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An Improved Empirical Correlation for the Thermal Conductivity of Propane

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New experimental data on the thermal conductivity of propane have been reported since the wide-range correlations proposed by Holland et al. and by Younglove and Ely. These new experimental data, covering a temperature range of 110 to 700 K and a pressure range of 0.1 to 70 MPa, are used together with the previously available data to develop an improved empirical equation for the thermal conductivity of gaseous and liquid propane. The quality of the new data is such that the thermal-conductivity correlation for propane is estimated to have an uncertainty of about ±5% at a 95% confidence level, with the exception of state points near the critical point, where the uncertainty of the correlation increases to ±10%.

KEY WORDS: empirical correlation; *n*-alkane; propane; thermal conductivity; transport properties.

1. INTRODUCTION

Accurate thermophysical property data are required for industrially important fluids such as propane, to allow design of efficient chemical processes and equipment. The high uncertainty associated with existing theoretical predictions for the transport properties has motivated efforts to develop empirical correlations to represent the transport properties as functions of temperature and pressure (or density). These correlations must be based on accurate experimental data that cover the entire fluid region of interest. An international effort has been coordinated by the IUPAC Subcommittee on

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Transport Properties to develop accurate correlations for such fluids. These correlations require a careful selection of the best available experimental data, based on a critical analysis of the measurement techniques and comparisons with other reliable data. New experimental data on the thermal conductivity of propane have been reported since the wide-range correlations proposed by Holland et al. [1] in 1979 and Younglove and Ely [2] in 1987. The present work describes an improved empirical correlation for the thermal conductivity of propane incorporating these new data.

Although desirable, a complete theoretical analysis of the available experimental data for the thermal conductivity of propane in the limit of zero density and in the critical region cannot yet be performed. The thermal conductivity of polyatomic molecules is strongly influenced by inelastic collisions and the exchange of energy between translational and the internal modes (rotation, vibration, electronic) during collisions. The propane molecule is characterized by a significant number of excited degrees of freedom, including hindered rotations. Thus, the kinetic theory for the thermal conductivity in the dilute-gas phase of polyatomic molecules is still approximate and the calculations are heuristic [3]. In the critical region, the absence of a crossover equation of state for propane does not allow an adequate theoretically based description of the thermal conductivity enhancement, and thus, an empirical formulation was considered in this work.

Two wide-range empirical correlations for the thermal conductivity of propane have been published based on a comprehensive analysis of the data available to the authors. In 1979, Holland et al. [1] reported a correlation for propane at temperatures from 140 to 500 K and at pressures up to 50 MPa, which has an estimated uncertainty of 8% outside the critical region and 15% near the critical point. In 1987, Younglove and Ely [2] reported a correlation for propane at temperatures from 86 to 600 K and at pressures up to 100 MPa that has an estimated uncertainty of 5% outside the critical region and an uncertainty of 10% near the critical point. New experimental data with high accuracy, which cover a wide range of temperature and pressure, with improved coverage of the critical region where almost no data existed, motivated the development of this improved correlation. It is shown that systematic deviations between thermal-conductivity data and these two correlations [1, 2] can be significantly reduced in the critical region.

2. METHOD

The thermal conductivity is represented as the sum of three contributions,

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

where λ_0 is the dilute-gas thermal conductivity, which is dependent only on the temperature, $\Delta\lambda_e$ is the excess thermal conductivity, and $\Delta\lambda_c$ is the thermal-conductivity enhancement in the critical region. $\Delta\lambda_e$ and $\Delta\lambda_c$ depend on both density and temperature. This representation is useful since it allows the theoretically based analysis of each contribution to be considered separately. This is particularly useful when the dilute-gas thermal conductivity and the thermal-conductivity enhancement in the critical region are examined.

