

Thermal conductivity correlations for minor constituent fluids in natural gas: *n*-octane, *n*-nonane and *n*-decane[☆]

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Abstract

Natural gas, although predominantly comprised of methane, often contains small amounts of heavier hydrocarbons that contribute to its thermodynamic and transport properties. In this manuscript, we review the current literature and present new correlations for the thermal conductivity of the pure fluids *n*-octane, *n*-nonane, and *n*-decane that are valid over a wide range of fluid states, from the dilute-gas to the dense liquid, and include an enhancement in the critical region. The new correlations represent the thermal conductivity to within the uncertainty of the best experimental data and will be useful for researchers working on thermal conductivity models for natural gas and other hydrocarbon mixtures.

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1. Introduction

Natural gas is a mixture of many components. Wide-ranging correlations for the thermal conductivity of the lower alkanes, such as methane, ethane, propane, butane and isobutane, have already been developed and are available in the literature [1–6]. However, wide-ranging correlations are often not readily available for many of the higher alkanes and impurities such as carbon monoxide and hydrogen sulfide. These fluids may be present in small quantities in natural gas and are important when modeling the mixture properties. In this work, we survey the available literature for thermal conductivity and present correlations for the thermal conductivity in terms of temperature and density over a wide range of fluid states including the dilute-gas, condensed liquid and supercritical fluid for *n*-octane, *n*-nonane, and *n*-decane. The new correlations also contain a critical enhancement term.

2. Thermal conductivity correlation

We represent the thermal conductivity λ of a pure fluid as a sum of three contributions:

$$\lambda(\rho, T) = \lambda_0(T) + \Delta\lambda_r(\rho, T) + \Delta\lambda_c(\rho, T) \quad (1)$$

where λ_0 is the dilute-gas thermal conductivity that depends only on temperature, $\Delta\lambda_r$ the residual thermal conductivity, and $\Delta\lambda_c$ the enhancement of the thermal conductivity in the critical region. Both $\Delta\lambda_r$ and $\Delta\lambda_c$ are functions of temperature and density, with the density provided by an equation of state (EOS). In this work, we use the equation of state of Span [7] for *n*-octane, and the recent equations of state by Lemmon and Span [8] for *n*-nonane and *n*-decane. The EOS for *n*-octane has upper temperature, pressure, and density limits of 600 K, 100 MPa, and 6.69 mol/L, respectively. The EOS for *n*-nonane has upper temperature, pressure, and density limits of 575 K, 800 MPa, and 6.06 mol/L, while the EOS for *n*-decane has upper temperature, pressure, and density limits of 700 K, 800 MPa, and 5.41 mol/L. Some of the thermal conductivity data in the literature exceed these limits,

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and the results of these extrapolations should be viewed with caution.

2.1. Dilute-gas thermal conductivity

We represent the dilute-gas thermal conductivity as a polynomial in reduced temperature:

$$\lambda_0(T) = \sum_{k=0}^3 A_k \left(\frac{T}{T_c} \right)^k \quad (2)$$

where T is the temperature in K, T_c the critical temperature in K, and the thermal conductivity is in W/(m K).

2.2. Residual thermal conductivity

We used a polynomial in temperature and density to represent the residual contribution to the thermal conductivity:

$$\Delta\lambda_r(\rho, T) = \sum_{i=1}^4 \left(B_{i,1} + B_{i,2} \left(\frac{T}{T_c} \right) \right) \left(\frac{\rho}{\rho_c} \right)^i \quad (3)$$

where ρ and ρ_c are the density and critical density in mol/L, and the thermal conductivity is in W/(m K). This form has recently been shown to accurately represent other hydrocarbon fluids such as propane [3], butane [4], isobutane [5], and most recently, *n*-dodecane [9].

2.3. Critical enhancement

Olchoway and Sengers [10] developed a theoretically based, but complex, model for the thermal conductivity enhancement in the critical region. We use a simplified version of their crossover model [11]:

$$\Delta\lambda_c(T, \rho) = \frac{\rho C_p R_0 k_B T}{6\pi\eta\xi} (\Omega - \Omega_0) \quad (4)$$

where the heat capacity at constant pressure, $C_p(T, \rho)$, is obtained from the equation of state, $R_0 = 1.03$ is a universal constant [12], and the viscosity, $\eta(T, \rho)$, is obtained from separate correlations for *n*-octane, *n*-nonane and *n*-decane developed in a previous work [13]. The crossover functions Ω and Ω_0 are determined by

$$\Omega = \frac{2}{\pi} \left[\left(\frac{C_p - C_v}{C_p} \right) \arctan(q_D \xi) + \frac{C_v}{C_p} (q_D \xi) \right] \quad (5)$$

$$\Omega_0 = \frac{2}{\pi} \left[1 - \exp \left(\frac{-1}{(q_D \xi)^{-1} + (1/3)(q_D \xi) \rho_c / \rho^2} \right) \right] \quad (6)$$

