

# Reference Correlation of the Thermal Conductivity of Sulfur Hexafluoride from the Triple Point to 1000 K and up to 150 MPa

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This paper contains new, representative reference equations for the thermal conductivity of SF<sub>6</sub>. The equations are based in part upon a body of experimental data that has been critically assessed for internal consistency and for agreement with theory whenever possible. Although there are a sufficiently large number of data at intermediate temperatures, data at very low or very high temperatures as well as near the critical region are scarce. In the case of the dilute-gas thermal conductivity, a theoretically based correlation was adopted in order to extend the temperature range of the experimental data. Moreover, in the critical region, the experimentally observed enhancement of the thermal conductivity is well represented by theoretically based equations containing just one adjustable parameter. The correlations are applicable for the temperature range from the triple point to 1000 K and pressures up to 150 MPa. The overall uncertainty (considered to be estimates of a combined expanded uncertainty with a coverage factor of two) of the proposed correlation is estimated, for pressures less than 150 MPa and temperatures less than 1000 K, to be less than 4%. © 2012 by the U.S. Secretary of Commerce on behalf of the United States. All rights reserved. [<http://dx.doi.org/10.1063/1.4708620>]

Key words: critical phenomena; SF<sub>6</sub>; thermal conductivity; transport properties.

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## 1. Introduction

Sulfur hexafluoride was originally synthesized in 1900 by Moissan and Lebeau, in the laboratories of the Faculté de Pharmacie in Paris. A stable gas was obtained following the exothermic reaction of sulfur with fluorine gas obtained by electrolysis. Following this, the physical and chemical properties of SF<sub>6</sub> were established in a series of publications.<sup>1-5</sup>

In 1937, the General Electric Company was probably the first to research the possibility of employing the gas for insulation in electrical plants. In 1939, Thomson-Houston patented the principle of using SF<sub>6</sub> in insulating cables and capacitors. Immediately after World War II, a wide range of applications of SF<sub>6</sub> began to appear. In 1947 work on transformer insulation started, while in 1948 Allied Chemical Corporation and Pennwalt started the industrial manufacture of SF<sub>6</sub>. In 1960, the large scale commercialization of SF<sub>6</sub> manufacture for use in electrical plant construction in the USA and in Europe coincided with the appearance of the first SF<sub>6</sub> circuit-breakers and switches at high voltage (HV) and extra high voltage (EHV). The unique properties of SF<sub>6</sub> have led to its adoption for a number of industrial and scientific applications including, for example,

- medical applications: electrical insulation in medical equipment (e.g., x-ray machines) for surgery,
- electrical insulation in scientific equipment (electron microscopes, particle accelerators such as Van de Graaff generators),
- acoustic insulation in double glazed windows,
- tracer gas for studying airflow in ventilation systems (for instance in mines) or in the high atmosphere,
- tracer for leak detection in pressurized systems, and
- special atmosphere for metallurgical processing (aluminum and magnesium) or for military purposes.

Recently, Guder and Wagner<sup>6</sup> have reviewed the thermodynamic properties of SF<sub>6</sub> and developed an accurate, wide-ranging equation of state. Recommended tabular values for the thermal conductivity of SF<sub>6</sub> are available in the handbook of Vargaftik.<sup>7</sup> Furthermore, Quiñones-Cisneros *et al.*<sup>8</sup> recently published a correlation for the viscosity of SF<sub>6</sub> from the triple point to 1000 K and pressures up to 50 MPa. The goal of this work is to critically assess the available literature data, and provide a wide-ranging correlation for the thermal conductivity of SF<sub>6</sub> that is valid over gas, liquid, and super-

critical states, and that incorporates densities provided by the equation of state of Guder and Wagner.<sup>6</sup> It should further be noted that, although there are some alternative approaches today for such correlations (e.g., neural networks), we preferred to follow a procedure based upon kinetic theory and our previous work, as will be discussed in the following sections.

## 2. Methodology

The thermal conductivity  $\lambda$  is expressed as the sum of three independent contributions, as

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

where  $\rho$  is the density,  $T$  is the temperature, and the first term,  $\lambda_o(T) = \lambda(0, T)$ , is the contribution to the thermal conductivity in the dilute-gas limit, where only two-body molecular interactions occur. The final term,  $\Delta\lambda_c(\rho, T)$ , the critical enhancement, arises from the long-range density fluctuations that occur in a fluid near its critical point, which contribute to divergence of the thermal conductivity at that point. Finally, the term  $\Delta\lambda(\rho, T)$ , the residual property, represents the contribution of all other effects to the thermal conductivity of the fluid at elevated densities including many-body collisions, molecular-velocity correlations, and collisional transfer.

The identification of these three separate contributions to the thermal conductivity and to transport properties in general is useful because it is possible, to some extent, to treat both  $\lambda_o(T)$  and  $\Delta\lambda_c(\rho, T)$  theoretically. In addition, it is possible to derive information about  $\lambda_o(T)$  from experiment. In contrast, there is almost no theoretical guidance concerning the residual contribution,  $\Delta\lambda(\rho, T)$ , so that its evaluation is based entirely on experimentally obtained data.

