# Thermal Conductivity of Sulfur Hexafluoride

**J. Kestin**[1] **and N. Imaishi**[1,2]

This paper reports new measurements of the thermal conductivity of sulfur hexafluoride at the nominal temperature of 27.5°C as a function of density in the range up to 200 kg · m$^{-3}$. The measurements were performed in a transient, hot-wire instrument. When combined with earlier measurements of the viscosity of the gas, they allow us to calculate the rather large contribution stemming from the internal degrees of freedom. The present measurements compare well with those in the literature. All of them suggest that the excess thermal conductivity is a unique function of density in the present range of states. An empirical correlation of our measurements can serve users in the ranges $0 < t < 100$°C and $0 < \rho < 200$ kg · m$^{-3}$.

## 1. INTRODUCTION

The present account ends a series of measurements of the thermal conductivity of a number of gases at 27.5°C as a function of density. Measurements were performed in our transient, hot-wire apparatus [1]. The series started with monatomic gases [1] and progressively encompassed gases of increasing structural complexity [2–6]. The present system, sulfur hexafluoride, has the most complex structure in the series. The molecule consists of seven heavy atoms, but its field of forces is still simple, being spherical. Sulfur hexafluoride was chosen for the present study because we have at our disposal precise measurements of its viscosity [7] which can be used to determine the translational contribution of its ther-

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[1] Division of Engineering, Brown University, Providence, Rhode Island 02912, USA.
[2] Present address: Chemical Research Institute of Nonaqueous Solutions, Tohoku University, Sendai, Japan.

mal conductivity. On the other hand, the internal, vibrational modes are excited even at room temperature.

The present measurements range from 0.8 to 2.2 MPa (52 to 190 $kg \cdot m^{-3}$).

## 2. EXPERIMENTAL PROCEDURES

We omit a detailed description of the instrument and of the procedures employed because they were identical with those in Ref. 1. We merely add that the purity of the $SF_6$ used was 99.99% and that check measurements made with nitrogen before the start of the series did not differ from a previous correlation in Ref. 5 by more than 0.3%. This gave us an assurance that the instrument functioned reliably.

The density of $SF_6$ was calculated on the basis of the work of Sigmund et al. [8].

There was some concern that the state of the gas in the instrument became too close to the critical as the highest pressure was approached. Even though some sensitivity to temperature rise in the platinum wire was
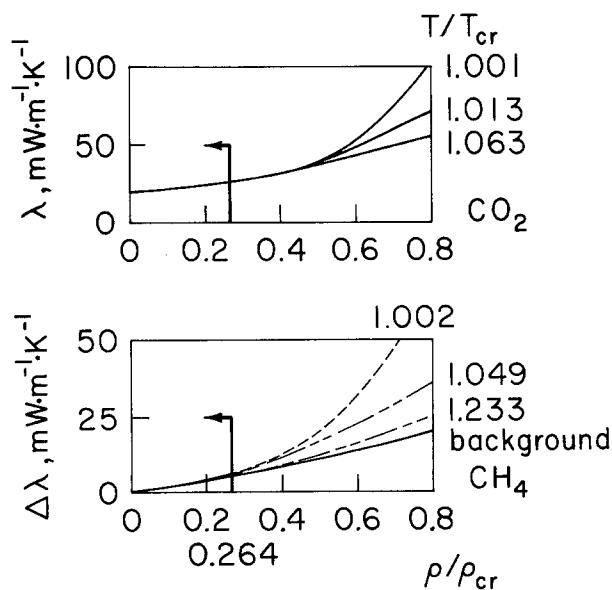


Fig. 1. The zone of critical enhancement in $CO_2$ and $CH_4$. The location of the maximum value of density covered in our measurements corresponds to $\rho/\rho_{cr} = 0.264$. The isotherm is at $T/T_{cr} = 0.94$.

experienced, and counteracted by limiting this rise to 2.5°C, we could verify that critical enhancement was not to be expected.

