# The Thermal Conductivity of Methane and Tetrafluoromethane in the Limit of Zero Density

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M. J. Assel, J. Millat, V. Vesovic, and W. A. Wakeham



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# The Thermal Conductivity of Methane and Tetrafluoromethane in the Limit of Zero Density

#### M.J. Assael<sup>a</sup>, J. Millat<sup>b</sup>, V. Vesovic, and W.A. Wakeham

IUPAC Transport Properties Project Centre, Department of Chemical Engineering and Chemical Technology, Imperial College of Science and Technology, London, SW7 2BY, UK

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The paper presents accurate representations of the thermal conductivity of methane and tetrafluoromethane in the limit of zero density. The theoretically-based correlations provided are valid for the temperature range 120-1000 K and 280-750 K for methane and tetrafluoromethane respectively. The methane correlation has associated uncertainties of  $\pm 2\%$  between 300 and 500 K, rising to  $\pm 2.5\%$  at the low, and  $\pm 4\%$  at the high, temperature extremes. The tetrafluoromethane correlation has uncertainties of 1% between 280 K and 450 K, rising to  $\pm 5\%$  at the highest temperature. A comparison with some earlier correlations is given. The paper also includes an improved correlation for the temperature dependence of the zero-density viscosity of tetrafluoromethane.

Keywords: carbon tetrafluoride; correlations; methane; polyatomic gases; tetrafluoromethane; thermal conductivity of gases; transport properties.

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## 1. Introduction

The importance of accurate values of the thermophysical properties of fluids to the optimum design of chemical process equipment has been illustrated by a number of papers<sup>1-3</sup>. Since these values should be included within computer-aided design software accurate representations

Department of Chemical Engineering, Aristotle University of Thessaloniki, GR - 540.06, Thessaloniki.

<sup>&</sup>lt;sup>b</sup>Permanent address: Sektion Chemie, der Wilhelm-Pieck Universität Rostock, Buchbinderstr. 9, Rostock 1, DDR-2500.

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of the properties over a wide range of thermodynamic states are essential. In the case of the transport properties the establishment of the correlations usually begins with the behaviour of the property in the limit of zero-density. For example, the thermal conductivity may be written as the sum of three different contributions

$$\lambda(\rho, T) = \lambda_0(T) + \Delta\lambda(\rho, T) + \Delta\lambda_c(\rho, T)$$
(1)

where the term  $\lambda_0(T)$  represents the thermal conductivity in the limit of zero-density, while the terms  $\Delta\lambda(\rho,T)$ and  $\Delta\lambda_c(\rho,T)$  represent the excess thermal conductivity and its critical enhancement respectively. In this paper we extend earlier studies of the zero-density viscosity of nitrogen<sup>4</sup>, oxygen<sup>4</sup>, carbon dioxide<sup>5</sup>, methane<sup>5</sup>, sulphur hexafluoride<sup>5</sup> and of the zero-density thermal conductivity of nitrogen and carbon monoxide<sup>6</sup> to that of methane and tetrafluoromethane.

The justification for an up-to-date evaluation of the thermal conductivity of these two gases derives from new experimental and theoretical results. The transient hot wire technique has been developed to the state of a primary standard instrument for the experimental determination of the thermal conductivity. With the aid of this method, new measurements for methane and tetrafluoromethane have been made and provide a suitable basis for an improved correlation.

At the same time, the kinetic theory of polyatomic gases has advanced<sup>7-10</sup> to a stage where it can be used as a tool to assess the validity of experimental data and to provide a basis for correlation schemes even though it is not yet at a comparable stage to that for monatomic systems<sup>7</sup>. The representations given here for the thermal conductivity of methane and tetrafluoromethane are limited to temperatures above 120 K and 280 K respectively. The range therefore does not encompass the entire fluid range<sup>c</sup> for reasons given later.

