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Measurement and Correlation of the Thermal Conductivity of *cis*-1,1,1,4,4,4-hexafluoro-2-butene^{†,§}

Richard A. Perkins^{*}, Marcia L. Huber

Thermophysical Properties of Fluids Group, National Institute of Standards and Technology, 325 Broadway, Boulder, Colorado, 80305-3337, United States

Abstract

New experimental data for the thermal conductivity of *cis*-1,1,1,4,4,4-hexafluoro-2-butene (R-1336mzz(Z)) are reported for vapor, liquid and supercritical states. These data were obtained with transient hot-wire apparatus over the temperature range from 192 K to 498 K and at pressures from 0.05 MPa to 69 MPa. These data were used to develop a wide-range correlation for the thermal conductivity of the vapor, liquid, and supercritical fluid. The experimental data reported here have an uncertainty of 1 % for the liquid and supercritical regions (densities above 600 kg·m⁻³), 1.5 % for vapor and supercritical regions (pressures greater than or equal to 1 MPa and densities less than 200 kg·m⁻³), 3 % for supercritical states (densities between 200 kg·m⁻³ and 600 kg·m⁻³), and 3 % for vapor and supercritical states (pressures below 1 MPa). The thermal-conductivity correlation developed in this work is estimated to have an expanded relative uncertainty, at a 95 % confidence level, ranging from approximately 1.4 % to 4.2 % depending on the temperature and pressure, with larger uncertainties in the critical region.

Keywords

cis-1,1,1,4,4,4-hexafluoro-2-butene; R1336mzz(Z); thermal conductivity

1. Introduction

The chemical *cis*-1,1,1,4,4,4-hexafluoro-2-butene, also known as R-1336mzz(Z) is a highly fluorinated butene. It has recently been investigated for applications including as a working fluid in high-temperature heat pumps,[1,2] for use in Organic Rankine cycles for waste heat recovery from heavy duty internal combustion engines,[3] and for micro-scale low temperature applications.[4] It has a CAS number of 692-49-9, chemical formula C₄H₂F₆, and molar mass 164.056 g·mol⁻¹. Part of the interest in this fluid is due to its low global

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^{*}Corresponding author. richard.perkins@nist.gov.

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Supporting Information

Tabulated experimental values (73 pages) are reported in the supporting information.

warming potential (100 year time horizon, GWP_{100}) of 2,[5] zero ozone depletion potential (ODP), an atmospheric lifetime of 22 days, a favorable toxicity profile,[6] and that it is non-flammable at 60 °C and 100 °C.[5]

McLinden and Akasaka[7] recently developed an equation of state (EOS) to provide thermodynamic properties of R-1336mzz(Z). In this work, we use this EOS (as implemented in REFPROP[8]) to calculate all densities for given T, p state points and for the saturation boundary. The EOS is valid from the triple point (182.65 K) to 500 K at pressures up to 46 MPa and has uncertainties in liquid density of 0.01 % and 0.02 % for vapor densities. In addition, we adopt the critical temperature, pressure, and density consistent with this EOS, namely 444.5 K, 2.903 MPa, and $3.044 \text{ mol}\cdot\text{l}^{-1}$ ($499.386 \text{ kg}\cdot\text{m}^{-3}$). The viscosity of R-1336mzz(Z) was investigated by Miyara et al.[9] and Alam et al.[10] and most recently by Sun et al.[11] In a separate study, Alam et al.[12] presented measurements of the thermal conductivity of R-1336mzz(Z) of the liquid and the gas phase at pressures to 4 MPa and also included simplified correlations for the thermal conductivity of both the saturated liquid and vapor. The data of Alam et al.[12] were used to develop a corresponding-states-based model for the full thermal conductivity surface,[13] but the lack of adequate data over a wide range of temperatures and pressures limits model development. There remains a need for comprehensive thermal conductivity measurements for R-1336mzz(Z) over a wide range of temperatures and pressures covering state points in the gas, liquid, and supercritical regions.

In this work, we report wide-ranging measurements for the thermal conductivity of R-1336mzz(Z) with temperatures ranging from 192 K to 498 K and with pressures up to 69 MPa. We use these data to develop a correlation for R-1336mzz(Z) that is valid from the triple point to 500 K at pressures up to 70 MPa for all fluid states including gas, liquid and supercritical states over this range of conditions. This correlation requires extrapolation of the equation of state[7] for pressures above 46 MPa.

