The Thermal Conductivity of Propane

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This paper presents thermal conductivity measurements of propane over the temperature range of 192-320 K, at pressures to 70 MPa, and densities to 15 mol. L^{-1} , using a transient line-source instrument. The precision and reproducibility of the instrument are within ± 0.5 %. The measurements are estimated to be accurate to ± 1.5 %. A correlation of the present data, together with other available data in the range 110-580 K up to 70 MPa, including the anomalous critical region, is presented. This correlation of the over 800 data points is estimated to be accurate within $+ 7.5 \%$.

KEY WORDS: high pressure; propane; thermal conductivity.

1. INTRODUCTION

In this paper, absolute measurements of the thermal conductivity of propane are reported in the range of 193-300 K at pressures to 70 MPa. These data, together with those from other sources $\lceil 1-5 \rceil$ in the range 120-580 K at pressures to 70 MPa, including the anomalous critical region, are correlated within $+7.5\%$.

Previous work on the measurement and correlation of the thermal conductivity of propane include that reported in the temperature range 111-300 K [1, 2] and that reported by Tufeu and Le Neindre [3] in the range of 300-480 K. The maximum pressure in the above cases was limited to about 70 MPa.

Holland et al. $\lceil 6 \rceil$ present a correlation in the range of 140–500 K from 1 to 50 MPa. This correlation, however, has a large uncertainty, due

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primarily to the lack of reliable data available at the time it was made. The present work, therefore, permits comparison of the latest experimental measurements and provides a correlation of the data over a wider range of temperature than earlier studies.

The precision and reproducibility of the instrument used for the thermal conductivity measurement are estimated to be $+0.5\%$ and the measurements are estimated to be accurate within $+ 1.5\%$ [7].

2. EXPERIMENTAL

The investigation was carried out with a transient hot-wire instrument of the compensating type [7]. The calibration coefficients and length and diameter of the wires used are given in Table I. The principle of the measurement, as well as various components of the apparatus (e.g., the conductivity cell, the thermostat, the pressurizing system, the measurement

	(a) Calibration equation	
	$R = a_0 + a_1 T + a_2 T^2 + bP$ T (°C), P (MPa)	
	(b) Wire specification and calibration coefficients	
	Long wire	Short wire
Purity $(\%)$	99.999	99.999
Length (m)	$8.661E - 02$	$4.6816E - 02$
Diameter μ m)	12.7	12.7
a_0	68.39340	36.67749
a ₁	0.265132	0.142398
a ₂	$-3.95057E - 05$	$-2.021200E - 05$
b	$-1.22823E - 03$	$-6.62392E - 04$
	(c) Specification of the test fluid	
Test fluid	Propane	
Purity	99.99 % pure	
$T_{\scriptscriptstyle\rm TP}$	85.47 K	
T_{cr}	369.80 K	
P_{cr}	4.24204 MPa	
ρ_{cr}	4.96 mol \cdot L ⁻¹ (0.2187 g \cdot cm ⁻³)	
\overline{M}	44.097	

Table I. Calibration Coefficients and Specifications of the Wire and Test Fluid

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system, and the uncertainty in the results) are described in detail elsewhere $[7, 8]$.

A hot wire immersed vertically in the fluid, initially in thermal equilibrium, is subjected to a step voltage at $t = 0$. The transient temperature rise (AT_w) of the wire is obtained by the solution of Fourier's equation $[9]:$

$$
\Delta T = \frac{Q_1}{4\pi\lambda(\rho, T)} \ln \left[\frac{4\alpha t}{a^2 C} \right] \tag{1}
$$

$$
T_{\rm re} = T_0 + \frac{1}{2} [\Delta T(t_1) + \Delta T(t_2)] \tag{2}
$$

$$
\Delta T = \Delta T_{\rm w} + \sum \delta T_i \tag{3}
$$

where ΔT_w is the experimentally measured temperature rise of the hot wire.⁴ The corrections, δT_i , are described in detail elsewhere [9, 10].

A straight line is fitted to the $AT \sim \ln(t)$ data by linear regression over selected ranges of time. The thermal conductivity is calculated from the slope of this line and the applied power, using Eq. (1). The applied power, which decreases by up to 2% for a 5 K temperature rise of the hot wire, is determined from simultaneous measurements of the current and the outof-balance voltage across the wires. These measurements arc also used to evaluate the temperature rise of each wire.

Experimental runs obtained with low-pressure propane vapor show the expected linear $AT \sim ln(t)$ behavior at large times; at shorter times, the effect of thermal accommodation can be seen [11]. Results obtained with liquid propane are linear over the period 200-1000 ms.

