i}$ (mW m^{-1} K^{-1})	$B_{2,i}$ (mW m^{-1} K^{-1})
1	$-3.462\,92 \times 10^1$	$4.558\,79 \times 10^1$
2	$7.577\,35 \times 10^1$	$-5.944\,73 \times 10^1$
3	$-6.743\,78 \times 10^1$	$5.500\,12 \times 10^1$
4	$2.769\,50 \times 10^1$	$-2.555\,22 \times 10^1$
5	$-3.742\,38 \times 10^0$	$4.188\,05 \times 10^0$

Perkins *et al.*[24] also for the effective cutoff wavelength $\overline{q}_D^{-1}$; thus found equal to 7.11×10^{-10} m. The viscosity required for Eq. (7) was estimated by an extended corresponding-states method of Huber *et al.*[44] The reference temperature T_{ref}, far above the critical temperature where the critical enhancement is negligible, was calculated by $T_{ref} = (3/2)T_c$,[45] which for *o*-xylene is 945.4 K. The coefficients $B_{1,i}$ and $B_{2,i}$ of Eq. (6) obtained are shown in Table 3.

Table 4 summarizes comparisons of the primary data with the correlation. We have defined the percent deviation as PCTDEV $= 100^*(\lambda_{exp}-\lambda_{fit})/\lambda_{fit}$, 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 AAD $= (\sum|\text{PCTDEV}|)/n$, where the summation is over all n points, the bias percent is found with the expression BIAS $= (\sum\text{PCTDEV})/n$. We estimate the uncertainty (at the 95% confidence level) for thermal conductivity at liquid and supercritical densities up to 918 kg m^{-3} and temperatures from the triple point to 400 K, to be 2.6%, and 4% at higher temperatures For the thermal conductivity of the dilute gas, we estimate the uncertainty to be 2%. Uncertainties in the critical region are much larger, since the thermal conductivity approaches infinity at the critical point and is very sensitive to small changes in density.

Figure 5 shows the percentage deviations of all primary thermal-conductivity data from the values calculated by Eqs. (1), (6)–(10), and (12), as a function of the density, while Figs. 6 and 7 show the same deviations but as a function of the temperature and pressure, respectively.

Table 5 shows the AAD and the bias for the secondary data. Finally, Fig. 8 shows a plot of the thermal conductivity of *o*-xylene as a function of temperature for different pressures, while in Table 6 recommended values for the thermal

TABLE 4. Evaluation of the *o*-xylene thermal-conductivity correlation for the primary data

1st Author	Year Publ.	AAD (%)	BIAS (%)
Watanabe[27]	2004	1.57	−1.57
Assael[25]	1988	0.37	−0.37
Taxis[26]	1988	0.74	0.28
Naziev[28]	1987	0.60	0.16
Kashiwagi[29]	1982	0.67	−0.05
Mustafaev[30]	1977	1.89	−1.30
Rastorguev[31]	1970	1.02	0.85
Akhundov[32]	1970	1.44	0.61
Entire data set		**1.30**	**−0.54**

FIG. 5. Percentage deviations of primary experimental data of *o*-xylene from the values calculated by the present model Eqs. (1), (6)–(10), and (12), as a function of density. Assael *et al.*[25] (□), Taxis *et al.*[26] (+), Watanabe and Kato[27] (●), Kashiwagi *et al.*[29] (Δ), Mustafaev and Gabulov[30] (×), Rastorguev and Pugash[31] (◊), Akhundov and Gasanova[32] (♦), Kostrovskii and Prostov[46] (▲).

FIG. 7. Percentage deviations of primary experimental data of *o*-xylene from the values calculated by the present model, Eqs. (1), (6)–(10), and (12), as a function of pressure. Assael *et al.*[25] (□), Taxis *et al.*[26] (+), Watanabe and Kato[27] (●), Kashiwagi *et al.*[29] (Δ), Mustafaev and Gabulov[30] (×), Rastorguev and Pugash[31] (◊), Akhundov and Gasanova[32] (♦), Kostrovskii and Prostov[46] (▲).

conductivity are shown. For checking computer implementations of the correlation, the density for the point at 300 K and 70 MPa is 914.85 kg m^{-3}. A point with critical enhancement is 635.0 K, 270.0 kg m^{-3}, where the thermal conductivity is 96.4 mW m^{-1} K^{-1} and the viscosity used in the correlation was 28.59 μPa s.

3.2. The correlation for *m*-xylene

Table 7 summarizes, to the best of our knowledge, the experimental measurements of the thermal conductivity of *m*-xylene reported in the literature. Nineteen sets are included in the table. From these sets, ten were considered as primary data.

The measurements of eight investigators[25–27,29–32,47] in Table 7 were already characterized as primary data in the
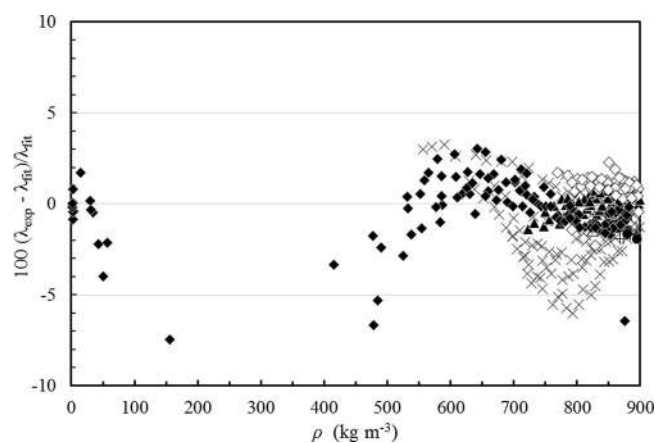

FIG. 6. Percentage deviations of primary experimental data of *o*-xylene from the values calculated by the present model, Eqs. (1), (6)–(10), and (12), as a function of temperature. Assael *et al.*[25] (□), Taxis *et al.*[26] (+), Watanabe and Kato[27] (●), Kashiwagi *et al.*[29] (Δ), Mustafaev and Gabulov[30] (×), Rastorguev and Pugash[31] (◊), Akhundov and Gasanova[32] (♦), Kostrovskii and Prostov[46] (▲).

case of *o*-xylene, and hence in the case of *m*-xylene for the same reasons are also considered as primary data. Two additional sets were added to the primary data set for *m*-xylene. Perkins[48] employed an absolute transient hot-wire instrument, backed by the full theory, with an uncertainty of 0.5% for the measurement of the thermal conductivity. His measurements have been successfully employed in previous thermal conductivity reference correlations.[1–4] Finally, the vapor-phase measurements of Kostrovskii and Prostov,[46] performed in a hot-wire instrument with a 2% uncertainty, have been included as they have also successfully been employed in previous thermal conductivity reference correlations.[4,5]

Figures 9 and 10 show the ranges of the primary measurements outlined in Table 7; the saturation curve is also shown in Fig. 10. Temperatures for all data were converted to the ITS-90 temperature scale.[41] The development of the correlation requires densities; Zhou *et al.*[10] in 2012 reviewed the thermodynamic properties of *m*-xylene and developed an accurate, wide-ranging equation of state valid for single-phase and saturation states from the triple point to 700 K at pressures up to 200 MPa and a maximum density of 921 kg m^{-3}, with an uncertainty in density of 0.2% in the compressed liquid region, and up to 1% in the critical and vapor regions. Again, we note that the maximum density of the correlation imposes a pressure

TABLE 5. Evaluation of the *o*-xylene thermal-conductivity correlation for the secondary data

1st author	Year Publ.	AAD (%)	BIAS (%)
Tarzimanov[33]	2002	1.65	−1.65
Briggs[34]	1977	6.83	6.83
Kerimov[35]	1970	2.22	0.93
Bachmann[36]	1969	6.98	6.98
Filippov[37]	1965	1.73	1.73
Gudzinowicz[38]	1964	7.80	−7.80
Frontasev[39]	1959	0.79	0.79
Linder[40]	1956	2.09	0.69
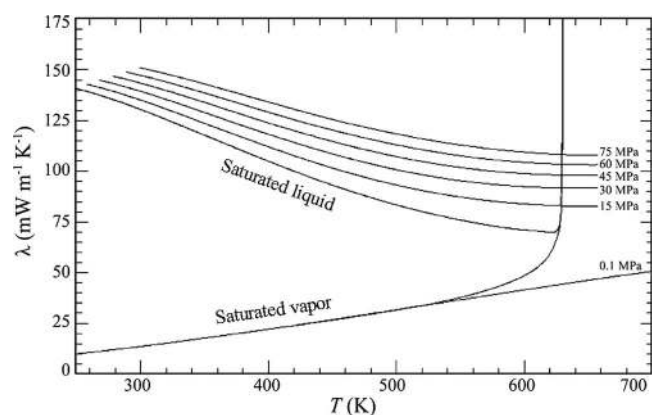
FIG. 8. Thermal conductivity of o-xylene as a function of temperature for different pressures.

limit in the present measurements shown in Table 7 (e.g., at 250 K the maximum pressure is approximately 40 MPa, at 300 K is ∼120 MPa, while over 400 K it is above 200 MPa). We also adopt their values for the critical temperature, T_c, the critical density, ρ_c, and the triple-point temperature, as 616.89 K, 282.9297 kg m^{-3}, and 225.3 K, respectively. Finally, as already discussed, the isobaric ideal-gas heat capacity proposed by Zhou et al.[10] (estimated by a group contribution method) was also employed.