The diagram in Fig. 1 reproduces portions of the graphs of the thermal conductivity of carbon dioxide and methane from the work of Hanley et al. [9]. Our conditions corresponded to a density ratio $\rho/\rho_{cr} = 0.264$ at the highest pressure, and the isotherm was one of $T/T_{cr} = 0.94$. It is apparent that our measurements cover a range which stays just clear of the region of critical enhancement.

In spite of all the precautions, and in spite of the location of the state points relative to the region of critical enhancement, we observed a slightly larger degree of scatter from the straight line in the $\Delta T$ versus $\ln t$ plot, which determines the thermal conductivity. As the pressure in the instrument was decreased, this scatter attenuated at first and then increased again, as it always does. In the present case, we decided to restrict the low end of the pressure range to 0.8 MPa to avoid excessive scatter.

## 3. EXPERIMENTAL RESULTS

The experimental results are listed in Table I. Reduction to the nominal temperature of 27.5°C was performed linearly with the aid of the constant factor[3]

$$(\partial\lambda/\partial T)_{27.5°C} = 0.072 \text{ mW} \cdot \text{m}^{-1} \cdot \text{K}^{-2} \tag{1}$$

The usual statistical fit to the virial expansion in density

$$\lambda = a_0 + a_1\rho + a_2\rho^2 + \cdots \tag{2}$$

presented difficulties because of the absence of measured data at densities below $\rho = 52 \text{ kg} \cdot \text{m}^{-3}$ due to the cutoff in pressure mentioned earlier. The coefficients in Eq. (2) are listed in Table II as a function of the limiting density, $\rho'$, employed for the respective order, $n$, of the polynomial. The zero value, $a_0$, of thermal conductivity reproduces itself reasonably well between $n = 1$ and $n = 2$. The first slope, $a_1$, does not reproduce very well, but given its uncertainty, the result is acceptable. In contrast, the third-order polynomial leads to seriously different values of $a_0$ and $a_1$. We interpret these results as meaning that the lower end of the $\lambda(\rho)$ curve is compatible with the assumption that the function is a virial expansion which ceases to be valid at $\rho'$ exceeding $100 \text{ kg} \cdot \text{m}^{-3}$ or so.

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[3] This value was deduced with the aid of an estimate based on Ref. 10; it is confirmed in Section 5.

**Table I.** Thermal Conductivity of Sulfur Hexafluoride ($SF_6$) at $T_{nom} = 27.5°C$

| Pressure $P$ (MPa) | Equilibrium temperature $T_0$ (°C) | Density at equil. temp. $\rho_0(P,T_0)$ (kg·m$^{-3}$) | Reference temperature $T_r$ (°C) | Density at ref. temp. $\rho_r(P,T_r)$ (kg·m$^{-3}$) | Thermal conductivity $\lambda(T_r,\rho_r)$ (mW·m$^{-1}$·K$^{-1}$) | $\lambda(T_{nom},\rho_r)$ (mW·m$^{-1}$·K$^{-1}$) |
|---|---|---|---|---|---|---|
| 0.7995 | 24.51 | 52.24 | 26.89 | 51.66 | 13.58 | 13.62 |
| 0.9023 | 24.51 | 59.86 | 26.87 | 59.18 | 13.65 | 13.70 |
| 1.003 | 24.51 | 67.58 | 26.87 | 66.76 | 13.76 | 13.80 |
| 1.10 | 24.51 | 75.34 | 26.87 | 74.41 | 13.88 | 13.92 |
| 1.10 | 24.51 | 75.38 | 26.87 | 74.42 | 13.82 | 13.86 |
| 1.20 | 24.52 | 83.63 | 26.87 | 82.51 | 13.97 | 14.02 |
| 1.29 | 24.53 | 90.90 | 26.87 | 89.63 | 14.11 | 14.15 |
| 1.40 | 24.53 | 101.2 | 26.85 | 99.67 | 14.20 | 14.24 |
| 1.50 | 24.53 | 110.1 | 26.85 | 108.3 | 14.45 | 14.49 |
| 1.60 | 24.54 | 120.4 | 26.87 | 118.4 | 14.64 | 14.68 |
| 1.70 | 24.53 | 130.9 | 26.88 | 128.4 | 14.95 | 15.00 |
| 1.83 | 24.56 | 144.8 | 26.88 | 141.9 | 15.22 | 15.27 |
| 1.91 | 24.56 | 154.4 | 26.88 | 151.0 | 15.39 | 15.43 |
| 1.98 | 24.56 | 163.9 | 26.88 | 160.0 | 15.73 | 15.78 |
| 2.11 | 24.55 | 181.2 | 26.89 | 176.3 | 16.27 | 16.31 |
| 2.20 | 24.56 | 195.0 | 26.89 | 189.1 | 16.70 | 16.74 |

