Reference Correlation of the Thermal Conductivity of ethanol from the Triple Point to 660 K and up to 245 MPa

E. A. Sykioti, M. J. Assael, M. L. Huber, and R. A. Perkins

Reference Correlation of the Thermal Conductivity of Methanol from the Triple Point to 660 K and up to 245 MPa

E. A. Sykioti and M. J. Assael

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

M. L. Huber[a] **and R. A. Perkins**

Applied Chemicals and Materials Division, National Institute of Standards and Technology, 325 Broadway, Boulder, Colorado 80305, USA

This paper contains new, representative reference equations for the thermal conductivity of methanol. 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. The correlation is applicable for the temperature range from the triple point to 660 K and pressures up to 245 MPa. The overall uncertainty (at the 95% confidence level) of the correlation over its range of applicability for the liquid and supercritical phases, excluding the critical region, is estimated to be less than 4.4%. The dilute gas region has an estimated uncertainty of 3%, and the liquid at atmospheric pressure is represented to 2%. Uncertainty in regions where data are unavailable for comparison, such as the dense gas region, may be larger. *© 2013 by the U.S. Secretary of Commerce on behalf of the United States. All rights reserved.* [http://dx.doi.org/10.1063/1.4829449]

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

CONTENTS

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] SF_6,[2] toluene,[3] benzene,[4] *n*-hexane,[5] *n*-heptane,[6] and ethanol,[7] covering a wide range of conditions of temperature and pressure, were reported. In this paper, the work is extended to the thermal conductivity of methanol.

The goal of this work is to critically assess the available literature data, and provide a wide-ranging correlation for the thermal conductivity of methanol that is valid over gas, liquid, and supercritical states, and that incorporates densities provided by the equation of state of de Reuck and Craven.[8]

2. Methodology

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

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

where ρ is the density, T is the temperature, and the first term, $\lambda_o(T) = \lambda(0, T)$, is the contribution to the thermal conductivity in the dilute-gas limit, where only two-body molecular interactions occur. The final term, $\Delta\lambda_c(\rho, T)$, the critical enhancement, arises from the long-range density fluctuations that occur in a fluid near its critical point, which contribute to divergence of the thermal conductivity at 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 $\lambda_o(T)$ and $\Delta\lambda_c(\rho, T)$ theoretically. In addition, it is possible to derive information about $\lambda_o(T)$ from experiment. In contrast, there is almost no theoretical guidance concerning the residual contribution, $\Delta\lambda(\rho, T)$, so that its evaluation is based entirely on experimentally obtained data.

The analysis described above should be applied to the best available experimental data for the thermal conductivity. Thus, a prerequisite to the analysis is a critical assessment of the experimental data. For this purpose, two categories of experimental data are defined: primary data employed in the development of the correlation, and secondary data used simply for comparison purposes. According to the recommendation adopted by the Subcommittee on Transport Properties (now known as The International Association for Transport Properties) of the International Union of Pure and Applied Chemistry, the primary data are identified by a well-established set of criteria.[9] These criteria have been successfully employed to establish standard reference values for the viscosity and thermal conductivity of fluids over wide ranges of conditions, with uncertainties in the range of 1%. However, in many cases, such a narrow definition unacceptably limits the range of the data representation. Consequently, within the primary data set, it is also necessary to include results that extend over a wide range of conditions, albeit with a poorer accuracy, provided they are consistent with other more accurate data or with theory. In all cases, the accuracy claimed for the final recommended data must reflect the estimated uncertainty in the primary information.

3. The Correlation

Table 1 summarizes, to the best of our knowledge, the experimental measurements[10–59] of the thermal conductivity of methanol reported in the literature. Fifty sets are included in the table. From these sets, six were considered as primary data.

The data of Assael *et al.*[11] were obtained in an absolute transient hot-wire instrument employing two anodized tantalum wires. The operation of this instrument 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 (e.g., *n*-hexane,[5] *n*-heptane,[6] benzene,[4] toluene,[3] ethanol,[7] hydrogen,[1] and water[60]). Hence, this set was considered as primary data. The measurements of Mukhamedzyanov and Usmanov,[14] also considered as primary data, were similarly obtained in a transient hot-wire instrument in an absolute manner but with a slightly inferior uncertainty of 2%. These measurements are very useful as they cover a very wide range of temperatures and pressures. Furthermore, they have also been successfully employed in previous thermal conductivity reference correlations (e.g., *n*-hexane,[5] *n*-heptane,[6] and ethanol[7]). Finally, Takizawa *et al.*[12] also performed measurements employing a transient hot-wire instrument in an absolute manner, checked also by measuring the thermal conductivity of water. This group, headed by A. Nagashima, has produced measurements

TABLE 1. Thermal conductivity measurements of methanol

1st author	Year Publ.	Technique employed[a]	Purity (%)	Uncertainty (%)	No. of data	Temperature range (K)	Pressure range (MPa)
Primary Data							
Naziev[10,b]	2004	CAL	na	1.9	126	292–601	0.1–60
Assael[11]	1988	THW-Abs	99.8	0.5	9	301–326	0.1
Takizawa[12]	1978	THW-Abs	na	1.5	7	263–313	0.1
Tarzimanov[13,b]	1974	HW	99.97	1.5	19	340–662	0.016–0.099
Mukhamezyanov[14]	1971	THW-Abs	na	2	82	297–473	0.1–245
Golubev[15,b]	1969	HW	na	3	523	290–570	0.1–40
Secondary Data							
Ohmori[16]	2001	LITG	99.5	na	39	513–540	4.0–50
Fujii[17]	1997	THW	na	2	2	294–299	0.1
Wang[18]	1995	CAL	99.5	1	1	298	0.1
Cai[19]	1993	THW	99.4	0.8	1	303	0.1
Bailey[20]	1987	TL	na	na	13	321–341	0.003–0.083
Baroncini[21]	1987	THW-Rel	na	2	6	298–348	0.1
Atalla[22]	1981	ACHW	na	2.2	1	293	0.1
Frurip[23,b]	1981	HW	na	1	139	337–419	0.013–0.242
Raal[24]	1981	HW	99.5	1	6	259–313	0.1
Renner[25]	1977	HW	99.9	10	119	307–345	0.007–0.102
Mallan[26]	1972	THW-Rel	na	1.3	15	296–362	0.1
Papadopoulos[27]	1971	SSHW	na	0.7	1	298	0.1
Perry[28]	1968	HW	na	2	6	298–317	0.1
Venart[29]	1967	THW	na	1	11	293–335	0.1
Geller[30]	1966	CC	na	1.5	1	313	0.1
Sale[31]	1966	HW	na	2	1	293	0.1
Tufeu[32]	1966	CC	na	1	1	293	0.1
Poltz[33]	1965	GHP	na	0.5	1	298	0.1
Jamieson[34]	1964	HW	99.7	5	3	298–323	0.1
Jobst[35]	1964	THW-Abs	na	2	5	312–383	0.1
Schlunder[36]	1964	HW	na	na	1	364	0.026
Fritz[37]	1962	GHP	na	0.5	1	293	0.1
Scheffy[38]	1961	CC	99.5	na	1	391	0.1
Gerts[39]	1960	HW	na	1	1	303	0.1
Abaszade[40]	1957	HW	na	na	23	273–293	0.004–5.78
Hildenbrand[41]	1957	HW	na	na	1	303	0.1
Cecil[42]	1956	HW	na	na	1	298	0.1
Sakiadis[43]	1955	SSPP	na	1.5	5	310–330	0.1
Mason[44]	1954	CC	na	2.7	5	302–323	0.1
Vines[45,b]	1954	HW	na	1	5	352–343	0.1
Vines[46,b]	1953	HW	na	1	11	351–382	0.017–0.101
Bromley[47]	1952	HW	na	4	2	373–400	0.1
Riedel[48]	1951	CC	99.7	2	9	203–333	0.1
Lambert[49,b]	1950	HW	na	na	26	339–358	0.002–0.045
Dittman[50]	1949	CC	na	2	1	306	0.1
van der Held[51]	1949	THW	na	2	1	288	0.1
Vargaftik[52]	1949	HW	na	2	1	303	0.1
Shushpanov[53]	1939	HW	na	0.5?	12	332–400	0.1
Bates[54]	1938	HW	na	na	5	283–323	0.1
Shiba[55]	1931	SSHW	na	na	1	303	0.1
Bridgman[56]	1923	CC	na	4	13	303	0.1–1177
Goldschmidt[57]	1911	HW	na	na	1	273	0.1
Lees[58]	1898	PP	na	na	2	298–320	0.1
Weber[59]	1886	na	na	na	1	293	0.1