The heat capacity at constant volume, $C_v(T, \rho)$, is obtained from the equation of state, and the correlation length ξ is given by

$$\xi = \xi_0 \left[\frac{P_c \rho}{\Gamma \rho_c^2} \right]^{v/\gamma} \left[\frac{\partial \rho(T, \rho)}{\partial P} \Big|_T - \frac{T_R}{T} \frac{\partial \rho(T_R, \rho)}{\partial P} \Big|_T \right]^{v/\gamma} \quad (7)$$

The partial derivative $\partial \rho / \partial P|_T$, is evaluated with the equation of state at the system temperature T and a reference temperature, T_R . For the reference temperature, we select a value where the critical enhancement is assumed to be negligible: $T_R = 1.5T_c$. The exponents $\gamma = 1.239$ and $\nu = 0.63$ are universal constants [12]. The critical amplitudes Γ and ξ_0 are system-dependent and are determined by the asymptotic behavior of the equation of state in the critical region. The thermal conductivity at the critical point itself is infinite. We have chosen to use values that we consider reasonable [5] for this family of fluids: $\Gamma = 0.0496$ and $\xi_0 = 1.94 \times 10^{-10}$ m. The only parameter left to be determined is the cutoff wave number q_D (or alternatively, its inverse q_D^{-1}). When sufficient experimental data are available, q_D is obtained from regression. We note that the theoretical analysis of the critical enhancement of thermal conductivity is limited by both the lack of reliable data near the critical point and the increased uncertainty of compressibilities and specific heats calculated from the classical equation of state in the critical region. These increased uncertainties translate to increased uncertainty in the critical enhancement calculated with the simplified crossover theory. While improvements might be possible through the use of a crossover equation of state, this does not seem warranted unless reliable thermal conductivity data become available in the critical region, and in this work we use classical equations of state [7,8] for all thermodynamic properties.

3. Results

We surveyed the literature for experimental data on *n*-octane, *n*-nonane and *n*-decane with computer databases, including the NIST TRC Source [14], and DIPPR DIADDEM [15], as well as on-line search resources. In addition, several compilations of the thermal conductivity of these fluids exist in the literature. Touloukian et al. [16] provided recommended values for thermal conductivity for these three fluids; however they were based on extremely limited data. Vargaftik et al. [17,18] gave tables of recommended values for all three fluids. Vargaftik et al. [18] also gave a corresponding states correlation for the thermal conductivity of the dilute-gas for *n*-alkanes. Jamieson et al. [19] made a comprehensive data survey of liquid thermal conductivity to 1973, and Stephan et al. [20] surveyed data to 1981. We discuss each fluid individually below.

3.1. *n*-Octane

In order to obtain the coefficients for the thermal conductivity of the dilute-gas in the limit of zero density, Eq. (2), one can extrapolate the thermal conductivity at constant temperature to zero density. For reliable extrapolation it is necessary to have data over a reasonable range of density. However, only limited gas-phase data were found for *n*-octane, and it was not possible to obtain estimates in this manner. We

Table 1

Summary of experimental data and comparison of the correlation with primary and selected secondary experimental thermal conductivity data for *n*-octane

Ref.	Method	Uncertainty	Purity	<i>T</i> (K)	<i>P</i> (MPa)	No. Pts.	AAD (%)	Bias (%)	RMS, %	Maximum deviation (%)
[25]	CB			293–343	0.1	3	2.34	0.86	2.20	2.81
[26]	HW			223–373	0.1	16	1.80	−1.67	0.95	−2.50
[27]	THW	1	99	282–337	Sat.	21	3.30	−3.30	0.39	−3.87
[21] ^a	SC		99.8	294–378	0.0	6	2.18	−1.86	1.97	−4.90
[28]	HS	2	99.1	293–373	0.1	9	18.2	−18.2	2.67	−21.67
[29]	THW	5	99.81	272–386	Sat.	4	1.00	−1.00	0.66	−1.65
[30]	THW	2	99	298–348	0.1	5	1.90	−1.90	0.27	−2.24
[31]	HW			303	0.0	1	7.88	−7.88	0	−7.88
[32] ^{ab}	THW	0.3	99.9	307–362	7.3–591	75	0.46	−0.28	0.51	−1.34
[33]	THW	2		299–370	0.8	9	2.47	−2.47	1.58	−5.23
[22] ^{ab}	CB	2		418–678	0.1	29	1.12	1.06	0.91	3.08
[34]	HW	1.5		233–373	0.1	9	3.15	−2.91	2.02	−4.92
[35]	HW			304–383	0.1	11	4.18	−4.18	0.76	−5.30
[23] ^{ab}	CT	2		245–620	0.1–100	200	1.06	−0.17	1.33	−4.09
[36] ^b	CT	2		403–629	0.1–1	14	1.40	1.39	1.28	4.39
[37]	CT	1.5		293–333	0.1	3	7.50	−7.50	0.91	−8.61
[38]	THW	5		282–337	Sat.	24	2.69	−2.69	0.46	−3.47
[39]	THW	0.4	99.95	295–335	Sat.	8	1.33	−1.13	0.96	−2.24
[40]	PP	3	99.54	293–343	0.1	6	6.11	−6.11	2.29	−9.46
[41]	THW	0.8	99.81	272–386	Sat.	12	1.22	−1.22	0.62	−1.98
[42]	TC	4		303	Sat.	1	6.92	−6.92	0	−6.92
[43]	na			313	0.1	1	2.50	−2.50	0	−2.50
[44]	THW	2		303	0.1	1	0.72	−0.72	0	−0.72
[45]	THW	2		303	0.1	1	0.95	−0.95	0	−0.95
[46]	PP	1.5	99	311	0.1	1	7.17	−7.17	0	−7.17
[47]	CC			303–373	0.1	6	17.19	−17.19	2.46	−20.03
[48] ^b	THW	1	99	283–373	0.1–200	46	1.24	−1.06	1.08	−4.54
[49] ^b	CyC			273–633	0.1–49	162	11.66	−10.56	6.26	−31.16
[50]	THW	0.5		268–333	Sat.	41	0.30	−0.28	0.18	−0.80
[51] ^a	THW	0.5	98.0	258–335	Sat.	21	0.28	0.21	0.35	0.91

