# Reference Correlation of the Thermal Conductivity of Cyclohexane from the Triple Point to 640 K and up to 175 MPa

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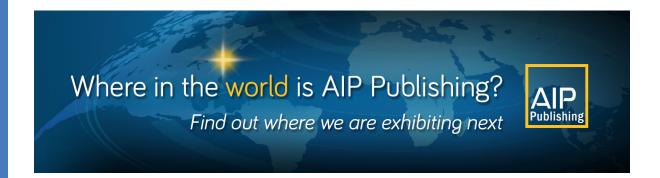
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# Reference Correlation of the Thermal Conductivity of Cyclohexane from the Triple Point to 640 K and up to 175 MPa

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New, wide-range reference equations for the thermal conductivity of cyclohexane as a function of temperature and density are 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. We estimate the uncertainty (at the 95% confidence level) for the thermal conductivity of cyclohexane from the triple point (279.86 K) to 650 K at pressures up to 175 MPa to be 4% for the compressed liquid and supercritical phases. For the low-pressure gas phase (up to 0.1 MPa) over the temperature range 280–680 K, the estimated uncertainty is 2.5%. 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. © 2017 by the U.S. Secretary of Commerce on behalf of the United States. All rights reserved. [http://dx.doi.org/10.1063/1.4974325]

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

CONTENTS			4.	Evaluation of the cyclohexane thermal-conductivity correlation for the secondary data
1. 2.	Introduction	2 2	5.	Recommended values of cyclohexane thermal conductivity
3.	The Correlation	2		conductivity
-	3.1. The dilute-gas limit	3		
	3.2. The residual thermal conductivity	5		
	3.3. The critical enhancement	5		List of Figures
	3.4. Recommended values	6		
4.	Conclusion	7	1.	Temperature-pressure range of the primary
5.	References	7		experimental thermal-conductivity data for cyclo- hexane
	List of Tables		2.	Temperature–density range of the primary experimental thermal-conductivity data for cyclohexane.
1.	Thermal-conductivity measurements of cyclohexane	3	3.	Dilute-gas limit thermal conductivity of cyclohexane as a function of temperature
2.	Coefficients of Eq. (5) for the residual thermal		4.	Percentage deviations of the dilute-gas limit ther-
3.	conductivity of cyclohexane  Evaluation of the cyclohexane thermal-	5		mal conductivity of cyclohexane from the scheme of Eqs. (3)–(5), as a function of temperature
J.	conductivity correlation for the primary data	5	5.	Percentage deviations of primary experimental data of cyclohexane from the values calculated by the present model, Eqs. 1, 6–11, as a function of density
assa	thor to whom correspondence should be addressed; Electronic rel@auth.gr 017 by the U.S. Secretary of Commerce on behalf of the United St		6.	Percentage deviations of primary experimental data of cyclohexane from the values calculated by the present model, Eqs. 1, 6–11, as a function of

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6

temperature.....

6

- 7. Percentage deviations of primary experimental data of cyclohexane from the values calculated by the present model, Eqs. 1, 6–11, as a function of pressure......
- 8. Thermal conductivity of cyclohexane as a function of temperature for different pressures......
- 9. Thermal conductivity of cyclohexane as a function of density for different temperatures......

# 1. Introduction

In a series of recent papers, new reference correlations for the thermal conductivity of many fluids (normal and parahydrogen, water, sulfur hexafluoride, toluene, benzene, n-hexane, n-heptane, methanol, ethanol, ortho-xylene, meta-xylene, para-xylene and ethylbenzene, cyclopentane, iso-pentane and n-pentane, carbon dioxide, and ethene and propene xwere reported. In this paper, the work is extended to the thermal conductivity of cyclohexane.