TABLE 6. Recommended values of o-xylene thermal conductivity (mW m^{-1} K^{-1})

Pressure (MPa)	Temperature (K)					
	250	300	400	500	600	700
0	10.06	13.68	22.4	32.0	41.6	50.9
0.1	141.5	130.2	104.9	32.0	41.6	51.0
20		136.5	114.4	96.2	86.8	87.0
40		142.2	122.4	105.9	96.4	94.8
60		147.4	129.7	114.2	104.6	101.6
70		149.8	133.0	118.0	108.3	104.9

3.2.1. The dilute-gas limit of *m*-xylene

From the primary measurements shown in Table 7, only two investigators[32,46] performed measurements near the dilute-gas limit. These measurements were employed together with Eqs. (3)–(5) in order to obtain the coefficients a_0 and a_1 of Eq. (5) as

$$S_\lambda = 0.3037 + 362.08/T. \qquad (13)$$

Equations (3)–(5) and (13) represent the dilute-gas thermal conductivity to within 5.5% at the 95% confidence level.

The values of the dilute-gas limit thermal conductivity, $\lambda_0(T)$ in mW m^{-1} K^{-1}, obtained by the scheme of Eqs. (3)–(5)

TABLE 7. Thermal conductivity measurements of m-xylene

1st author	Year Publ.	Technique employed[a]	Purity (%)	Uncertainty (%)	No. of data	Temperature range (K)	Pressure range (MPa)
			Primary data				
Watanabe[27]	2004	THW	98	0.4	18	258–392	0.1
Naziev[47]	1991	CC	99.7	1.9	67	248–473	0.1–50
Assael[25]	1988	THW	99	0.5	10	301–359	0.1
Taxis[26]	1988	THW	99	0.3	83	308–360	0.3–200[b]
Perkins[48]	1983	THW	99	0.5	36	328–604	0.4–14
Kashiwagi[29]	1982	THW	99	2	6	298–358	0.1
Mustafaev[30]	1977	CC	na	2	139	306–672	0.1–98
Kostrovskii[46,c]	1974	HW	na	2	30	300–663	0–2.5
Rastorguev[31]	1970	SSHF	High Purity[d]	1.5	70	293–453	0.1–152
Akhundov[32,c]	1970	THW	99	2	114	302–698	0.002–30
			Secondary data				
Tarzimanov[33]	2002	THW	na	1	5	293–493	0.001–0.59
Briggs[34]	1977	CC	95	3	8	293–363	0.1
Kerimov[35]	1970	HW	na	na	3	298–353	0.1
Bachmann[36]	1969	THW	na	2	13	233–353	0.1
Poltz[49]	1967	PP	na	2	3	298–328	0.1
Frontasev[39]	1959	HW	na	0.5	1	293	0.1
Linder[40]	1956	PP	99	3.5	5	310–345	0.1
Abas-Zade[50]	1949	HW	na	na	22	273–619	0.1–3.8
Goldschmidt[51]	1911	HW	na	na	1	273	0.1

[a]CC, coaxial cylinder; HW, hot wire; na, not available; PP, parallel plate; SSHF, steady-state hot filament; THW, transient hot wire.
[b]Measurements restricted to 921 kg m^{-3} (restriction imposed by the density limit of the equation of state[10])
[c]Includes vapor data employed to derive the dilute-gas thermal-conductivity correlation.
[d]'High Purity' grade was quoted in the paper.

FIG. 9. Temperature-pressure ranges of the primary experimental thermal conductivity data for *m*-xylene.

FIG. 11. Dilute-gas thermal conductivity of *m*-xylene as a function of temperature. Akhundov and Gasanova[32] (○), Yaws[42] (- -), Vargaftik[43] (●), Kostrovskii and Prostov[46] (◊), Eq. (14) (–).
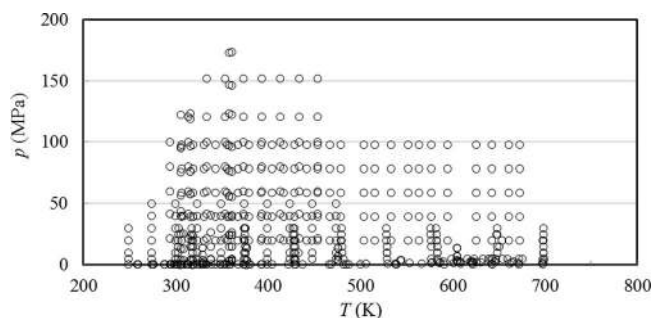
and (13), were fitted as a function of the reduced temperature $T_r = T/T_c$ for ease of use to the following equation:

$$\lambda_0(T) = \frac{0.242107 + 13.522T_r - 123.168T_r^2 + 296.882T_r^3 - 107.973T_r^4 + 18.686T_r^5 - 1.29167T_r^6}{-0.850118 + 3.11646T_r + 0.0001T_r^2}. \qquad (14)$$

Values calculated by Eq. (14) do not deviate from the values calculated by the scheme of Eqs. (3)–(5) and (13) by more than 0.2% over the temperature range from 226 to 2000 K. Equation (14) is hence employed in the calculations that will follow.

Figure 11 shows the dilute-gas thermal conductivity values of Akhundov and Gasanova[32] and Kostrovskii and Prostov,[46] and the values calculated by Eq. (14), as a function of the temperature. In addition to these values, the values recommended by Vargaftik[43] and a more recent correlation proposed by Yaws[42] are also shown. In Fig. 12, percentage deviations of the dilute-gas thermal conductivity of *m*-xylene from the scheme of Eqs. (3)–(5) and (13) are also shown. Based on the measurements of Akhundov and Gasanova[32] and Kostrovskii and Prostov,[46] the uncertainty of the correlation is estimated to be 6%. We note that sources employed by Yaws[42] are not known, while the sources employed by Vargaftik[43] include the measurements of Akhundov and Gasanova.[32]

3.2.2. The residual and the critical enhancement contributions of *m*-xylene

As already mentioned, the coefficients $B_{1,i}$ and $B_{2,i}$ in Eq. (6) were fitted with ODRPACK (Ref. 22) to the primary data for the thermal conductivity of *m*-xylene. It should however be noted that the highest two isobars of Mustafaev and Gabulov[30] were not considered, as they seemed to deviate considerably from the rest of the data in that area. The crossover model requires the system-dependent amplitudes Γ and ξ_0. For this work, we adopted the value $\Gamma = 0.057$ and estimated $\xi_0 = 2.35 \times 10^{-10}$ m, using a universal representation of the critical enhancement of the thermal conductivity (based on a simplified solution of mode-coupling theory with fluid-specific
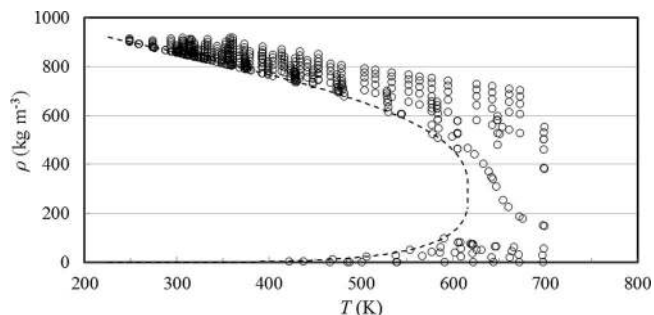

FIG. 10. Temperature-density ranges of the primary experimental thermal conductivity data for *m*-xylene. (- -) saturation line.