The analysis described above should be applied to the best available experimental data for the thermal conductivity. Thus, a prerequisite to the analysis is a critical assessment of the experimental data. For this purpose, two categories of experimental data are defined: primary data employed in the development of the correlation and secondary data used simply for comparison purposes. According to the recommendation adopted by the Subcommittee of Transport Properties (now known as The International Association for Transport Properties) of the International Union of Pure and Applied Chemistry, the primary data are identified by the following criteria:<sup>9</sup>

- (i) Measurements must have been made with a primary experimental apparatus, *i.e.*, one for which a complete working equation is available.
- (ii) The form of the working equation should be such that sensitivity of the property measured to the principal variables does not magnify the random errors of measurement.
- (iii) All principal variables should be measurable to a high degree of precision.
- (iv) The published work should include description of purification methods and a guarantee of the purity of the sample.

- (v) The data reported must be unsmoothed data. While graphs and fitted equations are useful summaries for the reader, they are not sufficient for standardization purposes.
- (vi) The lack of accepted values of the thermal conductivity of standard reference materials implies that only absolute and not relative measurement results can be considered.
- (vii) Explicit quantitative estimates of the uncertainty of reported values should be given, taking into account the precision of experimental measurements and possible systematic errors.
- (viii) Owing to the desire to produce low-uncertainty reference values, limits must be imposed on the uncertainties of the primary data sets. These limits are determined after critical evaluation of the existing data sets.

These criteria have been successfully employed to establish standard reference values for the viscosity and thermal conductivity of fluids over wide ranges of conditions, with uncertainties in the range of 1%. However, in many cases, such a narrow definition unacceptably limits the range of the data representation. Consequently, within the primary data set, it is also necessary to include results that extend over a wide range of conditions, albeit with a poorer accuracy, provided they are consistent with other more accurate data or with theory. In all cases, the accuracy claimed for the final recommended data must reflect the estimated uncertainty in the primary information.

### 3. The Correlation

Table 1 summarizes, to the best of our knowledge, the experimental measurements of the thermal conductivity of SF<sub>6</sub> reported in the literature. Seventeen sets are included in the table. From these sets, seven were considered as primary data.

The data of Perkins *et al.*<sup>10</sup> were measured in an absolute transient hot-wire instrument with an uncertainty of approximately 1% for the liquid, increasing to 3% in the critical region and for dilute gas at pressures below 1 MPa, and this set was considered as primary data. The measurements of Kestin and Imaishi<sup>11</sup> were also performed in an absolute transient hot-wire instrument with an uncertainty of 0.3%, and this set is part of the primary data. The measurements of Bakulin and Ulybin<sup>12</sup> were performed in transient hot-wire instruments but of slightly higher uncertainty, and were also considered as primary data. Although the measurements of Choy and Raw<sup>14</sup> were performed on a relative basis in a transient hot-wire instrument, they were also considered as primary data, as they extended to 703 K. Rastorguev *et al.*<sup>13</sup> and Lis and Kellard<sup>15</sup> measured the thermal conductivity of SF<sub>6</sub> employing concentric-cylinders instruments. These two sets were considered as part of the primary data. Finally the measurements of Venart,<sup>16</sup> performed in a radial heat-flow instrument, were also considered as primary data.

Jany and Straub<sup>17</sup> and Letaief *et al.*<sup>18</sup> measured the thermal diffusivity of SF<sub>6</sub> near the critical point. Both sets were considered as secondary data, as conversion to thermal conductivity near the critical point is subject to large uncertainties,

TABLE 1. Thermal conductivity measurements of SF<sub>6</sub>

1st author	Year Publ.	Technique employed <sup>a</sup>	Purity (%)	Uncertainty (%)	No. of data	Temperature range (K)	Pressure range (MPa)
<b>Primary data</b>							
Perkins <sup>10</sup>	2012	THW	99.996	1–3	1902	226–348	0.08–68
Kestin <sup>11</sup>	1985	THW	99.99	0.3	16	300	0.8–2.2
Bakulin <sup>12</sup>	1978	HF	98.00	2.5	100	230–350	0.1–50
Rastorguev <sup>13</sup>	1977	CC	99.78	1.5	210	250–473	2–113
Choy <sup>14</sup>	1966	THW (Rel)	98.00	2.0	7	325–703	0.1
Lis <sup>15</sup>	1965	CC	99.00	1.5	66	311–365	0.6–5.1
Venart <sup>16</sup>	1964	RHF	99.90	2.0	2	293,303	0.1
<b>Secondary data</b>							
Jany <sup>17</sup>	1987	DLS	na	na	310	283–353	1.5–12
Letaief <sup>18</sup>	1986	CC	na	2.0	51	280–411	1.3–5
Totskii <sup>19</sup>	1984	THW	99.97	1.8–5.0	18	291–364	3.9–40
Totskii <sup>20</sup>	1984	THW	99.97	1.8–2.3	45	291–319	2–3.9
Cherneeva <sup>21</sup>	1983	PP (Rel)	na	1.8	42	323–423	0.1–2
Burinskii <sup>22</sup>	1981	THW	99.90	2.0	130	293–363	0.1–20
Tanaka <sup>23</sup>	1979	CC (Rel)	99.50	2.0	115	298–373	0.1–7
Bakulin <sup>24</sup>	1976	HF	98.00	2.5	14	300–1000	0.1
Donaldson <sup>25</sup>	1970	CCaps (Rel)	na	2.0	17	283–347	0.1
Plank <sup>26</sup>	1958	na	na	na	1	303	0.012

<sup>a</sup>CC, coaxial cylinder; CCaps, concentric capsule; DLS, dynamic light scattering; HF, hot filament; na, not available; PP, parallel plate; RHF, radial heat flow; Rel, relative; THW, transient hot wire.