#### 2. Experimental Data

From a direct comparison of the entire set of published thermal conductivity data for methane and tetrafluoromethane, it is apparent that there are substantial discrepancies between various authors' results. Since it is extremely difficult to decide on the accuracy of reported data solely on the basis of the available literature we have employed two complementary methods of assessing, in particular, the older experimental data. First, we use a comparison with new experimental data acquired with improved, modern equipment of proven accuracy. Secondly, we attempt to establish confidence in experimental data by recourse to the available kinetic theory<sup>11,12</sup>. Thus, we commence our analysis by dividing the experimental data into the categories<sup>4,5,13,14</sup> of primary and secondary data. Under primary data we consider the results of measurements made with apparatus of high

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precision for which a complete working equation and a detailed knowledge of all corrections is available. However, because this would reduce the temperature range studied unduly, we have also included in the primary data set those results obtained by different techniques, which prove consistent with the high precision data and theoretical results<sup>11</sup>.

Secondary data are the results of measurements which are of inferior accuracy to primary data. This inferior accuracy may arise from operation at extreme conditions or from incomplete characterisation of the apparatus.

For methane as well as tetrafluoromethane, we have carried out a survey of the available data and assigned them to one of the above-mentioned categories. Only primary data were used in the formulation of the final correlations. In the following sections the data selected as primary for each system are detailed, together with our estimate of their uncertainty, a summary of which is included in Table 1.

TABLE 1.	Primary experimental data for the thermal conductivity or
	methane and tetrafluoromethane

Reference	Technique	Temperature range (K)	Ascribed uncertainty (%)
	Metha	ne	
Millat et al. <sup>15</sup>	THW	309-426	±0.5
Assael et al.16	THW	308	$\pm 0.5$
Clifford et al.17	THW	301	$\pm 0.5$
Clifford et al.18	HW	303	$\pm 1.0$
Roder <sup>19</sup>	THW	133-310	±2.0
Johnston et al. <sup>20</sup>	HW	125-384	±3.0
Tufeu et al. <sup>21</sup>	CC	298-725	±2.5
	Tetrafluoror	nethane	
Millat et al. <sup>15</sup>	THW	308-426	±0.5
Imaishi et al.25	THW	301	$\pm 0.5$
Clifford et al.18	HW	303	±1.0

THW = Transient hot-wire.

HW = Hot-wire.

CC = Concentric cylinders.

#### 2.1. Thermal Conductivity Data

#### 2.1.1. Methane

The most accurate of the thermal conductivity measurements have been carried out with transient hot-wire instruments at Imperial College<sup>15,16</sup>, and Brown University<sup>17</sup>. These measurements, as well as those reported by other authors, were conducted over a range of densities and the value of the thermal conductivity at zero density,  $\lambda_0$ , derived by modest extrapolation. In all cases we have employed the value of  $\lambda_0$  quoted by the authors since the manner of extrapolation employed is always that which we would have used. The measurements at Imperial College extend over the temperature range 308–426 K, whereas at Brown<sup>17</sup>,

<sup>&</sup>lt;sup>c</sup>The triple point temperatures of CH<sub>4</sub> and CF<sub>4</sub> are approximately 90.6 K and 89.4 K; respectively.

only one isotherm at 300.65 K has been measured. The uncertainty we ascribe to the zero-density values derived from these measurements is  $\pm 0.5\%$ .

Other measurements made with the transient hot-wire technique are those of Clifford et al.18 and Roder19 and they are estimated to have an accuracy of  $\pm 1.0\%$  and  $\pm 2.0\%$  respectively. The remaining primary data are the measurements of Johnston and Grilly<sup>20</sup> and Tufeu et al.<sup>21</sup> made with steady state techniques. Although the sets of data included in Refs. 19-21 have a significantly greater uncertainty than the rest available the temperature range covered by the primary data set is substantially expanded by their inclusion. By definition, all other experimental data are included in the category of secondary data and employed for comparison purposes. Consequently, in the interests of brevity we have not been comprehensive in collating this information and use instead for our comparisons earlier representations<sup>22-24</sup> in which these data were included.