[a]Abs, absolute; ACHW, Alternating-current hot wire; CAL, calorimetry; CC, coaxial cylinder; GHP, guarded hot plate; HW, hot wire; na, not available; LITG, laser induced transient grating; PP, parallel plate; Rel, relative; SSHW, steady-state hot wire; SSPP, steady-state parallel plate; THW, transient hot wire; TL, thermal lens.

[b]Include vapor data employed to derive the dilute-gas thermal-conductivity correlation.

of very high quality that were part of the primary data in the reference correlations for the thermal conductivity of water[60] and ethanol.[7]

The group of Tarzimanov and Mashirov[13] has been involved in the measurement of the thermal conductivity of vapors of hydrocarbons and alcohols. A steady-state hot-wire instrument was employed, with a 1.5% uncertainty, covering a wide range of temperature with a low uncertainty. As they have produced very good measurements, employed in the development of the reference correlations of the thermal conductivity of
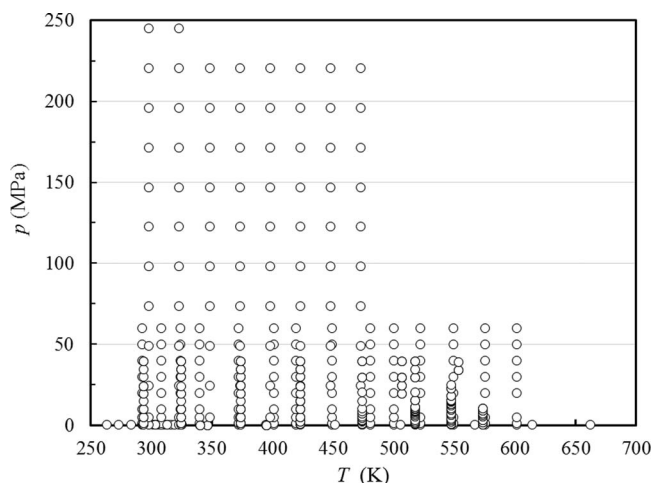
FIG. 1. Temperature and pressure ranges of the primary experimental thermal conductivity data for methanol.

n-heptane,[6] benzene,[4] ethanol,[7] and water,[60] they were also considered here as part of the primary data set. Finally, it was decided to also include in the primary dataset the measurements of the laboratory of Naziev *et al.*,[10] and Golubev and Vasilkovskaya.[15] The measurements of Golubev and Vasilkovskaya[15] were performed in a hot-wire instrument with a 3% uncertainty, while the more recent ones of Naziev *et al.*[10] were obtained in a calorimeter with a 1.9% uncertainty. Both sets extend to high temperatures and pressures. Furthermore, they have been included as primary data in the development of the thermal-conductivity reference correlations of *n*-hexane,[5] *n*-heptane,[6] toluene,[3] and ethanol.[7] The remaining datasets shown in Table 1 formed the secondary dataset group.

Figure 1 shows the temperature and pressure range of the primary measurements outlined in Table 1. Temperatures for all data were converted to the ITS-90 temperature scale.[61] The development of the correlation requires densities; de Reuck and Craven[8] in 1993 reviewed the thermodynamic properties of methanol and developed an accurate, wide-ranging equation of state valid for single-phase and saturation states from the triple point to 620 K at pressures up to 800 MPa, with an uncertainty in density of 0.1%. This equation behaves in a physically reasonable manner at temperatures above its recommended range, so we have included primary data that extend to 662 K, and adopt 660 K as the upper limit of our correlation. We also adopt their values for the critical temperature, T_c, the critical density, ρ_c, and the triple-point temperature, as 512.6 K, 275.563 kg m^{-3}, and 175.61 K, respectively. Finally, the isobaric ideal-gas heat capacity proposed by de Reuck and Craven[8] with an uncertainty of less than 0.1% was also employed.

3.1. The dilute-gas limit

From the primary measurements shown in Table 1, three investigators performed measurements near the dilute-gas limit.[10,13,15] To increase the number of measurements, four more studies (Frurip *et al.*,[23] Vines and Bennett,[45] Vines,[46] and

Lambert *et al.*[49]), initially classified as secondary data, were also included. The vapor measurements of these investigators were performed in hot-wire instruments, and although their description of method and uncertainty do not justify inclusion in the primary data, they were also considered in developing only the dilute-gas limit correlation. This procedure has been adopted in similar reference correlation papers, and on these grounds the measurements of Frurip were included in developing the dilute-gas limit thermal conductivity of water,[60] the measurements of Vines in *n*-hexane[5] and water,[60] and the measurements of Lambert in *n*-hexane[5] and *n*-heptane.[6]

The vapor measurements of Renner *et al.*[25] were not included as their uncertainties were far too high (10%). For the same reason, the measurements of Bailey *et al.*,[20] obtained with a thermal-lens technique, were not included. Finally, the vapor measurements of Abaszade[40] showed very high deviations from all the rest, and were consequently not considered. No measurements are ever performed at zero pressure; the values of thermal conductivity are usually obtained by extrapolating the data along an isotherm to a dilute-gas limit. All investigators performed the measurements at sufficiently low pressures that the zero-pressure correction would be smaller than 0.3%, and hence we have used their quoted values as the dilute-gas thermal conductivity and marginally increased their claimed uncertainty.