$(\partial \lambda / \partial T)_{27.5°C} = 0.071$ mW·m$^{-1}$·K$^{-2}$

**Table II.** Coefficients of Virial Expansion, Eq. (2)

| $\rho'$ (kg·m$^{-3}$) | Highest power in density $n$ | $a_0 \pm \sigma(a_0)$ (mW·m$^{-1}$·K$^{-1}$) | $a_1 \pm \sigma(a_1)$ ($\mu$W·m$^2$·kg$^{-1}$·K$^{-1}$) | $a_2 \pm \sigma(a_2)$ (nW·m$^5$·kg$^{-2}$·K$^{-1}$) | $a_3 \pm \sigma(a_3)$ (pW·m$^8$·kg$^{-3}$·K$^{-1}$) |
|---|---|---|---|---|---|
| 83 | 1 | $12.97 \pm 0.07$ | $12.79 \pm 0.96$ | — | — |
| 100 | 2 | $13.05 \pm 0.24$ | $9.38 \pm 6.54$ | $27.6 \pm 43.1$ | — |
| 176 | 3 | $13.26 \pm 0.30$ | $3.40 \pm 8.87$ | $61.7 \pm 82.5$ | $94.6 \pm 242$ |

For further work, we shall assume averages and accept that

$$\lambda^0 \equiv a_0 = 13.01 \text{ mW} \cdot \text{m}^{-1} \cdot \text{K}^{-1},$$
$$\lambda_1 \equiv a_1 = 11.0 \ \mu\text{W} \cdot \text{m}^2 \cdot \text{kg}^{-1} \cdot \text{K}^{-1} \tag{3}$$

The entire range of data can be correlated by a truncated cubic polynomial

$$\lambda = \lambda^0 + \lambda_1 \rho + \lambda_2 \rho^2 + \lambda_3 \rho^3 \tag{4}$$

The coefficients of the truncated cubic polynomial are listed in Table III. The diagram in Fig. 2 contains a deviation plot which proves that the data depart from the smooth correlation in Eq. (4) by at most 0.6%; the standard deviation of the fit is 0.3%, and we accept it as a measure of our current precision.

## 4. ANALYSIS

We do not think that the behavior of the coefficients in Table II and the observed increased scatter in individual measurements mentioned before justify a full analysis in terms of statistical mechanics. We merely note that in the sum

$$\lambda^0 = \lambda^0_{\text{tr}} + \lambda_{\text{int}} \tag{5}$$

**Table III.** Coefficients of Cubic Correlation, Eq. (3)

$\lambda^0 = 13.01 \text{ mW} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ (at 27.5°C)
$\lambda_1 = 11.00 \ \mu\text{W} \cdot \text{m}^2 \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$
$\lambda_2 = -7.615 \text{ nW} \cdot \text{m}^5 \cdot \text{kg}^{-2} \cdot \text{K}^{-1}$
$\lambda_3 = 288.7 \text{ pW} \cdot \text{m}^8 \cdot \text{kg}^{-3} \cdot \text{K}^{-1}$
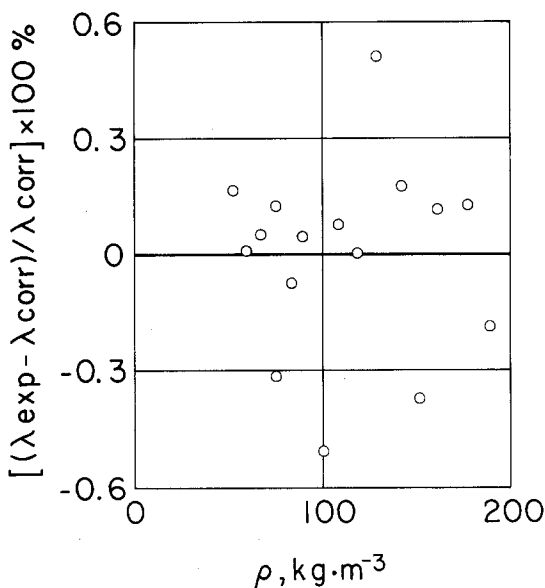
**Fig. 2.** Deviation of experimental results from Eq. (4).