To analyze the thermal conductivity in terms of density and temperature, the density of the fluid must be determined from the temperatures and pressures reported by each author. The modified Benedict–Webb–Rubin (MBWR) equation of state of Younglove and Ely [2] was used. This equation of state is valid at pressures up to 100 MPa and at temperatures between the triple point and 600 K. With the exception of the more recent results of Yata et al. [4], all experimental data and the equation of state were reported prior to 1990, when the ITS-90 temperature scale was adopted. Therefore, the reported temperatures were converted to this scale according to the recommendations of IUPAC [5] and all calculations are based on the ITS-90 temperature scale. All densities are in $\mathrm{mol \cdot L^{-1}}$, temperatures are in K, and stated uncertainties are at the 95% (2σ) confidence level.

The available experimental data were initially grouped into categories of primary and secondary data according to the criteria described by Nieto de Castro et al. [6]. However, this requirement of absolute measurements with uncertainties less than 2% would have excluded all the data prior to 1982 except for one gas point and relied on only four remaining sets of data, thus confining the present correlation to a very limited range of temperature and pressure. Measurements of thermal conductivity made with relative instruments (calibrated through measurements with one or more reference fluids) have often been unreliable and have additional uncertainties that are poorly characterized. Consequently, it was decided to exclude all the relative measurements and to include absolute results with uncertainties of up to ±5% that are consistent with other data sets with lower uncertainties. A summary of the primary data for propane [4, 7–18], together with the ranges in temperature and pressure, the experimental technique, and the assigned uncertainty, is provided in Table I.

3. CORRELATION PROCEDURES AND RESULTS

3.1. Zero-Density Limit

The zero-density or dilute-gas limit is determined from the extrapolation of a particular transport property in terms of density, held at constant

Table I. Primary Experimental Data for the Thermal Conductivity of Propane

Reference(s)	Temperature range (K)/ pressure range (MPa)	Technique[a]	Number of points	Estimated uncertainty (%)
Mann and Dickins [7]	275–285 ~0.1	SSHW	6	5
Leng and Comings [8]	323–413 0.1–30	CC	83	5
Smith et al. [9]	323–423 0.1	CC	3	5
Carmichael et al. [10]	277–444 0.1–35	SC	33	5
Brykov and Mukhamedzyanov [11]	93–223 0.1	SSHW	14	5
Clifford et al. [12]	303 0.1	THW	1	1
Aggarwal and Springer [13]	400–725 0.1–0.6	CC	41	3
Roder and Nieto de Castro [14, 15]	110–300 1–70	THW	400	1.5
Zheng et al. [16]	323.75 0.1–1	CC	6	3
Tufeu and Le Neindre [17]	298–578 1–70	CC	175	2
Prasad et al. [18]	192–320 0.2–70	THW	128	1.5
Yata et al. [4]	254–315 1–30	THW	16	1

[a] SSHW, steady-state hot wire; THW, transient hot wire; CC, concentric cylinders; SC, spherical cell.

temperature, to zero density [3]. Consequently, dilute-gas transport properties cannot be directly measured. Reliable extrapolation of low-density vapor data requires that the data span a reasonable range of density. This is not possible at the lowest temperatures, where the vapor pressure of propane is of the order of a bar and there is an insufficient density range covered to allow extrapolation to zero density. For these cases, thermal conductivity data near atmospheric pressure are used along with the extrapolated, dilute-gas values. Table II summarizes the primary data used for correlating the zero-density thermal conductivity. The data sets that allow extrapolation are designated in Table II. Systematic errors in the correlated dilute-gas

Table II. Primary Experimental Data for the Thermal Conductivity of Propane in the Dilute-Gas Phase

Reference	Temperature range (K)	Technique[a]	Number of points	Estimated uncertainty (%)
Mann and Dickins [7]	275–285	SSHW	6	5
Leng and Comings [8][b]	323–413	CC	5	5
Smith et al. [9]	323–423	CC	3	5
Carmichael et al. [10]	277–444	SC	6	5
Clifford et al. [12]	303	THW	1	5
Aggarwal and Springer [13][b]	400–725	CC	8	3
Zheng et al. [16][b]	323.75	CC	1	3
Tufeu and Le Neindre [17][b]	298–578	CC	5	2

[a] SSHW, steady-state hot wire; THW, transient hot wire; CC, concentric cylinders; SC, spherical cell.