and resulted in values that deviated far too much from all other measurements. The measurements of Burinskii *et al.*<sup>22</sup> and Totskii *et al.*,<sup>19,20</sup> performed in the same laboratory in a transient hot-wire instrument, produced values that are much higher than other sets in this range. The measurements of Cherneeva<sup>21</sup> were considered as secondary data, as the measurements are presented only in a very unclear diagram. The data of Tanaka *et al.*<sup>23</sup> were performed on a relative basis, and thus were part of the secondary data set. The high-temperature data of Bakulin *et al.*<sup>24</sup> were also considered as secondary data, as they were lower than other measurements which was possibly attributed (according to his paper) to the decomposition of SF<sub>6</sub>. The measurements of Donaldson,<sup>25</sup> performed on a relative basis in an instrument consisting of two concentric capsules, were also part of the secondary data set, together with the measurement of Plank<sup>26</sup> performed in 1958.

Figure 1 shows the temperature and pressure range of the primary measurements outlined in Table 1. Temperatures for all data were converted to the ITS-90 temperature scale. The development of the correlation requires densities; the equation of state of Guder and Wagner,<sup>6</sup> valid from the melting line to 625 K extrapolated to 1000 K and up to 150 MPa, was used to provide the density for each experimental state point from the experimental temperature and pressure. We also adopt the values for the critical point and triple point from their equation of state; the critical temperature,  $T_c$ , the critical pressure,  $p_c$ , and the critical density,  $\rho_c$ , were taken to be equal to 318.7232 K, 3.75498 MPa, and 742.297 kg m<sup>-3</sup>, respectively. The triple-point temperature is 223.555 K.<sup>27</sup> It should be noted that, for this equation of state, the uncertainties in density from an input of temperature and pressure are 0.02% for temperatures less than 340 K (<30 MPa), 0.03% for temperatures below 500 K (<30 MPa), 0.1% increasing to 0.3% at temperatures above 500 K, and 0.2% for all temperatures at pressures above 30 MPa increasing to 1% at the pressure limits of the equation of state. The uncertainties in heat capacities are generally within 2%, decreasing to 0.2% at the lowest pressures in the vapor phase; below 400 K and above 20 MPa, the uncertainties are 5%.

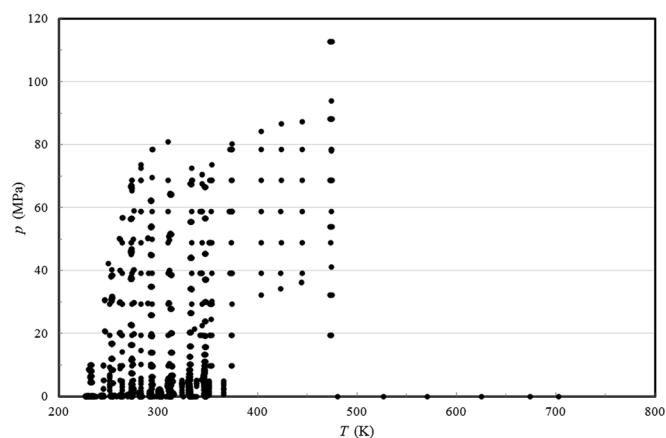


FIG. 1. Temperature and pressure ranges of the experimental thermal-conductivity data for SF<sub>6</sub>.

### 3.1. The dilute-gas limit

From the primary measurements shown in Table 1, only five investigators (Perkins *et al.*,<sup>10</sup> Bakulin and Ulybin,<sup>12</sup> Choy and Raw,<sup>14</sup> Lis and Kellard,<sup>15</sup> and Venart<sup>16</sup>) performed measurements near the dilute-gas limit. As only one of these sets (Choy and Raw<sup>14</sup>) extends to 700 K, a theoretically based scheme was preferred in order to correlate the dilute-gas limit thermal conductivity,  $\lambda_o(T)$ , over a wide temperature range.

A reasonable estimate of the thermal conductivity,  $\lambda_o(T)$ , of a pure dilute gas may be obtained from the viscosity,  $\eta_o(T)$ , and ideal-gas heat capacity at constant volume,  $C_{Vo}$ , through the modified Eucken correlation,<sup>28</sup>

$$f_{Eu} = \frac{\lambda_o(T)M}{\eta_o(T)C_{Vo}} = 1.32 + 1.77 \left( \frac{R}{C_{Vo}} \right). \quad (2)$$

In the above equation,  $M$  represents the molar mass of sulfur hexafluoride<sup>29</sup> (146.05 g/mol), and  $R$  the universal gas constant<sup>30</sup> (8.3144721 J mol<sup>-1</sup> K<sup>-1</sup>). To employ the above equation, the dilute-gas viscosity and the ideal-gas heat capacity at constant volume are required. Although recently Quiñones-Cisneros *et al.*<sup>8</sup> published a correlation for the dilute-gas viscosity, a different approach (not optimized for the viscosity), allowing more flexibility, was preferred. Hence, the dilute-gas viscosity can easily be written as a function of the reduced collision integral  $\Omega^*(T^*)$ , as

$$\eta_o(T) = \frac{5}{16} \left[ \frac{MRT}{\pi} \right]^{1/2} \frac{1}{\sigma^2 \Omega^*(T^*)} = 0.0266957 \frac{\sqrt{MT}}{\sigma^2 \Omega^*(T^*)}, \quad (3)$$