The goal of this work is to critically assess the available literature data, and provide wide-ranging correlations for the thermal conductivity of cyclohexane that are valid over gas, liquid, and supercritical states, and incorporate densities provided by the equation of state of Zhou *et al.*<sup>14</sup>

# 2. Methodology

The thermal conductivity  $\lambda$  is expressed as the sum of three independent contributions, as

$$\lambda(\rho, T) = \lambda_0(T) + \Delta\lambda(\rho, T) + \Delta\lambda_c(\rho, T), \tag{1}$$

where  $\rho$  is the density, T is the temperature, and the first term,  $\lambda_{\rm o}(T)=\lambda(0,T)$ , is the contribution to the thermal conductivity in the dilute-gas limit, where only two-body molecular interactions occur. The final term,  $\Delta\lambda_{\rm c}(\rho,T)$ , 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.

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  $\lambda_{\rm o}(T)$  and  $\Delta\lambda_{\rm c}(\rho,T)$  theoretically. In addition, it is possible to derive information about  $\lambda_{\rm o}(T)$  from experiment. In contrast, there is almost no theoretical guidance concerning the residual contribution,  $\Delta\lambda(\rho,T)$ ; 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 wellestablished set of criteria.<sup>15</sup> 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 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<sup>16–38</sup> of the thermal conductivity of cyclohexane reported in the literature. From the 23 sets shown in the table, nine were considered as primary data.

The measurements of Li *et al.*, <sup>18</sup> extending to high pressures, were obtained in an absolute transient hot-wire instrument with an uncertainty of 0.3%. Measurements performed by this group (of W.A. Wakeham of Imperial College London) have already been successfully employed in many thermal conductivity reference correlations, <sup>2,4–6,10–13</sup> and are part of the primary dataset. The transient hot-wire technique was also employed by Watanabe and Kato, <sup>16</sup> Tanaka *et al.*, <sup>17</sup> and Kashiwagi *et al.* <sup>19</sup> with corresponding uncertainties of 0.5, 1, and 2%, respectively. Measurements from these three groups have already been successfully employed in previous correlations as primary data (Watanabe and Kato <sup>16</sup> in Refs. 4, 6, 7, 10, and 11, Tanaka *et al.* <sup>17</sup> in Refs. 6 and 7, and Kashiwagi *et al.* <sup>19</sup> in Refs. 4–7 and 10).

Naziev *et al.*<sup>21</sup> and Grigoriev and Ishkanov<sup>20</sup> employed concentric-cylinder instruments to measure the thermal conductivity with 1.6% and 1.5% uncertainty, respectively. The measurements of Naziev *et al.*<sup>21</sup> have successfully been employed in previous reference correlations, <sup>6,7,9–11,13</sup> and therefore here are also considered as primary data. The measurements of Grigoriev and Ishkanov<sup>20</sup> were included in the primary data set as they extend to higher pressures (50 MPa) and higher temperatures (633 K).

Finally, the low-pressure vapor-phase measurements of Vines, <sup>23</sup> Vines and Bennett, <sup>22</sup> and Lambert *et al.*, <sup>24</sup> performed in hot-wire instruments with 0.3%, 1%, and 1% uncertainty, respectively, were also included in the primary data set. Measurements from both groups have previously successfully been employed in other thermal-conductivity reference correlations (Vines<sup>23</sup> and Vines and Bennett<sup>22</sup> in Refs. 2, 8, and 11, and Lambert *et al.*<sup>24</sup> in Refs. 6–8, 11, and 13). The remaining sets were considered as secondary data.