#### 2.1.2. Tetrafluoromethane

The sources of experimental data for tetrafluoromethane are more limited.

Again, we include the data from Imperial College<sup>15</sup> and Brown University<sup>25</sup> in the primary data set. The former extend over the temperature range 308–426 K and we ascribe an uncertainty of  $\pm 0.5\%$ ; the single point from Brown at 300.65 K has the same estimated accuracy.

The final datum included in the primary data set is that of Clifford *et al.*<sup>18</sup> at 303 K, which has an estimated uncertainty of  $\pm 1\%$ .

The measurement of Lambert  $et al.^{26}$  at 339.15 K has been classified as secondary.

The uncertainties ascribed by us normally exceed those claimed by the various authors, no doubt reflecting the original authors' tendency to wishful thinking, although, in most cases, the adjustment is minor. The uncertainties have been used to weight the various data in all subsequent linear regressions in the standard manner as described in detail elsewhere.<sup>4</sup>

### **3. Kinetic Theory Analysis**

A kinetic theory analysis of the experimental data serves to confirm the selection of primary data and to provide the basis for the final representation. Because the details of this analysis have been given elsewhere for carbon dioxide<sup>13</sup>, nitrogen<sup>6</sup> and carbon monoxide<sup>6</sup> we present only a condensed version here and assume that the reader has the earlier papers to hand.

According to the kinetic theory the thermal conduclivity of a polyatomic gas in the limit of zero-density can be related<sup>6,13</sup> to the effective cross-sections  $\mathfrak{S}\begin{bmatrix} p & q & r & s \\ p' & q' & r' & s' \end{bmatrix}$  that incorporate all the information about binary molecular collisions. Furthermore, it can be shown that if the measurements of the viscosity,  $\eta$ , thermal conductivity,  $\lambda$ , internal isochoric heat capacity per molecule,  $c_{int}$  collision number,  $\zeta_{int}$ , and the relative change at saturation in thermal conductivity owing to a magnetic field,  $(\Delta \lambda'' / \lambda)_{sat}$ , are available then all of the cross-sections appearing in the expression for the thermal conductivity of a gas can be evaluated consistently. The required information is available for both methane<sup>5,27-30</sup> and tetrafluoromethane<sup>28-39</sup> and the sources are listed in Table 2.

TABLE 2. Sources of auxiliary data for the kinetic theory analysis of the thermal conductivity

Property	Cross-section	Reference	Temperature range (K)
	Metha	ane	an and a take to get
Viscosity	S(2000)	[5]	120-1000
Collision number	S(0001)	[28]	120-1000
$C_{\rho}^{0}$	<u> </u>	[27]	95-1000
$(\Delta \lambda'' / \lambda)_{sat}$	= - 0.0017	[29,30] temp	erature independent
	Tetrafluoro	methane	
		at the	
V ISCOSILY	S(2000)	[31–38]	150-1100
Collision number	S(0001)	[28]	280-750
$C_p^0$		[39]	100-1100
$(\Delta\lambda''/\lambda)_{sat}$	= - 0.0028	[29,30] temp	erature independen

Among the cross-sections that can be evaluated two quantities are of particular significance to the analysis of experimental data and subsequently to its representation. The first is the ratio<sup>6,11</sup>, of the diffusion coefficient for internal energy,  $D_{int}$ , to the self diffusion coefficient, D

$$\frac{D_{\rm int}}{D} = \frac{\mathfrak{S}(1000)}{[\mathfrak{S}(1001) - \frac{1}{2}\mathfrak{S}(0001)]}$$
(2)

while the second is the Thijsse cross-section<sup>9,10</sup>  $\mathfrak{S}_{\tau}(10E)$  in terms of which the thermal conductivity may be written

$$\lambda_{0} = \frac{5k^{2}T}{2m\langle\nu\rangle_{0}} \frac{(1+r^{2})}{\mathfrak{S}_{T}(10E)}$$
(3)

where

and

$$\langle \nu \rangle_0 = 4(kT/\pi m)^{\frac{1}{2}} \tag{4}$$

$$c_{\rm int}/5k)^{\frac{1}{2}}$$
 (5)