where the viscosity is expressed in  $\mu\text{Pa s}$ , the temperature is in kelvins, and  $\sigma$  is in nm. The reduced collision integral can be calculated<sup>31</sup> as a function of the reduced temperature,  $T^* = T (k_B/\epsilon)$ , for the range  $0.3 < T^* < 100$ , as

$$\begin{aligned} \Omega^*(T^*) &= 1.16145(T^*)^{-0.14874} + 0.52487 e^{-0.7732T^*} \\ &+ 2.16178 e^{-2.43787T^*} - 6.435 \times 10^{-4} (T^*)^{0.14874} \\ &\times \sin \left[ 18.0323(T^*)^{-0.7683} - 7.27371 \right], \quad (4) \end{aligned}$$

and the ideal-gas heat capacity at constant volume,  $C_{Vo}$ , can be obtained from the heat capacity at constant pressure,  $C_{Po}$  (J mol<sup>-1</sup> K<sup>-1</sup>), (as  $C_{Po} - C_{Vo} = R$ ), as this is given by<sup>6</sup>

$$\frac{C_{Po}(T)}{R} = 4 + \sum_{i=1}^3 n_i^o (\theta_i^o \tau)^2 \frac{\exp(\theta_i^o \tau)}{[\exp(\theta_i^o \tau) - 1]^2}. \quad (5)$$

The coefficients  $n_i^o$  and  $\theta_i^o$  are given in Table 2, with the reduced temperature  $\tau = T_c/T$ . Equations (2)–(5) form a consistent scheme for the calculation of the dilute-limit thermal conductivity. It should be noted that the above equations assume that SF<sub>6</sub> behaves like a Lennard-Jones gas, an assumption that is very reasonable due to its shape. Furthermore, the



TABLE 2. Coefficients of Eq. (5) for the dilute-gas thermal conductivity of SF<sub>6</sub>

$i$	$n_i^0$	$\theta_i^0$
1	3.661 182 320	1.617 282 065
2	7.878 851 030	2.747 115 139
3	3.459 816 790	4.232 907 175

fixed numerical value employed in the modified Eucken correlation, Eq. (2), was preferred, as it was simpler and at the same time produced very good results.

In the above scheme, the only unknowns are the Lennard-Jones parameters,  $\sigma$  and  $\varepsilon/k_B$ . The five sets of thermal conductivity measurements in the dilute limit were used to optimize these two parameters. The values thus obtained were  $\sigma = 0.508$  nm and  $\varepsilon/k_B = 265$  K. These values also predict the viscosity values of Strehlow and Vogel<sup>32</sup> within  $\pm 5\%$ . The experimental dilute-limit thermal-conductivity values as well as the values predicted by the scheme of Eqs. (2)–(5) are shown in Fig. 2, while Fig. 3 presents the percentage deviations of the dilute-gas experimental data from the values calculated by this scheme. The only experimental value with large deviations ( $\sim 10\%$ ) is the first measurement at 52 °C of the high-temperature data of Choy and Raw,<sup>14</sup> which could be attributed to inaccurate furnace operation at low temperatures. This point is also an outlier in the correlation of Kestin and Imaishi.<sup>11</sup>

Figure 3 also shows the deviations of previous schemes from the proposed scheme of Eqs. (2)–(5), as

- The theoretical correlation of Altunin,<sup>33</sup> covering the temperature range of 230–1000 K, was based on the data of Choy and Raw<sup>14</sup> and Lis and Kellard,<sup>15</sup> and agrees well with the present correlation. The larger deviations below 300 K are attributed to the choice of data employed for that region.
- Uribe *et al.*,<sup>34</sup> covering the temperature range of 250–3000 K and published in 1990, is a theoretically based cor-

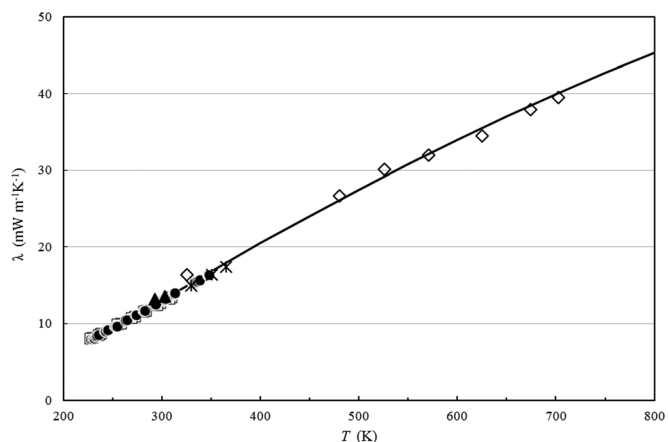


FIG. 2. Dilute-gas limit thermal conductivity as a function of temperature. Perkins *et al.*<sup>10</sup> (●), Bakulin and Ulybin<sup>12</sup> (□), Choy and Raw<sup>14</sup> (◇), Lis and Kellard<sup>15</sup> (×), Venart<sup>16</sup> (▲), (—) Eqs. (2)–(5).