TABLE 1. Thermal-conductivity measurements of cyclohexane

1st author	Year publ.	Technique employed <sup>a</sup>	Purity (%)	Uncertainty (%)	No. of data	Temperature range (K)	Pressure range (MPa)		
Primary data									
Watanabe <sup>16</sup>	2004	THW	99.8	0.4	12	281-319	0.1		
Tanaka <sup>17</sup>	1988	THW	99.5	1	45	284-374	0.1-175		
Li <sup>18</sup>	1984	THW	99.5	0.3	48	309-361	5-145		
Kashiwagi <sup>19</sup>	1982	THW	99.0	2	4	303-333	0.1		
Grigoriev <sup>20</sup>	1981	CC	na	1.5	70	298-455	0.1-146		
Naziev <sup>21</sup>	1974	CC	na	1.6	141	293-633	0.1 - 50		
Vines <sup>22</sup>	1954	HW	na	1	7	373-435	0.1		
Vines <sup>23</sup>	1953	HW	na	0.3	17	348-383	0.0-0.1		
Lambert <sup>24</sup>	1950	HW	na	1	17	339–358	0.0-0.04		
	Secondary data								
Voss <sup>25</sup>	1989	THW	na	2	24	326-450	0.4-10		
Rowley <sup>26</sup>	1988	THW	na	1.0	1	313	0.1		
Shakhverdiev <sup>27</sup>	1980	CC	na	na	40	293-493	0.1-40		
Nefedov <sup>28</sup>	1979	HF	na	1.5	50	290-618	2-30		
Andersson <sup>29</sup>	1978	THW	99.5	3	15	305-339	0.1-75		
Mogilevskii <sup>30</sup>	1970	THW	99.9	na	4	282-298	0.1		
Filippov <sup>31</sup>	1968	CC	na	1.9	4	283-313	0.1		
Barnette <sup>32</sup>	1967	PP	na	1.5	1	298	0.1		
Mukhamedzyanov <sup>33</sup>	1964	HW	na	na	9	303-349	0.1		
Horrocks <sup>34</sup>	1963	THW	na	na	5	295-345	0.1		
Briggs <sup>35</sup>	1957	CC	na	3	5	293-333	0.1		
Sakiadis <sup>36</sup>	1957	PP	99	1	8	309-348	0.1		
Riedel <sup>37</sup>	1948	CC	na	1.0	1	293	0.1		
Moser <sup>38</sup>	1913	HW	na	na	1	375	0.1		

<sup>&</sup>lt;sup>a</sup>CC, coaxial cylinder; HF, hot filament; HW, hot wire; na, not available; PP, parallel plate; THW, transient hot wire.

Figures 1 and 2 show the range of the primary measurements outlined in Table 1, and the saturation curve may be seen in Fig. 2. Temperatures for all data were converted to the ITS-90 temperature scale.<sup>39</sup> The development of the correlation requires accurate values for the density; Zhou *et al.*<sup>14</sup> have reviewed the thermodynamic properties of cyclohexane and developed an accurate, wide-ranging equation of state. For the density, the estimated uncertainty of the new equation of state is less than 0.1% (liquid and vapor) up to 500 K, and 0.2% above 500 K, with higher uncertainties within the critical region. Between 283 and 473 K with pressures lower than 30 MPa, the uncertainty is as low as 0.03% in density in the liquid phase.

We also adopt their values for the critical temperature,  $T_c$ , the critical density,  $\rho_c$ , and the triple-point temperature as 553.6 K, 271.33 kg m<sup>-3</sup>, and 279.86 K, respectively. Finally, the isobaric ideal-gas heat capacity was also obtained from the same source.

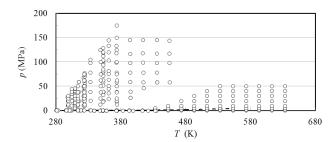


Fig. 1. Temperature–pressure range of the primary experimental thermal-conductivity data for cyclohexane.