In order to be able to extrapolate the temperature range of the aforementioned measurements (337 to 662 K), 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.[62,63] However, it is possible to derive an equivalent kinetic theory expression for thermal conductivity by making use of the approach of Thijsse *et al.*,[64,65] 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,[62-65] $S(10E)$, as

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

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 methanol [(0.03204216/6.02214 × 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 $r^2 = 2 C_{int}^o/5k_B$, 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 heat capacity C_v^o.

Recent classical trajectory calculations[66-68] 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^2), and rewrite Eq. (2) for the dilute-gas

TABLE 2. Coefficients of Eq. (4)

i	d_i $(-)$	g_i $(-)$
1	3.900 79	–
2	10.992 7	4.126 05
3	18.336 8	3.269 97
4	−16.366 0	3.775 20
5	−6.223 23	2.935 95
6	2.803 54	8.238 07
7	1.077 81	10.332 0
8	0.969 66	0.533 30

limit thermal conductivity of methanol, $\lambda_o(T)$ (mW m^{-1} K^{-1}), as

$$\lambda_o(T) = 0.0985496 \frac{(C_P^o/k_B)\sqrt{T}}{S_\lambda}. \quad (3)$$

The ideal-gas isobaric heat capacity of methanol, C_P^o ($=C_{int}^o + 2.5k_B$) can be obtained from de Reuck and Craven:[8]

$$\frac{C_P^o}{k_B} = d_1 + \sum_{i=2}^{8} d_i \frac{u_i^2 e^{u_i}}{(e^{u_i}-1)^2}, \quad (4)$$

where $u_i = g_i \tau$, $\tau = T_c/T$, and constants d_i and g_i are given in Table 2.[8] It has been previously noted,[65] and recently confirmed for smaller molecules,[62] that the cross section $S(10E)$ exhibits a nearly linear dependence on the inverse temperature.

In order to develop the correlation, we have fitted the effective cross section S_λ (nm^2), obtained from experimental data[10,13,15,23,45,46,49] by means of Eq. (3), to a polynomial in inverse temperature, resulting in the following expression,

$$S_\lambda = 0.1472 + 134.31/T. \quad (5)$$

Equations (3)–(5) form a consistent set of equations for the calculation of the dilute-gas limit thermal conductivity of methanol. The experimental dilute-limit thermal-conductivity values as well as the values calculated by Eqs. (3)–(5) are shown in Fig. 2, while Fig. 3 presents the percentage deviations of the dilute-gas experimental data from the values calculated by Eqs. (3)–(5). The majority of the selected data are represented to within ±3%, which is commensurate with the uncertainty of the data. No obvious systematic trends are observed.

Since methanol is a polar molecule, some more points can be made concerning the approach adopted. We note, however, that a full discussion of the validity of this approach is to be submitted soon.[69] Nevertheless, a further indication of its
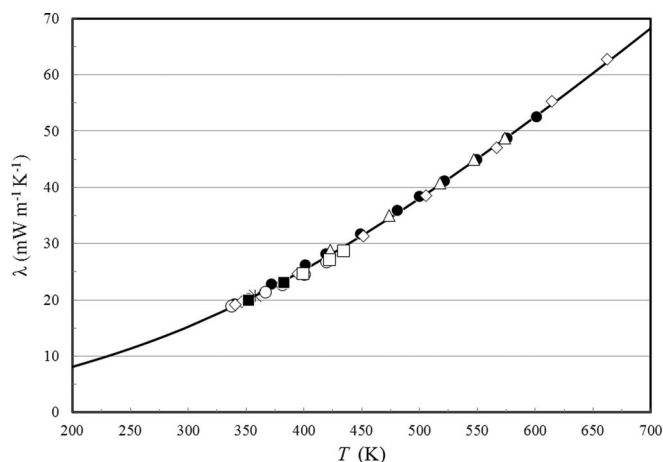

FIG. 2. Dilute-gas limit thermal conductivity as a function of temperature. Naziev et al.[10] (●), Tarzimanov and Mashirov[13] (◊), Golubev and Vasilkovskaya[15] (Δ), Frurip et al.[23] (○), Vines and Bennett[45] (□), Vines[46] (■), Lambert et al.[49] (✕), Eq. (8) (—).

validity can be provided if the thermal-conductivity values derived are employed to calculate accurate dilute-gas viscosity values. Vogel et al.[70] have accurately measured the viscosity of methanol at the dilute-gas limit. A modified Eucken equation can be employed to calculate approximately the dilute-gas limit viscosity, $\eta_o(T_o)$. Such an equation[71] is

$$\lambda_o(T) = \frac{\eta_o(T)k_B}{m}\left\{\frac{5}{2}\frac{C_{tr}^o}{k_B} + \left(\frac{\rho D}{\eta_o(T)}\right)\frac{C_{int}^o}{k_B}\right\}, \quad (6)$$

where C_{tr}^o denotes the translational contribution to the ideal-gas isochoric heat capacity, and D the diffusion coefficient. In Ref. 71 it is also proposed to employ as an approximation

$$\frac{\rho D}{\eta_o(T)} = A^*, \quad (7)$$

where A^* is a reduced collision integral. Vogel et al.[70] employed approximately $A^* = 1.1$ for methanol. If we employ this value in the above equations, the viscosity values measured by Vogel et al.[70] are predicted within 5%. We note that employing $A^* = 1.15$ improves the agreement to less than 2%.