3. RESULTS

The thermal conductivity of propane was measured along six isotherms at nominal temperatures of 193, 209, 220, 229, 252, and 261 K at pressures up to 70 MPa. In all, 129 measurements are reported covering the density range $0.01 < \rho < 15$ mol. L⁻¹.

In addition to the temperature $(T_0; K)$, pressure $(P; kPa)$, and thermal conductivity (λ ; mW \cdot m⁻¹ \cdot K ⁻¹), the fluid density (ρ ; mol \cdot L ⁻¹) is also tabulated in Table II. The density of propane was obtained from Ref. 12.

The accuracy of the present measurement can, in part, be inferred

⁴ Definitions of terms are given under Nomenclature, below.

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Table II. (Continued) Table **II.** *(Continued)*

Fig. 1. Deviation in measurements of the thermal conductivity of propane obtained with various power levels.

from measurements made over a range of power levels as shown in Fig. 1. These measurements can be adjusted to a mean reference value within a maximum variation of $+0.7\%$ and $+1.2\%$ for the liquid and vapor states, **respectively. There appears to be no systematic variation with power for both states. As shown later, the present measurements for liquid propane** are found to be within $+1.2\%$ of the available reliable overlapping data **[1, 2]. The accuracy of the present measurement is, therefore, estimated to** be better than $+1.5\%$.

The propane sample purity was certified to be 99.99 %. The ciritcal properties of propane were obtained from Ref. 12 and are listed in Table I.

4. COMPARISON OF THE PRESENT DATA

The measurements reported (Table II) for the liquid fall within the experimental range covered by Refs. 1 and 2. The measurements were, therefore, compared with the correlation used by them [6]. It is seen that the measurements on liquid propane are generally lower, but within 1% of the correlation (Fig. 2). At low densities, in the vapor state, the present measurements are about 4 to 6% lower. The dilute-gas correlation employed in Refs. 1 and 2, however, was that recommended by Holland et al. [6] and had an estimated uncertainty of about $\pm 8\%$. Figure 3 shows the deviation of the thermal conductivity at low densities ($\rho < 1.13$ mol \cdot L⁻¹) **reported here (Table II) as well as that for data reported by others [4, 5,**

Fig. 2. Deviation plot of present data from the correlation of Refs. 1 and 2 for the thermal conductivity of liquid propane.

Fig. 3. Deviation plot of present data from the correlation of Refs. 1, 2, and 6 for the thermal conductivity of low-density propane vapor.

13, 14] at similar densities. It is seen that all these measurements are consistently lower, by up to 8% , than those obtained with the correlation of Eq. (6), indicating the need for increased data and improved correlation in this region.

5. CORRELATION

5.1. General Correlation

A correlation of the present data together with those of others $\lceil 1-5 \rceil$ was attempted using the model suggested by Sengers et al. [15].

$$
\lambda(\rho, T) = \lambda_{\text{bg}}(\rho, T) + \Delta \lambda_{\text{cr}}(\rho, T) \tag{4}
$$

$$
\lambda_{\text{bg}}(\rho, T) = \lambda_0(T) + \varDelta \lambda_{\text{e}}(\rho, T) \tag{5}
$$

5.2. Thermal Conductivity for the Dilute Vapor

The available thermal conductivity data for propane in the lowdensity region are inconsistent as shown in Ref. 6 as well as Fig. 3. A new correlation for λ_0 based on our measurements was, therefore, not attempted and the expression recommended by Holland et al. [6] and employed by Roder and his co-worker [1, 2] was used:

$$
\lambda_0(T) = a_1 T^{-1} + a_2 T^{-2/3} + a_3 T^{-1/3} + a_4 + a_5 T^{1/3} + a_6 T^{2/3}
$$

+
$$
a_7 T + a_8 T^{4/3} + a_9 T^{5/3}
$$
 (6)

The empirical coefficients a_n (n=1 to 9) are given in Ref. 6 and Table III. Below 150 K the correlation is unreliable since both correlations severely diverge from the low temperature behavior expected of a lowdensity vapor theoretically and empirically.

5.3. The Excess Thermal Conductivity, $\Delta\lambda_e$

Measurements in the high-density region indicate an increase in the excess thermal conductivity, $\Delta\lambda_e$, with an increase in density along any isotherm. The data of Tufeu and Le Neindre [3] show the critical-point thermal conductivity enhancement along isotherms in the range 357-388 K. On the basis of preliminary analyses, measurements showing the anomalous critical-region increase and near the liquid-vapor saturation line were excluded for the correlation of the excess thermal conductivity, $\Delta\lambda_e$. In this low-density region ($\rho < 1$ mol \cdot L⁻¹), five data points from

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Ref. 4, two from Ref. 5, and one from Ref. 14, showing deviations greater than 10%, were also excluded.

