Measurement and Correlation of the Thermal Conductivity of Butane from 135 K to 600 K at Pressures to 70 MPa[†]

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New experimental data for the thermal conductivity of butane are reported that allow improved correlations to be developed. Previous correlations have been limited by a lack of thermal conductivity data for the vapor and compressed liquid at temperatures below 300 K and near the critical point. In addition, significant discrepancies were noted in the high-temperature dilute-gas thermal conductivity. These new experimental data, covering the temperature range from the triple point at 135.86 K to 600 K and the pressure range 0.1 MPa to 70 MPa, are used together with the previously available data to develop improved correlations for the thermal conductivity of butane. The data reported here are estimated to have an uncertainty of ±1% for measurements removed from the critical point and at pressures above 1 MPa, which increases to ±3% in the critical region and ±4% at low pressures (<1 MPa) at a 95% confidence level. The quality of the new data is such that the thermal-conductivity correlation for butane is estimated to have an uncertainty of about 3% at a 95% confidence level, with the exception of state points near the critical point and the dilute gas, where the uncertainty of the correlation increases to 5%.

Introduction

Accurate thermophysical property data are required for industrially important fluids such as butane to allow the design of efficient chemical processes and equipment. The large 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 International Union of Pure and Applied Chemistry (IUPAC) Subcommittee on 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 are reported here for the thermal conductivity of butane that were not available during development of the wide-range correlations proposed by Younglove and Ely[1] in 1987 and Ramires *et al.*[2] in 1996. The present work describes improved empirical correlations incorporating these new data for the thermal conductivity of butane.

Although desirable, a complete theoretical analysis of the available experimental data for the thermal conductivity of butane 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 butane 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 butane does not allow an adequate theoretically based description of the enhancement of thermal conductivity and, thus, an empirical formulation was also considered in this work.

The literature contains two previous wide-range empirical correlations for the thermal conductivity of butane based on a comprehensive analysis of the data available at the time of publication. In 1987, Younglove and Ely[1] reported a correlation for butane at temperatures from 86 K 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. In 1996, Ramires *et al.*[2] reported a correlation for butane at temperatures from 192 K to 725 K and at densities up to 17 mol·L^{-1} that has an estimated uncertainty of 5% outside the critical region and an uncertainty of 10% near the critical point. The experimental data reported here, which cover a wide range of temperature and pressure, with improved coverage of the critical region and low-temperature vapor region where almost no data existed, motivated the development of improved correlations. We show that systematic deviations between thermal-conductivity data and the previous correlations[1,2] can be significantly reduced in the critical region and for the dilute vapor.

Experimental Section

The purity of the butane sample studied was verified to be 99.92 mol % by a gas-chromatographic mass-spectro-

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metric method. The most significant impurity was air at a concentration of 0.08 mol %. The present measurements of thermal conductivity were obtained with two hot-wire instruments, operated in both transient and steady-state modes, that have been described in detail.[4,5] Both instruments used dual hot wires that are 4 μm in diameter and made from tungsten. The outer cavity around the hot wires is stainless steel and has a diameter of 9 mm. The low-temperature instrument is capable of operation from 30 K to 340 K at pressures to 70 MPa in the liquid, vapor, and supercritical gas phases. The high-temperature instrument is capable of operation from 250 K to 750 K at pressures to 70 MPa in the liquid, vapor, and supercritical gas phases. Temperatures are determined with a reference platinum resistance thermometer with an uncertainty of ±0.01 K, and pressures are determined with a pressure transducer with an uncertainty of ±7 kPa. The basic theory that describes the operation of the transient hot-wire instrument is given by Healy *et al.*[6] Each hot-wire cell is designed to approximate a transient line source as closely as possible, and deviations from this model are treated as corrections to the experimental temperature rise. The ideal temperature rise ΔT_{id} is given by

$$\Delta T_{id} = \frac{q}{4\pi\lambda}\left[\ln(t) + \ln\left(\frac{4a}{r_0^2 C}\right)\right] = \Delta T_w + \sum_{i=1}^{10}\delta T_i \quad (1)$$

where q is the power applied per unit length, λ is the thermal conductivity of the fluid, t is the elapsed time, $a = \lambda/(\rho C_p)$ is the thermal diffusivity of the fluid, ρ is the density of the fluid, C_p is the isobaric heat capacity of the fluid, r_0 is the radius of the hot wire, $C = 1.781...$ is the exponential of Euler's constant, ΔT_w is the measured temperature rise of the wire, and δT_i are corrections[6] to account for deviations from ideal line-source conduction.

Both thermal conductivity and thermal diffusivity can be determined with the transient hot-wire technique, but only the thermal-conductivity results are considered here. For gas-phase measurements there are two significant corrections[6–10] that must be carefully considered. First, since the thermal diffusivity of the gas is much different from that of the wire, the correction for the finite wire radius becomes very significant. Second, the thermal diffusivity of the dilute gas varies inversely with the pressure, so it is possible for the transient thermal wave to penetrate to the outer boundary of the gas region during an experiment performed at low pressures.[7–10] The preferred method to deal with such corrections is to minimize them by proper apparatus design. For instance, the correction for finite wire radius can be minimized with wires of extremely small diameter (4–7) μm, and penetration of the thermal wave to the outer boundary can be eliminated with a cell that has a large-diameter outer boundary. However, such designs are often not optimum for a general-purpose instrument, where extremely fine wires may be too fragile and large outer dimensions may require too much of a scarce sample, particularly in the liquid phase.