2. Experimental

The thermal conductivity of R-1336mzz(Z) was measured over a wide range of temperature and pressure with a transient hot-wire apparatus. The following sections presents details on the sample and the experimental technique.

2.1. Sample Material.

The R-1336mzz(Z) sample was supplied by Chemours in a 1000 cm^3 steel gas cylinder, and was also used in a companion study at our institute to develop an equation of state[7]. The supplier reported a purity of 0.9999 mole fraction. Our own analysis by gas chromatography/quadrupole time-of-flight mass spectrometry (GC/QToF-MS) indicated a purity of 0.9999 mole fraction. The sample was degassed by multiple freeze-thaw cycles in liquid nitrogen with evacuation of the vapor space until the final pressure over the frozen sample was $<1 \times 10^{-4} \text{ Pa}$. Table 1 gives the characterization of the sample.

2.2. Hot-Wire Systems.

We measured the thermal conductivity using two different hot-wire systems that covered the temperature range from 192 K to 498 K. The low-temperature system can measure thermal

conductivity at temperatures from 60 K to 345 K and has a copper cell with sample volume of 25 ml with two hot wires for cancellation of axial conduction effects.

The high-temperature system can measure thermal conductivity at temperatures from 300 K to 750 K and can be used with both single-wire and double-wire cells. The high-temperature single-wire cell had a volume of 5 ml and was made from 316 stainless steel. In both hot-wire cells, small platinum hot wires of 12.7 μm diameter approximate line-source electrical heaters and simultaneously function as resistance thermometers to measure the temperature rise. The resistance of each of the hot wires is calibrated in-situ as a function of the measured temperature and pressure so that the measurement of the resistance increase permits the determination of the temperature increase. The steady-state mode was used for vapor-phase measurements, while transient measurements were used for the liquid, vapor, and supercritical fluid states of R-1336mzz(Z). Due to the increasing thermal diffusivity of the gas with decreasing pressure at low pressures (which leads to increasingly more significant corrections to transient measurements for finite wire diameter and penetration to the outer boundary), the steady-state measurements have lower uncertainty for dilute-gas measurements compared to transient measurements.

At low temperatures (below 343 K), the thermal conductivity was measured with the low-temperature cryostat system.[14] The temperature of this hot-wire cell is controlled with a multilayer copper cryostat cooled by immersion in liquid nitrogen. The two hot-wires are supported at the top of their respective cylindrical cavities of 9 mm diameter and are tensioned with small weights at the bottom end. A Wheatstone bridge records the difference between the response of the long and short hot wires. The recorded bridge signal is effectively from the central portion of the long wire with the two half-lengths of the short-wire response removed. It is this region, near the wire end supports, where axial temperature gradients exist during an experiment. The initial cell temperature, T_i , is measured with an expanded uncertainty of $U(T_i)=0.005$ K with a platinum resistance thermometer. The fluid pressure, p_e , is determined with a quartz pressure transducer with an expanded uncertainty of $U(p_e)=7$ kPa over the pressure range from (0 to 69) MPa.

At higher temperatures (from 311 K to 498 K), the thermal conductivity was measured with a high-temperature thermostat system. The thermostat consists of a DC-powered furnace with an isothermal shield enclosing the hot-wire cell. The single platinum hot wire is supported at the top and tensioned with a spring arrangement at the bottom in a commercial microreactor with an 8 mm diameter bore. As in the low-temperature apparatus, a Wheatstone bridge circuit is used to measure the resistance increase and temperature rise of the wire. The correction for axial conduction during data analysis for the single-wire cell is based on the model of Woodfield et al.[15] The initial cell temperature, T_i , is measured with an expanded uncertainty of $U(T_i)=0.005$ K with a platinum resistance thermometer. The fluid pressure, p_e , is determined with a quartz pressure transducer with an expanded uncertainty of $U(p_e)=7$ kPa over the pressure range from (0 to 69) MPa. All reported expanded uncertainties are for a coverage factor of $k=2$, approximately a 95 % confidence interval.