The values of the dilute-gas limit thermal conductivity, $\lambda_o(T)$, in mW m^{-1} K^{-1}, 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:

$$\lambda_o(T) = \frac{-3.57796 + 62.9638T_r - 37.3047T_r^2 - 52.1182T_r^3 + 231.607T_r^4 + 44.1575T_r^5}{3.33313 - 6.08398T_r + 8.18739T_r^2 - 0.261074T_r^3 + T_r^4}. \quad (8)$$
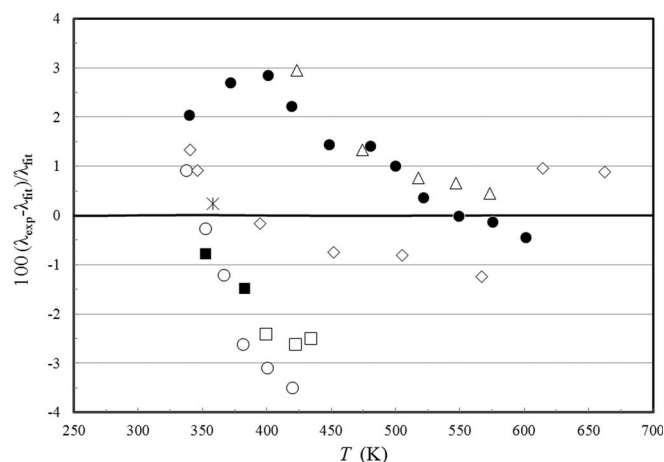
FIG. 3. Percentage deviations of primary experimental data for dilute-gas limit thermal conductivity of methanol from the values calculated by Eqs. (3)–(5). Naziev *et al.*[10] (●), Tarzimanov and Mashirov[13] (◊), Golubev and Vasilkovskaya[15] (Δ), Frurip *et al.*[23] (○), Vines and Bennett[45] (□), Vines[46] (■), Lambert *et al.*[49] (✳), Eq. (8) (—). Note that on the scale of this figure Eq. (8) is almost indistinguishable from the zero line representing the full correlation.

Values calculated by Eq. (8) do not deviate from the values calculated by the scheme of Eqs. (3)–(5) by more than 0.05% over the temperature range from 176 to 2000 K. Equation (8) is hence employed in the calculations that will follow. Finally, based upon the aforementioned discussion, Eqs. (3)–(5) or Eq. (8) represent the dilute-gas limit thermal conductivity to within 2.9% at the 95% confidence level.

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.[72–74] The density-dependent terms for thermal conductivity can be grouped according to Eq. (1) as $[\Delta\lambda(\rho, T) + \Delta\lambda_c(\rho, T)]$. To assess the critical enhancement either theoretically or empirically, we need to evaluate, in addition to the dilute-gas thermal conductivity, the residual thermal-conductivity contribution. The procedure adopted during this analysis used ODRPACK (Ref. 75) 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 obtained by Eq. (8). The density values employed were obtained by the equation of state of de Reuck and Craven.[8]

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

$$\Delta\lambda(\rho, T) = \sum_{i=1}^{5} \left(B_{1,i} + B_{2,i}(T/T_c) \right)(\rho/\rho_c)^i. \quad (9)$$

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

TABLE 3. Coefficients of Eq. (9) for the residual thermal conductivity of methanol

i	$B_{1,i}$ (W m^{-1} K^{-1})	$B_{2,i}$ (W m^{-1} K^{-1})
1	$5.569\ 18 \times 10^{-2}$	$1.047\ 71 \times 10^{-2}$
2	$1.121\ 74 \times 10^{-1}$	$-7.452\ 72 \times 10^{-2}$
3	$-8.438\ 93 \times 10^{-2}$	$6.375\ 69 \times 10^{-2}$
4	$1.975\ 25 \times 10^{-2}$	$-2.468\ 26 \times 10^{-2}$
5	$-1.525\ 30 \times 10^{-3}$	$4.346\ 56 \times 10^{-3}$

3.3. The critical enhancement

3.3.1. Simplified crossover model

The theoretically based crossover model proposed by Olchowy and Sengers[72–74] 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.[76] The critical enhancement of the thermal conductivity from this simplified model is given by

$$\Delta\lambda_c = \frac{\rho C_p R_D k_B T}{6\pi\bar{\eta}\xi} \left(\bar{\Omega} - \bar{\Omega}_0 \right), \quad (10)$$

with

$$\bar{\Omega} = \frac{2}{\pi} \left[\left(\frac{C_p - C_v}{C_p} \right) \arctan(\bar{q}_D \xi) + \frac{C_v}{C_p} \bar{q}_D \xi \right] \quad (11)$$

and

$$\bar{\Omega}_0 = \frac{2}{\pi} \left[1 - \exp\left(-\frac{1}{(\bar{q}_D \xi)^{-1} + (\bar{q}_D \xi \rho_c/\rho)^2/3} \right) \right]. \quad (12)$$

In Eqs. (10)–(12), k_B is Boltzmann's constant, $\bar{\eta}$ is the viscosity, and C_p and C_v are the isobaric and isochoric specific heat capacities from Ref. 8. To estimate the viscosity, the correlation of Xiang *et al.*[77] implemented in the REFPROP (Ref. 78) program was employed. The correlation length ξ is given by

$$\xi = \xi_0 \left(\frac{p_c \rho}{\Gamma \rho_c^2} \right)^{\nu/\gamma} \left[\frac{\partial\rho(T, \rho)}{\partial p} \bigg|_T - \left(\frac{T_{ref}}{T} \right) \frac{\partial\rho(T_{ref}, \rho)}{\partial p} \bigg|_T \right]^{\nu/\gamma}. \quad (13)$$

As already mentioned, the coefficients $B_{1,i}$ and $B_{2,i}$ in Eq. (9) and $\bar{q}_D$ in Eqs. (10)–(13) were fitted with ODRPACK (Ref. 75) to the primary data for the thermal conductivity of methanol. This crossover model requires the universal constants[76] $R_D = 1.03$, $\nu = 0.63$, and $\gamma = 1.239$, and system-dependent amplitudes Γ and ξ_0. For this work, we adopted the values $\Gamma = 0.05283$ and estimated $\xi_0 = 1.487 \times 10^{-10}$ m, using the method presented by Perkins *et al.*[79] Employing the primary experimental data, the effective cutoff wavelength $\bar{q}_D^{-1}$ was found equal to 7.0×10^{-10} m, which is very near the value of 7.2×10^{-10} m estimated by the scheme of Perkins *et al.*[79] The reference temperature T_{ref}, far above the critical temperature where the critical enhancement is negligible, was calculated by $T_{ref} = (3/2)T_c$,[80] which for methanol is 768.9 K.

TABLE 4. Evaluation of the methanol thermal-conductivity correlation for the primary data

1st Author	Year Publ.	AAD (%)	BIAS (%)
Naziev[10]	2004	2.07	−0.67
Assael[11]	1988	0.43	0.07
Takizawa[12]	1978	0.65	0.22
Tarzimanov[13]	1974	1.39	−0.56
Mukhamezyanov[14]	1971	1.31	−0.46
Golubev[15]	1969	2.76	−1.31
Entire data set		**2.21**	**−0.73**

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 $= (\sum |\,\mathrm{PCTDEV}\,|\,)/n$, where the summation is over all n points, and the bias percent is found with the expression BIAS $= (\sum \mathrm{PCTDEV})/n$. It can be seen that the uncertainty (at the 95% confidence level), for pressures less than 245 MPa and temperatures from the triple point to the upper temperature limit of the data, 662 K, is 4.4%, while the bias of the data is −0.73%. 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 4 shows the percentage deviations of all primary thermal-conductivity data from the values calculated by Eqs. (1) and (8)–(13) as a function of the density, while Figs. 5 and 6 show the same deviations but as a function of the temperature and pressure, respectively.