## 3.1. 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,  $\lambda_0(T)$ , over a wide temperature range. The traditional kinetic approach for thermal conductivity results in an expression involving three generalized cross sections. 40,41 However, it is possible to derive an equivalent kinetic theory expression for thermal conductivity by making use of the approach of Thijsse et al. 42 and Millat et al.,43 where one considers expansion in terms of total energy, rather than separating translational from internal energy as is done traditionally. In this case, the dilutegas limit thermal conductivity,  $\lambda_0(T)$  (mW m<sup>-1</sup> K<sup>-1</sup>), of a polyatomic gas can be shown to be inversely proportional to a single generalized cross section,  $^{40-43}$  S(10E) (nm<sup>2</sup>), as

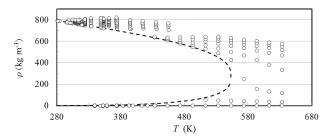


Fig. 2. Temperature–density range of the primary experimental thermal-conductivity data for cyclohexane. (– –) saturation curve.

$$\lambda_{\rm o}(T) = 1000 \frac{5k_{\rm B}^2(1+r^2)T}{2m\langle v\rangle_{\rm o} S(10E)} f_{\lambda},$$
 (2)

where  $k_{\rm B}$  is the Boltzmann constant  $(1.380\,648\,52\times10^{-23}\,{\rm J~K^{-1}})$ , T (K) is the absolute temperature,  $f_{\lambda}$  (–) is the dimensionless higher-order correction factor, m (kg) is the molecular mass of cyclohexane [ $(0.084\,159\,48/6.022\,140\,857\times10^{23})\,{\rm kg}$ ], and  $\langle \nu \rangle_{\rm o} = 4\sqrt{k_{\rm B}T/\pi m}\,{\rm (m/s)}$  is the average relative thermal speed. The quantity  $r^2$  is defined by  $r^2=2C_{\rm int}^o/5k_{\rm B}$ , where  $C_{\rm int}^o$  is the contribution of both the rotational,  $C_{\rm rot}^o$ , and the vibrational,  $C_{\rm vib}^o$ , degrees of freedom to the isochoric ideal-gas heat capacity  $C_{\rm p}^o$ .

The recent classical trajectory calculations<sup>44–46</sup> 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  $S_{\lambda}$  (= $S(10E)/f_{\lambda}$ ) (nm<sup>2</sup>), and rewrite Eq. (2) for the dilute-gas limit thermal conductivity of cyclohexane,  $\lambda_{\rm o}(T)$  (mW m<sup>-1</sup> K<sup>-1</sup>), as

$$\lambda_{\rm o}(T) = 0.060\,808\,5\,\frac{(C_p^{\rm o}/k_{\rm B})\,\sqrt{T}}{S_{\lambda}}.$$
 (3)

The ideal-gas isobaric heat capacity,  $C_p^{\rm o}$  (=  $C_{\rm int}^{\rm o}$  + 2.5 $k_{\rm B}$ ) in (J/K), can be obtained from Zhou *et al.* <sup>14</sup> as

$$\frac{C_p^{\text{o}}}{k_{\text{B}}} = 4 + \sum_{k=1}^{4} v_k \left(\frac{u_k}{T}\right)^2 \frac{\exp(u_k T)}{\left[\exp(u_k T) - 1\right]^2},\tag{4}$$

where the values of the coefficients  $v_k$  and  $u_k$  are  $v_1 = 0.83775$ ,  $v_2 = 16.036$ ,  $v_3 = 24.636$ ,  $v_4 = 7.1715$ ,  $u_1 = 773 \text{ K}$ ,  $u_2 = 941$ ,  $u_3 = 2185 \text{ K}$ ,  $u_4 = 4495 \text{ K}$ .

It has been previously noted, <sup>43</sup> and recently confirmed <sup>41</sup> for smaller molecules, that the cross section S(10E) exhibits a nearly linear dependence on the inverse temperature. Hence, in order to develop the correlation, we have fitted the effective cross section  $S_{\lambda}$  (nm<sup>2</sup>), obtained from the low-pressure (<0.1 MPa) vapor measurements of Naziev *et al.*, <sup>21</sup> Vines and Bennett, <sup>22</sup> Vines, <sup>23</sup> and Lambert *et al.* <sup>24</sup> by means of Eq. (3), to a polynomial in inverse temperature, resulting in the following expression:

$$S_{\lambda} = 0.378 + 255.27/T. \tag{5}$$

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

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

$$\lambda_0(T) = \frac{6.52149 - 39.8399T_r + 65.3275T_r^2 - 202.857T_r^3 + 78.7909T_r^4}{-2.3043 + 1.83274T_r - 2.66787T_r^2 + T_r^3}.$$
(6)

Values calculated by Eq. (6) do not deviate from the values calculated by the scheme of Eqs. (3)–(5) by more than 0.04% over the temperature range from 280 to 680 K. Equation (6) is hence employed in the calculations that will follow.