we can calculate $\lambda_{tr}^0$ with the aid of the Viehland–Mason relation [10]. In this we obtain

$$\lambda_{tr}^0 = 2.71 \text{ mW} \cdot \text{m}^{-1} \cdot \text{K}^{-1} \tag{5a}$$

leading to

$$\lambda_{int}^0 = 10.30 \text{ mW} \cdot \text{m}^{-1} \cdot \text{K}^{-1} \tag{5b}$$

as the measured contribution of the internal degrees of freedom to the zero-density thermal conductivity.

## 5. OTHER MEASUREMENTS

We have located six earlier sets of measurements of the thermal conductivity of sulfur hexafluoride [11–16]. We omit from further consideration the single point measured by Choy and Raw [13] at atmospheric pressure and the two points measured by Venart [11]. The remaining four sets each, namely, Refs. 12 and 14–16, cover a range of pressures and temperatures. We refer to them as the *selected data.*

The succeeding analysis shows reasonable but not complete agreement with our measurements.
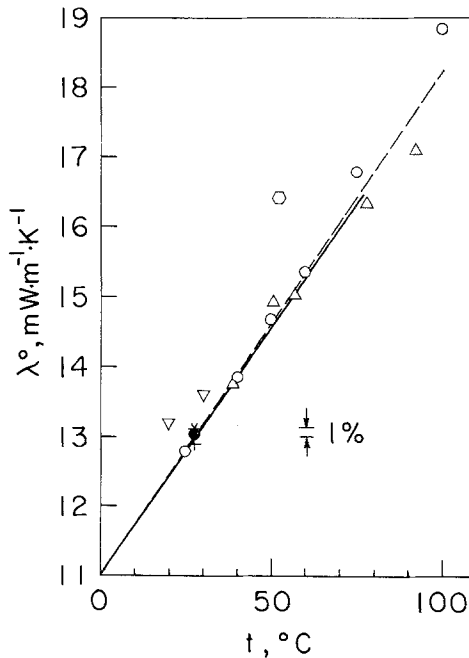
## 5.1. Zero Density

In order to facilitate intercomparison, we have first reduced all data to zero density by a smooth graphical extrapolation. The result is displayed in Fig. 3. In it we still show the data of Refs. 11 and 13, even though we assign to them a zero weight in the following.

All data admit a linear interpolation formula of the form

$$\lambda^0(T) = \lambda^0(27.5) \times [1 + b(t - 27.5°C/0°C]$$ (6)

The dashed line represents a best fit to all the data with[4]

$$b = 0.00549$$ (6a)



Fig. 3. Zero-density conductivity of sulfur hexafluoride. (●) This work; (▽) Ref. 11; (△) Ref. 12; (○) Ref. 13; (○) Ref. 15; (+) Ref. 14, reduced to 27.5°C; (*) Ref. 16, reduced to 27.5°C. (———) Recommended correlation in Ref. 14; (-----) Eqs. (6) and (6a).

[4] This factor yields $(\partial\lambda/\partial T)_{27.5°C} = 0.071$ mW · m$^{-1}$ · K$^{-2}$, which justifies *ex post* the estimate given in Eq. (1).

The solid line is the interpolation equation recommended by Bakulin and Ulybin [14] with the insignificantly different value of $b = 0.00541$.

We may assert that Eq. (6) with the value given in Eq. (6a) correlates our own and the selected data adequately. The range of validity can be taken as

$$0 < t < 100°C \tag{6b}$$

We note for further reference that all data suggest that the zero-density thermal conductivity is a linear function of temperature.