Since most of the secondary data consisted of one or two measurements at room temperature, Table 5 shows the AAD and the bias for the secondary data. The majority of the deviations are within 5% of the present correlation. Finally,

FIG. 5. Percentage deviations of primary experimental data of methanol from the values calculated by the present model as a function of temperature. Naziev et al.[10] (Δ), Assael et al.[11] (□), Takizawa et al.[12] (◊), Tarzimanov and Mashirov[13] (▲), Mukhamedzyanov and Usmanov[14] (○), Golubev and Vasilkovskaya[15] (×).

Fig. 7 shows a plot of the thermal conductivity of methanol as a function of the temperature for different pressures. Extrapolated values at 500 MPa are shown as a dotted line.

3.3.2. Empirical critical enhancement

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

$$\Delta\lambda_c(\rho, T) = \frac{C_1}{C_2 + |\Delta T_c|}\exp\left[-(C_3\Delta\rho_c)^2\right], \qquad (14)$$
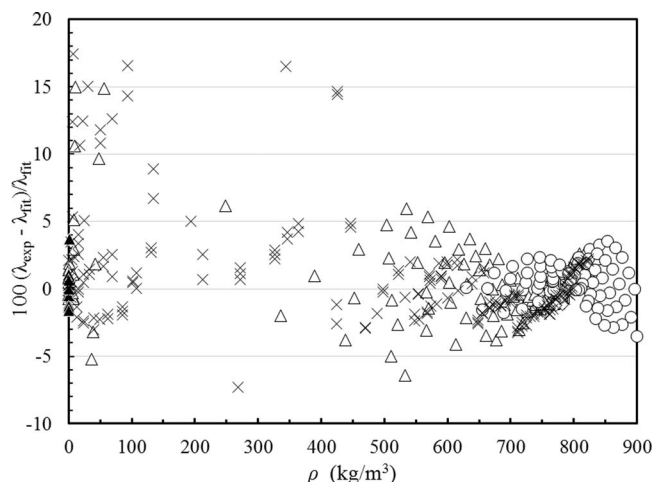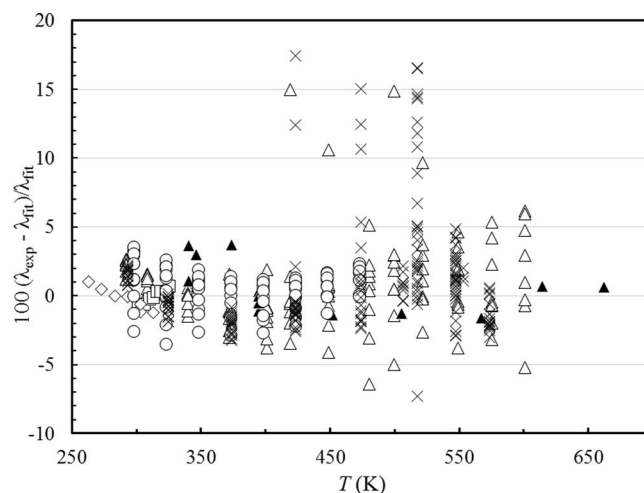

FIG. 4. Percentage deviations of primary experimental data of methanol from the values calculated by the present model as a function of density. Naziev et al.[10] (Δ), Assael et al.[11] (□), Takizawa et al.[12] (◊), Tarzimanov and Mashirov[13] (▲), Mukhamedzyanov and Usmanov[14] (○), Golubev and Vasilkovskaya[15] (×).
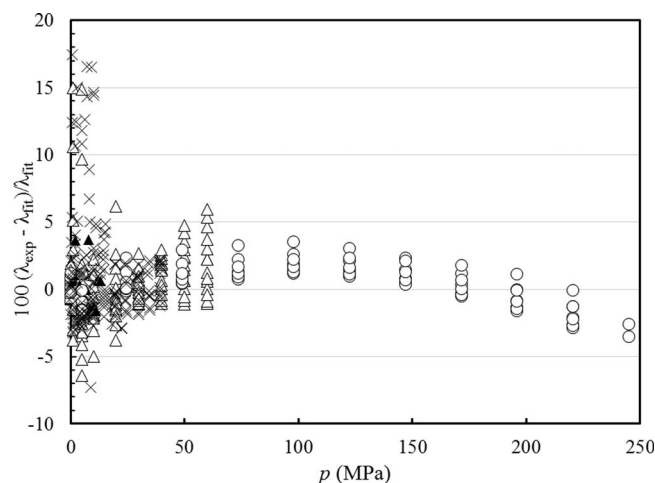

FIG. 6. Percentage deviations of primary experimental data of methanol from the values calculated by the present model as a function of pressure. Naziev et al.[10] (Δ), Assael et al.[11] (□), Takizawa et al.[12] (◊), Tarzimanov and Mashirov[13] (▲), Mukhamedzyanov and Usmanov[14] (○), Golubev and Vasilkovskaya[15] (×).

TABLE 5. Evaluation of the methanol thermal-conductivity correlation for the secondary data

1st author	Year Publ.	AAD	BIAS
Ohmori[16]	2001	6.52	5.32
Fujii[17]	1997	6.87	6.87
Wang[18]	1995	5.92	5.92
Cai[19]	1993	5.64	5.64
Bailey[20]	1987	16.9	7.89
Baroncini[21]	1987	8.54	8.54
Atalla[22]	1981	2.56	2.56
Frurip[23]	1981	5.57	−4.31
Raal[24]	1981	4.46	4.46
Renner[25]	1977	15.2	−15.2
Mallan[26]	1972	31.7	31.7
Papadopoulos[27]	1971	3.51	3.51
Perry[28]	1968	3.99	3.99
Venart[29]	1967	5.84	5.84
Geller[30]	1966	0.11	0.11
Sale[31]	1966	3.29	−3.29
Tufeu[32]	1966	3.43	−3.43
Poltz[33]	1965	5.81	5.81
Jamieson[34]	1964	3.25	3.25
Jobst[35]	1964	4.31	4.31
Schlunder[36]	1964	2.63	−2.63
Fritz[37]	1962	5.11	5.11
Scheffy[38]	1961	38.3	38.3
Gerts[39]	1960	3.33	3.33
Abaszade[40]	1957	8.23	3.31
Hildenbrand[41]	1957	9.54	−9.54
Cecil[42]	1956	1.61	−1.61
Sakiadis[43]	1955	19.9	19.9
Mason[44]	1954	2.26	2.26
Vines[45]	1954	4.12	4.12
Vines[46]	1953	1.42	1.12
Bromley[47]	1952	1.65	1.65
Riedel[48]	1951	3.23	3.20
Lambert[49]	1950	2.36	−1.75
Dittman[50]	1949	7.62	7.62
van der Held[51]	1949	6.39	6.39
Vargaftik[52]	1949	1.45	1.45
Shushpanov[53]	1939	1.83	1.83
Bates[54]	1938	2.28	−2.28
Shiba[55]	1931	1.99	−1.99
Bridgman[56]	1923	4.21	3.14
Goldschmidt[57]	1911	1.96	−1.96
Lees[58]	1898	7.36	7.36
Weber[59]	1886	1.53	1.53

FIG. 7. Thermal conductivity of methanol as a function of temperature for different pressures.