In all cases it has been found that Eq. (3) together with a representation of the temperature dependence of  $\mathfrak{S}_{T}(10E)$  provides a concise and accurate method of describing zero-density thermal conductivity data. In a limited number of cases, specifically those of linear molecules, theoretical results for the high temperature limiting behaviour of  $D_{int}/D$  have been available and it has therefore been possible to provide a reliable extrapolation of the available experimental thermal conductivity

(7)

data by means of Eq. (3). For the present gases there is less theoretical guidance and we must proceed more empirically, but the ratio  $D_{int}/D$  remains a valuable quantity upon which to base extrapolations.

#### 3.1 Results of the Analysis

The complete set of cross-section  $\mathfrak{S}\begin{bmatrix} p & q & r & s \\ p'q'r's' \end{bmatrix}$  for methane and tetrafluoromethane have been evaluated using the primary thermal conductivity data and information from the sources of data listed in Table 2. Each of the derived cross-sections,  $\mathfrak{S}(2000)$ ,  $\mathfrak{S}(0001)$ ,  $\mathfrak{S}(1001)$  as well as the ratio  $D_{int}/D$  has been represented by a correlation of the form

$$\ln \mathfrak{S}^{*}(p \ q \ r \ s) = \sum_{i=0}^{n} a_{i} (\ln T^{*})^{i}$$
(6)

where

and

6\*

$$(p q r s) = \mathfrak{S}(p q r s)/\pi\sigma^2$$

$$T^* = T/\epsilon \tag{8}$$

The scaling parameters for energy,  $\epsilon$ , and length,  $\sigma$ , employed in these representations are those employed in a corresponding states treatment of the viscosity. They are listed in Table 3 together with the various sets of optimum coefficients  $a_i$ .

 
 TABLE 3.
 Coefficients for the representation of the effective crosssections of methane and tetrafluoromethene

	S*(2000)	S*(0001)	©*(1001)	$D_{\rm int}/D$				
	Methane							
•	120 <i>≤T≤</i> 1000	120 <i>≤T≤</i> 1000	120 <i>≤T≤</i> 1000	120 <i>≤T≤</i> 425				
<i>a</i> <sub>0</sub>	0.226946	-1.1798458	0.2089968	-0.15144851				
$a_1$	-0.46460	- 1.4341041	-0.63328856	0.17920026				
$a_2$	-0.0063653	0.32467234	-0.13076870	-0.13875343				
$a_3$	0.10925	-1.0081271	-0.39838421	0.62378311				
$a_4$	-0.032954	0.55069572	0.99755096	-0.44258565				
a,	0.0	0.0	0.60647237	0.0				
$a_6$	0.0	-0.03383053	0.11753039	0.0				

M = 0.016043 kg mol<sup>-1</sup>;  $\epsilon/k = 163.558$  K;  $\sigma = .3709$  nm;  $D_{int}/D = 1.06$ ;  $T \ge 425$  K

	150 <i>≤T≤</i> 1100	$280 \leqslant T \leqslant 750$	280 <i>≤T≤</i> 750	280 <i>≤T≤</i> 640	
<i>a</i> 0	0.2157348	-0.9074313	0.1386481	-0.09436843	
$a_1$	-0.4072572	-2.1317093	-0.73472255	0.25055015	
$a_2$	-0.1202826	-0.71819067	0.38735265	-0.39719742	
<i>a</i> <sub>3</sub>	0.1894549	1.8498369	0.27158833	0.26404387	
a4	-0.0508102	-1.2789857	0.13444437	-0.05957666	
a <sub>5</sub>	0.0	0.46590585	-0.026452595	0.0	
$a_6$	0.0.	-0.072916970	0.0	0.0	
$M = 0.088005 \text{ kg mol}^{-1}$ ; $\epsilon/k = 164.444 \text{ K}$ ; $\sigma = .4543 \text{ nm}$ ; $D_{\text{int}}/D = 0.985$ ; $T > 640 \text{ K}$					