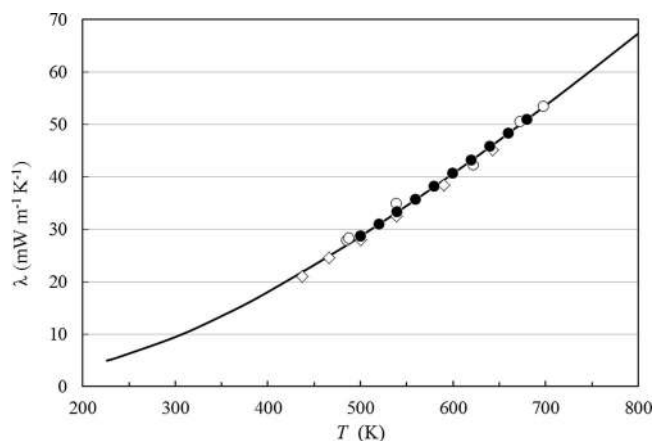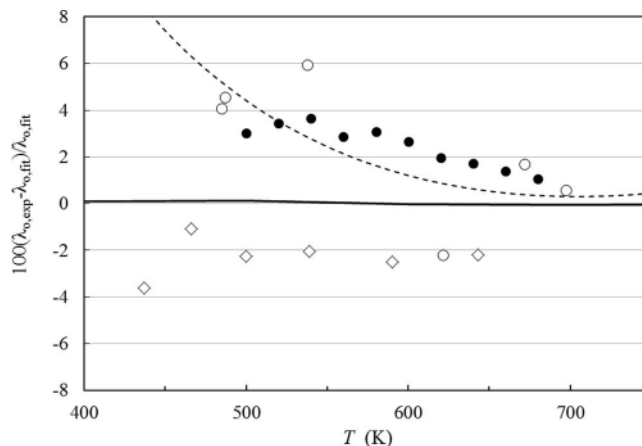FIG. 12. Percentage deviations of the dilute-gas thermal conductivity of *m*-xylene from the scheme of Eqs. (3)–(5) and (13). Akhundov and Gasanova[32] (○), Yaws[42] (- -), Vargaftik[43] (●), Kostrovskii and Prostov[46] (◊), Eq. (14) (–).

TABLE 8. Coefficients of Eq. (6) for the residual thermal conductivity of m-xylene

i	$B_{1,i}$ (mW m^{-1} K^{-1})	$B_{2,i}$ (mW m^{-1} K^{-1})
1	$-6.793\,14 \times 10^1$	$5.925\,37 \times 10^1$
2	$2.257\,78 \times 10^2$	$-1.626\,26 \times 10^2$
3	$-1.856\,93 \times 10^2$	$1.330\,36 \times 10^2$
4	$6.190\,06 \times 10^1$	$-4.490\,51 \times 10^1$
5	$-7.116\,64 \times 10^0$	$5.618\,60 \times 10^0$

parameters determined by a corresponding states method) by Perkins et al.[24] Furthermore, since very few data exist in the critical region, it was preferred to employ the method of Perkins et al.[24] also for the effective cutoff wavelength $\overline{q}_D^{-1}$; thus found equal to 7.13×10^{-10} m. The viscosity required for Eq. (7) was estimated by an extended corresponding-states method by Huber et al.[44] The reference temperature T_{ref}, far above the critical temperature where the critical enhancement is negligible, was calculated by $T_{ref} = (^3/_2)T_c$,[45] which for m-xylene is 925.3 K. The coefficients $B_{1,i}$ and $B_{2,i}$ of Eq. (6) obtained are shown in Table 8.

Table 9 summarizes comparisons of the primary data with the correlation We estimate the uncertainty (at the 95% confidence level) for thermal conductivity at liquid and supercritical densities up to 921 kg m^{-3} and temperatures from the triple point to 375 K, to be 3.6%, and 5% at higher temperatures. For the thermal conductivity of the dilute gas, due to inconsistencies in the experimental data, we estimate the uncertainty to be $\sim$7%. Uncertainties in the critical region are also much larger.

Figure 13 shows the percentage deviations of all primary thermal-conductivity data from the values calculated by Eqs. (1), (6)–(10), and (14), as a function of the density, while Figs. 14 and 15 show the same deviations but as a function of the temperature and pressure, respectively.

Table 10 shows the AAD and the bias for the secondary data. Except for Briggs[34] and Abas-Zade,[50] the rest of the deviations are within 5% of the present correlation. Finally, Fig. 16 shows a plot of the thermal conductivity of m-xylene as a function of temperature for different pressures, while in Table 11 recommended values for the thermal conductivity are shown. For checking computer implementations of the correlation, the

TABLE 9. Evaluation of the m-xylene thermal-conductivity correlation for the primary data

1st author	Year Publ.	AAD (%)	BIAS (%)
Watanabe[27]	2004	0.23	−0.23
Naziev[47]	1991	0.64	0.40
Assael[25]	1988	0.30	0.30
Taxis[26]	1988	0.85	0.05
Perkins[48]	1983	1.50	−0.82
Kashiwagi[29]	1982	0.76	0.76
Mustafaev[30]	1977	3.42	−2.48
Kostrovskii[46]	1974	2.15	0.90
Rastorguev[31]	1970	0.88	0.18
Akhundov[32]	1970	2.30	0.75
Entire data set		**1.81**	**−0.53**

FIG. 13. Percentage deviations of primary experimental data of m-xylene from the values calculated by the present model, Eqs. (1), (6)–(10), and (14), as a function of density. Assael et al.[25] (□), Taxis et al.[26] (+), Watanabe and Kato[27] (●), Kashiwagi et al.[29] (Δ), Mustafaev and Gabulov[30] (×), Rastorguev and Pugash[31] (◊), Akhundov and Gasanova[32] (♦), Kostrovskii and Prostov[46] (▲), Naziev et al.[47] (◒), Perkins[48] (■).

density for the point at 400 K and 200 MPa is 899.58 kg m^{-3}. A point with critical enhancement is 616.0 K, 220.0 kg m^{-3}, where the thermal conductivity is 82.8 mW m^{-1} K^{-1} and the viscosity used in the correlation was 36.41 μPa s.

3.3. The correlation for p-xylene

Table 12 summarizes, to the best of our knowledge, the experimental measurements of the thermal conductivity of p-xylene reported in the literature. Seventeen sets are included in the table. From these sets, eight were considered as primary data.

Measurements of several investigators[25–27,29–31,47,52] in Table 12 were already characterized as primary data in the case of o-xylene and m-xylene, and hence in the case of

FIG. 14. Percentage deviations of primary experimental data of m-xylene from the values calculated by the present model, Eqs. (1), (6)–(10), and (14), as a function of temperature. Assael et al.[25] (□), Taxis et al.[26] (+), Watanabe and Kato[27] (●), Kashiwagi et al.[29] (Δ), Mustafaev and Gabulov[30] (×), Rastorguev and Pugash[31] (◊), Akhundov and Gasanova[32] (♦), Kostrovskii and Prostov[46] (▲), Naziev et al.[47] (◒), Perkins[48] (■).
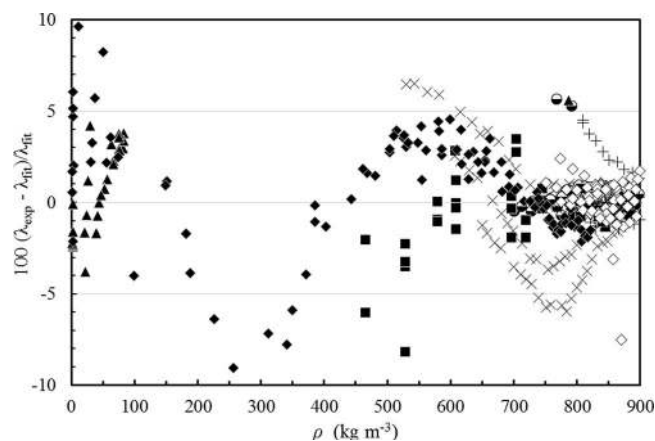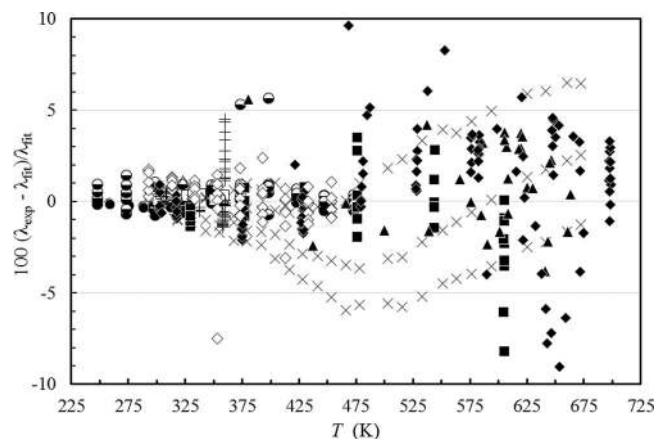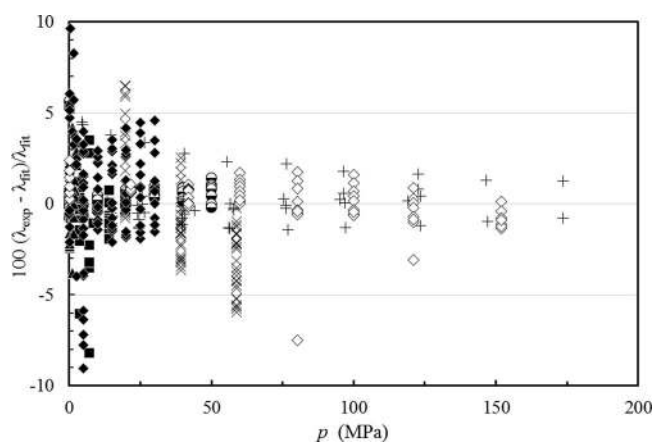
FIG. 15. Percentage deviations of primary experimental data of *m*-xylene from the values calculated by the present model Eqs. (1), (6)–(10), and (14), as a function of pressure. Assael *et al.*[25] (□), Taxis *et al.*[26] (+), Watanabe and Kato[27] (●), Kashiwagi *et al.*[29] (Δ), Mustafaev and Gabulov[30] (×), Rastorguev and Pugash[31] (◊), Akhundov and Gasanova[32] (♦), Kostrovskii and Prostov[46] (▲), Naziev *et al.*[47] (◓), Perkins[48] (■).