3.4. The 0.101 MPa liquid line

From the primary data of Table 1 measured at or near 0.101 MPa, investigators that exhibited uncertainty higher than 2% were excluded. The remaining investigators are Assael *et al.*[11] with quoted uncertainty of 0.5%, and Takizawa *et al.*,[12] Naziev *et al.*,[10] and Mukhamedzyanov and Usmanov,[14] with quoted uncertainties of 1.5%, 1.9%, and 2%, respectively. The percentage deviations of these data from the values obtained by the proposed scheme of Eqs. (1) and (8)–(13) are shown in Fig. 9. These data were fitted to a linear equation for the thermal conductivity, $\lambda_{0.101\text{ MPa}}$ in mW m^{-1} K^{-1}, as a function of the absolute temperature, T in K, as

$$\lambda_{0.101\text{MPa}} = 265.67 - 0.2191T. \quad (15)$$

FIG. 8. Percentage deviations of primary experimental data of methanol from the values calculated by Eqs. (1), (8), and (9) and the empirical critical enhancement of Eq. (14) as a function of temperature. Naziev *et al.*[10] (△), Assael *et al.*[11] (□), Takizawa *et al.*[12] (◇), Tarzimanov and Mashirov[13] (▲), Mukhamedzyanov and Usmanov[14] (○), Golubev and Vasilkovskaya[15] (×).

where $\Delta T_c = (T/T_c) - 1$ and $\Delta\rho_c = (\rho/\rho_c) - 1$. This equation does not require accurate information on the compressibility, specific heat, and viscosity of methanol in the critical region, as does the theory of Olchowy and Sengers.[73,76,79] The coefficients of Eqs. (8) and (9) were fixed, while the coefficients of Eq. (14) were fitted to the primary data. The values obtained were $C_1 = 2.6 \times 10^{-3}$ W m^{-1} K^{-1}, $C_2 = 3.0 \times 10^{-2}$, and $C_3 = 1.7$. Figure 8 shows the percentage deviations between the primary data and the values calculated by Eqs. (1), (8), (9), and (14), as a function of the temperature. By comparing Figs. 5 and 8, it can be seen that employing Eq. (14) results in very little deterioration in the representation of the data.
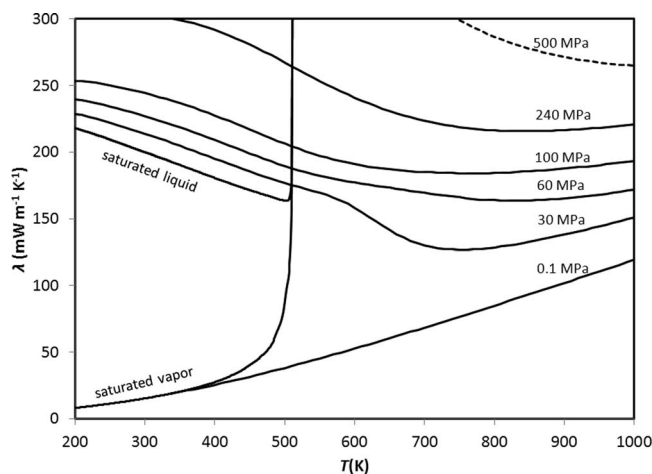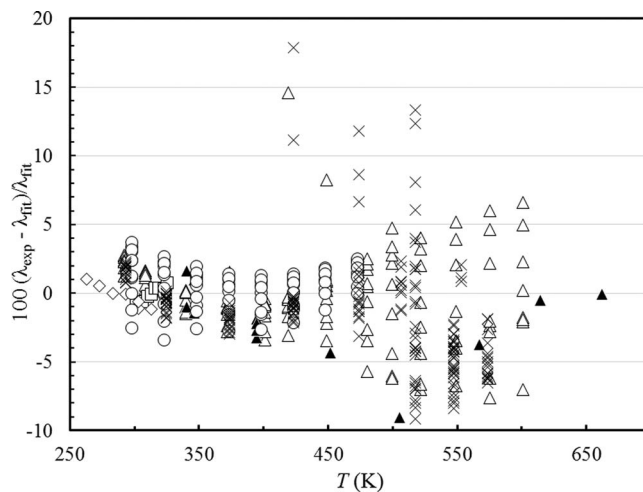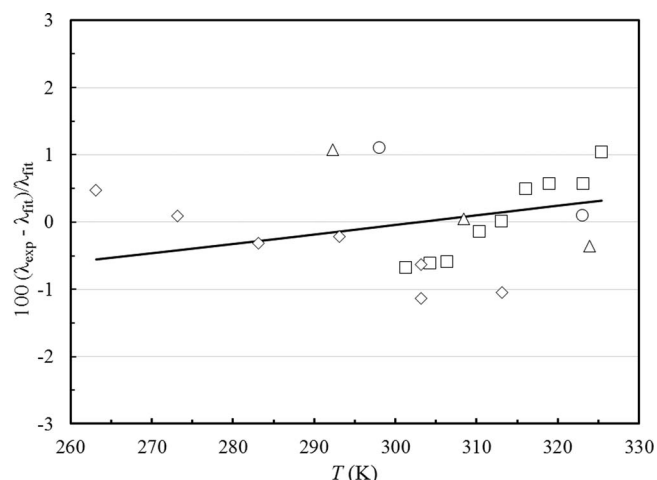
Fig. 9. Percentage deviations of selected primary experimental data of liquid methanol at 0.101 MPa from the values calculated by Eq. (15). Naziev *et al.*[10] ($\triangle$), Assael *et al.*[11] ($\square$), Takizawa *et al.*[12] ($\Diamond$), Mukhamedzyanov and Usmanov[14] ($\circ$), Eqs. (1), (8)–(13) (—).

Equation (15) represents the selected primary data at 0.101 MPa from 260 to 330 K with an uncertainty of 2% at the 95% confidence level (as the data are only accurate to 2%). In Fig. 9, the percentage deviations of the selected experimental data from the values calculated by Eq. (15) are shown. In the same figure, deviations of the values obtained by the proposed scheme of Eqs. (1) and (8)–(13) from those of Eq. (15) are also shown. The agreement is very good, as expected, since both are based upon the same data.