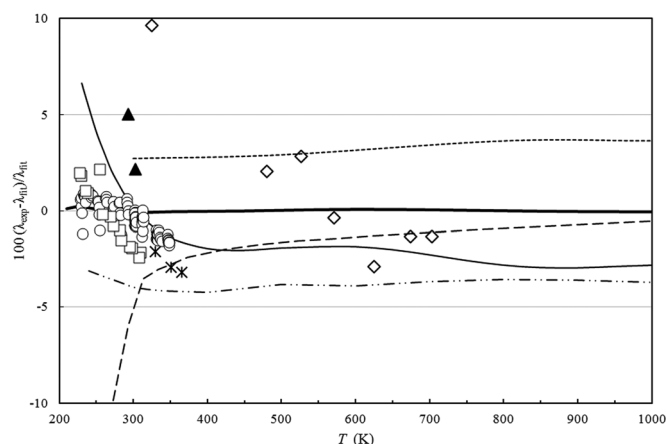


FIG. 3. Percentage deviations of the dilute-gas limit thermal conductivity measurements from the scheme described by Eqs. (2)–(5). Perkins *et al.*<sup>10</sup> (○), Bakulin and Ulybin<sup>12</sup> (□), Choy and Raw<sup>14</sup> (◇), Lis and Kellard<sup>15</sup> (×), Venart<sup>16</sup> (▲), Eq. (6) (—), Stefanov *et al.*<sup>35</sup> (---), Uribe *et al.*<sup>34</sup> (—), Altunin<sup>33</sup> (—), and Svehla<sup>36</sup> (---).

relation that employed the data of Tanaka *et al.*<sup>23</sup> and extrapolated values of Kestin and Imaishi.<sup>11</sup> This correlation agrees within 3% with the present correlation, over the temperature range 300–3000 K. The larger deviations in the temperature range 270–300 K cannot be explained.

- Stefanov *et al.*<sup>35</sup> presented a theoretically based correlation covering the temperature range 220–1000 K. His correlation employed the data of Bakulin and Ulybin,<sup>12</sup> Bakulin,<sup>24</sup> Tanaka *et al.*,<sup>23</sup> Cherneeva,<sup>21</sup> Burinskii *et al.*,<sup>22</sup> and extrapolated values of Kestin and Imaishi.<sup>11</sup> This correlation also agrees with the present correlation over its whole range within 4%.
- Finally, in the same figure the older theoretically based correlation of Svehla<sup>36</sup> is also included. This correlation agrees with the present correlation.

Based upon the aforementioned discussion, Eqs. (2)–(5) represent the dilute-gas limit thermal conductivity to within  $\pm 3.6\%$  at the 95% confidence level.

For ease of use, the values of the dilute-gas limit thermal conductivity,  $\lambda_o(T)$  (mW m<sup>-1</sup> K<sup>-1</sup>), obtained by the scheme of Eqs. (2)–(5), were fitted, which resulted in the equation,

$$\lambda_o(T) = \frac{1461860 - 18539.4T + 77.7891T^2 + 0.0241059T^3}{29661.7 + 505.67T + T^2} \quad (6)$$

Values calculated by this equation do not deviate from the values calculated by the scheme of Eqs. (2)–(5) by more than 0.3% over the temperature range 223–1000 K, and hence Eq. (6) was used for the dilute-gas limit thermal conductivity for the work described in all of the following sections.

### 3.2. The 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 residual values far away from the critical point.<sup>37–39</sup> The density-dependent terms for thermal conductivity can be grouped according to Eq. (1) as  $[\Delta\lambda(\rho, T) + \Delta\lambda_c(\rho, T)]$ . To assess the critical enhancement either theoretically or empirically, we need to evaluate, in addition to the dilute-gas thermal conductivity, the residual thermal-conductivity contribution. The procedure adopted during this analysis used ODRPACK (Ref. 40) to fit all the primary data simultaneously to the residual thermal conductivity and the critical enhancement, while maintaining the parameters in Eq. (6) already obtained from the fit of the dilute-gas thermal-conductivity data. The density values employed were obtained by the equation of state of Guder and Wagner.<sup>6</sup>

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

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

The coefficients  $B_{1,i}$  and  $B_{2,i}$  are shown in Table 3.

### 3.3. The critical enhancement

#### 3.3.1. Simplified crossover model

The theoretically based crossover model proposed by Olchowy and Sengers<sup>37–39</sup> 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.<sup>41</sup> The critical enhancement of the thermal conductivity from this simplified model is given by

$$\Delta\lambda_c = \frac{\rho C_p R_D k_B T}{6\pi\bar{\eta}\xi} (\bar{\Omega} - \bar{\Omega}_0), \quad (8)$$

with

$$\bar{\Omega} = \frac{2}{\pi} \left[ \left( \frac{C_p - C_v}{C_p} \right) \arctan(\bar{q}_D \xi) + \frac{C_v}{C_p} \bar{q}_D \xi \right] \quad (9)$$

and

$$\bar{\Omega}_0 = \frac{2}{\pi} \left[ 1 - \exp \left( - \frac{1}{(\bar{q}_D \xi)^{-1} + (\bar{q}_D \xi \rho_c / \rho)^2 / 3} \right) \right]. \quad (10)$$

TABLE 3. Coefficients of Eq. (7) for the residual thermal conductivity of SF<sub>6</sub>

$i$	$B_{1,i}$ (W m <sup>-1</sup> K <sup>-1</sup> )	$B_{2,i}$ (W m <sup>-1</sup> K <sup>-1</sup> )
1	$-2.837\,46 \times 10^{-2}$	$3.527\,68 \times 10^{-2}$
2	$2.074\,72 \times 10^{-2}$	$-4.330\,53 \times 10^{-2}$
3	$-5.571\,80 \times 10^{-3}$	$5.120\,84 \times 10^{-2}$
4	$5.328\,90 \times 10^{-3}$	$-2.902\,62 \times 10^{-2}$
5	$-1.616\,88 \times 10^{-3}$	$5.984\,38 \times 10^{-3}$