## 5.2. Higher Densities

In order to create a basis for comparison, we have reduced the selected data to the 27.5°C isotherm by a linear correction at constant density with the factor quoted in Eq. (1). This is justified given that $\lambda^0$ is a linear
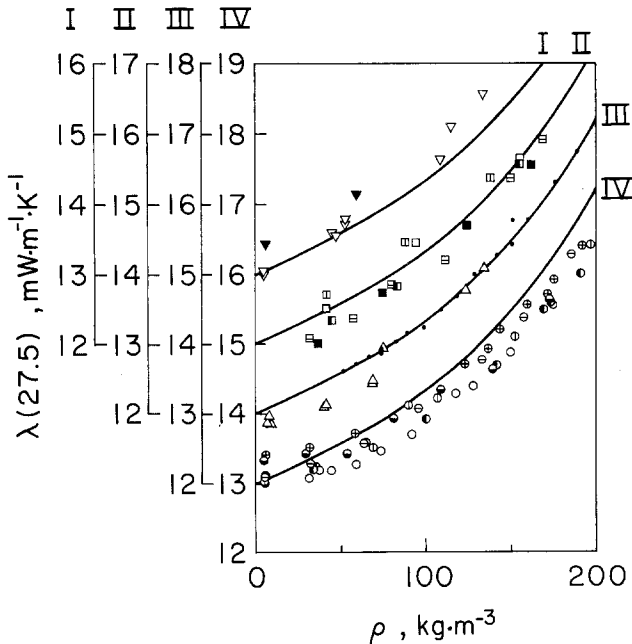


**Fig. 4.** Selected data, reduced to 27.5°C. (●) This work; (———) Eq. (4). I [16]: (▼) reduced from 21–22°C; (▽) reduced from 48–92°C. II [12]: (□) 38.8°C; (▥) 50.9°C; (▮) 57.0°C; (⊟) 78.0°C; (■) 92.5°C. III [14]: (△) reduced from 6–42°C. IV [15]: (○) 25.0°C; (⦶) 40.0°C; (◖) 50.0°C; (⊖) 60.0°C; (⊕) 75.0°C; (◓) 100.0°C.

**Table IV.** Values of $\lambda^0$ (27.5°C) at $\rho = 0$ Obtained by Different Experimenters

|  | $\lambda^0$ (27.5) $(\mathrm{mW \cdot m^{-1} \cdot K^{-1}})$ |
|---|---|
| I    (Ref. 16) | 13.12 |
| II   (Ref. 12) | 12.89 |
| III  (Ref. 14) | 12.90 |
| IV   (Ref. 15) | 13.08 |
| Present | 13.01 |
| Average | 13.03 |
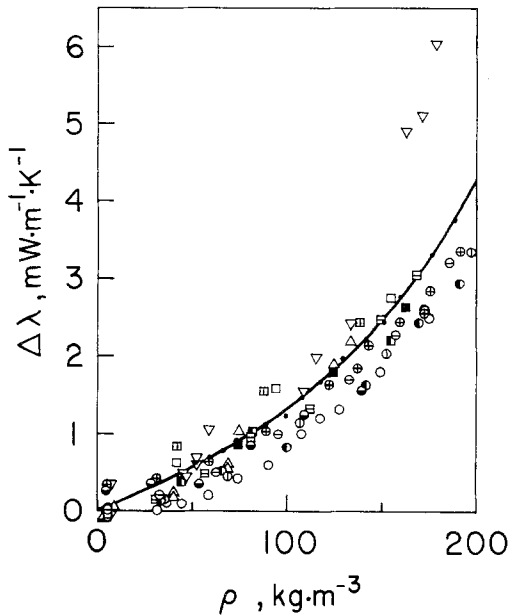


**Fig. 5.** Excess thermal conductivity of SF$_6$. ($\bullet$) This work; (———) Eq. (9). Ref. 12: ($\square$) 38.8°C; ($\boxdot$) 50.9°C; ($\blacksquare$) 57.0°C; ($\boxminus$) 78.0°C; ($\blacksquare$) 92.5°C. Ref. 14: ($\triangle$) 6–42°C. Ref. 15: ($\bigcirc$) 25.0°C; ($\oslash$) 40.0°C; ($\bullet$) 50.0°C; ($\ominus$) 60.0°C; ($\oplus$) 75.0°C; ($\ominus$) 100°C. Ref. 16: ($\triangledown$) 21–92°C.