2.3. Transient Measurements.

The hot-wire systems used in this work were designed based upon the early work of Healy *et al.*[16] In this approach, the ideal temperature rise, T_{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 applied power per unit length, λ is the fluid thermal conductivity, t is the time elapsed after application of power, ρ is the fluid density, C_p is the fluid isobaric specific heat capacity, $a = \lambda/(\rho C_p)$ is the fluid thermal diffusivity, r_0 is the hot-wire radius, and C is the exponential of Euler's constant. The ideal temperature rise is related to the measured temperature rise of the wire, T_W , and the summation of the temperature rise corrections, δT_i . [16] The thermal conductivity is determined from the slope of a plot of T_{id} as a function of $\ln(t)$ and the thermal diffusivity is found from the intercept. However, in the present work, we consider only the thermal conductivity from the slope of the fit line. During data analysis, a line is fit to Eq. 1 over an optimum time interval, typically from 0.1 s to 1.0 s where the magnitude of the corrections is small. The experimental temperature, T_e , associated with the thermal conductivity is the average wire temperature over the time interval that was fit for each experiment.

Four corrections were found to be significant during the present measurements on R-1336mzz(Z). The correction accounting for the finite diameter and heat capacity of the hot wire was generally the largest for both gas and liquid measurements at short experiment times of less than 0.1 s. As discussed above, the correction for finite wire length is not required for the low-temperature double-wire cell but is required for the high-temperature single-wire cell. The correction for finite wire length remains small relative to the finite wire diameter and outer boundary corrections for wires with a large length to diameter ratio like those used in the present work. The full heat correction for finite wire diameter[16] was applied to the present measurements.

Depending upon the thermal diffusivity of the gas and experimental elapsed time, it is possible for the transient temperature gradient to penetrate to the cavity wall during measurements of dilute-gas states.[15–20] Thus, the outer boundary correction also becomes very significant for some dilute-gas states. The end time for the fit interval was determined such that fluid convection was not significant, especially important for measurements in the critical region, and the outer boundary correction remained small during dilute-gas measurements. An experiment duration of 1 s was considered optimal for most transient experiments in the vapor, liquid, and supercritical states. A few dilute-gas experiments required reduction of the upper fit limit to times less than 1 s due to the large fluid thermal diffusivity, as did a few experiments near the gas-liquid critical point due to increasing fluid convection.

In the present hot-wire experiments, the thermal radiation correction remains relatively small at temperatures up to 500 K since, for small temperature rises, the thermal radiation correction is approximately proportional to $T^3 (T_1 - T_2)$. In both the gas and liquid phases we applied the transparent fluid correction.[16]

2.4. Steady-State Measurements.

Previous work[15, 21] has demonstrated for dilute-gas samples, that steady-state hot-wire measurements are reliable and require smaller corrections than transient hot-wire measurements. The steady-state solution of Fourier's law for concentric cylinders gives the fluid thermal conductivity, λ ,

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

in terms of the cell geometry and temperature rise for a given applied power per unit length, q . In Eq. 2, r_1 and T_1 are the radius and temperature of the hot wire, while r_2 and T_2 are the radius and temperature of the concentric cylindrical cavity containing the fluid. Due to the large mass and heat capacity of the cell, the temperature T_2 is assumed to be constant at the initial cell temperature measured with the platinum resistance thermometer.

A detailed discussion of steady-state measurements of dilute gases with the transient hot-wire method is given by Roder et al.[21] Fluid convection corrections increase with increasing pressure and density in the dilute gas, but at pressures below 0.7 MPa remain small. The transparent fluid correction for thermal radiation is applied in the present work. Due to the small wire diameter, the correction for eccentricity between the hot wire and the outer boundary is small.

3. Experimental Results

The thermal conductivity data for R-1336mzz(Z) are available in the Supporting Information. At each initial state point there are generally five transient or steady-state experimental results. The Helmholtz EOS of McLinden and Akasaka[7, 8] was used to calculate the densities reported in the Supporting Information. It also was used to obtain corrections required during analysis of the hot-wire temperature rise data at each measured temperature and pressure. Figure 1 shows the temperature and pressure range covered by the present measurements along with the saturation boundary for R-1336mzz(Z)[7, 8] calculated by the EOS. There were 134 transient vapor and 661 transient liquid measurements at temperatures from 192 K to 344 K, with pressures up to 69 MPa, reported from the low-temperature double-wire instrument. There were 491 steady-state vapor, 542 transient vapor, and 662 transient liquid measurements at temperatures from 311 K to 498 K reported from the high-temperature single-wire instrument. There were 804 transient supercritical measurements at temperatures from 457 K to 498 K reported from the high-temperature single-wire instrument. The average temperatures of the 14 transient vapor isotherms were (303, 312, 313, 328(twice), 341, 343, 356, 370, 385, 399, 414, 429, and 444) K. The 328 K vapor isotherm was measured in both the high-temperature and in the low-temperature apparatus. The average temperatures of the 13 steady-state vapor isotherms were (312, 327, 340, 355, 369, 384, 398, 414, 428, 443, 458, 478, and 497) K. Three supercritical isotherms at (458, 478, and 498) K were measured in the transient mode. The average temperatures of the 11 liquid isotherms were (192, 223, 252, 282, 312 (twice), 341, 342, 370, 399, and 428) K. The 312 K liquid isotherm was measured in both the low-temperature and in the high-