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#### 3.1.1. Methane

Figure 1 shows the derived values of  $D_{int}/D$  for methane using the various primary data sources for the thermal conductivity. The sensitivity of  $D_{int}/D$  to the thermal conductivity data is apparent from the large scatter in this diagram. Indeed, a sensitivity analysis indicates that an uncertainty of  $\pm 1\%$  in the thermal conductivity data propagates to an uncertainty of  $\pm 2\%$  in the ratio of  $D_{\rm int}/D$ . The scatter of  $D_{\rm int}/D$  values seen in Fig. 1 is similar to that observed for other molecules studied<sup>6,13</sup> as is the trend, discernible within the scatter, in the temperature dependence of the ratio, which approaches a high temperature limiting value from below as the temperature increases. For non-vibrating linear molecules, this asymptotic behaviour has been predicted with theoretical analysis revealing a high temperature limit of  $D_{\rm int}/D = 1$ . For vibrating, non-linear molecules theoretical calculations are still beyond the scope of even the fastest computers, but it is plausible to assert that the same qualitative trend will pertain, especially when supported by the empirical evidence of Fig. 1. Consequently, we can make use of this observation to extend the temperature range of our representation of  $D_{int}/D$ , and hence the thermal conductivity, by adopting a constant value of  $D_{int}/D = 1.06$  for  $T \ge 425$  K as shown by the solid line in Fig. 1. Below that temperature a representation by means of a weighted fit to an equation of the form of Eq. (6) has been used.

The representations of the effective cross-sections contained in Eqs. (6)-(8) and Table 3, when combined with a representation of the ideal gas heat capacity, are sufficient to permit an evaluation of the thermal conductivity of methane over a wide range of temperature. The limits of the range are dictated by the availability of the auxiliary data, Table 2. Figure 2 compares the results of the calculation of the thermal conductivity by this route with the primary experimental data. It can be seen that the maximum deviation amounts to about 3% with data from Refs. 19 and 21. The scatter is relatively large compared with our earlier results for nitrogen and carbon monoxide. This is due to the fact that even for the transient hot-wire measurements unexpectedly large differences have been found<sup>15</sup>. The solid lines in Fig. 2 delineate the estimated error in the calculated thermal conductivity.

Figure 3 contains a comparison of the computed thermal conductivity with selected earlier correlations. As has already been shown for carbon dioxide<sup>13</sup>, nitrogen and carbon monoxide<sup>6</sup> most older correlations underestimate the high temperature values of  $\lambda_0$  owing to systematic errors associated with the input thermal conductivity data. Also, Fig. 3 shows a comparison with the result of a corresponding states analysis ("universal correlation") performed by Uribe *et al.*<sup>24</sup>. It is worth noting that the rapidly increasing differences at low temperatures compared with our "individual correlation" seem to be typical of comparisons between these two treatments. For nitrogen it has recently been shown that the be-







FIG. 2. Deviation plot for the primary thermal conductivity data set for methane.

haviour of the universal correlation at low temperatures is not consistent with experiment<sup>40</sup>.

#### 3.1.2. Tetrafluoromethane

For this gas there is no high quality representation of the viscosity in the limit of zero-density. Consequently, in order to carry out the analysis described above, a representation of the viscosity based upon the data of references 31–38 has been developed following the procedure outlined in Ref. 5 and will be presented elsewhere.