[b] Extrapolated to zero density.

thermal conductivity due to the inclusion of the data at atmospheric pressure (not extrapolated to zero density) are less than the uncertainty of the data sets.

The experimental thermal conductivity data were correlated with a quadratic polynomial in temperature:

$$\lambda_0(T) + A_1 + A_2 T + A_3 T^2 \tag{2}$$

where λ_0 is the dilute-gas thermal conductivity in $\mathrm{W \cdot m^{-1} \cdot K^{-1}}$ and T is the absolute temperature in K. Weighted-least-squares analysis was used to fit this equation with the weight factors reflecting the uncertainty of the data given in Table II.

Table III contains the coefficients A_i together with the standard deviations. The maximum deviation of the primary experimental data is 4%. The deviations of the primary data from the correlation are presented in Fig. 1, where it is clearly shown that, except for the lower-temperature data point of Smith et al. [9] and the highest-temperature data point of Tufeu

Table III. Coefficients for the Representation of the Thermal Conductivity of Propane in the Limit of Zero Density, Eq. (2)

A_1	$-1.25 \times 10^{-2} \pm 1.13 \times 10^{-3}$
A_2	$8.42 \times 10^{-5} \pm 5.56 \times 10^{-6}$
A_3	$6.02 \times 10^{-8} \pm 6.55 \times 10^{-9}$

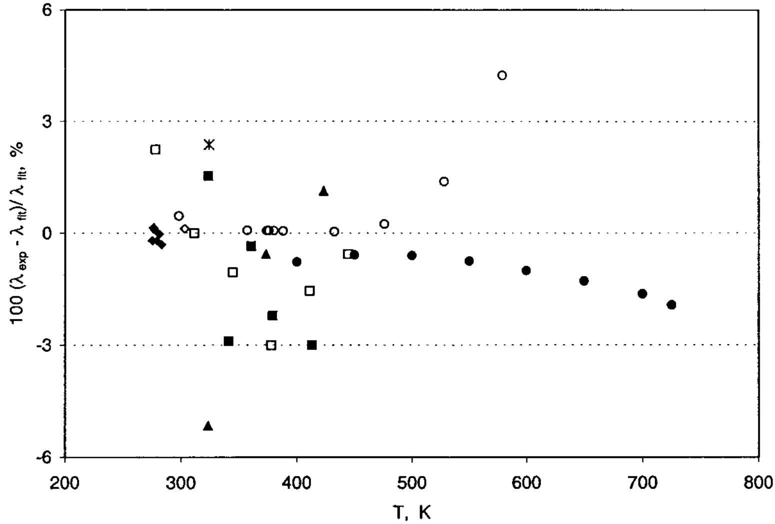

Fig. 1. Deviations of the primary experimental data for the dilute-gas phase of propane from Eq. (2); ◆, Mann and Dickins [7]; ■, Leng and Comings [8]; ▲, Smith et al. [9]; □, Carmichael et al. [10]; ◇, Clifford et al. [12]; ●, Aggarwal and Springer [13]; ∗, Zheng et al. [16]; ○, Tufeu and Le Neindre [17].

and Le Neindre [17], all of the data are reproduced within their assigned experimental uncertainties of ±2 to 5%.

3.2. Excess Thermal Conductivity and Critical Enhancement

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 non-singular background values far away from the critical point [19, 20]. The density-dependent terms for thermal conductivity can be grouped according to Eq. (3),

$$\lambda(\rho, T) = \bar{\lambda}(\rho, T) + \Delta\lambda_c(\rho, T) \tag{3}$$

where $\bar{\lambda}(\rho, T) = \lambda_0(T) + \Delta\lambda_e(\rho, T)$ is the background contribution.