The present transient hot-wire wires are as small as practical to minimize corrections for the finite wire radius during such dilute-gas measurements. However, measurement times must be carefully selected to minimize the correction for penetration to the outer boundary due to the relatively small diameter of the outer boundary. For the measurements reported here, application of the full correction[4] for the finite wire dimensions was considered essential. For a few of the measurements at the lowest pressures, the outer boundary was encountered during the

1 s duration of the experiment and the experiment time was reduced to minimize the magnitude of the correction for the outer boundary. The largest thermal diffusivity for any of the present measurements on a gas was 2×10^{-5} m^2·s^{-1}. This conclusion is consistent with previous work on light gases such as argon and nitrogen at 1 bar to 2 bar,[4,5] where the outer boundary was encountered at times below 1 s when the thermal diffusivity was greater than 9×10^{-6} m^2·s^{-1}.

At very low pressures, the steady-state hot-wire technique has the advantage of not requiring significant corrections. The working equation for the steady-state mode is based on a different solution of Fourier's law, but the geometry is still that of concentric cylinders. The solution can be found in standard texts for the case of constant thermal conductivity (see, for example, ref 11, p 114). This equation can be solved for the thermal conductivity of the fluid, λ,

$$\lambda = \frac{q \ln\left(\frac{r_2}{r_1}\right)}{2\pi(T_1 - T_2)} \quad (2)$$

where q is the applied power per unit length, r_2 is the internal radius of the outer cylinder, r_1 is the external radius of the inner cylinder (hot wire), and $\Delta T = (T_1 - T_2)$ is the measured temperature difference between the hot wire and its surrounding cavity.

For the concentric-cylinder geometry described above, the total radial heat flow per unit length, q, remains constant and is not a function of radial position. Assuming that the thermal conductivity is a linear function of temperature, such that $\lambda = \lambda_0(1 + b_\lambda T)$, it can be shown that the measured thermal conductivity is given by $\lambda = \lambda_0(1 + b_\lambda(T_1 + T_2)/2)$. Thus, the measured thermal conductivity corresponds to the value at the mean temperature of the inner and outer cylinders

$$\bar{T} = (T_1 + T_2)/2 \quad (3)$$

This assumption of a linear temperature dependence for the thermal conductivity is valid for experiments with small temperature differences. The density assigned to the measured thermal conductivity is calculated with an equation of state at the temperature from eq 3 and the experimentally measured pressure. An assessment of corrections during steady-state hot-wire measurements is available.[12]

Experimental Results

The results of measurements of the thermal conductivity of the vapor phase of butane are tabulated in the Supporting Information. The range of state points covered by the present measurements is shown in Figure 1 relative to the vapor pressure curve of butane and the previous measurements that are available in the literature. There are a total of 335 steady-state measurements and 2333 transient measurements tabulated at temperatures from the triple point to 600 K with pressures to 70 MPa. The measurements are reported on the ITS-90 temperature scale and are estimated to have an uncertainty of ±1% for transient measurements of liquid and gas removed from the critical point, increasing to ±3% in the critical region and the low-pressure gas region (<1 MPa) at a 95% confidence level. The steady-state vapor measurements are estimated to have an uncertainty of ±2%. A summary of these measurements is given in Table 1, while the complete data set is

Table 1. Summary of Present Measurements on Butane

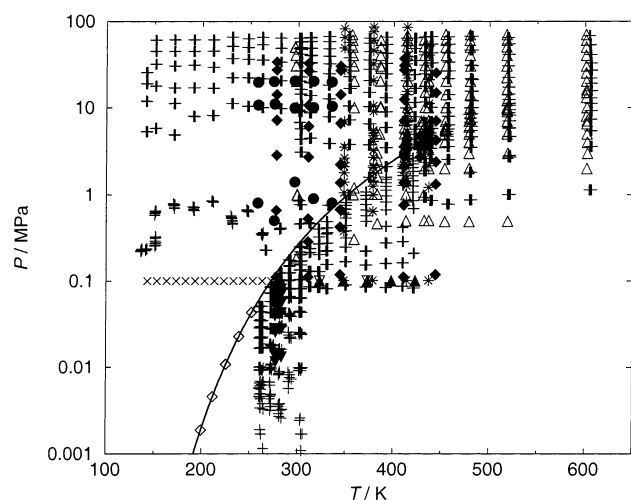| technique	temp range/K	pressure range/MPa	no. of points	estimated uncertainty
steady-state hot wire (low temp)	260 to 300	0.001 to 0.25	246	±2%
steady-state hot wire (high temp)	310 to 420	0.008 to 0.22	89	±2%
transient hot wire (low temp)	136 to 300	0.01 to 70.0	880	±1−2%
transient hot wire (high temp)	300 to 606	0.08 to 70.0	1453	±1−3%

Figure 1. Distribution of thermal conductivity data for butane reported here and available in the literature: +, present work; ●, Yata;[14] ◇, Kandiyoti *et al.*;[17] ▽, Parkinson and Gray;[18] △, Nieto de Castro *et al.*;[19] ▼, Mann and Dickins;[20] ▲, Smith *et al.*;[21] ∗, Kramer and Comings;[22] ◆, Carmichael and Sage;[23] ×, Brykov and Mukhamedzyanov;[24] ○, Ehya *et al.*[25]

available in the Supporting Information. Many of these vapor measurements were made at temperatures below the normal boiling point of butane. It should be emphasized that there are many difficulties associated with such measurements due to the small quantity of sample in the cell and to possible contamination with air impurities and material adsorbed on the surface of the cell and wires.[13] The uncertainty of measurements for dilute vapors is larger than that for the measurements in the liquid or vapor phase at higher reduced temperatures and pressures due to sample handling as well as relatively large corrections for transient measurements. It is necessary to have an equation of state[1] during the data analysis to make the corrections to the measured temperature rise as described above.