Method key: CB, cylindrical bicalorimeter; CC, concentric cylinder; CT, cylindrical tricalorimeter; CyC, cylindrical calorimeter; HS, hot strip; HW, hot wire; PP, parallel plate; SC, spherical cell; TC, thermal comparator; THW, transient hot wire.

^a Indicates data used in the regression.

^b Contained points with temperatures, densities and/or pressures exceeding the range of validity of the EOS.

therefore approximated the dilute-gas in the limit of zero density by fitting experimental data at pressures of 0.1 MPa or lower. Carmichael and Sage [21] measured gas-phase thermal conductivity of *n*-octane with a spherical cell, steady-state apparatus at six temperatures between 294 and 378 K, at 0.003 MPa. Mustafaev [22] obtained gas-phase thermal conductivity at one atmosphere over a higher temperature range, 418–678 K in a cylindrical bicalorimeter. Naziev [23] included some measurements in the gas-phase at atmospheric pressure with his cylindrical tricalorimeter apparatus. These three sets were selected as the basis to obtain the parameters for Eq. (2). In addition, we supplemented the data with estimates of the zero-density thermal conductivity obtained from a corresponding states method [24]. We relied primar-

ily on the experimental data discussed above, and only used two points from the extended corresponding states method, in order to stabilize the behavior of the correlation at very low and very high temperatures where experimental data is unavailable, so that the correlation is not overly influenced by the estimated points. A summary of all experimental data for *n*-octane is given in Table 1, along with the experimental method used, estimated uncertainty and the sample purity, when known. Table 2 gives the coefficients obtained from regression of data for the dilute-gas thermal conductivity, Eq. (2).

The data situation for the liquid-phase thermal conductivity of *n*-octane is much better than that for the vapor phase, as the many entries in the summary in Table 1 demonstrate.

Table 2

Parameters used in the representation of the dilute-gas thermal conductivity, Eq. (2)

	<i>n</i> -Octane	<i>n</i> -Nonane	<i>n</i> -Decane
a_0	$7.7293 \times 10^{-3} \pm 1.1 \times 10^{-3}$	$8.7877 \times 10^{-3} \pm 3.1 \times 10^{-3}$	$1.05542680 \times 10^{-2} \pm 1.5 \times 10^{-3}$
a_1	$-3.7114 \times 10^{-2} \pm 3.7 \times 10^{-3}$	$-4.1351 \times 10^{-2} \pm 9.1 \times 10^{-3}$	$-5.14530090 \times 10^{-2} \pm 5.2 \times 10^{-3}$
a_2	$9.7758 \times 10^{-2} \pm 3.7 \times 10^{-3}$	$1.0479 \times 10^{-1} \pm 8.5 \times 10^{-3}$	$1.18978971 \times 10^{-1} \pm 5.6 \times 10^{-3}$
a_3	$-2.8871 \times 10^{-2} \pm 1.2 \times 10^{-3}$	$-3.2003 \times 10^{-2} \pm 2.6 \times 10^{-3}$	$-3.72442104 \times 10^{-2} \pm 1.8 \times 10^{-3}$

However, many of these data sets are quite old and did not account adequately for convection in their analysis, and thus their measurements tend to give values that are higher than the actual thermal conductivity. In general, selection as a primary data set involved consideration of sample purity, the authors' estimate of uncertainty (when given), discrepancies with other sets of data, and the experimental procedure used, with preference given to data covering a wide range of conditions. For the saturated liquid phase, we selected the data of Watanabe and Seong [51] that were obtained with a transient hot-wire apparatus and has an estimated uncertainty of 0.5%, and cover the temperature range 258–335 K. For the pressure dependence, we selected the set of Li et al. [32] that extends to 591 MPa over 307–362 K and was measured with a transient hot-wire apparatus. A final data set included in the primary data are the data of Naziev [23] who made wide-ranging measurements from 245 to 629 K at pressures from 0.1–100 MPa with a cylindrical tricalorimeter, and reports an uncertainty of 2%.