FIG. 16. Thermal conductivity of *m*-xylene as a function of temperature for different pressures.

p-xylene for the same reasons they are also considered as primary data. The remaining sets are considered as secondary data.

Figures 17 and 18 show the ranges of the primary measurements outlined in Table 12; the saturation curve is also shown in Fig. 18.

Temperatures for all data were converted to the ITS-90 temperature scale.[41] The development of the correlation requires densities; Zhou *et al.*[10] in 2012 reviewed the thermodynamic properties of *p*-xylene and developed an accurate, wide-ranging equation of state valid for single-phase and saturation states from the triple point to 700 K at pressures up to 200 MPa and a maximum density of 866 kg m^{-3}, with an uncertainty in density of 0.2% in the liquid region, and up to 1% in the critical and vapor regions. It should be noted that the maximum density of the correlation imposes a pressure limit in the present measurements shown in Table 12 (e.g., at 290 K the maximum pressure is approximately 3 MPa, at 400 K is ∼130 MPa, while over 500 K it is above 200 MPa). We adopt the temperature and pressure limits of the equation of state as the limits of the thermal conductivity correlation. We also

adopt their values for the critical temperature, T_c, the critical density, ρ_c, and the triple-point temperature, as 616.168 K, 286.00 kg m^{-3}, and 286.40 K, respectively. Finally, as already discussed, the isobaric ideal-gas heat capacity proposed by Zhou *et al.*[10] (estimated by a group contribution method) was also employed.

3.3.1. The dilute-gas limit of *p*-xylene

From the primary measurements shown in Table 12, only Akhundov and Gasanova[52] performed measurements near the dilute-gas limit. These measurements were employed together with Eqs. (3)–(5) in order to obtain the coefficients a_0 and a_1 of Eq. (5), as

$$S_\lambda = 0.4383 + 279.52/T. \qquad (15)$$

Equations (3)–(5) and (15) represent the dilute-gas thermal conductivity to within 5.5% at the 95% confidence level.

The values of the dilute-gas limit thermal conductivity, $\lambda_0(T)$ in mW m^{-1} K^{-1}, obtained by the scheme of Eqs. (3)–(5) and (15), were fitted as a function of the reduced temperature $T_r = T/T_c$ for ease of use to the following

TABLE 10. Evaluation of the *m*-xylene thermal-conductivity correlation for the secondary data

1st author	Year Publ.	AAD (%)	BIAS (%)
Tarzimanov[33]	2002	2.84	−2.84
Briggs[34]	1977	60.1	58.6
Kerimov[35]	1970	2.26	2.12
Bachmann[36]	1969	2.86	2.86
Poltz[49]	1967	0.70	−0.70
Frontasev[39]	1959	0.19	0.19
Linder[40]	1956	2.02	0.44
Abas-Zade[50]	1949	37.5	−23.6
Goldschmidt[51]	1911	5.26	5.26

TABLE 11. Recommended values of *m*-xylene thermal conductivity (mW m^{-1} K^{-1})

Pressure (MPa)	Temperature (K)					
	240	300	400	500	600	700
0	5.60	9.45	18.04	28.6	40.6	53.7
0.1	143.2	129.4	103.7	28.4	40.5	53.7
20	147.4	135.7	113.5	95.8	86.0	84.7
40		141.3	121.8	105.8	96.6	94.6
60		146.3	129.0	114.4	105.6	103.0
80		150.9	135.6	122.2	113.7	110.7
100		155.1	141.6	129.2	121.1	117.9
120			147.2	135.7	128.0	124.7
140			152.4	141.9	134.5	131.2
160			157.4	147.8	140.8	137.4
180			162.0	153.3	146.7	143.4
200			166.4	158.6	152.4	149.2

TABLE 12. Thermal conductivity measurements of *p*-xylene

1st author	Year Publ.	Technique employed[a]	Purity (%)	Uncertainty (%)	No. of data	Temperature range (K)	Pressure range (MPa)
			Primary data				
Watanabe[27]	2004	THW	98	0.4	12	286–328	0.1
Naziev[47]	1991	CC	99.7	1.9	51	320–494	0.1–50
Assael[25]	1988	THW	99	0.5	11	295–365	0.1
Taxis[26]	1988	THW	99	0.3	66	305–360	0.3–124[b]
Kashiwagi[29]	1982	THW	99	2	6	298–358	0.1
Mustafaev[30]	1977	CC	na	2	132	306–672	0.1–98
Rastorguev[31]	1970	SSHF	High Purity[c]	1.5	68	292–492	0.1–152[b]
Akhundov[52,d]	1969	THW	99.78	2	164	300–700	0.001–30
			Secondary data				
Tarzimanov[33]	2002	THW	na	1	5	293–493	0.001–0.59
Powell[53]	1991	THW	na	2.5	1	298	0.1
Ogiwara[54]	1980	PP	99.4	na	6	293–343	0.1
Briggs[34]	1977	CC	95	3	8	293–363	0.1
Mallan[55]	1972	THW	na	1.3	10	299–384	0.1
Kerimov[35]	1970	HW	na	na	3	298–353	0.1
Bachmann[36]	1969	THW	na	2	13	233–353	0.1
Frontasev[39]	1959	HW	na	0.5	1	293	0.1
Linder[40]	1956	PP	99	3.5	5	310–345	0.1

[a]CC, coaxial cylinder; HW, hot wire; na, not available; PP, parallel plate; SSHF, steady-state hot filament; THW, transient hot wire.
[b]Measurements restricted to 866 kg m^{-3} (restriction imposed by the density limit of the equation of state[10]).
[c]'High Purity' grade was quoted in the paper.
[d]Includes vapor data employed to derive the dilute-gas thermal-conductivity correlation.

equation:

$$\lambda_0(T) = \frac{-3.88568 + 29.4648T_r - 81.5299T_r^2 + 77.1534T_r^3 + 7.55487T_r^4 - 3.8897T_r^5 + 0.406892T_r^6}{0.00404188 - 0.424893T_r + T_r^2}. \quad (16)$$

Values calculated by Eq. (16) do not deviate from the values calculated by the scheme of Eqs. (3)–(5) and (15) by more than 0.05% over the temperature range from 290 to 2000 K. Equation (16) is hence employed in the calculations that will follow.

Figure 19 shows the dilute-gas thermal conductivity values of Akhundov and Gasanova,[52] and the values calculated by Eq. (16), as a function of the temperature. In addition to these values, the values recommended by Vargaftik[43] and a more
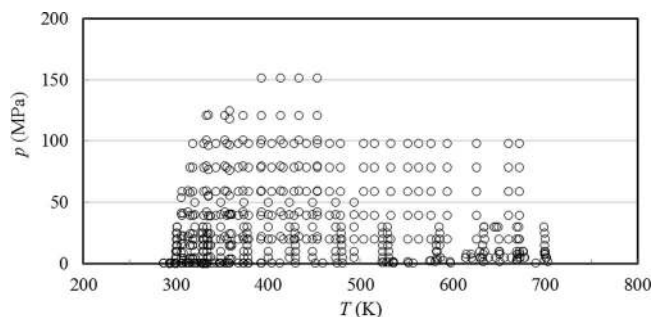
recent correlation proposed by Yaws[42] are also shown. In Fig. 20, percentage deviations of the dilute-gas thermal conductivity of *p*-xylene from the scheme of Eqs. (3)–(5) and (15) are also shown. Based on the measurements of Akhundov and Gasanova,[52] the uncertainty of the correlation is believed to be 2.5%. We note that sources employed by Yaws[42] are not known, while the sources employed by Vargaftik[43] include the measurements of Akhundov and Gasanova.[52]

FIG. 17. Temperature-pressure ranges of the primary experimental thermal conductivity data for *p*-xylene.