Correlation Development

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

$$\lambda(\rho, T) = \lambda_0(T) + \Delta\lambda_r(\rho, T) + \Delta\lambda_c(\rho, T) \tag{4}$$

where λ_0 is the dilute-gas thermal conductivity, which depends only on the temperature, $\Delta\lambda_r$ is the residual thermal conductivity, and $\Delta\lambda_c$ is the thermal-conductivity enhancement in the critical region. $\Delta\lambda_r$ 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)

Table 2. Primary Experimental Data for the Thermal Conductivity of Butane

ref	temp range/K oressure range/MPa	technique[a]	no. of points	estimated uncertainty/%
14	258−335 1−20	THW	15	±1
17	148−252 0.1	THW	42	±2
19	298−601 0.1−70	CC	215	±2
18	323−373 0.1	SSHW	2	±2

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

equation of state of Younglove and Ely[1] was used. This equation of state is valid at pressures up to 70 MPa and at temperatures between the triple point and 500 K. Some of the data reported here are at temperatures above the 500 K limit of the equation of state. For these cases, the equation of state was used beyond its recommended limits, so the results should be viewed with caution. With the exception of the more recent results of Yata et al.,[14] 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[15] and all calculations are based on the ITS-90 temperature scale. All densities are in mol·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.[16] However, this requirement of absolute measurements with uncertainties less than 2% excluded all the data prior to 1983 and considers only four sets of data. 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. A summary of the primary data for butane,[14,17−19] together with the ranges in temperature and pressure, the experimental technique, and the assigned uncertainty, is provided in Table 2. A summary of the secondary data for butane,[20−25] together with the ranges in temperature and pressure, the experimental technique, and the assigned uncertainty, are provided in Table 3.

The need for improved correlations for the thermal conductivity of butane is evident when the literature data and the present results are compared with the previous correlations. The relative deviations between the literature data and the correlation of Younglove and Ely[1] are shown in Figure 2. In the critical region, deviations range from 15% to 30%. The relative deviations between the present measurements and the correlation of Younglove and Ely[1] are shown in Figure 3. At temperatures significantly above the critical temperature (425.16 K) and near the critical density (3.920 mol·L⁻¹), the measurements of Nieto de Castro et al.[19] and the present measurements are 10% lower than the correlation.[2] At temperatures above 450 K,

Table 3. Secondary Experimental Data for the Thermal Conductivity of Butane

ref	temp range/K pressure range/MPa	technique[a]	no. of points	estimated uncertainty/%
20	275–285 ∼ 0.1	SSHW	5	±5
21	323–423 0.1	CC	3	±5
22	348–427 0.1–100	CC	97	±5
23	277–444 0.1–35	SC	45	±5
24	143–273 0.1	SSHW	14	±5
25	300–1000 0.1	SSHW	fit equation	±5

[a] SSHW, steady-state hot wire; CC, concentric cylinders; SC, spherical cell.
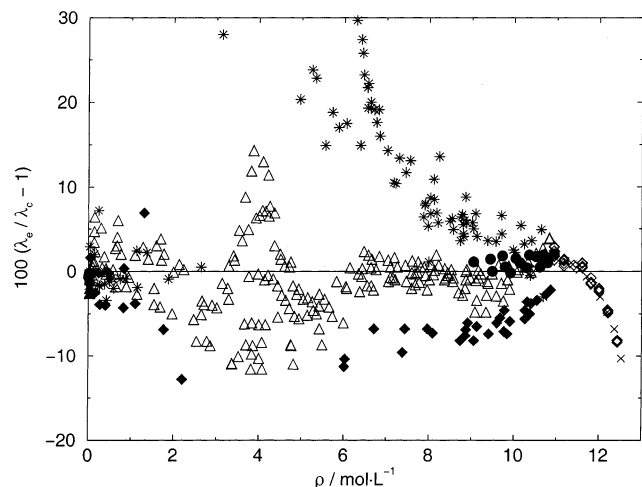
Figure 2. Relative deviations between literature values for the thermal conductivity of butane and the correlation of Younglove and Ely:[1] ●, Yata;[14] ◇, Kandiyoti *et al.*;[17] ▽, Parkinson and Gray[18] △, Nieto de Castro *et al.*;[19] ▼, Mann and Dickins;[20] ▲, Smith *et al.*;[21] ∗, Kramer and Comings;[22] ◆, Carmichael and Sage;[23] ×, Brykov and Mukhamedzyanov;[24] ○, Ehya *et al.*[25]
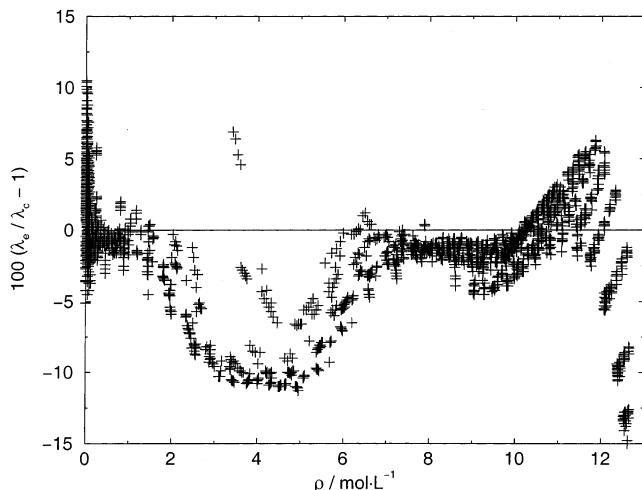