In order to obtain the parameters for the residual contribution, the dilute-gas coefficients in Eq. (2) were fixed at the values given in Table 2, and the fitting program ODRPACK [52] was used to fit the primary experimental data to determine the coefficients in Eqs. (3)–(7). We used the critical point consistent with the equation of state of Span [7]; $T_c = 569.32$ K, $P_c = 2.497$ MPa, and $\rho_c = 234.9$ kg/m³. The coefficients obtained from the regression are given in Table 3, and Table 1 gives the average absolute deviation, bias, root-mean-square, and maximum deviations of the correlation from the experimental data. In the tables, we use the following definitions: average absolute deviation $AAD = 100 \sum |(\lambda_i^{\text{calc}}/\lambda_i^{\text{exp}} - 1)|/n$, bias $= 100 \sum (\lambda_i^{\text{calc}}/\lambda_i^{\text{exp}} - 1)/n$, and root-mean-square deviation $RMS^2 = 100 \sum (\lambda_i^{\text{calc}}/\lambda_i^{\text{exp}} - 1)^2/n - \text{bias}^2$, where each summation ranges from $i = 1$ to n . Some of the data points exceeded the limits of the EOS; their results are still presented in Table 1, but we recommend the use of caution when extrapolating outside of the limits of the EOS. Along the saturation boundary, the estimated uncertainty of the correlation, at a 95% confidence level, is 3%, reflecting the level of consistency between the literature values. In the dense liquid, we estimate the correlation also has an uncertainty of approximately 3%. In the vapor region, the uncertainties are larger; we estimate 5%.

Fig. 1a illustrates the deviations of the present correlation from selected experimental data, as a function of density, while Fig. 1b shows the deviations as a function of temperature. There is generally agreement of $\pm 3\%$ between the 16 data sets shown in these figures even though the correlation is based only on the first five data sets. There are limited supercritical data available from Mustafaev [22] and Naziev [23,36] with a significant data gap at densities from 0.4 to 3 mol/L. These wide-range data sets [22,23,36] were made with steady-state techniques and agree well with the recent transient hot-wire measurements at more moderate temperatures. It is apparent in both figures that the

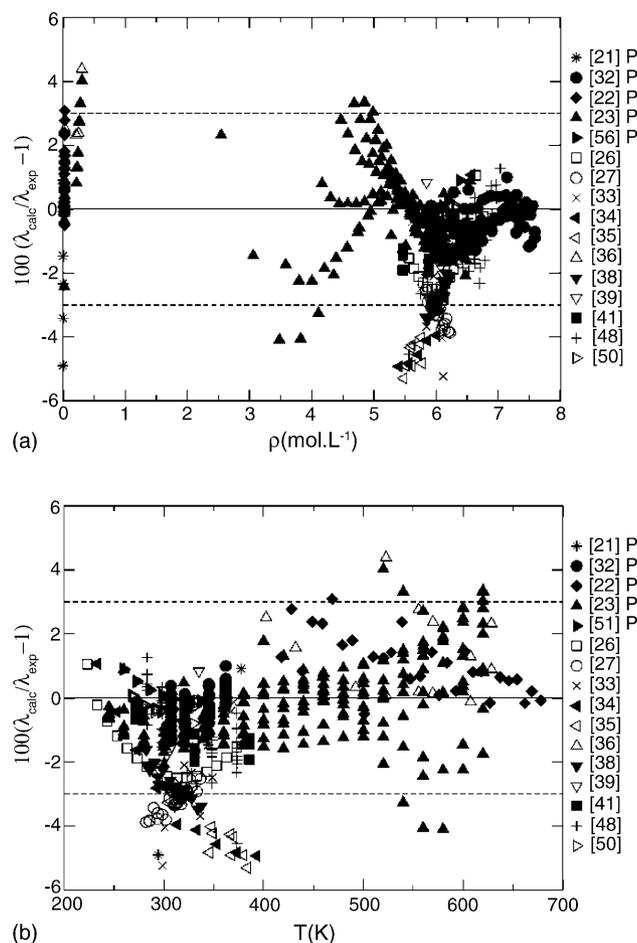


Fig. 1. Deviations of the correlation for thermal conductivity as a function of (a) density and (b) temperature from primary and selected secondary experimental data for *n*-octane.

temperature and density dependencies of measurements by various researchers differ from each other and the correlation near 320 K. The most dramatic examples are the data sets of Mukhamedzyanov et al. [34,35] and Nieto de Castro et al. [38,39] compared to the data sets of Brykov and Mukhamedzyanov [26], Calado et al. [27], and Mallan et al. [33]. It is noted that the primary dilute vapor data of Carmichael and Sage [21] have a temperature dependence that differs from that of the correlation, with a maximum deviation of 4.9%.