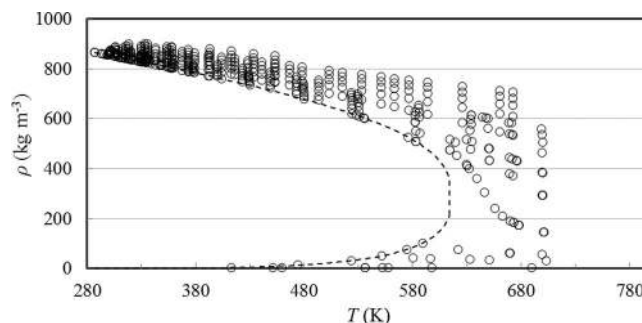FIG. 18. Temperature-density ranges of the primary experimental thermal conductivity data for *p*-xylene. (- -) saturation line.

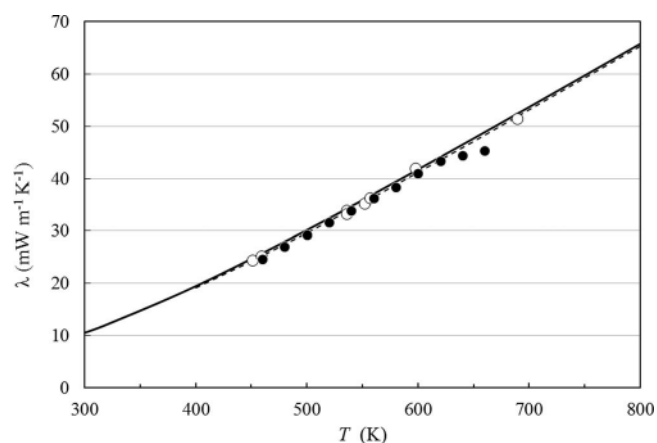FIG. 19. Dilute-gas thermal conductivity of *p*-xylene as a function of temperature. Akhundov and Gasanova[52] (○), Yaws[42] (- -), Vargaftik[43] (●), Eq. (16) (–).

3.3.2. The residual and the critical enhancement contributions of *p*-xylene

As already mentioned, the coefficients $B_{1,i}$ and $B_{2,i}$ in Eq. (6) were fitted with ODRPACK (Ref. 22) to the primary data for the thermal conductivity of *p*-xylene. This crossover model requires the system-dependent amplitudes Γ and ξ_0. For this work, we adopted the value $\Gamma = 0.056$ and estimated $\xi_0 = 2.35 \times 10^{-10}$ m, using a universal representation of the critical enhancement of the thermal conductivity (based on a simplified solution of mode-coupling theory with fluid-specific parameters determined by a corresponding states method) by Perkins *et al.*[24] Furthermore, since very few data exist in the critical region, it was preferred to employ the method of Perkins *et al.*[24] also for the effective cutoff wavelength $\overline{q}_D^{-1}$; thus found equal to 7.10×10^{-10} m. The viscosity required for Eq. (7) was estimated by an extended corresponding-states method by Huber *et al.*[44] The reference temperature T_{ref}, far above the critical temperature where the critical enhancement is negligible, was calculated by $T_{ref} = (3/2)T_c$,[45] which for *p*-xylene is 924.3 K. The coefficients $B_{1,i}$ and $B_{2,i}$ of Eq. (6) obtained are shown in Table 13.
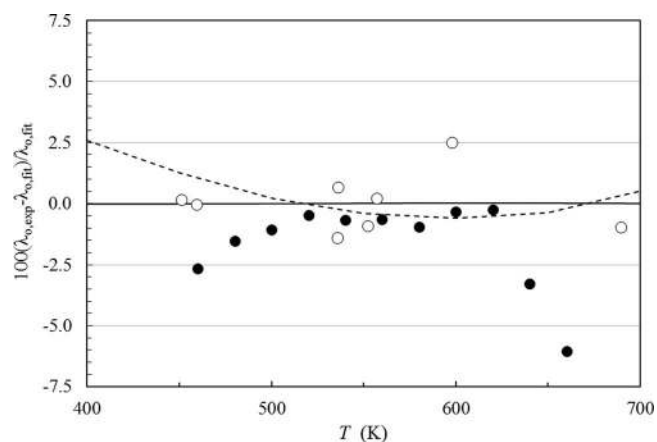

FIG. 20. Percentage deviations of the dilute-gas thermal conductivity of *p*-xylene from the scheme of Eqs. (3)–(5) and (15). Akhundov and Gasanova[52] (○), Yaws[42] (- -), Vargaftik[43] (●), Eq. (16) (–).

TABLE 13. Coefficients of Eq. (6) for the residual thermal conductivity of *p*-xylene

i	$B_{1,i}$ (mW m^{-1} K^{-1})	$B_{2,i}$ (mW m^{-1} K^{-1})
1	$-1.010\,22 \times 10^2$	$1.075\,31 \times 10^2$
2	$2.248\,28 \times 10^2$	$-2.054\,99 \times 10^2$
3	$-1.591\,00 \times 10^2$	$1.503\,48 \times 10^2$
4	$4.994\,90 \times 10^1$	$-5.025\,84 \times 10^1$
5	$-5.624\,22 \times 10^0$	$6.440\,51 \times 10^0$

Table 14 summarizes comparisons of the primary data with the correlation. We estimate the uncertainty (at the 95% confidence level) for thermal conductivity at liquid and super-critical densities up to 866 kg m^{-3} and temperatures from the triple point to 700 K, to be 3.6%, and for the dilute gas, the estimated uncertainty is 5%. Uncertainties in the critical region are much larger.

Figure 21 shows the percentage deviations of all primary thermal-conductivity data from the values calculated by Eqs. (1), (6)–(10), and (16), as a function of the density, while Figs. 22 and 23 show the same deviations but as a function of the temperature and pressure, respectively.

Table 15 shows the AAD and the bias for the secondary data. Deviations are within 10% of the present correlation. Finally, Fig. 24 shows a plot of the thermal conductivity of *p*-xylene as a function of temperature for different pressures, while in Table 16 recommended values for the thermal conductivity are shown. For checking computer implementations of the correlation, the density for the point at 500 K and 200 MPa is 853.89 kg m^{-3}. A point with critical enhancement is 620.0 K, 287.0 kg m^{-3}, where the thermal conductivity is 107.7 mW m^{-1} K^{-1} and the viscosity used in the correlation was 23.98 µPa s.

3.4. The correlation for ethylbenzene

Table 17 summarizes, to the best of our knowledge, the experimental measurements of the thermal conductivity of ethylbenzene reported in the literature. Twelve sets are included in the table. From these sets, seven were considered as primary data.

Measurements of six investigators[27,29–31,46,56] in Table 17 were already characterized as primary data in the case of the xylene isomers and hence in the case of ethylbenzene for the

TABLE 14. Evaluation of the *p*-xylene thermal-conductivity correlation for the primary data

1st Author	Year Publ.	AAD (%)	BIAS (%)
Watanabe[27]	2004	0.06	−0.02
Naziev[47]	1991	1.86	0.70
Assael[25]	1988	0.67	0.65
Taxis[26]	1988	0.37	−0.25
Kashiwagi[29]	1982	1.76	1.76
Mustafaev[30]	1977	1.60	0.46
Rastorguev[31]	1970	3.49	2.74
Akhundov[52]	1969	2.09	−1.41
Entire data set		**1.78**	**0.05**

FIG. 21. Percentage deviations of primary experimental data of *p*-xylene from the values calculated by the present model, Eqs. (1), (6)–(10), and (16), as a function of density. Assael *et al.*[25] (□), Taxis *et al.*[26] (+), Watanabe and Kato[27] (●), Kashiwagi *et al.*[29] (△), Mustafaev and Gabulov[30] (×), Rastorguev and Pugash[31] (◊), Naziev *et al.*[47] (◒), Akhundov and Gasanova[52] (♦).