4. Computer-Program Verification

Table 6 is provided to assist the user in computer-program verification. The thermal-conductivity calculations are based on the tabulated temperatures and densities. Note that Eq. (8) was employed for the dilute-gas correlation.

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

T (K)	ρ (kg m^{-3})	λ (mW m^{-1} K^{-1})
300.00	850.00	241.48
400.00	2.00	25.803
400.00	690.00	183.59
500.00	10.00	40.495[a]
500.00	10.00	43.742[b]

[a]Computed with modified Olchowy-Sengers critical enhancement; the viscosity at this point for use in Eq. (10) was taken as $\eta = 16.157$ µPa s (see Sec. 3.3.1). Density derivative values required for the enhancement term are from Ref. 8.
[b]Computed with empirical critical enhancement Eq. (14).

5. Conclusion

A new wide-ranging correlation for the thermal conductivity of methanol was developed based on critically evaluated experimental data. The correlation is valid from the triple point to 660 K, and at pressures up to 245 MPa. The correlation is expressed in terms of temperature and density, and the densities were obtained from the equation of state of de Reuck and Craven.[8] Based on comparisons with experimental data, the overall uncertainty (at the 95% confidence level) of the correlation over its range of applicability for the liquid and supercritical phases, excluding the critical region, is estimated to be less than 4.4%. Deviations in the critical region are larger. The dilute gas region has an estimated uncertainty of 3%, and the liquid at atmospheric pressure is represented to 2%. Uncertainties in regions where data are unavailable for comparison, such as the dense gas region, may be larger. However, the correlation behaves in a physically reasonable manner at pressures up to 500 MPa.

Acknowledgments

6. References

[1]M. J. Assael, J. A. M. Assael, M. L. Huber, R. A. Perkins, and Y. Takata, J. Phys. Chem. Ref. Data **40**, 033101 (2011).

[2]M. J. Assael, I. A. Koini, K. D. Antoniadis, M. L. Huber, I. M. Abdulagatov, and R. A. Perkins, J. Phys. Chem. Ref. Data **41**, 023104 (2012).

[3]M. J. Assael, S. K. Mylona, M. L. Huber, and R. A. Perkins, J. Phys. Chem. Ref. Data **41**, 023101 (2012).

[4]M. J. Assael, E. K. Mihailidou, M. L. Huber, and R. A. Perkins, J. Phys. Chem. Ref. Data **41**, 043102 (2012).

[5]M. J. Assael, S. K. Mylona, C. A. Tsiglifisi, M. L. Huber, and R. A. Perkins, J. Phys. Chem. Ref. Data **42**, 013106 (2013).

[6]M. J. Assael, I. Bogdanou, S. K. Mylona, M. L. Huber, R. A. Perkins, and V. Vesovic, J. Phys. Chem. Ref. Data **42**, 023101 (2013).

[7]M. J. Assael, E. A. Sykioti, M. L. Huber, and R. A. Perkins, J. Phys. Chem. Ref. Data **42**, 023102 (2013).

[8]K. M. de Reuck and R. J. B. Craven, *Methanol, International Thermodynamic Tables of the Fluid State - 12, IUPAC* (Blackwell Scientific Publications, London, 1993).

[9]M. J. Assael, M. L. V. Ramires, C. A. Nieto de Castro, and W. A. Wakeham, J. Phys. Chem. Ref. Data **19**, 113 (1990).

[10]Y. M. Naziev, M. M. Bashirov, and I. M. Abdulagatov, Fluid Phase Equilib. **226**, 221 (2004).

[11]M. J. Assael, E. Charitidou, and C. A. Nieto de Castro, Int. J. Thermophys. **9**, 813 (1988).

[12]S. Takizawa, H. Murata, and A. Nagashima, Bull. JSME **21**, 273 (1978).

[13]A. A. Tarzimanov and V. E. Mashirov, "Experimental determination of the coefficient of thermal conductivity of vapors of N-alkanes, spirits and acids," in *Thermophysical Properties of Matter and Substances* (Amerind Pub. Co. Ltd, New Delhi, 1974), Vol. 2, pp. 240–253.

[14]G. K. Mukhamedzyanov and A. G. Usmanov, Proc. Kazan Chem. Tech. Inst. S.W. Kirov **44**, 57 (1971).

[15]I. F. Golubev and T. N. Vasilkovskaya, Teploenergetika **16**(5), 77 (1969).

[16]T. Ohmori, Y. Kimura, N. Hirota, and M. Terazima, Phys. Chem. Chem. Phys. **3**, 3994 (2001).

[17]M. Fujii, X. Zhang, N. Imaishi, S. Fujiwara, and T. Sakamoto, Int. J. Thermophys. **18**, 327 (1997).

[18]C. Y. Wang and M. L. Yang, Thermochim. Acta **255**, 365 (1995).

[19]G. Q. Cai, H. X. Zong, Q. S. Yu, and R. S. Lin, J. Chem. Eng. Data **38**, 332 (1993).

[20]R. T. Bailey, F. R. Cruickshank, D. Pugh, and I. J. M. Weir, Chem. Phys. Lett. **134**, 311 (1987).

[21]C. Baroncini, G. Latini, and F. Piazza, High Temp. - High Press. **19**, 51 (1987).

[22]S. R. Atalla, A. A. El-Sharkawy, and F. A. Gasser, Int. J. Thermophys. **2**, 155 (1981).

[23]D. J. Frurip, L. A. Curtiss, and M. Blander, Int. J. Thermophys. **2**, 115 (1981).

[24]J. D. Raal and R. L. Rijsdijk, J. Chem. Eng. Data **26**, 351 (1981).

[25]T. A. Renner, G. H. Kucera, and M. Blander, J. Chem. Phys. **66**, 177 (1977).

[26]G. M. Mallan, M. S. Michaelian, and F. J. Lockhart, J. Chem. Eng. Data **17**, 412 (1972).

[27]C. Papadopoulos, Chem. Ind. 932 (1971).

[28]M. G. Perry and H. A. S. Jangda, in *Proceedings of Symposium on Physical Properties of Liquids and Gases for Plant and Process Design* (National Engineering Laboratory, East Kilbride, Glasgow, 1968).

[29]J. E. S. Venart and C. Krishnamurthy, in *Proceedings of the Seventh Conference on the Thermal Conductivity*, NBS Special Publication 302 (National Bureau of Standards, Gaithersburg, Maryland, 1967), pp. 659–669.

[30]Z. I. Geller, Y. L. Rastorguev, and Y. A. Ganiev, Izv. Vyssh. Uchebn. Zaved., Neft Gaz **9**, 88 (1966).