Figure 3. Relative deviations between the present measurements for the thermal conductivity of butane and the correlation of Younglove and Ely.[1]

the dilute-gas thermal conductivity data are systematically higher than the correlation[1] by up to 10%. Problems are also apparent in the low-temperature liquid, where the present measurements are up to 15% lower than the correlation[1] near the triple-point temperature (134.86 K). The relative deviations between the literature data and the
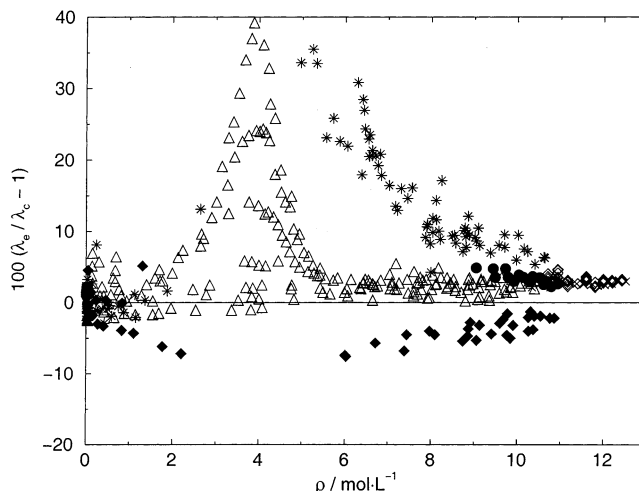

Figure 4. Relative deviations between literature values for the thermal conductivity of butane and the correlation of Ramires *et al.*:[2] ●, Yata;[14] ◇, Kandiyoti *et al.*;[17] ▽, Parkinson and Gray;[18] △, Nieto de Castro *et al.*;[19] ▼, Mann and Dickins;[20] ▲, Smith *et al.*;[21] ∗, Kramer and Comings;[22] ◆, Carmichael and Sage;[23] ×, Brykov and Mukhamedzyanov.[24]
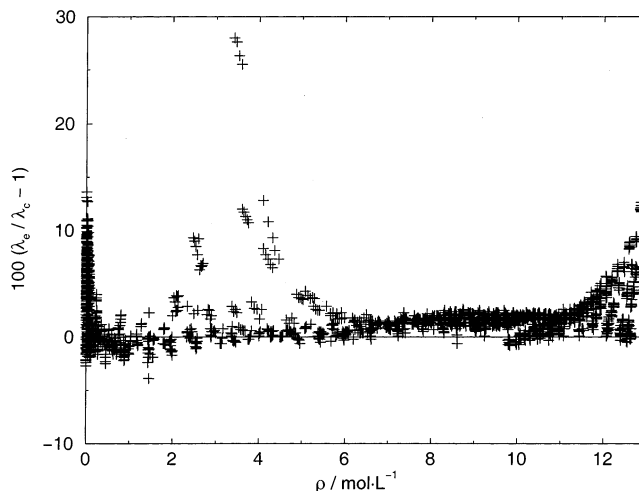

Figure 5. Relative deviations between the present measurements for the thermal conductivity of butane and the correlation of Ramires *et al.*[2]

correlation of Ramires *et al.*[2] are shown in Figure 4. The relative deviations between the present measurements and the correlation of Ramires *et al.*[2] are shown in Figure 5. In the critical region, deviations range from 10% to 40%. The correlation of Ramires *et al.*[2] does much better than the correlation of Younglove and Ely[1] for the low-temperature saturated liquid. The deviations between the present data and the correlation of Ramires *et al.*[2] increase to 10% for the low-temperature compressed liquid as the pressure increases to 70 MPa. The correlation of Younglove and Ely[1] does somewhat better than the correlation of Ramires *et al.*[2] at high temperatures near the critical density. Improved correlations are needed for the thermal conductivity of butane based on both the literature data and the present measurements.

Zero-Density Limit. The zero-density or dilute-gas limit is determined from the extrapolation of a particular transport property, held at constant temperature, to zero density.[3] Consequently, transport properties of a dilute gas 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 tem-
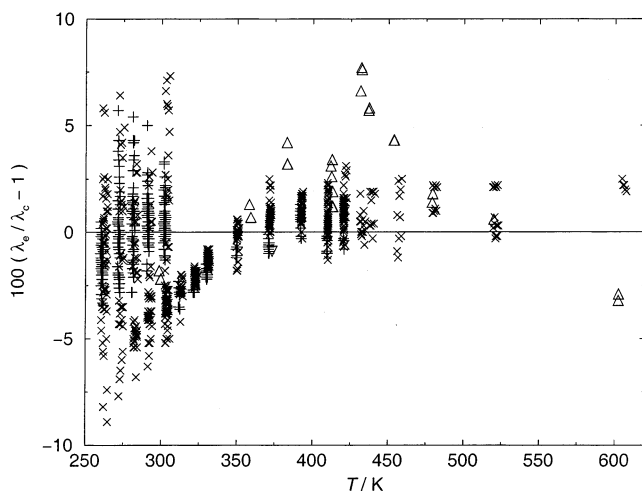
Figure 6. Relative deviations between the present steady-state (+) and transient (×) measurements for the thermal conductivity of butane and the dilute-gas thermal conductivity calculated with eq 5. Deviations between the dilute-vapor data of Parkinson and Gray[18] (▽) and Nieto de Castro et al.[19] (△) are also shown.

Table 4. Coefficients for the Representation of the Thermal Conductivity of Butane in the Limit of Zero Density, Eq 5

$A_1/(W \cdot m^{-1} \cdot K^{-1})$	$1.626\,76 \times 10^{-3} \pm 9.0478 \times 10^{-4}$
$A_2/(W \cdot m^{-1} \cdot K^{-1})$	$9.757\,03 \times 10^{-4} \pm 2.3654 \times 10^{-3}$
$A_3/(W \cdot m^{-1} \cdot K^{-1})$	$2.898\,87 \times 10^{-2} \pm 1.5170 \times 10^{-3}$

peratures, where the vapor pressure of butane is of the order of 0.1 MPa and there is an insufficient density range covered to allow extrapolation to zero density. It was assumed that at low densities, with pressures less than 1 MPa, the density dependence is linear with a constant slope. Thus, the available thermal conductivity data for the vapor phase over the full range of temperature, at pressures less than 1 MPa or the vapor pressure at any given temperature, are fit with a polynomial in reduced temperature with a linear density dependence to allow extrapolation to the true zero-density dilute-gas limit.