FIG. 22. Percentage deviations of primary experimental data of *p*-xylene from the values calculated by the present model, Eqs. (1), (6)–(10), and (16), as a function of temperature. Assael *et al.*[25] (□), Taxis *et al.*[26] (+), Watanabe and Kato[27] (●), Kashiwagi *et al.*[29] (△), Mustafaev and Gabulov[30] (×), Rastorguev and Pugash[31] (◊), Naziev *et al.*[47] (◒), Akhundov and Gasanova[52] (♦).
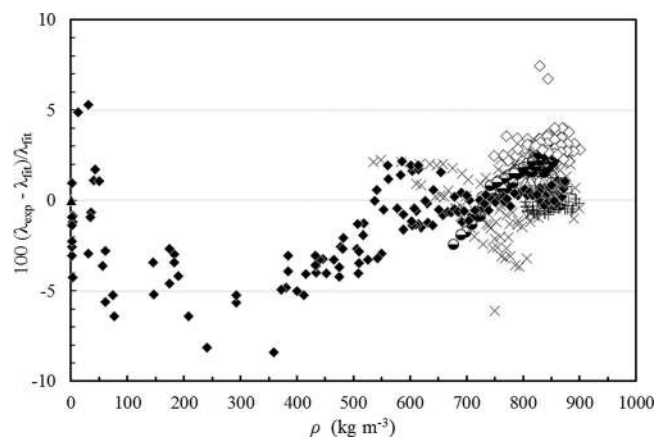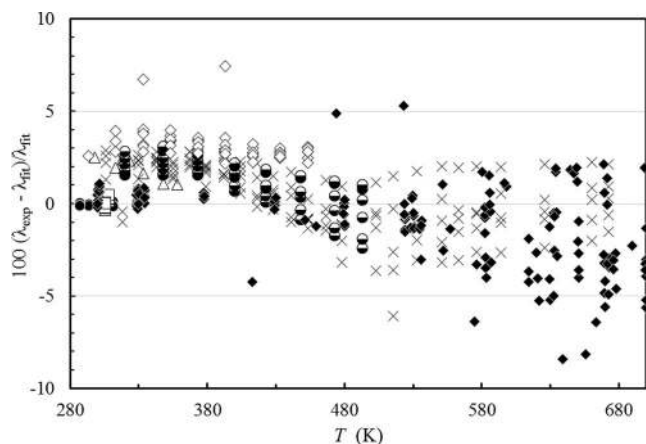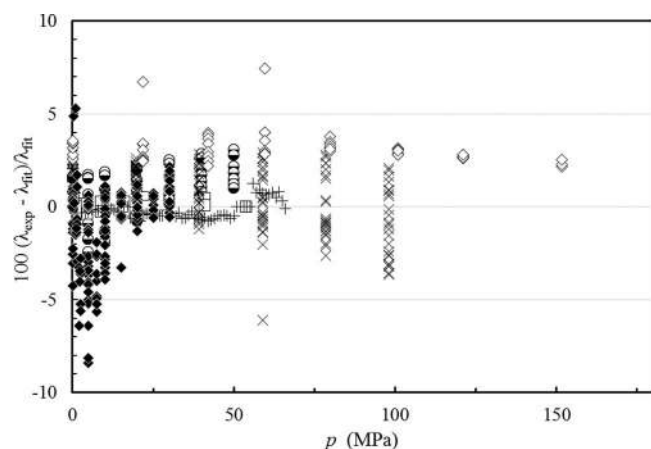

FIG. 23. Percentage deviations of primary experimental data of *p*-xylene from the values calculated by the present model, Eqs. (1), (6)–(10), and (16), as a function of pressure. Assael *et al.*[25] (□), Taxis *et al.*[26] (+), Watanabe and Kato[27] (●), Kashiwagi *et al.*[29] (△), Mustafaev and Gabulov[30] (×), Rastorguev and Pugash[31] (◊), Naziev *et al.*[47] (◒), Akhundov and Gasanova[52] (♦).

TABLE 15. Evaluation of the *p*-xylene thermal-conductivity correlation for the secondary data

1st author	Year Publ.	AAD (%)	BIAS (%)
Tarzimanov[33]	2002	1.84	−1.68
Powell[53]	1991	8.18	−8.18
Ogiwara[54]	1980	4.04	4.04
Briggs[34]	1977	10.5	10.5
Mallan[55]	1972	2.16	1.22
Kerimov[35]	1970	2.96	2.96
Bachmann[36]	1969	2.42	2.42
Frontasev[39]	1959	4.21	4.21
Linder[40]	1956	2.69	2.16

same reasons, these are also considered as primary data. In addition to these investigators, the measurements of Brykov,[57] performed in a concentric-cylinders instrument with a 2% uncertainty, are also included in the primary dataset, as they extend in temperature to as low as 183 K. The remaining sets are considered as secondary data.

Figures 25 and 26 show the ranges of the primary measurements outlined in Table 17; the saturation curve is also shown in Fig. 26.

Temperatures for all data were converted to the ITS-90 temperature scale.[41] The development of the correlation requires densities; Zhou *et al.*[10] in 2012 reviewed the thermodynamic properties of ethylbenzene and developed an accurate, wide-ranging equation of state valid for single-phase and saturation states from the triple point to 700 K at pressures up to 60 MPa and a maximum density of 968 kg m^{-3}, with an uncertainty in density of 0.1% below 5 MPa, and up to 1% in the critical and vapor regions. It should be noted that in the case of ethylbenzene the maximum pressure of 60 MPa of the correlation imposes a pressure limit in the present measurements shown in Table 17. We also adopt their values for the critical temperature, T_c, the critical density, ρ_c, and the triple-point temperature, as 617.12 K, 291.00 kg m^{-3}, and 178.2 K, respectively. Finally, as already discussed, the isobaric ideal-gas heat capacity proposed by Zhou *et al.*[10] (estimated by a group contribution method) was also employed.
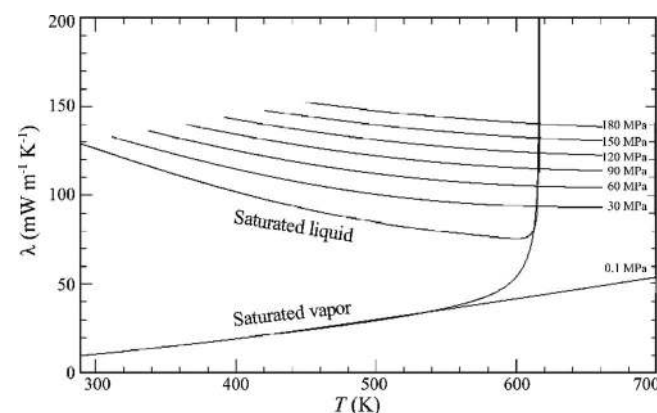

FIG. 24. Thermal conductivity of *p*-xylene as a function of temperature for different pressures.

TABLE 16. Recommended values of *p*-xylene thermal conductivity (mW m^{-1} K^{-1})

Pressure (MPa)	Temperature (K)				
	300	400	500	600	700
0	10.57	19.48	30.17	41.73	53.68
0.1	126.2	102.2	30.06	41.76	53.82
20		111.0	96.21	89.59	90.19
40		118.6	104.9	98.36	98.30
60		125.3	112.4	105.8	105.0
80		131.6	119.2	112.5	111.0
100		137.4	125.5	118.8	116.8
120		142.9	131.6	124.7	122.3
140			137.3	130.5	127.7
160			142.8	136.0	133.0
180			148.2	141.4	138.1
200			153.3	146.7	143.2

FIG. 25. Temperature-pressure ranges of the primary experimental thermal conductivity data for ethylbenzene.

3.4.1. The dilute-gas limit of ethylbenzene

From the primary measurements shown in Table 17, only Akhundov[56] and Kostrovskii and Prostov[46] performed measurements near the dilute-gas limit. These measurements were employed together with Eqs. (3)–(5) in order to obtain the coefficients a_0 and a_1 of Eq. (5), as

$$S_\lambda = 0.3439 + 344.07/T. \tag{17}$$

Equations (3)–(5) and (17) represent the dilute-gas thermal conductivity to within 2.7% at the 95% confidence level.

The values of the dilute-gas limit thermal conductivity, $\lambda_0(T)$ in mW m^{-1} K^{-1}, obtained by the scheme of Eqs. (3)–(5) and (17), were fitted as a function of the reduced temperature $T_r = T/T_c$ for ease of use to the following equation:

Values calculated by Eq. (18) do not deviate from the values calculated by the scheme of Eqs. (3)–(5) and (17) by more than 0.1% over the temperature range from 290 to 2000 K. Equation (18) is hence employed in the calculations that will follow.