The experimental dilute-limit thermal-conductivity values as well as the values calculated by Eq. (6) are shown in Fig. 3, while Fig. 4 presents the percentage deviations of the dilutegas experimental data from the values calculated by Eq. (6).

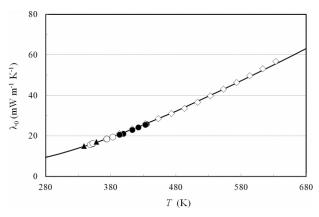


Fig. 3. Dilute-gas limit thermal conductivity of cyclohexane as a function of temperature. Naziev *et al.*<sup>21</sup> ( $\diamondsuit$ ), Vines and Bennett<sup>22</sup> ( $\bullet$ ), Vines<sup>23</sup> ( $\circ$ ), Lambert *et al.*<sup>24</sup> ( $\blacktriangle$ ), and Eq. (6) (—).

The selected data are represented within  $\pm 2.5\%$ , which is commensurate with the uncertainty of the data. No obvious systematic trends are observed.

Therefore, based on the aforementioned discussion, Eqs. (3)–(5) or Eq. (6) represent the dilute-gas limit thermal conductivity to within 2.5% at the 95% confidence level.

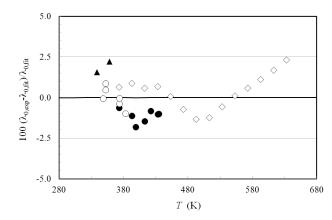


Fig. 4. Percentage deviations of the dilute-gas limit thermal-conductivity measurements of cyclohexane from the scheme of Eqs. (3)–(5) as a function of temperature. Naziev *et al.*<sup>21</sup> ( $\diamond$ ), Vines and Bennett<sup>22</sup> ( $\bullet$ ), Vines<sup>23</sup> ( $\circ$ ), Lambert *et al.*<sup>24</sup> ( $\blacktriangle$ ), and Eq. (6) (—). Note that on the scale of this figure Eq. (6) is almost indistinguishable from the zero line representing the full correlation.

#### 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. 47-49 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 theoretically, 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. 50) 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 equation of state of Zhou et al. 14 The primary data were weighted in inverse proportion to the square of their uncertainty.

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

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

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

### 3.3. The critical enhancement

The theoretically based crossover model proposed by Olchowy and Sengers<sup>47–49</sup> 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.<sup>51</sup> The critical enhancement of the thermal conductivity from this simplified model is given by

$$\Delta \lambda_{\rm c} = \frac{\rho C_p R_{\rm D} k_{\rm B} T}{6\pi \bar{\eta} \xi} \left( \bar{\Omega} - \bar{\Omega}_0 \right), \tag{8}$$

with

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

and

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

Table 2. Coefficients of Eq. (5) for the residual thermal conductivity of cyclohexane

$B_{1,i} \text{ (mW m}^{-1} \text{ K}^{-1}\text{)}$	$B_{2,i} \text{ (mW m}^{-1} \text{ K}^{-1})$
$1.897 \ 32 \times 10^{1}$	$2.14942 \times 10^{0}$
$-6.27889 \times 10^{1}$	$3.15482 \times 10^{1}$
$1.007 48 \times 10^{2}$	$-6.29082 \times 10^{1}$
$-4.77988 \times 10^{1}$	$3.22047 \times 10^{1}$
$7.32262 \times 10^{0}$	$-4.878\ 01 \times 10^{0}$
	$1.897 32 \times 10^{1}$ $-6.278 89 \times 10^{1}$ $1.007 48 \times 10^{2}$ $-4.779 88 \times 10^{1}$