Given the need for thermal conductivity data for butane vapor at low temperatures and pressures, it was decided that the present steady-state measurements were the most reliable and should form the basis for the dilute-gas thermal conductivity of butane. The present thermal conductivity data from steady-state measurements were correlated with a quadratic polynomial in temperature:

$$\lambda_0(T) = A_1 + A_2(T/T_c) + A_3(T/T_c)^2 \quad (5)$$

where λ_0 is the dilute-gas thermal conductivity, T is the absolute temperature, and T_c is the critical temperature. Table 4 contains the coefficients A_i together with their uncertainties at a confidence level of 1 standard deviation. The maximum deviation between the present steady-state and transient measurements of the dilute-gas thermal conductivity is about 5% at 260 K and the lowest pressures. The maximum deviation of the primary literature data is 8% at the temperature 450 K. The deviations of the present measurements and the primary data from eq 5 are presented in Figure 6. Good agreement is found between the present steady-state measurements, the steady-state measurements of Nieto de Castro et al.,[19] and the transient measurements of Parkinson and Gray.[18] Good agreement is also found between the present transient measurements (uncertainty of 3% for dilute vapor) and the present steady-state measurements (uncertainty of 2%). The transient

measurements are up to 5% higher than the steady-state measurements at 600 K. This difference is systematic and has been observed for other hydrocarbons and alternative refrigerants. No theoretical basis for this difference is available, but steady-state measurements at low density are considered more reliable, since significant corrections are required for the transient measurements at these conditions. The uncertainty of the dilute-gas thermal conductivity calculated with eq 5 is estimated to be 5% at a confidence level of 95%.

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 nonsingular background values far away from the critical point.[26-29] The density-dependent terms for thermal conductivity can be grouped according to eq 3:

$$\lambda(\rho, T) = \bar{\lambda}(\rho, T) + \Delta\lambda_c(\rho, T) \quad (6)$$

where $\bar{\lambda}(\rho, T) = \lambda_0(T) + \Delta\lambda_r(\rho, T)$ is the background contribution and ρ is the fluid density.

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 residual-thermal-conductivity contributions. The procedure adopted during this analysis used ODRPACK V. 2.01[24] to fit all the primary data simultaneously to the residual thermal conductivity and the critical enhancement, while maintaining the parameters already obtained from the fit of the dilute-gas thermal-conductivity data.

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

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

where ρ is the density and ρ_c is the critical density.

Empirical Critical Enhancement. For applications at state points that are relatively distant from the critical region, the critical enhancement is adequately represented by the following empirical expression

$$\Delta\lambda_c(\rho, T) = \frac{C_1}{C_2 + |\Delta T_c|}\exp[-(C_3\Delta\rho_c)^2] \quad (8)$$

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 and specific heat of butane in the critical region, as does the theory of Olchowy and Sengers.[26-29] The critical point is taken as that from Younglove and Ely,[1] with $T_c = 425.12$ K (425.16 K on IPTS-68) and $\rho_c = 3.920$ mol·L^{-1} (227.8 kg·m^{-3}). The coefficients of eq 5 were fixed while the coefficients of eqs 7 and 8 were fit with ODRPACK V. 2.01[30] to the present transient and steady-state data for the thermal conductivity of butane. Table 5 lists the optimum coefficients for eqs 7 and 8 together with their uncertainties at a confidence level of 1 standard deviation. Figure 7 shows a plot of deviations of the experimental data from the surface correlation of eqs 5, 7, and 8 incorporating this empirical equation for the representation of the critical enhancement. Around the critical region, and despite the lack of a crossover equation of state, the primary data are generally reproduced within ±6%, with the two near-

Table 5. Coefficients for the Representation of the Residual Thermal Conductivity of Butane, Eq 7 with the Empirical Critical Enhancement of Eq 8

$\Delta\lambda_r$	$B_{i,1}/(\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1})$	$B_{i,2}/(\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1})$
$i = 1$	$-3.183\,63 \times 10^{-2} \pm 1.7578 \times 10^{-3}$	$4.441\,32 \times 10^{-2} \pm 1.8108 \times 10^{-3}$
$i = 2$	$1.843\,89 \times 10^{-1} \pm 4.4958 \times 10^{-3}$	$-1.662\,50 \times 10^{-1} \pm 4.2170 \times 10^{-3}$
$i = 3$	$-1.670\,00 \times 10^{-1} \pm 4.2735 \times 10^{-3}$	$1.525\,11 \times 10^{-1} \pm 3.5549 \times 10^{-3}$
$i = 4$	$5.913\,97 \times 10^{-2} \pm 1.5354 \times 10^{-3}$	$-5.522\,70 \times 10^{-2} \pm 1.2432 \times 10^{-3}$
$i = 5$	$-7.064\,92 \times 10^{-3} \pm 1.8623 \times 10^{-4}$	$7.235\,62 \times 10^{-3} \pm 1.5379 \times 10^{-4}$

$\Delta\lambda_c$	$C_i/(\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1})$
$i = 1$	$4.499\,30 \times 10^{-4} \pm 3.5025 \times 10^{-5}$
$i = 2$	$1.317\,51 \times 10^{-2} \pm 2.3619 \times 10^{-3}$
$i = 3$	$2.661\,69 \times 10^{0°} \pm 5.4307 \times 10^{-2}$