Accordingly the viscosity is written in the form

$$\eta_0(T) = \frac{kT}{\langle \nu \rangle_0} \frac{1}{\pi \sigma^2 \mathfrak{S}^*(2000)} \tag{9}$$

and  $\mathfrak{S}^*$  (2000) is represented in the manner of Eq.(6) with the coefficients listed in Table 3. The correlation is valid in the temperature range 150 to 1100 K with an uncertainty rising from  $\pm 0.5\%$  near room temperature to  $\pm 1.5\%$  at the extremes of the range. The scaling parameters  $\epsilon$  and  $\sigma$  given here are to be preferred to the ones recently published in a comparative study on thermal conductivity<sup>41</sup>. The discrepancy is the result of an error in treating the viscosity data in the earlier work, which has now been corrected.

Only three sets of measurements of the thermal conductivity of gas have been classified as primary and they extend over the temperature range 300 K  $\leq T \leq 430$  K. Thus, when the ratio  $D_{int}/D$  is evaluated directly from the experimental data it is not possible to discern any trend capable of extrapolation in temperature. Consequently, we have adopted another approach in order to extend the temperature range which is founded upon an empirical observation of the temperature dependence of the cross-section  $\mathfrak{S}_{T}(10E)$ . In our examination of a number of different gases of various shapes<sup>11</sup> it has been observed that the cross-section is approximately linear in 1/T within one experimeter's data. Normally the systematic differences between different data sets reveal themselves as a different absolute value for the cross-section  $\mathfrak{S}_{\tau}(10E)$  and/or a different slope. For the limited range of temperature covered by the available experimental information for CF<sub>4</sub> the same has been found to hold so that we have chosen to extrapolate this linear relationship to higher temperatures. Such an extrapolation allows then the evaluation of the ratio  $D_{int}/D$  over a wide range of temperature. The results are shown in Fig. 4 where the values of  $D_{int}/D$  determined from experiment are indicated by discrete points and those derived from extrapolation by the solid line. The predicted value of the ratio  $D_{int}/D$  increases with increasing temperature and assumes an almost constant value  $D_{int}/D = 0.985$ above 640 K. Given the similarity of this quantitative behaviour to that found for other gases<sup>6,11-13</sup> some confidence is established in this substantial extrapolation. However its empirical nature means that it would be prudent to limit its range to temperatures in the range for the upper band of experimental data up to 750 K.



FIG. 3. Deviation plot for the selected correlations of thermal conductivity data for methane.

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No attempt has been made to extend the range to lower temperatures, since there is no theoretical guidance on the behaviour of  $D_{int}/D$  and because there is no evidence that the linearity of  $\mathfrak{S}_T(10E)$  vs 1/T remains valid.

A representation of the entire temperature variation of  $D_{int}/D$  has been developed based on the form of Eq. (6) and the appropriate coefficients are included in Table 3 together with those for the other reduced effective cross-sections. The availability of the complete, consistent set of cross-sections permits the evaluation of the thermal conductivity of CF<sub>4</sub> over a wide range of temperature. Figure 5 contains a plot of the deviations of the experimental data from those calculated; these do not exceed  $\pm 0.5\%$ . Figure 5 also compares the results of the present calculation of the thermal conductivity with that of the universal correlation of Uribe *et al.*<sup>24</sup>. The agreement is within the estimated error bands.

As the estimated error bands in Fig. 5 indicate, there is considerable scope for improved measurements of the thermal conductivity of the gas at both high and low temperatures.

## 4. The Final Correlation

Although the formalism set out in Sec. 3 provides a means of calculating the thermal conductivity of methane and tetrafluoromethane from a combination of experimental data and theory, it does not represent a particularly convenient form for a practical correlation. Consequently, we prefer to adopt as a practical correlation a representation based on the approximate, theoretical equation of Thijsse *et al.*<sup>9</sup>. Rewriting Eq. (3), the zero-density thermal conductivity is given by

$$\lambda_0 = \frac{1.39463(T/M)^{\frac{1}{2}} (1+2 C_{\text{inl}}/5R)}{\pi \sigma^2 \mathfrak{S}_1^* (10E)}$$
(10)