In Eqs. (8)–(10),  $k_{\rm B}$  is Boltzmann's constant,  $\bar{\eta}$  (Pa s) is the viscosity, and  $C_p$  and  $C_v$  (J kg<sup>-1</sup> K<sup>-1</sup>) are the isobaric and isochoric specific heat obtained from the equation of state. The correlation length  $\xi$  (m) is given by

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

As already mentioned, the coefficients  $B_{1,i}$  and  $B_{2,i}$  in Eq. (7) were fitted with odrpack (Ref. 50) to the primary data for the thermal conductivity of cyclohexane. This crossover model requires the universal amplitude,  $R_{\rm D}=1.02$  (–), and the universal critical exponents,  $\nu=0.63$  and  $\gamma=1.239$ , and the system-dependent amplitudes  $\Gamma$  and  $\xi_0$ . For this work, we adopted the values  $\Gamma=0.058$  (–) and  $\xi_0=0.230\times 10^{-9}$  m, using the universal representation of the critical enhancement of the thermal conductivity by Perkins  $et\ al.^{52}$  In the particular case of cyclohexane, as there were very few measurements in the critical region, it was preferred to adopt for the effective cutoff wavelength  $\bar{q}_{\rm D}^{-1}({\rm m})$ , the value of  $6.68\times 10^{-10}$  m, proposed by the aforementioned scheme of Perkins  $et\ al.^{52}$ 

The viscosity required for Eq. (8) was calculated with the correlation of Tariq *et al.*<sup>53</sup> The reference temperature  $T_{\rm ref}$ , far above the critical temperature where the critical enhancement is negligible, was calculated by  $T_{\rm ref} = (^{3}/_{2}) T_{\rm c}$ , which for cyclohexane is 830.4 K.

Table 3 summarizes comparisons of the primary data with the correlation. We note that measurements of Naziev et al.21 at densities above 650 kg/m3 were excluded, as they started to deviate from all the other measurements, and measurements of lower uncertainty exist in that region. We have defined the percentage deviation as PCTDEV = 100 \*  $(\lambda_{\rm exp} - \lambda_{\rm fit})/\lambda_{\rm fit}$ , where  $\lambda_{\rm exp}$  is the experimental value of the thermal conductivity and  $\lambda_{\rm fit}$  is the value calculated from the correlation. Thus, the average absolute percentage deviation (AAD) is found with the expression AAD =  $(\sum |PCTDEV|)/n$ , where the summation is over all n points, and the bias percent is found with the expression BIAS =  $(\sum PCTDEV)/n$ . We estimate the uncertainty (at the 95% confidence level) for the thermal conductivity in the liquid and supercritical phases from the triple point (279.86 K) to 680 K and up to 175 MPa, to be 4%. Uncertainties in the critical region are much larger, since the thermal conductivity approaches infinity

Table 3. Evaluation of the cyclohexane thermal-conductivity correlation for the primary data

1st author	Year publ.	AAD (%)	BIAS (%)
Watanabe <sup>16</sup>	2004	0.21	-0.19
Tanaka <sup>17</sup>	1988	1.81	-1.39
Li <sup>18</sup>	1984	0.37	0.19
Kashiwagi <sup>19</sup>	1982	3.33	3.33
Grigoriev <sup>20</sup>	1981	1.43	-1.42
Naziev <sup>21</sup>	1974	2.06	0.45
Vines <sup>22</sup>	1954	2.02	-2.02
Vines <sup>23</sup>	1953	0.49	0.12
Lambert <sup>24</sup>	1950	1.70	1.70
Entire d	ata set	1.41	-0.28