Table 6. Coefficients for the Representation of the Residual Thermal Conductivity of Butane, Eq 7 with Simplified Crossover Critical Enhancement of Eqs 9–12

$\Delta\lambda_r$	$B_{i,1}/(\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1})$	$B_{i,2}/(\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1})$
$i = 1$	$-3.043\,37 \times 10^{-2} \pm 1.7187 \times 10^{-3}$	$4.183\,57 \times 10^{-2} \pm 1.7371 \times 10^{-3}$
$i = 2$	$1.658\,20 \times 10^{-1} \pm 4.6841 \times 10^{-3}$	$-1.471\,63 \times 10^{-1} \pm 4.1710 \times 10^{-3}$
$i = 3$	$-1.481\,44 \times 10^{-1} \pm 4.4439 \times 10^{-3}$	$1.335\,42 \times 10^{-1} \pm 3.6327 \times 10^{-3}$
$i = 4$	$5.255\,00 \times 10^{-2} \pm 1.5908 \times 10^{-3}$	$-4.854\,89 \times 10^{-2} \pm 1.2550 \times 10^{-3}$
$i = 5$	$-6.293\,67 \times 10^{-3} \pm 1.9252 \times 10^{-4}$	$6.443\,07 \times 10^{-3} \pm 1.5148 \times 10^{-4}$

$\Delta\lambda_c$	
$\bar{q}_D^{-1}/\text{m}$	$(8.753\,50 \times 10^{-10} \pm 4.8938 \times 10^{-11})$
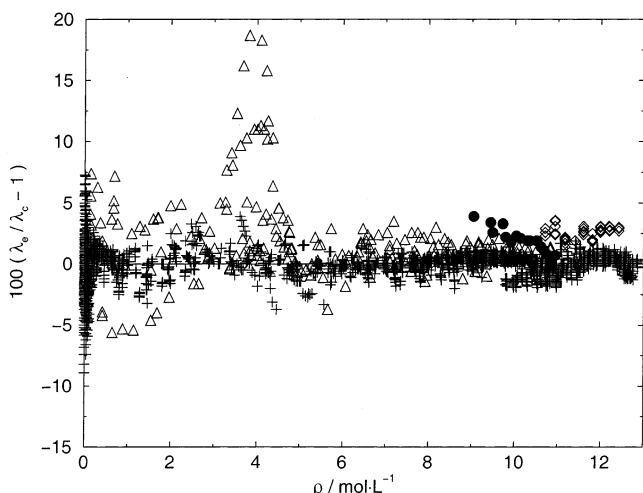
Figure 7. Relative deviations between the present measurements (+) and the primary literature values of Yata[14] (●), Kandiyoti *et al.*[17] (◇), Parkinson and Gray[18] (▽), and Nieto de Castro *et al.*[19] (△) for the thermal conductivity of butane and the correlation with the empirical expression for the critical enhancement of eqs 5, 7, and 8.

critical isotherms of Nieto de Castro *et al.*[19] exhibiting the largest deviations (up to 20%). The present transient and steady-state measurements are represented to within 4% at a confidence level of 95%.

Simplified Crossover Model. The theoretically based crossover model proposed by Olchowy and Sengers[26–28] 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.[29] The critical enhancement of the thermal conductivity is given by

$$\Delta\lambda_c = \frac{\rho C_p R k_b T}{6\pi\bar{\eta}\xi}(\bar{\Omega} - \bar{\Omega}_0) \qquad (9)$$

with

$$\bar{\Omega} = \frac{2}{\pi}\left[\left(\frac{C_p - C_v}{C_p}\right)\arctan(\bar{q}_D\xi) + \frac{C_v}{C_p}\bar{q}_D\xi\right] \qquad (10)$$

and

$$\bar{\Omega}_0 = \frac{2}{\pi}\left\{1 - \exp\left[-\frac{1}{(\bar{q}_D\xi)^{-1} + (\bar{q}_D\xi\rho_c/\rho)^2/3}\right]\right\} \qquad (11)$$

In eqs 9–11, k_B is Boltzmann's constant, $\bar{\eta}$ is the background viscosity, and $\bar{q}_D$ is the effective wavenumber cutoff determined by fitting thermal conductivity data in the critical region. The correlation length ξ is given by

$$\xi = \xi_0\left[\frac{P_c\rho}{\Gamma\rho_c^2}\right]^{\nu/\gamma}\left[\frac{\partial\rho(T,\rho)}{\partial P}\bigg|_T - \left(\frac{T_r}{T}\right)\frac{\partial\rho(T_r,\rho)}{\partial P}\bigg|_T\right]^{\nu/\gamma} \qquad (12)$$

The coefficients of eq 5 were fixed while the coefficients of eqs 7 and 9–12 were fit with ODRPACK V. 2.01[30] to the present transient and steady-state data for the thermal conductivity of butane. This crossover model requires the universal constants $R = 1.03$, $\nu = 0.063$, and $\gamma = 1.239$; system-dependent amplitudes $\Gamma = 0.0496$ and $\xi_0 = 1.94 \times 10^{-10}$ m; critical-point properties including the critical pressure $P_c = 3.796$ MPa; and a reference temperature where the critical enhancement is negligible $T_r = {}^3/_2 T_c = 637.68$ K. Table 6 lists the optimum coefficients for eqs 7 and 9–12 together with their uncertainties at a confidence level of one standard deviation. Figure 8 shows a plot of deviations of the primary experimental data from the surface correlation with this simplified theory for the representation of the critical enhancement. Despite the limitations of the equation of state in the critical region, the data are generally reproduced within ±5% at a level of uncertainty of 95%. Systematic deviations of up to 15% are observed in the critical region for the two near-critical isotherms of Nieto de Castro *et al.*[19] These deviations for the near critical isotherms are likely due to the limitations of the present equation of state.[1] The reference temperature T_R for the critical-enhancement theory is 637.68 K and is significantly above the upper recommended temperature of 500 K for the equation of state[1].