Figure 27 shows the dilute-gas thermal conductivity values of Akhundov[56] and Kostrovskii and Prostov,[46] and the values calculated by Eq. (18), as a function of the temperature. In addition to these values, the values recommended by Vargaftik[43] and a more recent correlation proposed by Yaws[42] are also shown. In Fig. 28, percentage deviations of the dilute-gas thermal conductivity of ethylbenzene from the scheme of Eqs. (3)–(5) and (17) are also shown. Based on the measurements of Akhundov[56] and Kostrovskii and Prostov,[46] the uncertainty of the correlation is estimated to be 2.5%. We

$$\lambda_0(T) = \frac{-1.10708 + 10.8026T_r - 28.9015T_r^2 + 41.9227T_r^3 + 20.9133T_r^4 - 4.01492T_r^5}{0.259475 - 0.343879T_r + T_r^2}. \tag{18}$$

TABLE 17. Thermal conductivity measurements of ethylbenzene

1st author	Year Publ.	Technique employed[a]	Purity (%)	Uncertainty (%)	No. of data	Temperature range (K)	Pressure range (MPa)
			Primary data				
Watanabe[27]	2004	THW	98	0.4	15	258–330	0.1
Kashiwagi[29]	1982	THW	99	2	6	298–358	0.1
Mustafaev[30]	1977	CC	na	2	114	306–672	0.1–60[b]
Akhundov[56,c]	1974	THW	99.96	2	140	287–683	0.002–30
Kostrovski[46,c]	1974	HW	na	2	15	423–643	0–2
Brykov[57]	1970	CC	na	2	23	183–404	0.1
Rastorguev[31]	1970	SSHF	High Purity[d]	1.5	43	293–453	0.1–60[b]
			Secondary data				
Tarzimanov[33]	2002	THW	na	1	21	293–592	0.001–30
Guseinov[58]	1975	CC	99.4	3	5	419–581	0.1
Kerimov[35]	1970	HW	na	na	2	298–353	0.1
Bachmann[36]	1969	THW	na	2	7	198–348	0.1
Smith[59]	1936	CC	na	13	1	303	0.1

[a]CC, coaxial cylinder; HW, hot wire; na, not available; SSHF, steady-state hot filament; THW, transient hot wire.
[b]Measurements restricted to 60 MPa (restriction imposed by the density limit of the equation of state[10]).
[c]Includes vapor data employed to derive the dilute-gas thermal-conductivity correlation.
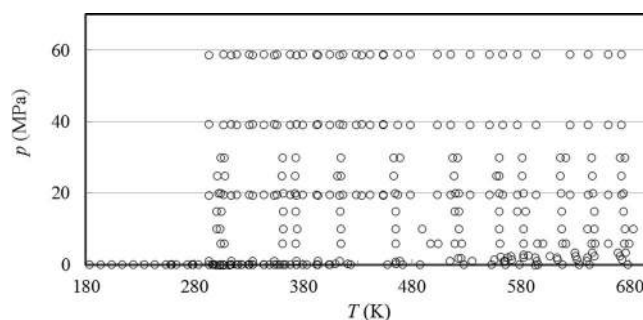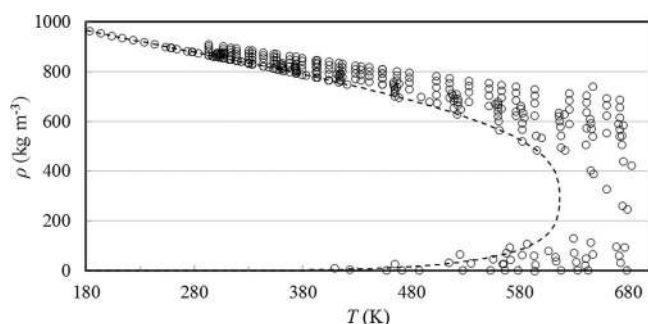[d]'High Purity' grade was quoted in the paper.

FIG. 26. Temperature-density ranges of the primary experimental thermal conductivity data for ethylbenzene. (- -) saturation line.

FIG. 28. Percentage deviations of the dilute-gas thermal conductivity of ethylbenzene from the scheme of Eqs. (3)–(5) and (17). Yaws[42] (- -), Vargaftik[43] (●), Kostrovskii and Prostov[46] (◊), Akhundov[56] (○), Eq. (18) (–).

note that sources employed by Yaws[42] are not known, while the sources employed by Vargaftik[43] include the measurements of Akhundov.[56]

3.4.2. The residual and the critical enhancement contributions of ethylbenzene

As already mentioned, the coefficients $B_{1,i}$ and $B_{2,i}$ in Eq. (6) were fitted with ODRPACK (Ref. 22) to the primary data for the thermal conductivity of ethylbenzene. This crossover model requires the system-dependent amplitudes Γ and ξ_0. For this work, we adopted the value $\Gamma = 0.056$ and estimated $\xi_0 = 2.35 \times 10^{-10}$ m, using a universal representation of the critical enhancement of the thermal conductivity (based on a simplified solution of mode-coupling theory with fluid-specific parameters determined by a corresponding states method) by Perkins et al.[24] Furthermore, since very few data exist in the critical region, it was preferred to employ the method of Perkins et al.[24] also for the effective cutoff wavelength $\overline{q}_D^{-1}$; thus found equal to 7.06×10^{-10} m. The viscosity required for Eq. (7) was estimated by an extended corresponding-states method by Huber et al.[44] The reference temperature T_{ref}, far above the critical temperature where the critical enhancement is negligible, was calculated by $T_{ref} = (^3/_2)T_c$,[45] which for p-
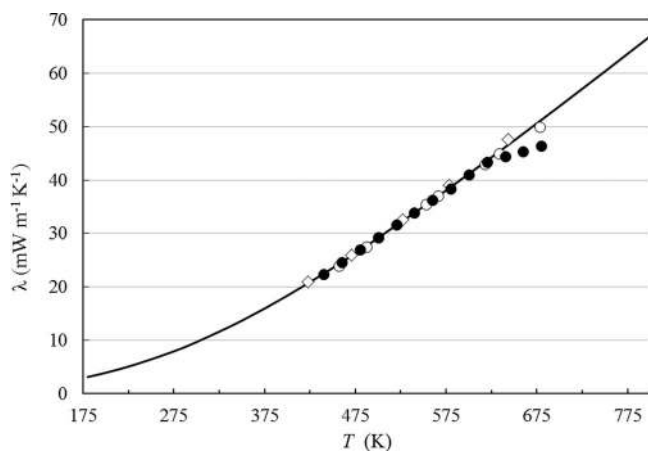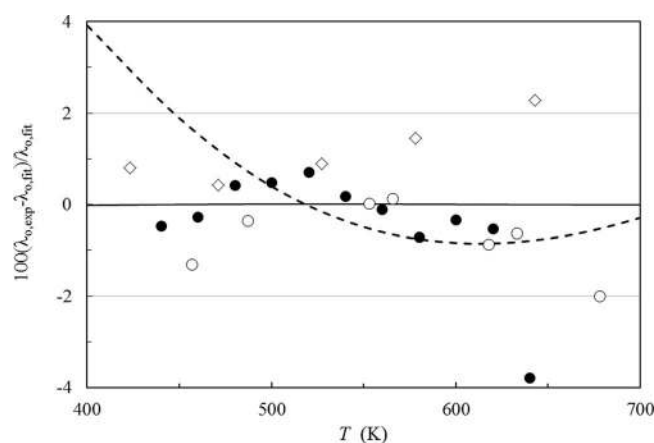
xylene is 925.7 K. The coefficients $B_{1,i}$ and $B_{2,i}$ of Eq. (6) obtained are shown in Table 18.

Table 19 summarizes comparisons of the primary data with the correlation. We estimate the uncertainty (at the 95% confidence level) for thermal conductivity, at liquid and supercritical densities up to 968 kg m^{-3} and temperatures from the triple point to 400 K, to be 2.8%. For the thermal conductivity of the dilute gas, we estimate the uncertainty to be 4%, with larger uncertainties in the critical region.

Figure 29 shows the percentage deviations of all primary thermal-conductivity data from the values calculated by Eqs. (1), (6)–(10), and (18), as a function of the density, while Figs. 30 and 31 show the same deviations but as a function of the temperature and pressure, respectively.

Table 20 shows the AAD and the bias for the secondary data. The measurements of Guseinov and Mirzoev[58] exhibit large deviations from all other investigators. Similarly the measurements of Smith[59] show large deviations from the correlation; however in this case the quoted uncertainty was 13%. The remaining data are within 4% of the present correlation. Finally, Fig. 32 shows a plot of the thermal conductivity of ethylbenzene as a function of temperature for different pressures, while in Table 21 recommended values for the thermal conductivity are shown. For checking computer implementations of the correlation, the density for the point at 300 K and 60 MPa is 897.95 kg m^{-3}. A point with critical enhancement is 617.0 K, 316.0 kg m^{-3}, where the thermal conductivity is 140.2 mW m^{-1} K^{-1} and the viscosity used in the correlation was 33.22 μPa s.

FIG. 27. Dilute-gas thermal conductivity of ethylbenzene as a function of temperature. Yaws[42] (- -), Vargaftik[43] (●), Kostrovskii and Prostov[46] (◊), Akhundov[56] (○), Eq. (18) (–).