[31]P. Sale, Bull. Inst. Refrig. **2**, 65 (1966).

[32]M. R. Tufeu, B. Le Neindre, and P. Johannin, C. R. Acad. Sci. **262B**, 229 (1966).

[33]H. Poltz, Int. J. Heat Mass Transfer **8**, 609 (1965).

[34]D. T. Jamieson and J. S. Tudhope, J. Inst. Pet. **50**, 150 (1964).

[35]W. Jobst, Int. J. Heat Mass Transfer **7**, 725 (1964).

[36]E. U. Schlunder, Chem.-Ing.-Tech. **36**, 115 (1964).

[37]W. Fritz and H. Poltz, Int. J. Heat Mass Transfer **5**, 307 (1962).

[38]W. J. Scheffy and E. F. Johnson, J. Chem. Eng. Data **6**, 245 (1961).

[39]I. G. Gerts and L. P. Filippov, Zhur. Fiz. Khim. **30**, 2424 (1956).

[40]A. K. Abaszade, Dokl. Akad. Nauk SSSR **99**, 227 (1954).

[41]D. L. Hildenbrand and J. A. Happe, J. Phys. Chem. **61**, 1415 (1957).

[42]O. B. Cecil and R. H. Munch, Ind. Eng. Chem. **48**, 437 (1956).

[43]B. C. Sakiadis and J. Coates, AIChE J. **1**, 275 (1955).

[44]H. L. Mason and D. C. Washington, Trans. ASME **76**, 817 (1954).

[45]R. G. Vines and L. A. Bennett, J. Chem. Phys. **22**, 360 (1954).

[46]R. G. Vines, Aust. J. Chem. **6**, 1 (1953).

[47]L. A. Bromley, *Thermal Conductivity of Gases at Moderate Pressures* (UCRL-1852, Berkeley, 1952).

[48]L. Riedel, Chem.-Ing.-Tech. **23**, 465 (1951).

[49]J. D. Lambert, E. N. Staines, and S. D. Woods, Proc. R. Soc. London, Ser. A **200**, 262 (1950).

[50]F. W. Dittman and C. C. Winding, Ind. Eng. Chem. **41**, 543 (1949).

[51]E. F. M. van der Held and F. G. van Drunen, Physica **15**, 865 (1949).

[52]N. B. Vargaftik, Izv. Vses. Teplotekhn. Inst. **18**, 6 (1949).

[53]P. I. Shushpanov, J. Exp. Theor. Phys. **9**, 875 (1939).

[54]O. K. Bates, G. Hazzard, and G. Palmer, Ind. Eng. Chem. - Anal. Ed. **10**, 314 (1938).

[55]H. Shiba, Inst. Phys. Chem. Res. **16**, 205 (1931).

[56]P. W. Bridgman, Proc. Am. Acad. Arts Sci. **59**, 141 (1923).

[57]R. Goldschmidt, Phys. Z. **12**, 417 (1911).

[58]C. H. Lees, Philos. Trans. R. Soc. London, Ser. A **191**, 399 (1898).

[59]H. F. Weber, Rep. Phys. **22**, 116 (1886).

[60]M. L. Huber, R. A. Perkins, D. G. Friend, J. V. Sengers, M. J. Assael, I. N. Metaxa, K. Miyagawa, R. Hellmann, and E. Vogel, J. Phys. Chem. Ref. Data **41**, 033102 (2012).

[61]H. Preston-Thomas, Metrologia **27**, 3 (1990).

[62]R. Hellmann, E. Bich, E. Vogel, and V. Vesovic, J. Chem. Eng. Data **57**, 1312 (2012).

[63]F. R. W. McCourt, J. J. M. Beenakker, W. E. Köhler, and I. Kučšer, *Nonequilibrium Phenomena in Polyatomic Gases* (Clarendon, Oxford, 1990).

[64]B. J. Thijsse, G. W. Thooft, D. A. Coombe, H. F. P. Knaap, and J. J. M. Beenakker, Physica A **98**, 307 (1979).

[65]J. Millat, V. Vesovic, and W. A. Wakeham, Physica A **148**, 153 (1988).

[66]S. Bock, E. Bich, E. Vogel, A. S. Dickinson, and V. Vesovic, J. Chem. Phys. **120**, 7987 (2004).

[67]R. Hellmann, E. Bich, E. Vogel, A. S. Dickinson, and V. Vesovic, J. Chem. Phys. **130**, 124309 (2009).

[68]R. Hellmann, E. Bich, E. Vogel, and V. Vesovic, Phys. Chem. Chem. Phys. **13**, 13749 (2011).

[69]V. Vesovic, E. A. Sykioti, and M. J. Assael, "A New Way to Correlate the Dilute-Gas Limit Thermal Conductivity," Int. J. Thermophys. (submitted).

[70]E. Vogel, E. Bich, and R. Nimz, Physica A **139**, 188 (1986).

[71]J. Millat, V. Vesovic, and W. A. Wakeham, in *Transport Properties of Fluids. Their Correlation, Prediction and Estimation*, edited by J. MIllat, J. H. Dymond, and C. A. Nieto de Castro (Cambridge University Press, New York, 1996), Chap. 4, p. 47.

[72]G. A. Olchowy and J. V. Sengers, Phys. Rev. Lett. **61**, 15 (1988).

[73]R. Mostert, H. R. van den Berg, P. S. van der Gulik, and J. V. Sengers, J. Chem. Phys. **92**, 5454 (1990).

[74]R. A. Perkins, H. M. Roder, D. G. Friend, and C. A. Nieto de Castro, Physica A **173**, 332 (1991).

[75]P. T. Boggs, R. H. Byrd, J. E. Rogers, and R. B. Schnabel, ODRPACK, Software for Orthogonal Distance Regression, NISTIR 4834, v2.013 (National Institute of Standards and Technology, Gaithersburg, MD, 1992).

[76]G. A. Olchowy and J. V. Sengers, Int. J. Thermophys. **10**, 417 (1989).

[77]H. W. Xiang, A. Laesecke, and M. L. Huber, J. Phys. Chem. Ref. Data **35**, 1597 (2006).

[78]E. W. Lemmon, M. L. Huber, and M. O. McLinden, REFPROP, NIST Reference Fluid Thermodynamic and Transport Properties, NIST Standard Reference Database 23, Version 9.0 (National Institute of Standards and Technology, Gaithersburg, MD, 2010).

[79]R. A. Perkins, J. V. Sengers, I. M. Abdulagatov, and M. L. Huber, Int. J. Thermophys. **34**, 191 (2013).

[80]V. Vesovic, W. A. Wakeham, G. A. Olchowy, and J. V. Sengers, J. Phys. Chem. Ref. Data **19**, 763 (1990).