In Eqs. (8)–(10),  $k_B$  is Boltzmann's constant,  $\bar{\eta}$  is the viscosity obtained from the correlation of Quiñones-Cisneros *et al.*,<sup>8</sup> and  $C_p$  and  $C_v$  are the isobaric and isochoric specific heat obtained from the Guder and Wagner<sup>6</sup> equation of state. The correlation length  $\xi$  is given by

$$\xi = \xi_0 \left( \frac{p_c \rho}{\Gamma \rho_c^2} \right)^{\nu/\gamma} \left[ \left. \frac{\partial \rho(T, \rho)}{\partial p} \right|_T - \left( \frac{T_{\text{ref}}}{T} \right) \left. \frac{\partial \rho(T_{\text{ref}}, \rho)}{\partial p} \right|_T \right]^{\nu/\gamma}. \quad (11)$$

As already mentioned, the coefficients  $B_{1,i}$  and  $B_{2,i}$  in Eq. (7) and  $\bar{q}_D$  in Eqs. (8)–(11) were fitted with ODRPACK (Ref. 40) to the primary data for the thermal conductivity of SF<sub>6</sub>. This crossover model requires the universal constants<sup>41</sup>  $R_D = 1.01$ ,  $\nu = 0.63$ , and  $\gamma = 1.2415$ , and system-dependent amplitudes  $\Gamma$  and  $\xi_0$ . For this work we adopted the values  $\Gamma = 0.052$  and estimated  $\xi_0 = 1.9 \times 10^{-10}$  m, using the method presented in Ref. 10. The effective wavenumber cut-off  $\bar{q}_D$  was found to be equal to  $3.5 \times 10^{-10}$  m. The reference temperature  $T_{\text{ref}}$ , far above the critical temperature where the critical enhancement is negligible, was calculated by  $T_{\text{ref}} = (3/2) T_c$ ,<sup>42</sup> which for SF<sub>6</sub> is 717.12 K.

Table 4 summarizes comparisons of the primary data with the correlation. We have defined the percent deviation as  $\text{PCTDEV} = 100 * (\lambda_{\text{exp}} - \lambda_{\text{fit}}) / \lambda_{\text{fit}}$ , where  $\lambda_{\text{exp}}$  is the experimental value of the thermal conductivity and  $\lambda_{\text{fit}}$  is the value calculated from the correlation. Thus, the average absolute percent deviation (AAD) is found with the expression  $\text{AAD} = (\sum |\text{PCTDEV}|) / n$ , where the summation is over all  $n$  points, the bias percent is found with the expression  $\text{BIAS} = (\sum \text{PCTDEV}) / n$ , and the standard deviation is  $\text{STDEV} = ([n \sum \text{PCTDEV}^2 - (\sum \text{PCTDEV})^2] / n^2)^{1/2}$ .

Figure 4 shows the percentage deviations of all primary thermal-conductivity data from the values calculated by Eqs. (1)–(11), as a function of the density, while Figs. 5 and 6 show the same deviations but as a function of the temperature and pressure. The primary data for SF<sub>6</sub> listed in Table 1 cover a wide range of conditions and extend to 150 MPa. Based on comparisons with the primary data, we estimate the uncertainty (considered to be estimates of a combined expanded uncertainty with a coverage factor of

TABLE 4. Evaluation of the SF<sub>6</sub> thermal-conductivity correlation for the primary data

1st author	Year Publ.	AAD (%)	BIAS (%)	STDEV (%)
Perkins <sup>10</sup>	2012	1.21	0.90	1.31
Kestin <sup>11</sup>	1985	0.27	-0.19	0.24
Bakulin <sup>12</sup>	1978	1.81	-0.97	2.27
Rastorguev <sup>13</sup>	1977	2.11	-1.78	2.09
Choy <sup>14</sup>	1966	2.83	-0.65	3.62
Lis <sup>15</sup>	1965	3.27	-1.88	4.04
Venart <sup>16</sup>	1964	3.08	-3.08	1.34
Entire data set		1.44	0.42	2.06

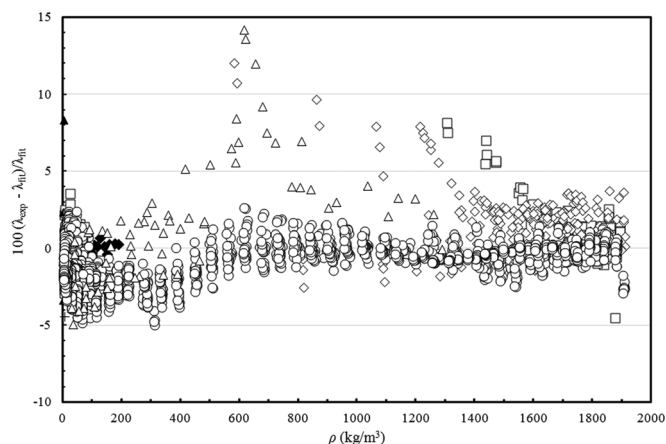


Fig. 4. Percentage deviations of primary experimental data of SF<sub>6</sub> from the values calculated by the present model as a function of density. Perkins *et al.*<sup>10</sup> (○), Bakulin and Ulybin<sup>12</sup> (□), Kestin and Imaishi<sup>11</sup> (◆), Rastorguev *et al.*<sup>13</sup> (◇), Choy and Raw<sup>14</sup> (▲), Lis and Kellard<sup>15</sup> (△), and Venart<sup>16</sup> (+).

two) for pressures less than 150 MPa and temperatures less than 1000 K to be less than 4%. Uncertainties in the critical region are much larger, since the thermal conductivity approaches infinity at the critical point.