temperature apparatus. Figure 2 shows the measured thermal conductivity data as a function of the calculated density. The critical enhancement is significant near the critical density for the subcritical and supercritical isotherms near the critical point. Figure 2 shows the strong dependence of the thermal conductivity on density that will be the basis of the correlation described below.

The expanded uncertainty of the reported thermal conductivity is 3 % for the gas phase at pressures below 1 MPa and 1 % for the liquid-phase measurements for the low-temperature double-wire cell. The expanded uncertainty of the reported thermal conductivity is 1.5 % for the vapor and supercritical measurements at pressures above 1 MPa and densities below 200 kg·m⁻³, 3 % for gas measurements at pressures less than 1 MPa and for the supercritical isotherms for densities between 200 kg·m⁻³ and 600 kg·m⁻³ for the high-temperature single-wire cell. The expanded uncertainty is 1 % for the liquid phase and supercritical measurements from the high-temperature single-wire cell at densities above 600 kg·m⁻³.

The steady-state thermal conductivity data have an expanded uncertainty of 3 %. All steady-state measurements are gas at low pressures (less than 0.7 MPa). In the Supporting Information, the tables of steady-state data provide the Rayleigh number, calculated according to the procedure given in Ref.([21]), that characterizes the level of convection during each experiment.

4. Correlation

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

$$\lambda(\rho, T) = \lambda_0(T) + \Delta\lambda_r(\rho, T) + \Delta\lambda_c(\rho, T), \quad (3)$$

where λ_0 is the thermal conductivity of the dilute gas, which depends only on temperature,

λ_r is the residual thermal conductivity, which depends strongly on density and more weakly on temperature, and λ_c is the thermal conductivity critical enhancement, which increases dramatically in the critical region. Both λ_r and λ_c are functions of temperature, T , and molar density, ρ , with ρ calculated with an equation of state for each experimental T and P . In this work, we use the Helmholtz EOS of McLinden and Akasaka[7, 8] which is valid at temperatures from the triple point, 182.65 K, to 500 K with pressures up to 46 MPa. The EOS was developed with methodology to support good extrapolation capability, and we use extrapolated results from the EOS to provide densities at pressures between 46 MPa and 69 MPa.

4.1. Dilute-gas thermal conductivity.

The dilute-gas thermal conductivity of R-1336mzz(Z) is represented as a polynomial in reduced temperature,

$$\lambda_0(T_r)/(W \cdot m^{-1} \cdot K^{-1}) = \frac{0.001\sqrt{T_r}}{\sum_{j=0}^2 a_j \left(\frac{1}{\sqrt{T_r}}\right)^j}, \quad (4)$$

with coefficients a_j given in Table 2, where T_r is the reduced temperature T/T_c where T is the temperature and T_c is the critical temperature.

4.2. Residual thermal conductivity.

A polynomial in temperature and density is used to represent the residual contribution to the thermal conductivity of R-1336mzz(Z),

$$\Delta\lambda_r(\rho, T)/(\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}) = \sum_{i=1}^5 (B_{1i} + B_{2i}(T/T_c))(\rho/\rho_c)^i. \quad (5)$$

with coefficients B_{ij} given in Table 2, where ρ is the molar density and ρ_c is the critical density. This functional form has been used successfully to represent the thermal conductivity of several promising new refrigerants such as (1,1,1,2,2,4,5,5,5-Nonafluoro-4-(trifluoromethyl)-3-pentanone,[22] R-1234yf,[23] R-1234ze(E),[23] and R-1233zd(E).[24]