Full Crossover Model. The full crossover equations proposed by Olchowy and Sengers[26–28] were also fit to the butane data. The critical enhancement of the thermal
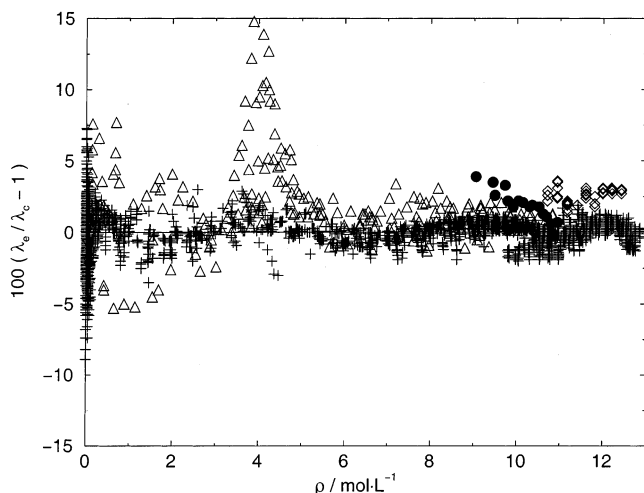
Figure 8. Relative deviations between the present measurements (+) and the primary literature values of Yata[14] (●), Kandiyoti *et al.*[17] (◇), Parkinson and Gray[18] (▽), and Nieto de Castro *et al.*[19] (△) for the thermal conductivity of butane and the correlation with the simplified theoretical expression[29] for the critical enhancement of eqs 5, 7, and 9−12.

conductivity is given by

$$\Delta\lambda_c = \frac{\rho C_p R k_b T}{6\pi\eta\xi}(\Omega - \Omega_0) \quad (13)$$

with

$$\Omega = \frac{2}{\pi}\left(\frac{1}{1+y_\gamma}\right) \times \left[y_D - \sum_{i=1}^{4}\left(\frac{(a_3 z_i^3 + a_2 z_i^2 + a_1 z_i + a_0)}{\prod_{j=1, j\neq i}^{4}(z_i - z_j)}\right)F(z_i, y_D)\right] \quad (14)$$

and

$$\Omega_0 = \frac{1 - \exp\{-[(q_D\xi)^{-1} + (q_D\xi\rho_c/\rho)^2/3]^{-1}\}}{\pi/2[1 + y_\alpha(y_D + y_\delta) + y_\beta(1 + y_\gamma)^{-1}]} \quad (15)$$

The correlation length ξ is again given by eq 12 as for the simplified crossover model, but q_D is the effective wavenumber cutoff ($\bar{q}_D \neq q_D$, since each effective wavenumber cutoff is model dependent) and is determined by a fit of thermal conductivity data in the critical region. The coefficients a_i in eq 14 are given by

$$a_0 = y_\gamma^2 - y_\alpha y_\gamma y_\delta$$

$$a_1 = y_\alpha y_\gamma y_D$$

$$a_2 = y_\gamma - y_\beta - y_\alpha y_\delta$$

$$a_3 = y_\alpha y_D \quad (16)$$

In eq 14, the z_i are the two real and two complex-conjugate roots of the equation

$$z^4 + y_\alpha y_D z^3 + (y_\gamma + y_\beta + y_\alpha y_\delta)z^2 + y_\alpha y_\gamma y_D z^2 + y_\alpha y_\gamma y_\delta z = 0 \quad (17)$$

The function F in eq 14 is given by

$$F(x, y_D) = \frac{1}{(1-x^2)^{1/2}}\ln\left[\frac{1 + x + (1-x^2)^{1/2}\tan(y_D/2)}{1 + x - (1-x^2)^{1/2}\tan(y_D/2)}\right] \quad (18)$$

The auxiliary functions are given by

$$y_D = \arctan(q_D\xi)$$

$$y_\delta = \frac{\arctan[q_D\xi/(1 + q_D^2\xi^2)^{1/2}] - y_D}{(1 + q_D^2\xi^2)^{1/2}} \quad (19)$$

$$y_\alpha = \rho k_B T/8\pi\bar{\eta}^2\xi$$

$$y_\beta = \bar{\lambda}/\bar{\eta}(C_p - C_v)$$

$$y_\gamma = C_v/(C_p - C_v)$$

$$y_\eta = (y_\delta + y_\beta/y_\alpha)/y_D$$

and

$$y_v = y_\gamma y_\delta/y_D$$

The coefficients of eq 5 were fixed while the coefficients of eqs 7 and 13−19 were fit with ODRPACK V. 2.01[30] to the present transient and steady-state data for the thermal conductivity of butane. This crossover model requires the universal constants $R = 1.03$, $z = 0.063$, and $\gamma = 1.239$; system-dependent amplitudes $\Gamma = 0.0496$ and $\xi_0 = 1.94 \times 10^{-10}$ m; and a reference temperature where the critical enhancement is negligible $T_R = {}^3/_2 T_c = 637.68$ K. Table 7 lists the optimum coefficients for eqs 7 and 13−19 together with their uncertainties at a confidence level of one standard deviation. Figure 9 plots deviations of the experimental data from the surface correlation with this theory for the representation of the critical enhancement. The deviations are comparable to those for the fit with the simplified theory for the criticial enhancement shown above, but they are up to 19% for the two near critical isotherms of Nieto de Castro *et al.*[19] Again, it is expected that a better equation of state would significantly reduce the deviations between the data and the full crossover theory in the critical region, similar to the simplified model.