Finally, a sample point for validating computer calculations is $T = 300$ K, $\rho = 6.1772$ mol/L, and $\lambda = 128.36$ mW/(m K). This point corresponds to a pressure of 10 MPa, and the viscosity at this state point is 553.60 $\mu\text{Pa s}$ [13]

3.2. *n*-Nonane

Two sets of gas-phase thermal conductivity data were found for *n*-nonane. Katz and Luchsinger [53] measured the thermal conductivity with a thick hot-wire cell from 320–359 K, while Mustafaev [54] made more comprehen-

Table 3
Parameters for the residual thermal conductivity contribution, Eqs. (3)–(7)

i	j	B_{ij} <i>n</i> -Octane	B_{ij} <i>n</i> -Nonane	B_{ij} <i>n</i> -Decane
1	1	$0.285553 \times 10^{-1} \pm 2.1 \times 10^{-3}$	$4.90087596 \times 10^{-3} \pm 2.0 \times 10^{-3}$	$-2.94394112 \times 10^{-2} \pm 5.3 \times 10^{-3}$
1	2	$-0.926155 \times 10^{-2} \pm 8.5 \times 10^{-4}$	$9.96486280 \times 10^{-3} \pm 5.0 \times 10^{-4}$	$1.50509474 \times 10^{-2} \pm 2.8 \times 10^{-3}$
2	1	$-0.171398 \times 10^{-1} \pm 1.1 \times 10^{-3}$	$-8.07305471 \times 10^{-3} \pm 1.2 \times 10^{-3}$	$4.99245356 \times 10^{-2} \pm 4.1 \times 10^{-3}$
2	2	0	0	0
3	1	$0.659971 \times 10^{-2} \pm 1.4 \times 10^{-4}$	$5.57430614 \times 10^{-3} \pm 1.8 \times 10^{-4}$	$-1.42700394 \times 10^{-2} \pm 1.2 \times 10^{-3}$
3	2	$0.153496 \times 10^{-2} \pm 9.8 \times 10^{-5}$	0	$-1.38857133 \times 10^{-2} \pm 1.1 \times 10^{-3}$
4	1	0	0	$1.50827597 \times 10^{-3} \pm 1.7 \times 10^{-4}$
4	2	0	0	$4.33326339 \times 10^{-3} \pm 2.8 \times 10^{-4}$
q_D	m^{-1}	$0.145713 \times 10^{10} \pm 1.1 \times 10^8$	$9.58722814 \times 10^8 \pm 9.1 \times 10^7$	$1.41115586 \times 10^9 \pm 4.8 \times 10^8$

sive measurements at atmospheric pressure with a cylindrical bicalorimeter for the temperature range 449–678 K. We supplemented these data with predicted values based on an extended corresponding states method [24] and obtained the coefficients presented in Table 2 for the dilute-gas thermal conductivity.

For the liquid phase along the saturation boundary, we selected the measurements of Watanabe and Seong [51] to be a primary data set. These measurements were made with a transient hot-wire apparatus with an estimated uncertainty of 0.5% over the temperature range 259–337 K. In addition, the atmospheric pressure, liquid-phase measurements of Brykov and Mukhamedzyanov [26], and the high pressure measurements of Menashe and Wakeham [55] were also selected as primary data. Menashe and Wakeham [55] used a transient hot-wire apparatus with estimated uncertainty of 0.7% to measure the thermal conductivity of *n*-nonane at pressures up to 503 MPa, but did not measure the saturation boundary. Mukhamedzyanov et al. [56] also measured the thermal conductivity of nonane as a function of temperature and pressure; however their pressure dependence is different from that of Menashe and Wakeham [55]. The data of Menashe and Wakeham [55] included a rigorous analysis of the influence of thermal radiation on their measurements and exhibit less scatter than the measurements of Mukhamedzyanov et al. [56] so we have opted to use the Menashe and Wakeham [55] data as the primary set for this region.

We fixed the dilute-gas coefficients in Eq. (2) at the values given in Table 2, and regressed the primary data with the fitting program ODRPACK [52] to determine the coefficients in Eqs. (3)–(7). We used the critical point consistent with the equation of state of Lemmon and Span [8]; $T_c = 594.55$ K, $P_c = 2.281$ MPa, and $\rho_c = 232.14$ kg/m³. The coefficients obtained from the regression are given in Table 3, and Table 4 gives the average absolute deviation, bias, root-mean-square, and maximum deviations of the correlation from the experimental data.

Along the saturation boundary, the estimated uncertainty of the correlation, at a 95% confidence level, is 3%, reflecting the level of consistency between the literature values. In the dense liquid, we also estimate the correlation has an

uncertainty of approximately 3%. In the vapor region, the uncertainties are larger; we estimate 5%.