4.3. Critical Enhancement.

The theoretically based mode-coupling theory of Olchowy and Sengers[25] accurately describes the thermal conductivity enhancement in the critical region. A simplified version of their crossover model [26] is used for the thermal conductivity of R-1336mzz(Z),

$$\Delta\lambda_c(T, \rho)/(\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}) = \frac{\rho C_p R_0 k_B T}{6\pi\eta\xi}(\Omega - \Omega_0), \quad (6)$$

where the isobaric heat capacity, $C_p(T, \rho)$, is obtained from the EOS,[7] $R_0 = 1.02$ is a universal constant,[27] k_B is Boltzmann's constant, and the viscosity, $\eta(T, \rho)$, is obtained from the extended corresponding states correlation of Huber.[13] In Eq. (6), ρ is in $\text{mol} \cdot \text{m}^{-3}$, C_p is in $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$, k_B is in $\text{J} \cdot \text{K}^{-1}$, T in K, η is in Pa·s, and the correlation length ξ defined below is in m.

In addition, the crossover functions Ω and Ω_0 in Eq. (6) depend upon the correlation length and are given by

$$\Omega = \frac{2}{\pi} \left[\left(\frac{C_p - C_V}{C_p} \right) \arctan(q_d \xi) + \frac{C_V}{C_p} (q_d \xi) \right], \quad (7)$$

$$\Omega_0 = \frac{2}{\pi} \left[1 - \exp \left(\frac{-1}{(q_d \xi) + \frac{1}{3} \left(\frac{(q_d \xi) \rho_c}{\rho} \right)^2} \right) \right]. \quad (8)$$

The isochoric heat capacity, $C_v(T, \rho)$, is obtained from the EOS, with the correlation length ξ given by

$$\xi = \xi_0 \left[\frac{P_c \rho}{\Gamma \rho_c^2} \right]^{\nu/\gamma} \left[\frac{\partial \rho(T, \rho)}{\partial P} \Big|_T - \frac{T_R}{T} \frac{\partial \rho(T_R, \rho)}{\partial P} \Big|_T \right]^{\nu/\gamma}, \quad (9)$$

where 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 partial derivative ρ/P is evaluated with the EOS at the system temperature T and at a reference temperature, T_R . For the reference temperature, we select a value where the critical enhancement is found to be negligible: $T_R = 1.5 T_c$. The exponents $\gamma = 1.239$ and $\nu = 0.63$ are universal constants. [26] We used fluid specific values of the critical amplitudes calculated from the generalized method of Perkins et al., [28] $\Gamma = 0.058$ and $\xi_0 = 2.21 \times 10^{-10}$ m. The cutoff wave number q_d (or, alternatively, its inverse, q_d^{-1}) is sensitive to thermal conductivity data in the critical region and is fit to the present R-1336mzz(Z) thermal conductivity data.

4.4. Data Fitting.

The dilute-gas measurements were fit first to obtain the coefficients of the dilute gas in the limit of zero density, Eq. (4). The data for gas-phase isotherms were extrapolated to zero density, and these points, along with estimated points at very high temperatures (2000 K and 5000 K) and one low-temperature point (200 K) were fit to obtain the values in Table 2. The estimated values were obtained from a method described in Huber; [13] these points are included only to loosely guide the extrapolation behavior to eliminate unphysical behavior such as poles or negative values. The complete experimental data set including the data from Alam et al. [12], with the dilute-gas coefficients fixed, was then fit with the fitting program ODRPACK [29] to obtain the coefficients B_{ij} in Eq. (5), given in Table 2, and the value of q_d^{-1} for the critical enhancement in Eqs. (6–9). We found $q_d^{-1} = 0.955$ nm.

The validity of the fitted coefficients in Table 2 was checked by comparisons of the standard deviation of each coefficient relative to the coefficient itself. In all cases, the standard deviation was at least an order of magnitude smaller than the coefficient. The behavior of the correlation was examined and found to be smooth with reasonable extrapolation behavior. Although the EOS is limited to 46 MPa, we use it to obtain density values up to 69 MPa as we expect the extrapolation to be reliable for these pressures. Table 3 provides calculated values of the thermal conductivity at several temperatures and pressures that allow readers to verify computer coding of the correlation reported here. Values of pressure shown in Table 3 are computed from the EOS of McLinden and Akasaka [7, 8] at the specified temperatures and densities in Table 3.