To assess the critical enhancement either theoretically or empirically, we need to evaluate the background contribution, which is the sum of the dilute gas and excess thermal conductivity contributions. The procedure adopted during this analysis was somewhat different since the regression

Table IV. Coefficients for the Representation of the Excess Thermal Conductivity of Propane, Eq. (4)

	$i=1$	$i=2$	$i=3$	$i=4$
$j=0$	$9.60\times10^{-3}\pm1.81\times10^{-3}$	$-4.71\times10^{-4}\pm3.34\times10^{-4}$	$-2.41\times10^{-5}\pm2.94\times10^{-5}$	$5.89\times10^{-6}\pm8.74\times10^{-7}$
$j=1$	-6.33 ± 1.42	$8.18\times10^{-1}\pm1.98\times10^{-1}$	$-5.38\times10^{-2}\pm1.45\times10^{-2}$	$1.36\times10^{-3}\pm4.47\times10^{-4}$
$j=2$	$1.35\times10^{3}\pm2.72\times10^{2}$	$-9.91\times10^{1}\pm2.19\times10^{1}$	$6.94\times10^{-2}\pm2.13\times10^{-2}$	$6.94\times10^{-2}\pm2.13\times10^{-2}$

software, ODRPACK V. 2.01 [21], allows a fit of all the primary data simultaneously to the excess thermal conductivity and the critical enhancement, while maintaining the parameters already obtained from the fit of the dilute-gas thermal-conductivity data.

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

$$\Delta\lambda_{\mathrm{e}}(\rho, T) = \sum_{i=1}^{4} \sum_{j=0}^{2} \frac{B_{i,j}\rho^{i}}{T^{j}} \tag{4}$$

where the density is in $\mathrm{mol \cdot L^{-1}}$ and the coefficient $B_{3,2} = B_{4,2}$.

For engineering purposes, the critical enhancement is represented by the following empirical expression,

$$\Delta\lambda_{\mathrm{c}}(\rho, T) = \frac{C_1}{C_2 + \Delta T_{\mathrm{c}}^2} \exp[-(C_3\, \Delta\rho_{\mathrm{c}})^2] \tag{5}$$

where $\Delta T_{\mathrm{c}} = (T/T_{\mathrm{c}}) - 1$ and $\Delta\rho_{\mathrm{c}} = (\rho/\rho_{\mathrm{c}}) - 1$. This equation does not require accurate information on the compressibility and specific heat of the fluids in the critical region, as does the theory of Olchowy and Sengers [19, 20]. The critical point is defined according to Younglove and Ely [2], with $T_{\mathrm{c}} = 369.82$ K (369.85 K on IPTS-68) and $\rho_{\mathrm{c}} = 5.000\ \mathrm{mol \cdot L^{-1}}$ (220.3 $\mathrm{kg \cdot m^{-3}}$). Tables IV and V contain the coefficients for Eqs. (4) and (5) together with their standard deviations.

To be consistent with future developments in the study of the thermal conductivity of propane, the critical enhancement is calculated with the theoretically based crossover equations proposed by Olchowy and Sengers [19, 20] using the parameters B_{ij} obtained in the previous fit from Eq. (4). Figure 2 shows a plot of deviations of the experimental data from the surface correlation using this theory for the representation of the critical enhancement. It can be seen that, around the critical region and in spite of the lack of a crossover equation of state, the data are reproduced within ±10%, although a systematic trend is observed in that region. However, outside this region, and with the exception of the data of Leng and Comings [8], almost all data are represented within a band of ±5%.

Table V. Coefficients for the Representation of the Critical Enhancement of Propane, Eq. (5)

C_1	$2.84 \times 10^{-5} \pm 1.57 \times 10^{-6}$
C_2	$1.04 \times 10^{-3} \pm 6.19 \times 10^{-5}$
C_3	$-3.05 \pm 5.50 \times 10^{-2}$