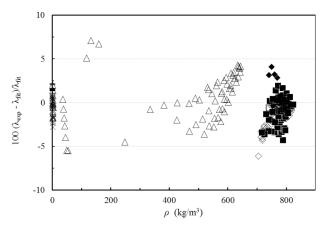


Fig. 5. Percentage deviations of primary experimental data of cyclohexane from the values calculated by the present model, Eqs. (1), (6)–(11), as a function of density. Watanabe and Kato<sup>16</sup> ( $\bullet$ ), Tanaka *et al.*<sup>17</sup> ( $\blacksquare$ ), Li *et al.*<sup>18</sup> ( $\square$ ), Kashiwagi *et al.*<sup>19</sup> ( $\bullet$ ), Grigoriev and Ishkanov<sup>20</sup> ( $\diamondsuit$ ), Naziev *et al.*<sup>21</sup> ( $\triangle$ ), Vines and Bennett<sup>22</sup> ( $\times$ ), Vines<sup>23</sup> ( $\bigstar$ ), Lambert *et al.*<sup>24</sup> (+).

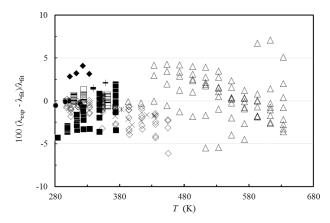


Fig. 6. Percentage deviations of primary experimental data of cyclohexane from the values calculated by the present model, Eqs. (1), (6)–(11), as a function of temperature. Watanabe and Kato<sup>16</sup> ( $\bullet$ ), Tanaka *et al.*<sup>17</sup> ( $\blacksquare$ ), Li *et al.*<sup>18</sup> ( $\square$ ), Kashiwagi *et al.*<sup>19</sup> ( $\bullet$ ), Grigoriev and Ishkanov<sup>20</sup> ( $\diamond$ ), Naziev *et al.*<sup>21</sup> ( $\triangle$ ), Vines and Bennett<sup>22</sup> ( $\times$ ), Vines<sup>23</sup> ( $\bigstar$ ), Lambert *et al.*<sup>24</sup> (+).

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) and (6)–(11), as a function of density. Figures 6 and 7 show the same deviations but as a function of temperature and pressure, respectively.

Table 4 shows the average absolute percentage deviation (AAD) and the bias for the secondary data. Finally, Figs. 8 and 9 show plots of the thermal conductivity of cyclohexane as a function of the temperature for different pressures, and as a function of the density for different temperatures.

#### 3.4. Recommended values

In Table 5, recommended values for the thermal conductivity of cyclohexane are shown. For checking computer implementations of the correlation, a point is provided for testing code with critical enhancement at 554.0 K and  $350.0 \text{ kg m}^{-3}$  (4.1718 MPa), where the thermal conductivity

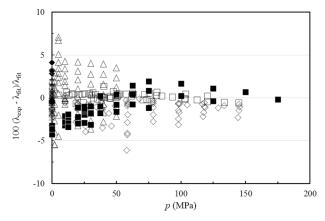


Fig. 7. Percentage deviations of primary experimental data of cyclohexane from the values calculated by the present model, Eqs. (1), (6)–(11), as a function of pressure. Watanabe and Kato<sup>16</sup> ( $\bullet$ ), Tanaka *et al.*<sup>17</sup> ( $\blacksquare$ ), Li *et al.*<sup>18</sup> ( $\square$ ), Kashiwagi *et al.*<sup>19</sup> ( $\bullet$ ), Grigoriev and Ishkanov<sup>20</sup> ( $\diamond$ ), Naziev *et al.*<sup>21</sup> ( $\triangle$ ), Vines and Bennett<sup>22</sup> ( $\times$ ), Vines<sup>23</sup> ( $\star$ ), Lambert *et al.*<sup>24</sup> (+).