Fig. 2a illustrates the deviations of the present correlation from selected experimental data, as a function of density, while Fig. 2b shows the deviations as a function of temperature. There is generally agreement of $\pm 3\%$ among the nine

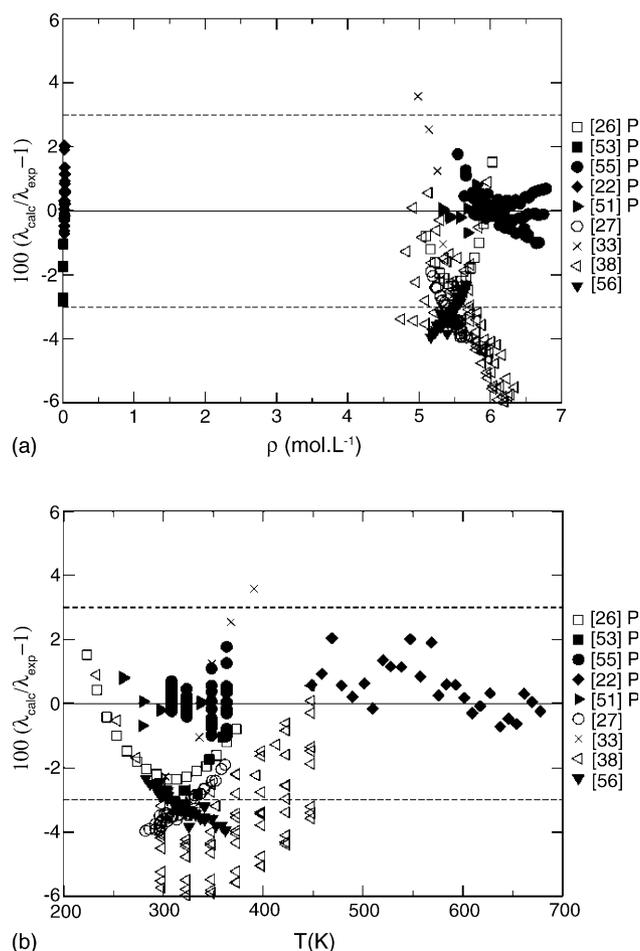


Fig. 2. (a) Deviations of the correlation for thermal conductivity as a function of density from primary and selected secondary experimental data for *n*-nonane. (b) Deviations of the correlation for thermal conductivity as a function of temperature from primary and selected secondary experimental data for *n*-nonane.

Table 4

Summary of experimental data and comparison of the correlation with primary and selected secondary experimental thermal conductivity data for *n*-nonane

Ref.	Method	Uncertainty	Purity	<i>T</i> (K)	<i>P</i> (MPa)	No. Pts.	AAD (%)	Bias (%)	RMS (%)	Maximum deviation (%)
[57]	SB	2.5		289–352	0.1–15	14	3.09	–3.09	1.23	–4.97
[25]	B			293–323	0.1	2	6.21	6.21	2.76	8.97
[26] ^a	HW			223–373	0.1	16	1.60	–1.35	1.06	–2.36
[27]	THW	1	99	282–362	Sat.	33	3.27	–3.27	0.55	–3.96
[58]	TO	10		293	0.1	1	3.24	–3.24	0	–3.24
[28]	HS	2	99.2	293–373	0.1	9	16.28	–16.28	1.77	–18.77
[59]	HW	2		336	Sat.	2	1.36	–1.36	0.52	–1.89
[53] ^a	HW	3		320–359	0–0.01	4	2.08	–2.08	0.73	–2.82
[33]	THW	2		302–391	0.8	5	2.14	0.81	2.18	3.58
[55] ^a	THW	0.7	99.9	308–363	35–503	64	0.39	0.03	0.52	1.77
[56]	THW	2	99.29	298–448	0.1–221	69	3.59	–3.59	1.52	–5.97
[34]	HW	1.5		233–413	0.1	10	2.16	–1.98	1.28	–3.28
[22] ^{ab}	CB	2		449–678	0.1	26	0.70	0.50	0.75	2.04
[38]	THW	5		282–362	Sat.	39	3.15	–3.15	0.42	–3.95
[40]	PP	3	99.44	293–343	0.1	6	7.07	–7.07	1.56	–9.35
[42]	TC	4		303	0.1	1	7.24	–7.24	0	–7.24
[46]	PP	1.5	99	311	0.1	1	8.37	–8.37	0	–8.37
[47]	CC		90	303–373	0.1	6	15.39	–15.39	2.67	–19.31
[51] ^a	THW	0.5	98.0	259–337	Sat.	15	0.30	0.05	0.42	0.83

Method key: B, bicalorimeter; CB, cylindrical bicalorimeter; CC, concentric cylinder; HS, hot strip; HW, hot wire; PP, parallel plate; SB, spherical bicalorimeter; TC, thermal comparator; THW, transient hot wire; TO, temperature oscill.

^a Indicates data used in the regression.

^b Contained points with temperatures, densities and/or pressures exceeding the range of validity of the EOS.

data sets shown in these figures even though the correlation is based only on the first five data sets. The vapor phase data of Katz et al. [53] and Mustafaev [22] agree with each other and the correlation to within 3%. The data of Mustafaev [22] are the only source for thermal conductivity at high temper-

atures and this is only for vapor at pressures of 1 bar. There are no liquid or high-density gas data available at temperatures above 460 K. As for *n*-octane, it is apparent in both figures that the temperature and density dependence of measurements by various researchers differ from each other and

Table 5

Summary of experimental data and comparison of the correlation with primary and selected secondary experimental thermal conductivity data for *n*-decane