TABLE 18. Coefficients of Eq. (6) for the residual thermal conductivity of ethylbenzene

i	$B_{1,i}$ (mW m^{-1} K^{-1})	$B_{2,i}$ (mW m^{-1} K^{-1})
1	$-4.978\ 37 \times 10^1$	$6.630\ 73 \times 10^1$
2	$1.067\ 39 \times 10^2$	$-1.462\ 79 \times 10^2$
3	$-6.851\ 37 \times 10^1$	$1.214\ 39 \times 10^2$
4	$2.261\ 33 \times 10^1$	$-4.622\ 45 \times 10^1$
5	$-2.794\ 55 \times 10^0$	$6.585\ 54 \times 10^0$

TABLE 19. Evaluation of the ethylbenzene thermal-conductivity correlation for the primary data

1st author	Year Publ.	AAD (%)	BIAS (%)
Watanabe[27]	2004	0.20	−0.20
Kashiwagi[29]	1982	0.78	0.17
Mustafaev[30]	1977	1.00	−0.41
Akhundov[56]	1974	1.87	−1.03
Kostrovski[46]	1974	1.43	−0.73
Brykov[57]	1970	1.44	1.37
Rastorguev[31]	1970	1.26	1.26
Entire data set		**1.43**	**−0.47**

FIG. 31. Percentage deviations of primary experimental data of ethylbenzene from the values calculated by the present model, Eqs. (1), (6)–(10), and (18), as a function of pressure. Watanabe and Kato[27] (●), Kashiwagi *et al.*[29] (Δ), Mustafaev and Gabulov[30] (×), Rastorguev and Pugash[31] (◊), Kostrovski and Prostov[46] (▲), Akhundov[56] (♦), Brykov[57] (□).
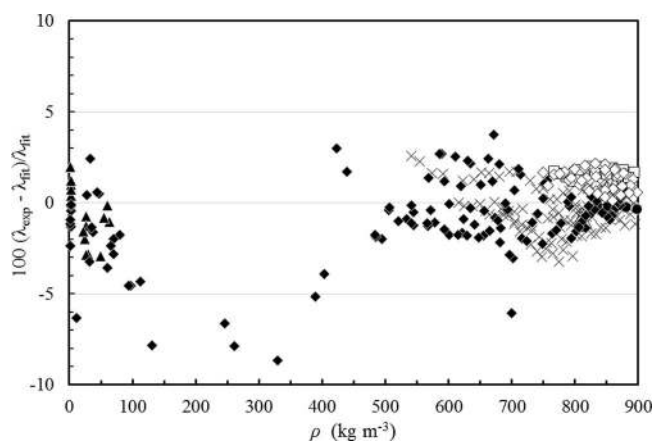

FIG. 29. Percentage deviations of primary experimental data of ethylbenzene from the values calculated by the present model, Eqs. (1), (6)–(10), and (18), as a function of density. Watanabe and Kato[27] (●), Kashiwagi *et al.*[29] (Δ), Mustafaev and Gabulov[30] (×), Rastorguev and Pugash[31] (◊), Kostrovski and Prostov[46] (▲), Akhundov[56] (♦), Brykov[57] (□).

TABLE 20. Evaluation of the ethylbenzene thermal-conductivity correlation for the secondary data

1st author	Year Publ.	AAD (%)	BIAS (%)
Tarzimanov[33]	2002	3.86	−3.86
Guseinov[58]	1975	35.0	35.0
Kerimov[35]	1970	2.24	2.24
Bachmann[36]	1969	2.66	2.66
Smith[59]	1936	14.4	14.4
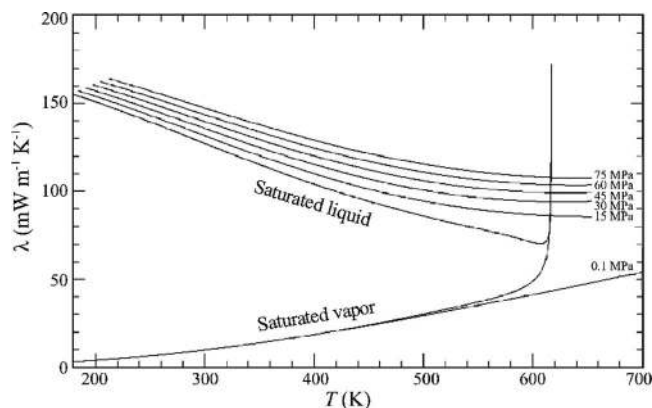
FIG. 32. Thermal conductivity of ethylbenzene as a function of temperature for different pressures.
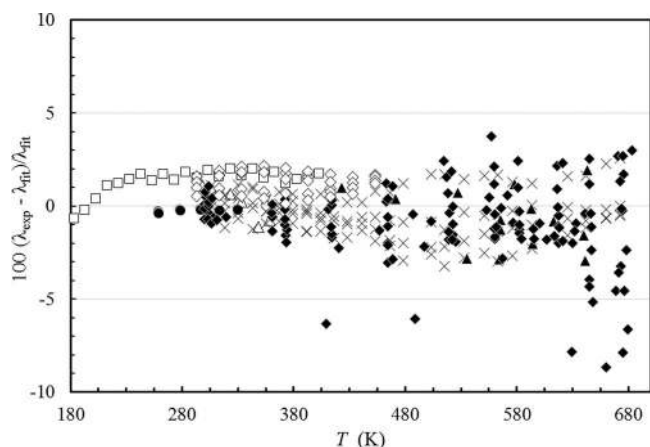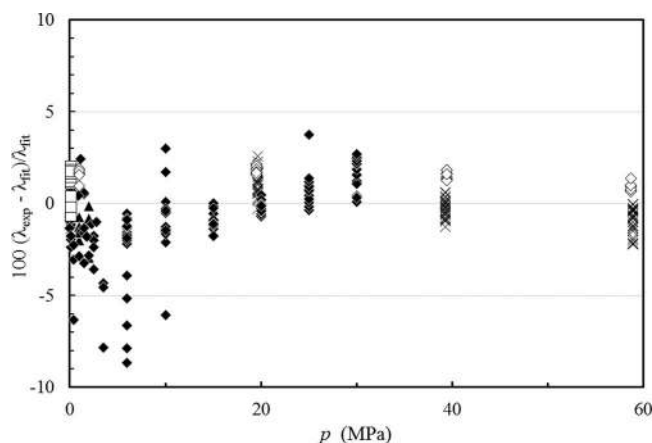

FIG. 30. Percentage deviations of primary experimental data of ethylbenzene from the values calculated by the present model, Eqs. (1), (6)–(10), and (18), as a function of temperature. Watanabe and Kato[27] (●), Kashiwagi *et al.*[29] (Δ), Mustafaev and Gabulov[30] (×), Rastorguev and Pugash[31] (◊), Kostrovski and Prostov[46] (▲), Akhundov[56] (♦), Brykov[57] (□).

TABLE 21. Recommended values of ethylbenzene thermal conductivity $(mW\,m^{-1}\,K^{-1})$

Pressure (MPa)	Temperature (K)					
	200	300	400	500	600	700
0	3.96	9.71	18.39	29.16	41.14	53.83
0.1	151.0	127.3	103.8	29.19	41.24	53.98
20	154.4	133.0	111.8	96.94	89.42	87.37
40	157.5	138.2	118.6	104.9	98.13	97.33
60		143.0	124.7	111.7	105.0	104.0

4. Conclusion

New, wide-range reference equations for the thermal conductivity of o-, m-, p-xylene, and ethylbenzene were presented. 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. 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. All four correlations are applicable for the temperature range from the triple point of each fluid to 700 K, and an upper pressure limit determined by the maximum density limit for the equation of state used to provide density. At the upper temperature limit of 700 K, the maximum pressure was 200 MPa for m-xylene and p-xylene, but 60 and 70 MPa for ethylbenzene and o-xylene, respectively. At lower temperatures, the maximum pressure is lower. The overall uncertainty (at the 95% confidence level) of the correlations of the thermal conductivity of the xylenes and ethylbenzene over their range of applicability varies for each fluid. For o-xylene, we estimate the uncertainty for liquid and supercritical densities for temperatures from the triple point to 400 K to be 2.6%, and 4% at higher temperatures, and in the dilute-gas region we estimate the uncertainty to be 2%. For m-xylene, the estimated uncertainty for liquid and supercritical densities at temperatures from the triple point to 375 K is 3.6%, and 5% at higher temperatures, and 6% for the dilute gas. For p-xylene, the estimated uncertainty for liquid and supercritical densities at temperatures from the triple point to 700 K is 3.6%, and 2.5% for the dilute gas. Finally, for ethylbenzene the estimated uncertainty for liquid and supercritical densities at temperatures from the triple point to 400 K is 2.8%, and 2.5% in the dilute-gas region. Uncertainties in the critical region for all four fluids are much larger, since the thermal conductivity approaches infinity at the critical point and is very sensitive to small changes in density.

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