The excess thermal conductivity, $\Delta\lambda_e$, was first correlated with density alone using the model:

$$
\Delta \lambda_e(\rho) = \sum_{n=0}^m b_n (\Delta \rho^*)^n \tag{7}
$$

Regression analysis of the data was performed with $m = 3$ to 7. Based on the maximum deviation and the nature of the plot from the resulting correlation, a correlation model, given by Eq. (7), with $m = 6$ was determined to represent the data best. Least-squares estimates of the correlation coefficients b_n (n = 0 to 6) are listed in Table III. Correlation of the data was to within $\pm 7.5\%$ (Fig. 4).

Table II1. Empirical Coefficients for Correlation of the Thermal Conductivity of Propane

(a) Correlation coefficient for λ_0 [1, 6]
$a_1 = -0.1089381103E + 04$
$a_2 = 0.8343297829E+03$
$a_3 = -0.2270902736E+03$
$a_4 = 0.1667866368E + 02$
$a_5 = 0.4347320565E + 01$
$a_6 = -0.1177734671E + 01$
$a_7 = 0.1215425833E + 00$
$a_8 = -0.6040596921E - 02$
$a_9 = 0.1207373681E - 03$
(b) Correlation coefficient for $\Delta \lambda$.
$b_0 = 0.01888627$
$b_1 = 0.02582971$
b_2 = 0.00462271
$b_3 = -0.00229670$
$b_4 = 0.00663134$
$b_5 = 0.00467437$
$b_6 = -0.00236672$
(c) Correlation coefficient for $\Delta \lambda_{cr}$
$c_1 = 0.00004432$
c_2 = 0.00142564
$c_3 = -0.01972275$
$c_4 = 2.75975351$
$n=0$

Fig. 4. Deviation plot: correlation of the excess thermal conductivity $(\Delta \lambda_e)$ for propane.

A correlation of the excess thermal conductivity in terms of density and temperature was next attempted with

$$
\Delta \lambda_{\rm e}(\rho, T) = \sum_{i=0}^{m} \sum_{j=0}^{n} b_{ij} T_{\rm r}^i \rho_{\rm r}^j \qquad (8)
$$

using $m = 5$ and $n = 4$. This correlation, as well as others with lower values of *m* and *n*, did not result in a lower maximum deviation; Eq. (7) was, therefore, preferred over Eq. (8).

5.4. The Anomalous Thermal Conductivity, $\Delta\lambda_{cr}$

The anomalous thermal conductivity, $\Lambda \lambda_{cr}$, was estimated by subtracting the background conductivity, λ_{bg} [Eqs. (5)–(7)], from the experimental data in the anomalous region. A correlation of $\Lambda\lambda_{\rm cr}$ in terms of density and temperature was attempted with the model $[16, 17]$.

$$
\varDelta \lambda_{\rm cr}(\rho, T) = A e^{-x^2} \tag{9}
$$

with

$$
A = C_1 / [(AT^*)^2 + C_2]
$$
 (10)

$$
X = C_4 \left[\Delta \rho^* - C_3 (A T^*)^n \right] \tag{11}
$$

This model is similar to the one recommended by Roder [16]; however, the expression for the amplitude term A \lceil Eqs. (9) and (10)] has been

Fig. 5. Deviation plot: correlation of the anomalous thermal conductivity $(\Lambda)_{cr}$ for propane.

modified [17] to ensure maximum enhancement along the critical isotherm. Correlation to within about $+8\%$ (Fig. 5) was obtained with $n = 0$ in Eq. (11). The estimates of the empirical coefficients C_n ($n = 1$ to 4) are listed in Table III.

6. DISCUSSION AND CONCLUSIONS

In summary, the thermal conductivity of propane in the range 192-320 K and up to 70 MPa was measured experimentally with a transient hot-wire instrument. These measurements are in excellent agreement $(\pm 1.2\%)$ with other reliable measurement [1, 2] and are estimated to be accurate within $+ 1.5 \%$.

The present measurements and data from other sources $\lceil 1-5 \rceil$ were employed to present a correlation in the range 110-480 K and up to 70 MPa including the critical region.

The present correlation expressed by Eqs. $(9)-(11)$ for the anomalous thermal conductivity is based on the data of Tufeu and Le Neindre [3] in the critical region, including some data at $AT^* = 0.01$ [15]. It is recommended that the method suggested by Sengers et al. [15] be employed for ΔT^* < 0.01 for this region.

The uncertainty in the correlation presented is estimated to be about $+8\%$.

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NOMENCLATURE

Greek symbols

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