Ref.	Method	Uncertainty	Purity	<i>T</i> (K)	<i>P</i> (MPa)	No. Pts.	AAD (%)	Bias (%)	RMS (%)	Maximum deviation (%)
[25]	B			293–343	0.1	3	6.38	6.38	4.00	12.03
[63]	THW	0.5	99.0	300–370	0.1	13	2.71	–2.71	0.13	–2.97
[64]	CC			293	0.1	1	8.06	–8.06	0	–8.06
[26]	HW	2		243–333	0.1	10	1.97	–1.97	0.28	–2.22
[60]	CS	2	99.5	278–444	0–34.5	60	8.11	7.47	4.77	–19.47
[28]	HS	2	99.0	293–373	0.1	9	16.04	–16.04	1.39	–17.89
[59]	HW	2		336	Sat.	2	1.04	–0.23	1.04	1.27
[30]	THW	2	99	303–373	0.1	7	0.95	–0.65	0.87	–1.70
[33]	THW	2		302–394	0.8	23	2.31	–2.31	0.99	3.98
[65] ^a	CB	2		469–678	0.1	24	0.82	–0.59	0.88	–2.69
[62] ^a	CB	2		308–678	1–400	191	0.72	0.08	0.87	–2.34
[34]	HW	2		253–433	0.1	10	3.80	–3.80	0.77	–4.56
[35]	HW			305–425	0.1	10	4.25	–4.25	0.49	–4.85
[66]	CB	2		313–593	0.1–14	105	7.50	–7.24	2.79	–9.46
[39]	THW	0.4	99.95	293–333	Sat.	8	1.15	–1.15	0.23	–1.60
[40]	PP	3	99.95	293–343	0.1	8	6.93	–6.93	1.39	–9.23
[42]	TC	4		303	0.1	1	6.12	–6.12	0	–6.12
[61] ^a	HW	1.3		303–458	0.1–49	58	1.94	1.94	0.50	3.06
[46]	PP	1.5		311	0.1	1	5.25	–5.25	0	–5.25
[47]	CC			303–373	0.1	6	13.28	–13.28	3.55	–19.15
[48] ^a	THW	1	99	283–373	0.1–200	90	0.82	–0.59	0.78	–2.32
[51] ^a	THW	0.5	99.0	259–338	Sat.	15	0.11	–0.02	0.12	0.20

Method key: B, bicalorimeter; CB, cylindrical bicalorimeter; CC, concentric cylinder; CS, concentric sphere; HS, hot strip; HW, hot wire; PP, parallel plate; TC, thermal comparator; THW, transient hot wire.

^a Indicates data used in the regression.

from the correlation near 320 K. The most dramatic examples are the data sets of Nieto de Castro et al. [38] compared to the data sets of Calado et al. [27] and Mallan et al. [33]. However, for *n*-nonane there is a clear maximum in the absolute deviations (with slope change in terms of both temperature and density) for the data of Mukhamedzyanov et al. [56] and Brykov and Mukhamedzyanov [26] at these conditions.

Finally, a sample point for validating computer calculations is $T = 300$ K, $\rho = 5.6194$ mol/L, and $\lambda = 130.31$ mW/(m K). This point corresponds to a pressure of 10 MPa, and the viscosity at this state point is 709.84 μ Pa s [13].

3.3. *n*-Decane

Mustafaev [54] measured the gas-phase thermal conductivity of *n*-decane at atmospheric pressure with a cylindrical bicalorimeter for the temperature range 469–678 K, with a reported uncertainty of 2%. These measurements were used as the primary data for the gas-phase. Carmichael and Sage [60] gave one point that is not consistent with the measurements of Mustafaev [54], and thus was not included in the primary data set. We supplemented the data of Mustafaev [54] with predicted values based on an extended corresponding states method [24] and obtained the coefficients presented in Table 2 for the dilute-gas thermal conductivity.

For the liquid phase along the saturation boundary, we selected the measurements of Watanabe and Seong [51] to be a primary data set. These measurements were made with a transient hot-wire apparatus with an estimated uncertainty of 0.5% over the temperature range 259–338 K. In addition, the high pressure measurements of Tanaka et al. [48] and Rastorguev et al. [61] were both included in the primary data set. Tanaka et al. [48] used a transient hot-wire apparatus with estimated uncertainty of 1% to measure the thermal conductivity of *n*-decane at pressures up to 200 MPa, while Rastorguev et al. [61] used a hot wire method and obtained thermal conductivities from 303–458 K at pressures to 49 MPa. For high temperatures, we also included the measurements of Mustafaev [62] in the primary set; these were obtained from 308 to 678 K at pressures to 400 MPa.

We fixed the dilute-gas coefficients in Eq. (2) at the values given in Table 2, and regressed the primary data with the fitting program ODRPACK [52] to determine the coefficients in Eqs. (3)–(7). We used the critical point consistent with the equation of state of Lemmon and Span [8]; $T_c = 617.7$ K, $P_c = 2.103$ MPa, and $\rho_c = 233.34$ kg/m³. The coefficients obtained from the regression are given in Table 3, and Table 5 gives the average absolute deviation, bias, root-mean-square, and maximum deviations of the correlation from the experimental data.