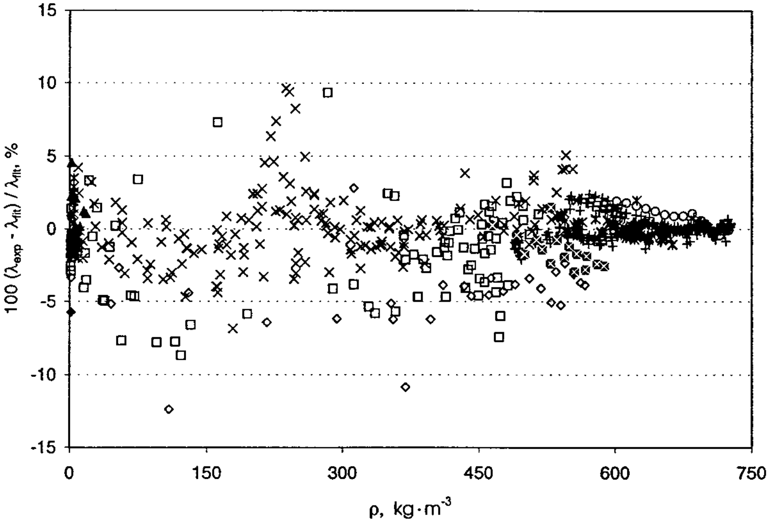

Fig. 2. Deviations of the primary experimental data for propane from the correlation of Eqs. (1)–(3), using the Olchowy and Sengers [19] theory for critical enhancement; ■, Mann and Dickins [7]; □, Leng and Comings [8]; ◆, Smith et al. [9]; ◇, Carmichael et al. [10]; ○, Brykov and Mukhamedzyanov [11]; ●, Clifford et al. [12]; △, Aggarwal and Springer [13]; +, Roder and Nieto de Castro [14, 15]; ▲, Zheng et al. [16]; ×, Tufeu and Le Neindre [17]; ∗, Prasad et al. [18]; ⊠, Yata et al. [4].

4. DISCUSSION

The thermal conductivity of propane, as given in Eq. (1), with the individual contributions given by Eqs. (2), (4), and (5), is valid in the temperature range from 192 to 725 K with densities up to 17 mol · L^{-1} (750 kg · m^{-3}) and pressures up to 70 MPa. The deviations of the primary data from the correlation are presented in Fig. 3, where it is clearly shown that, outside the critical region, almost all data are reproduced within ±5%. In Fig. 4, the deviations of the secondary data from the present correlation are shown. It can be seen that the deviations are in some cases larger than the experimental uncertainty claimed by the authors and are in some cases up to 100%.

An overall comparison between the deviations of the experimental data from this correlation and from the correlation of Ref. 2 is shown in Fig. 5. The differences between these correlations are small for densities below 1.7 mol · L^{-1} (75 kg · m^{-3}), that is, in the low-density region, and for densities higher than 7.9 mol · L^{-1} (350 kg · m^{-3}). However, near the critical density there are systematic deviations in the correlation of Ref. 2 that

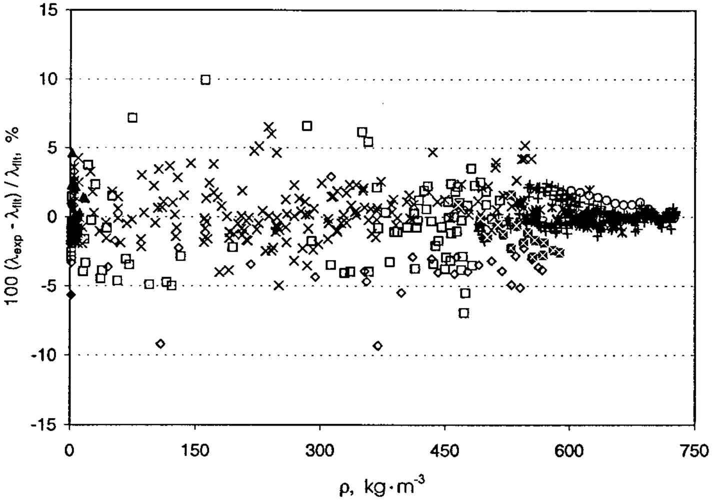

Fig. 3. Deviations of the primary experimental data for propane from the correlation of Eqs. (1)–(5); ■, Mann and Dickins [7]; □, Leng and Comings [8]; ◆, Smith et al. [9]; ◇, Carmichael et al. [10]; ○, Brykov and Mukhamedzyanov [11]; ●, Clifford et al. [12]; △, Aggarwal and Springer [13]; +, Roder and Nieto de Castro [14, 15]; ▲, Zheng et al. [16]; ×, Tufeu and Le Neindre [17]; $*$, Prasad et al. [18]; ⊠, Yata et al. [4].