Table 4. Evaluation of the cyclohexane thermal-conductivity correlation for the secondary data

1st author	Year publ.	AAD (%)	BIAS (%)
Voss <sup>25</sup>	1989	7.19	-7.19
Rowley <sup>26</sup>	1988	0.36	0.36
Shakhverdiev <sup>27</sup>	1980	6.00	6.00
Nefedov <sup>28</sup>	1979	11.37	-11.35
Andersson <sup>29</sup>	1978	2.99	-2.82
Mogilevskii <sup>30</sup>	1970	1.69	1.69
Filippov <sup>31</sup>	1968	4.37	4.37
Barnette <sup>32</sup>	1967	2.83	2.83
Mukhamedzyanov <sup>33</sup>	1964	3.45	3.45
Horrocks <sup>34</sup>	1963	1.16	1.16
Briggs <sup>35</sup>	1957	6.52	6.52
Sakiadis <sup>36</sup>	1957	2.35	2.35
Riedel <sup>37</sup>	1948	4.04	4.04
Moser <sup>38</sup>	1913	8.66	-8.66

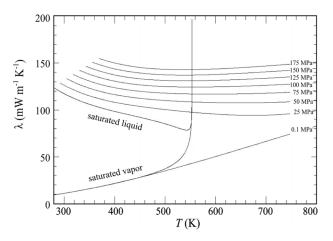


Fig. 8. Thermal conductivity of cyclohexane as a function of temperature for different pressures.

is 79.66 mW m<sup>-1</sup> K<sup>-1</sup>; the dilute-gas thermal conductivity,  $\lambda_o(554~\text{K}) = 43.09~\text{mW}~\text{m}^{-1}~\text{K}^{-1}$ , the residual term  $\Delta\lambda$  (350 kg m<sup>-3</sup>, 554 K) = 22.03 mW m<sup>-1</sup> K<sup>-1</sup>, and the critical enhancement term,  $\Delta\lambda_c(350.0~\text{kg m}^{-3}, 554~\text{K})$  = 14.54 mW m<sup>-1</sup> K<sup>-1</sup>. The viscosity used in the calculation of

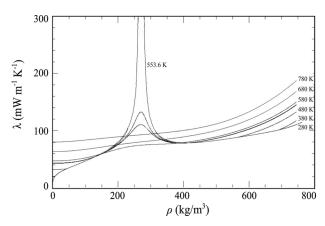


Fig. 9. Thermal conductivity of cyclohexane as a function of density for different temperatures.

Table 5. Recommended values of cyclohexane thermal conductivity (mW  $m^{-1}\ K^{-1}$ )

Pressure		Temperature (K)					
(MPa)	300	400	500	600	700		
0	11.0	21.7	35.0	50.2	66.4		
0.1	117.6	21.9	35.2	50.4	66.5		
50		116.0	110.0	108.8	110.6		
100		130.2	124.4	124.9	128.1		
150		143.2	136.6	137.3	141.2		

the enhancement for this state point is 44.42  $\mu$ Pa s, obtained from the correlation of Tariq *et al.*<sup>53</sup>

# 4. Conclusion

New, wide-ranging reference equations for the thermal conductivity of cyclohexane 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 guide the extrapolation behavior. In the critical region, the enhancement of the thermal conductivity is well represented by a theoretically based model.<sup>52</sup> The remaining contribution to the thermal conductivity was obtained by fitting critically assessed data to an empirical equation that is a function of temperature and density.

We estimate the uncertainty (at the 95% confidence level) for the thermal conductivity from the triple point (279.86 K) to 650 K at pressures up to 175 MPa to be 4% for the compressed liquid and supercritical phases. For the low-pressure gas phase (up to 0.1 MPa) over the temperature range 280–680 K, the estimated uncertainty is 2.5%. The equation of state of Zhou *et al.* <sup>14</sup> is valid from the triple point (279.86 K) to 700 K at pressures up to 250 MPa. The correlation behaves in a physically reasonable manner and we feel it can be used over this entire range, although the uncertainty will be larger where there were no experimental data. 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.

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