Figure 7 shows the deviations of the secondary data from the values calculated by the proposed scheme. This figure shows that the deviations rise up to 25%. However, most of the larger deviations refer to data in the vicinity of the critical point. Although the data of Burinski *et al.*<sup>22</sup> and Totskii *et al.*<sup>19,20</sup> were performed in the same laboratory, they also show large deviations among themselves, probably attributed to convection. The high-temperature atmospheric-pressure data of Bakulin *et al.*<sup>24</sup> are influenced by dissociation of the molecule according to the author, while the data of Cherneeva<sup>21</sup> are higher than all other data. Deviations up to 25% are also present in the data of Tanaka *et al.*<sup>23</sup> near the critical density.

The thermal diffusivity data of Jany and Straub<sup>17</sup> and Letaief *et al.*,<sup>18</sup> when converted to thermal-conductivity val-

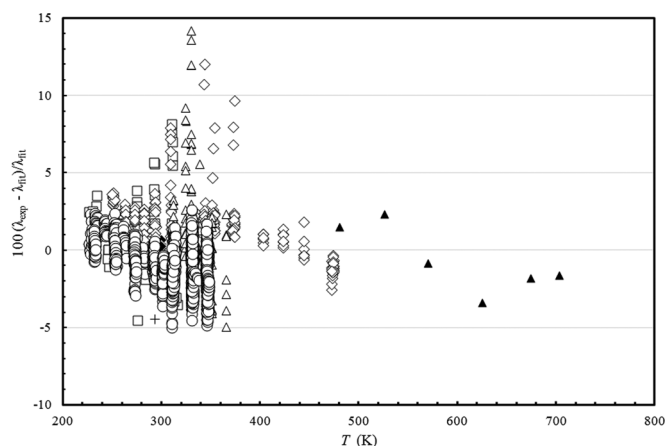


Fig. 5. Percentage deviations of primary experimental data of SF<sub>6</sub> from the values calculated by the present model as a function of temperature. Perkins *et al.*<sup>10</sup> (○), Bakulin and Ulybin<sup>12</sup> (□), Kestin and Imaishi<sup>11</sup> (◆), Rastorguev *et al.*<sup>13</sup> (◇), Choy and Raw<sup>14</sup> (▲), Lis and Kellard<sup>15</sup> (△), and Venart<sup>16</sup> (+).

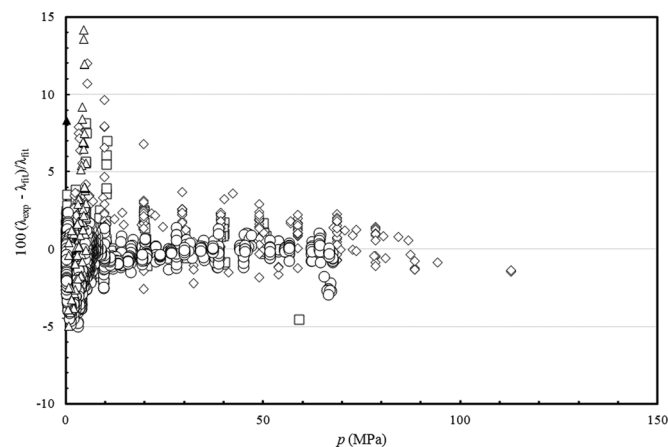


Fig. 6. Percentage deviations of primary experimental data of SF<sub>6</sub> from the values calculated by the present model as a function of pressure. Perkins *et al.*<sup>10</sup> (○), Bakulin and Ulybin<sup>12</sup> (□), Kestin and Imaishi<sup>11</sup> (◆), Rastorguev *et al.*<sup>13</sup> (◇), Choy and Raw<sup>14</sup> (▲), Lis and Kellard<sup>15</sup> (△), and Venart<sup>16</sup> (+).

ues, produced results which were too far away from all other data to be useful, as they were performed near the critical point.

Finally, Fig. 8 shows a plot of the thermal conductivity of SF<sub>6</sub> as a function of the temperature for different pressures.

### 3.3.2. Empirical critical enhancement

For applications at state points that are relatively distant from the critical point (at least 10–15 K from the critical temperature), the critical enhancement is adequately represented by the following empirical expression:

$$\Delta\lambda_c(\rho, T) = \frac{C_1}{C_2 + |\Delta T_c|} \exp\left[-(C_3\Delta\rho_c)^2\right], \quad (12)$$

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, specific heat, and viscosity of SF<sub>6</sub> in the critical region, as