4.5. Data Deviations.

The present work reports 3294 measurements of thermal conductivity of R-1336mzz(Z) in the liquid, gas, and supercritical regions from $T = 192$ K to 498 K at pressures to 69 MPa. Figure 3 shows deviations of the present experimental data and the data of Alam et al. [12] from the new correlation as a function of density over the temperature range from 302 K to 498 K for densities up to $60 \text{ kg}\cdot\text{m}^{-3}$, which corresponds to pressures no greater than 1 MPa. Figure 4 shows the deviations between the measurements and the correlation over the entire

density range of the measurements at temperatures from 192 K to 498 K with pressures up to 69 MPa. Although the gas-phase data of Alam et al.[12] are consistent with our measurements, their liquid-phase measurements are systematically ~8 to 10 % lower than our measurements. Our liquid-phase measurements were made in two different apparatus and are in agreement with each other. We do not at present have an explanation for the discrepancy with the data of Alam et al.[12] Figures 5 and 6 show deviations between all the thermal conductivity data and the correlation as a function of measured temperature and pressure, respectively. There are some single-wire steady-state vapor points shown in Figures 3 and 4, at densities between (30 and 40) $\text{kg}\cdot\text{m}^{-3}$, and Figure 5 near 360 K, with large relative deviations exceeding 8 %, likely due to convection. Finally, Figure 7 shows the data and the correlation for the supercritical isotherm at 458 K, which displays a noticeable critical enhancement.

One may note that there is a positive bias in some of the deviations that is most clearly visible in Figure 3. We based the dilute gas fit on the transient double wire (low temperatures) and the transient and steady-state results from the high-temperature single wire apparatus. Steady-state results are most accurate at the lowest densities where convection is not an issue. At increasing densities there is increased influence from convection as indicated by the Rayleigh number reported in the supporting information. We ultimately stop reporting steady-state data when the uncertainty due to this convection exceeds the uncertainty we report. However, any convection contribution remains systematically higher. It is never less than zero. The transient results have the opposite behavior with increasing uncertainty as the density decreases below 1 MPa due to increasing corrections for the finite wire diameter and for the outer boundary due to strongly increasing thermal diffusivity as the pressure/density is decreased. The transient results with these corrections applied tend to be systematically higher than they should be as the density is decreased. Thus, both the transient and steady-state results have regions that are systematically higher but still within the quoted uncertainty. The wide-range surface fit is further constrained by the density dependence at higher pressures and densities, with lower uncertainty, which seems to highlight the systematic nature of these deviations. This leads to the systematically higher data deviations in the low-density vapor.

The low-density gas-like data at pressures up to 1 MPa have an average absolute deviation (AAD) of 2.8 % for both the transient and steady-state measurements. We estimate the expanded uncertainty of the correlation in this region to be 4.2 % at a 95 % confidence level. For the liquid phase at pressures up to 69 MPa, the average absolute deviation between the measurements and the correlation is 0.5 % and the expanded uncertainty is estimated to be 1.4 % over the temperature range 192 K to 429 K. For the supercritical region, we estimate the uncertainty to be 2.8 % for densities below 200 $\text{kg}\cdot\text{m}^{-3}$, 1.8 % for intermediate densities between 200 and 800 $\text{kg}\cdot\text{m}^{-3}$, and 1.6 % for densities above 800 $\text{kg}\cdot\text{m}^{-3}$. The correlation represents the data at pressures to 69 MPa in a physically reasonable way even at pressures that exceed the recommended upper pressure limit (46 MPa) of the equation of state of McLinden and Akasaka.[7] A REFPROP[8]-compatible file implementing this correlation is available from the authors; it was not available at the time of the release of REFPROP version 10.0.

5. Conclusions

A total of 3294 points are reported for the thermal conductivity of R-1336mzz(Z) in the liquid, gas, and supercritical regions at pressures to 69 MPa. The experimental data reported here have an expanded uncertainty at a 95 % confidence level of 1 % for liquid measurements increasing to 3 % for gas at low pressures (less than 1 MPa) and in the critical region. Based on these measurements, a correlation is developed for the thermal conductivity surface of R-1336mzz(Z) covering the liquid, gas, and supercritical regions that may be used from the triple point to 500 K and pressures up to 70 MPa.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

Distribution of the data for the thermal conductivity of R-1336mzz(Z): $\square$, double-wire transient vapor; $\diamond$, single-wire steady-state vapor; $\circ$, double-wire transient liquid; $\times$, single-wire supercritical; $\odot$ single-wire transient vapor; $\triangle$, single-wire transient liquid. The solid curve shows the vapor-liquid saturation boundary, terminating at the critical point, *.