where T is in K,  $\sigma$  is in nm,  $C_{int}$  is in J K<sup>-1</sup> mol<sup>-1</sup>, R is the gas constant in J K<sup>-1</sup> mol<sup>-1</sup>, M is the relative molecular mass of the gas, and  $\lambda_0$  is in mW m<sup>-1</sup> K<sup>-1</sup>. From the thermal conductivity evaluated according to the procedure described in the previous sections, the reduced cross-section  $\mathfrak{S}^{*}_{T}(10E)$  has been calculated.

Subsequently, the temperature dependence of  $\mathfrak{S}_{\mathrm{T}}^*(10E)$  has been represented by a correlation of the form of Eqs. (6-8), where the coefficients securing the optimum fit are collected in Table 4 for both methane and tetrafluoromethane. To carry out this procedure one requires a representation of internal isochoric ideal gas heat capacity,  $C_{\mathrm{int}}$ , for the two gases and for the sake of completeness and convenience, we include the generating equation for  $C_{\mathrm{int}}$  for methane<sup>27</sup>

$$\frac{C_{p}^{\circ}}{R} = \frac{C_{\text{int}} + 2.5R}{R} = 4\left[\sum_{f}^{i=1} T^{i/3}\right] + \sum_{i=7}^{8} f_{i} T^{i-4} + f_{g} \frac{u^{2} e^{u}}{(e^{u-1})^{2}} \qquad (11)$$
$$u = f_{10}/T$$



FIG. 4. The ratio of the diffusion coefficients,  $D_{int}/D$  for the tetrafluoromethane.

and for tetrafluoromethane39

$$\frac{C_p^0}{R} = \frac{C_{\text{int}} + 2.5R}{R} = f_8 + \exp(f_9/X) \left[ \sum_{i=1}^7 f_i X^{6-i} \right] \quad (12)$$
$$X = T/f_{10}$$

where the coefficients,  $f_i$ , are given in Table 5<sup>d</sup>.

Naturally, the generated thermal conductivity data correlated in this way are not reproduced exactly. However, the maximum deviations between the correlation and the calculated data are less than  $\pm 0.1\%$  for methane as well as tetrafluoromethane. This additional error is a small fraction of the overall uncertainty that we ascribe to the practical correlation of the thermal conductivity which is one of  $\pm 2.0\%$  between 300 K and 500 K rising to  $\pm 2.5\%$  at the low temperature limit and to  $\pm 4.0\%$  at the high temperature extreme for methane and of  $\pm 1.0\%$  between 280 K and 450 K, rising to 5% at high temperature extreme (750 K) for tetrafluoromethane. It follows that the deviations of the primary experimental thermal conductivity from the practical correlation are essentially those displayed in Figs. 2 and 5 for methane and tetrafluoromethane respectively.

#### 5. Tabulations

The practical correlation described in the previous section has been employed to generate a set of recommended values for the thermal conductivity of methane in the temperature range 120 K  $\leq T \leq 1000$  K and for tetrafluoromethane in the temperature range 280 K  $\leq T \leq 750$  K. The thermal conductivity values are listed in Table 6 together with the viscosity for tetrafluoromethane. The tabulated values are subject to the uncertainties discussed in Sec. 4 and should be read in conjunction with the error limits displayed in Figs. 2 and 5.

TABLE 4. Coefficients for the practical correlation of the thermal conductivity

Coefficient	Methane	Tetrafluoromethane
	120 K≤ <i>T</i> ≤1000 K	280 K≤ <i>T</i> ≤750 K
<i>a</i> <sub>0</sub>	-0.05154269	-0.1893477
<i>a</i> <sub>1</sub>	-0.51986885	0.0
$a_2$	-0.045638189	-0.52825612
<i>a</i> <sub>3</sub>	0.0	0.34136039
<i>a</i> <sub>4</sub>	0.14228623	-0.070755579
u <sub>5</sub>	0.0	0.0
a <sub>6</sub>	-0.068641484	0.0
<b>a</b> <sub>7</sub>	0.020844530	0.0



FIG. 5. Deviation plot for the thermal conductivity data for tetrafluoromethane.