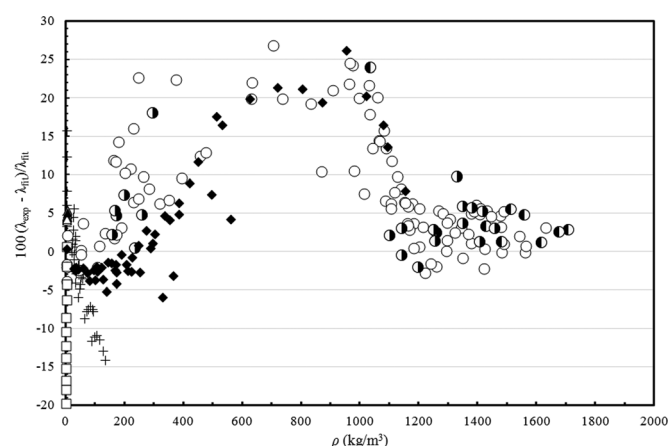


Fig. 7. Percentage deviations of secondary experimental data of SF<sub>6</sub> from the values calculated by the present model as a function of density. Cherneeva<sup>21</sup> (+), Burinski *et al.*<sup>22</sup> (○), Totskii *et al.*<sup>19</sup> (●), Totskii *et al.*<sup>20</sup> (⊙), Bakulin *et al.*<sup>24</sup> (□), Tanaka *et al.*<sup>23</sup> (◆), and Planck<sup>26</sup> (▲).

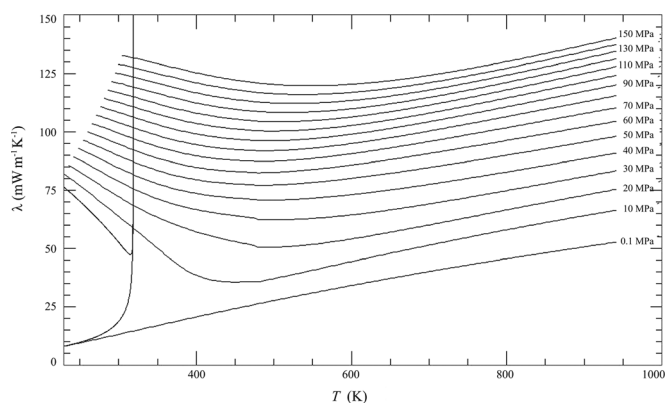


Fig. 8. Thermal conductivity of SF<sub>6</sub> as a function of temperature for different pressures.

does the theory of Olchowy and Sengers.<sup>37–39</sup> The coefficients of Eq. (7) were fixed, while the coefficients of Eq. (12) were fitted to the primary data. The values obtained were  $C_1 = 1.5 \times 10^{-3} \text{ W m}^{-1} \text{ K}^{-1}$ ,  $C_2 = 7.0 \times 10^{-2}$ , and  $C_3 = 1.8$ . Figure 9 shows the percentage deviations between the primary data and the values calculated by Eqs. (1), (6), (7), and (12) as a function of the temperature. By comparing Figs. 5 and 9, it can be seen that employing Eq. (12) results in little deterioration in the representation of the data.

#### 4. Computer-Program Verification

Table 5 is provided to assist the user in computer-program verification. The thermal-conductivity calculations are based on the tabulated temperatures and densities. Note that Eq. (6) was employed for the dilute-gas correlation.

#### 5. Conclusion

New wide-ranging correlations for the thermal conductivity of SF<sub>6</sub> were developed based on critically evaluated

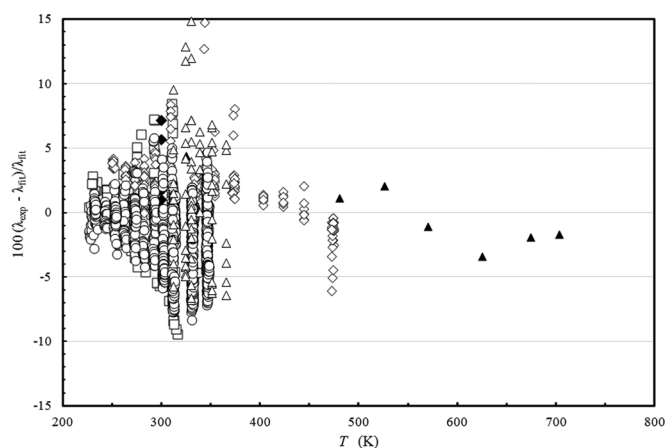


Fig. 9. Percentage deviations of primary experimental data of SF<sub>6</sub> from the values calculated by Eqs. (1), (6), (7), and (12) as a function of temperature. Perkins *et al.*<sup>10</sup> (○), Bakulin and Ulybin<sup>12</sup> (□), Kestin and Imaishi<sup>11</sup> (◆), Rastorguev *et al.*<sup>13</sup> (◇), Choy and Raw<sup>14</sup> (▲), Lis and Kellard<sup>15</sup> (△), and Venart<sup>16</sup> (+).

TABLE 5. Sample points for computer verification of the correlating equations

$T$ (K)	$\rho$ (kg m <sup>-3</sup> )	$\lambda$ (mW m <sup>-1</sup> K <sup>-1</sup> )
298.15	0.00	12.952
298.15	100.00	14.127
298.15	1600.00	70.747
310.00	0.00	13.834
310.00	1200.00	49.173 <sup>a</sup>
310.00	1200.00	48.946 <sup>b</sup>
480.00	100.00	28.863

<sup>a</sup>Computed with modified Olchowy-Sengers critical enhancement, the viscosity at this point for use in Eq. (8) was taken (Ref. 8) as  $\eta = 89.590 \mu\text{Pa s}$  and all other properties required for the enhancement term are from Guder and Wagner (Ref. 6).

<sup>b</sup>Computed with empirical critical enhancement, Eq. (12).

experimental data. The correlations are valid from the triple point to 1000 K and at pressures up to 150 MPa. The correlations are expressed in terms of temperature and density, and the densities were obtained from the equation of state of Guder and Wagner.<sup>6</sup>

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