Along the saturation boundary, the estimated uncertainty of the correlation, at a 95% confidence level, is 3%, reflecting the level of consistency between the literature values. In the dense liquid to 200 MPa, we also estimate the correlation has

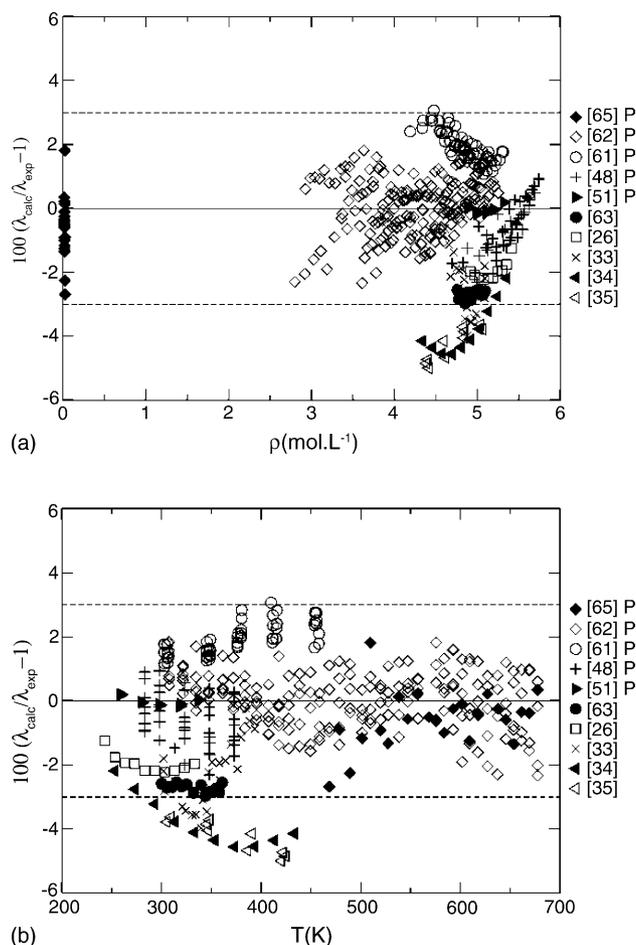


Fig. 3. (a) Deviations of the correlation for thermal conductivity as a function of density from primary and selected secondary experimental data for *n*-decane. (b) Deviations of the correlation for thermal conductivity as a function of temperature from primary and selected secondary experimental data for *n*-decane.

an uncertainty of approximately 3%. In the vapor region, the uncertainties are larger; we estimate 5%.

Fig. 3a illustrates the deviations of the present correlation from selected experimental data, as a function of density, while Fig. 3b shows the deviations as a function of temperature. There is generally agreement of $\pm 3\%$ between the 10 data sets shown in these figures even though the correlation is based only on the first five data sets. There are three data sets at high temperatures and densities from Mustafaev [62,65] and Naziev and Aliev [66]. Unfortunately, the deviations of Naziev and Aliev [66] range from -4 to -9.46% in the liquid phase, and so they could not be shown on these figures without expanding the deviation scale significantly. Similarly, since the deviations of Carmichael et al. [60] range from 3 to 13.3% in the liquid phase, they are not shown in the figures. There are limited supercritical data available from Mustafaev [62,65], with a significant data gap at densities from 0.1 to 3 mol/L. These wide-range data sets [62,65] were made with a steady-state technique and agree well with the recent transient hot-wire measurements at more moderate temperatures. There is

also the characteristic change in slope of the deviations with respect to temperature and density for some data sets, such as those of Brykov and Mukhamedzyanov [26] and Mallan et al. [33], in the liquid phase from 300 to 320 K. This is not as distinct as it was for *n*-octane and *n*-nonane but still seems to be present.

Finally, a sample point for validating computer calculations is $T=300$ K, $\rho=5.1504$ mol/L, and $\lambda=132.80$ mW/(mK). This point corresponds to a pressure of 10 MPa, and the viscosity at this state point is 926.37 μ Pa s [13].

4. Conclusions

We have presented correlations for the thermal conductivity surfaces of *n*-octane, *n*-nonane and *n*-decane that are applicable from the dilute-gas to the dense-fluid region, from the freezing point up to the limit of the respective equations of state. There are limited thermal conductivity data on the compressed liquid at temperatures below 300 K. In all cases, there are no data available in the critical region, and there is a shortage of reliable data at high temperatures for a range of densities centered about the critical density. The octane thermal conductivity surface has an uncertainty of 3% (based on a coverage factor of two) along the liquid saturation boundary and in the liquid phase, based on consistency between the literature values. The thermal conductivity in the vapor and supercritical regions is estimated to have an uncertainty of 5%. The correlation for the thermal conductivity of *n*-nonane has an uncertainty of 3% for the vapor and dense liquid and 5% in the supercritical regions. Finally the correlation for the thermal conductivity of *n*-decane has an estimated uncertainty of 3% in the liquid phase to 200 MPa, and 5% for the vapor and supercritical regions.

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