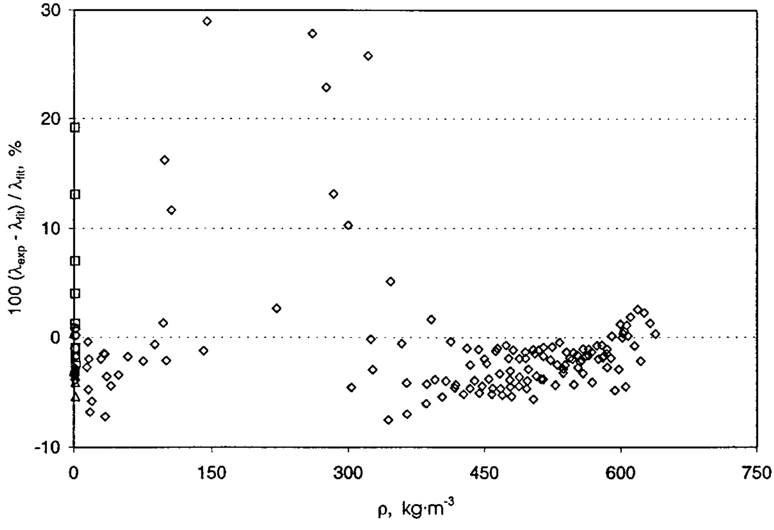

Fig. 4. Deviations of the secondary experimental data for propane from the correlation of Eqs. (1)–(5); ○, Vines and Bennett [22]; □, Senftleben [23]; ◇, Ryabtsev and Kazaryan [24]; △, Ehya et al. [25].

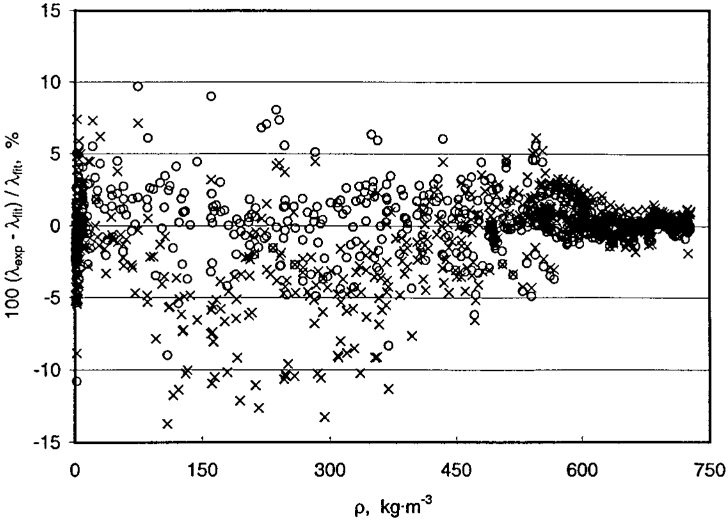

Fig. 5. Deviations of the primary experimental data for propane from (○) the present correlation of Eqs. (1)–(5) and (×) the correlation of Ref. 2.

are absent in the present correlation. The largest differences between the two correlations are found in the density range where more accurate data have become available and have been incorporated into the correlation presented here.

5. CONCLUSIONS

An improved empirical correlation for propane, valid in the temperature range from 192 to 725 K with densities to 17 mol · L^{-1} (750 kg · m^{-3}), has been presented. For temperatures higher than 600 K, this correlation must be used with caution, since the equation of state is valid only to 600 K and any extrapolation beyond this is subject to additional uncertainty. Nevertheless, the uncertainty of the calculated thermal-conductivity values at temperatures below 600 K is estimated to be $\pm 5\%$ when $\rho \leqslant 0.75\rho_c$ or $\rho \geqslant 1.25\rho_c$ and $\pm 10\%$ for densities from 0.75 to 1.25ρ_c.

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