**Table V.** Values of the Coefficients of the Correlation in Eq. (9)

| | $\alpha$ ($\mu W \cdot m^2 \cdot kg^{-1} \cdot K^{-1}$) | $\beta$ ($nW \cdot m^5 \cdot kg^{-2} \cdot K^{-1}$) | $\gamma$ ($pW \cdot m^8 \cdot kg^{-3} \cdot K^{-1}$) |
|---|---|---|---|
| Our data | 11.00 | −7.615 | 288.7 |
| All data | 3.270 | 108.5 | −163.7 |

function of temperature and that the excess thermal conductivity is a function of density only, as shown presently. The resulting four isotherms are depicted in Fig. 4 (note staggered ordinates). Each of the isotherms yields a slightly different value of $\lambda^0(27.5)$ which is listed in Table IV. We believe that the average

$$\lambda^0(27.5) = 13.0_3 \, mW \cdot m^{-1} \cdot K^{-1} \tag{7}$$

can be assigned a high degree of confidence.

The diagram in Fig. 4 and a full diagram of $\lambda$ versus $\rho$ for the isotherms of the selected data (not shown to save space) suggest that the excess thermal conductivity

$$\Delta\lambda = \lambda(T, \rho) - \lambda^0(T) \tag{8}$$
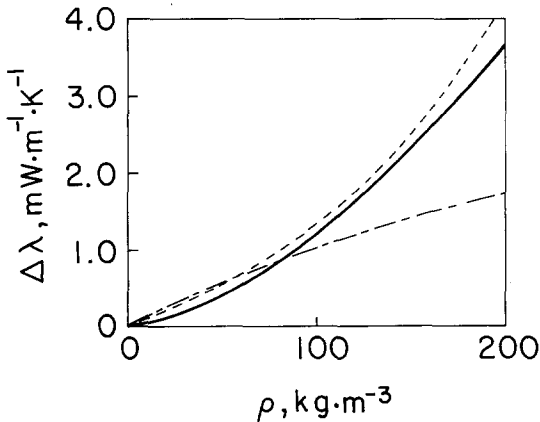


**Fig. 6.** Excess thermal conductivity of $SF_6$. (----) Eq. (9) for the present results; (——) Eq. (9) for the ensemble of the present results with the selected data; (— - —) recommended in Ref. 14.

can be correlated as a function of density alone, because no systematic influence of temperature could be discerned.

The diagram in Fig. 5 contains a plot of excess thermal conductivity against density, reduced to 27°C. It appears that our data together with those of Lis et al. [12] place themselves between the data of Burinskii et al. [16] on the one hand and the data of Makita et al. [15] on the other. All data can be correlated in the form of a cubic

$$\Delta\lambda = \alpha\rho + \beta\rho^2 + \gamma\rho^3 \qquad (9)$$

The coefficients in this equation are listed in Table V. In it, we specify two sets, one for the ensemble of our data with the selected data. The second set correlates our data alone.

The diagram in Fig. 6 shows that the two correlations are very close. Since our data show greater consistency, we recommend them to users. The graph also contains a line which corresponds to a recommendation made by Bakulin et al. [14] which is obviously in error.

The density correlation is valid in the density range

$$0 < \rho < 200 \text{ kg} \cdot \text{m}^{-3} \qquad (6c)$$

and the pressure range

$$0 < P < 3.5 \text{ MPa} \qquad (6d)$$

Evidently, the pressure range is indicated for convenience only and does not correspond to the density range at all temperatures.

### 5.3. Recommended Correlation

In summary, we recommend the use of Eqs. (6) and (4) with the constants listed in Eq. (6a) and Table III. The resulting values can be assigned an accuracy of the order of 0.5%.

### ACKNOWLEDGMENTS

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