Figure 2.

Thermal conductivity of R-1336mzz(Z) as a function of the density calculated at the measured temperature and pressure: $\square$, double-wire transient vapor; $\diamond$, single-wire steady-state vapor; $\circ$, double-wire transient liquid; $\times$, single-wire supercritical; $\ominus$, single-wire transient vapor; $\triangle$, single-wire transient liquid. The critical density is indicated by the dashed line.

Figure 3.

Relative deviation between the experimental data and the correlation for the thermal conductivity of R-1336mzz(Z) as a function of density for the gas and supercritical phases at pressures up to 1 MPa (□, double-wire transient vapor; ◇, single-wire steady-state vapor; ×, single-wire supercritical, ○, single-wire transient vapor); *, Alam et al.[12]

Figure 4.

Relative deviation between the experimental data and the correlation for the thermal conductivity of R-1336mzz(Z) as a function of density: $\square$, double-wire transient vapor; $\diamond$, single-wire steady-state vapor; $\bigcirc$, double-wire transient liquid; $\times$, single-wire supercritical, $\ominus$, single-wire transient vapor; $\triangle$, single-wire transient liquid; $*$, Alam et al.[12]. The critical density is indicated by the dashed line.

Figure 5.

Relative deviation between the experimental data and the correlation for the thermal conductivity of R-1336mzz(Z) as a function of temperature: □, double-wire transient vapor; ◇, single-wire steady-state vapor; ○, double-wire transient liquid; ×, single-wire supercritical; ⊙ single-wire transient vapor; △, single-wire transient liquid. ; *, Alam et al. [12], The critical temperature is indicated by the dashed line.

Figure 6.

Relative deviation between the present experimental data and the correlation for the thermal conductivity of R-1336mzz(Z) as a function of pressure: □, double-wire transient vapor; ◇, single-wire steady-state vapor; ○, double-wire transient liquid; ×, single-wire supercritical, ⊙, single-wire transient vapor; △, single-wire transient liquid.; *, Alam et al. [12]. The critical pressure is indicated by the dashed line.

Figure 7. Supercritical isotherm at 458 K. The circles are the experimental data, and the solid curve is the correlation. The dashed line indicates the critical density.

Table 1.

Sample Summary Table.

Chemical Name	Source	Initial Mole Fraction Purity	Purification Method	Final Mole Fraction Purity	Analysis Method
<i>cis</i> -1,1,1,4,4,4-hexafluoro-2-butene ^a	Chemours	0.9999	Freeze-Thaw Degassing	0.9999	GC/QToF-MS ^b

^aAlso known as R-1336mzz(Z), CAS number 692-49-9.

^bGas chromatography/quadrupole time-of-flight mass spectroscopy

Table 2.

Parameters for the dilute-gas and residual thermal conductivity of Eqs. 4 and 5 for R-1336mzz(Z).

Dilute-Gas Thermal Conductivity of Eq 4		
j	$a_j / (\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1})^{-1}$	
0	0.033207	
1	−0.089513	
2	0.101275	
Residual Thermal Conductivity of Eq 5		
i	j	$B_{ij} / (\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1})$
1	1	0.0182670
1	2	0.105672
1	3	−0.119719
1	4	0.0431845
1	5	−0.00497023
2	1	−0.0138014
2	2	−0.0756253
2	3	0.0919892
2	4	−0.0327931
2	5	0.00384035

Table 3.

Values of thermal conductivity calculated for R-1336mzz(Z) with the correlation (Eq. 3 to 9) at specified T and ρ , with the coefficients in Table 2. The value of viscosity used for $T=450$ K and $\rho=500.0$ kg·m⁻³ is 29.937 μPa·s, calculated with the correlation of Huber.[13]

T / K	ρ (kg·m ⁻³)	ρ / MPa [*]	λ (W·m ⁻¹ ·K ⁻¹)
300.0	0.00	0.00	0.011056
300.0	1363.0	0.98613	0.078701
450.0	0.00	0.00	0.022723
450.0	500.0	2.3261	0.053990
450.0	500.0	2.3261	0.038462 ^{**}

^{*} Pressures calculated with the equation of state of McLinden and Akasaka[7, 8]

^{**} Calculated with critical enhancement = 0.