Discussion

Three alternative correlations are developed for the thermal conductivity of butane that are valid over the temperature range from 135 K to 600 K with densities up to 13 mol·L⁻¹ (756 kg·m⁻³). These three correlations differ only in the expression used to account for the enhancement of the thermal conductivity in the critical region. The simple empirical expression is easy to implement and fits the present data quite well but is shown to have difficulty in dealing with the near critical isotherms of Nieto de Castro *et al.*[19] A simplified crossover theory[29] for the enhancement of the thermal conductivity is also relatively easy to implement, fits the present data well, and also predicts better the enhanced thermal conductivity of the near-critical isotherms of Nieto de Castro *et al.*[19] The full crossover theory[26−28] for the enhancement of the thermal conductivity appears to offer reduced performance relative to the simplified theory and is significantly more difficult to implement. The current barriers to theoretically accounting for the critical enhancement of butane are the lack

Table 7. Coefficients for the Representation of the Residual Thermal Conductivity of Butane, Eq 7 with Full Crossover Critical Enhancement of Eqs 13−19

$\Delta\lambda_r$	$B_{i,1}/(\text{W·m}^{-1}\text{·K}^{-1})$	$B_{i,2}/(\text{W·m}^{-1}\text{·K}^{-1})$
$i = 1$	$-3.088\,23 \times 10^{-2} \pm 1.8004 \times 10^{-3}$	$4.227\,11 \times 10^{-2} \pm 1.8427 \times 10^{-3}$
$i = 2$	$1.596\,98 \times 10^{-1} \pm 5.5260 \times 10^{-3}$	$-1.438\,67 \times 10^{-1} \pm 4.3780 \times 10^{-3}$
$i = 3$	$-1.416\,29 \times 10^{-1} \pm 5.6419 \times 10^{-3}$	$1.300\,43 \times 10^{-1} \pm 3.9539 \times 10^{-3}$
$i = 4$	$5.032\,52 \times 10^{-2} \pm 2.0308 \times 10^{-3}$	$-4.739\,21 \times 10^{-2} \pm 1.3500 \times 10^{-3}$
$i = 5$	$-6.043\,44 \times 10^{-3} \pm 2.4273 \times 10^{-4}$	$6.318\,24 \times 10^{-3} \pm 1.5847 \times 10^{-4}$

$\Delta\lambda_c$	
q_D^{-1}	$(6.129\,30 \times 10^{-10} \pm 2.3129 \times 10^{-11})/\text{m}$
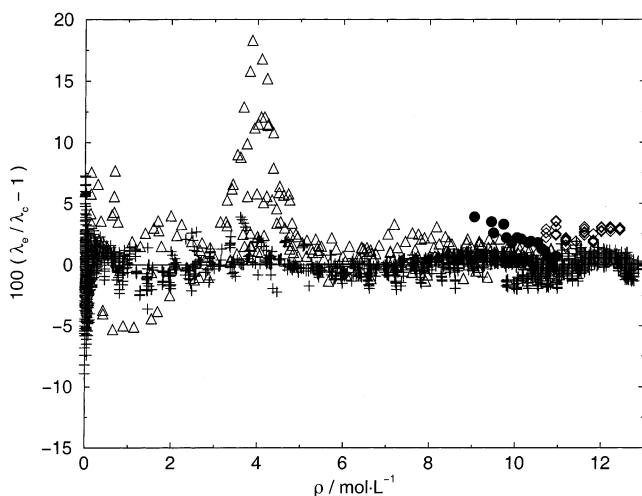
Figure 9. Relative deviations between the present measurements (+) and the primary literature values of Yata[14] (●), Kandiyoti *et al.*[17] (◇), Parkinson and Gray[18] (▽), and Nieto de Castro *et al.*[19] (△) for the thermal conductivity of butane and the correlation with the full theoretical expression[26−28] for the critical enhancement of eqs 5, 7, and 13−19.

of a crossover equation of state that is valid in the critical region and a classical equation of state that is valid at temperatures to 650 K. It is likely that the full theory for the critical enhancement would offer improved performance when used with such improved equations of state.

All three of the alternative correlations described above are shown to provide a significantly improved representation of the thermal conductivity of butane relative to earlier recommendations.[1,2] On the basis of simplicity and performance, the correlation based on the simplified crossover theory for the enhancement of thermal conductivity in the critical region is recommended relative to the other two formulations. The simplified crossover model fits all of the present steady-state and transient data, as well as the primary literature data, within ±5% at a level of uncertainty of 95%. This is particularly impressive, since the primary data sets, some of which are much closer to the critical point, were not used during the fitting process.

Conclusions

A total of 335 steady-state and 2333 transient hot-wire measurements of the thermal conductivity of butane are reported at temperatures from 135 K to 600 K with pressures to 70 MPa. These data are estimated to have an uncertainty of ±1% for measurements removed from the critical point and at pressures above 1 MPa, increasing to ±3% in the critical region and ±4% at low pressures (<1 MPa) at a 95% confidence level. This is a significant addition to the literature data that are available for the thermal conductivity of butane in terms of both the range of temperature and pressure studied and the reduction of uncertainty. Three alternative correlations are developed

on the basis of this new data, valid over the temperature range from 135 K to 600 K with densities up to 13 mol·L^{-1} (756 kg·m^{-3}). The simplified crossover model is recommended, since it fits all of the present steady-state and transient data for the thermal conductivity of butane, as well as the primary literature data, within ±5% at a confidence level of 95% at temperatures from 135 K to 600 K with pressures to 70 MPa, while remaining relatively simple to implement.

Supporting Information Available:

Tabulated experimental data. This material is available free of charge via the Internet at http://pubs.acs.org.

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