<sup>d</sup>A typographical error in the coefficient  $f_8$ , for methane given in Ref. 27 has been corrected.

## THERMAL CONDUCTIVITY OF METHANE AND TETRAFLUOROMETHANE

T

(K)

310.0

315.0

320.0

325.0

330.0

335.0

340.0

345.0

350.0

355.0

360.0

365.0

370.0

375.0

380.0

TABLE 5. Coefficients for the representation of the isobaric ideal gas heat capacity  $C_{\rho}^{*}(T)$ 

 TABLE 6. The thermal conductivity of methane and the thermal conductivity and viscosity of tetrafluoromethane

 — Continued

Methane

Thermal

conductivity

36.18

36.95

37.73

38.51

39.31

40.11

40.92

41.74

42.57

43.40

44.25

45.10

45.95

46.82

47.69

 $(mW m^{-1} K^{-1})$ 

<del>71</del> 	Methane	Tetrafluoromethane
fi	(95 K <i>≤T≤</i> 1000 K)	(100 K≤ <i>T</i> ≤1100 K)
fi	0.269386063023 .101	0.1524909458-10-3
f2	-0.213367335398-10 <sup>1</sup>	-0.5916481372.10-2
fs	····· 0.799266772081	0.10054126
fa	-0.160476700181	0.9681556225
fs	0.170796753887-10-1	0.5451235771-10 1
fe	-0.785578368269.10-3	-0.5750498772-10 <sup>1</sup>
fi	0.855930945735-10-7	0.161003220081.10
fs	-0.145719286035-10-10	4.0
fo	0.918971501008	-1.0
f10	2000.0	100.0

. . .

. . . .

TABLE 6. The thermal conductivity of methane and the thermal conductivity and viscosity of tetrafluoromethane

				385.0	48.57
· · · · · · · · ·	Methane	Tetrafluor	omethane	390.0	49.46
120 <u>7</u> 9				395.0	50.35
T	Thermal	Viscosity	Thermal	400.0	51,25
(K)	conductivity	(µPa s)	conductivity	405.0	52.16
	$(mW m^{-1} K^{-1})$	(n	$W m^{-1} K^{-1}$	410.0	53.07
<u> </u>	and the second	9.5		415.0	53.99
120.0	12.71	n ann an taine à	and the second second	420.0	54.91
125.0	13.24		. e	425.0	55.84
130.0	13.77	194 - A.		430.0	56.77
135.0	14.31			435.0	57.71
140.0	14.84		1	440.0	58.65
145.0	15.38			445.0	59.60
150.0	15.92	9.24		450.0	60.55
155.0	16.46	9.51		455.0	61.51
160.0	17.00	9.79		460.0	62.47
165.0	17.55	10.06		465.0	63.43
170.0	18.10	10.34		470.0	64.40
175.0	18.66	10.61		475.0	65.37
180.0	19.22	10.90		480.0	66.35
185.0	19.78	11.18		485.0	67.33
190.0	20.35	11.46		490.0	68.31
195.0	20.93	11.74		495.0	69.30
200.0	21.51	12.02		500.0	70.29
205.0	22.09	12.30		510.0	72.28
210.0	22.69	12.58		520.0	74.28
215.0	23.29	12.86		530.0	76.29
220.0	23.89	13.14		540.0	78.32
225.0	24.50	13.42		550.0	80.35
230.0	25.12	13.70		560.0	82.40
235.0	25.75	13.98		570.0	84.45
240.0	26.39	14.25		580.0	86.52
245.0	27.03	14.53		590.0	88.59
250.0	27.68	14.80		600.0	90.68
255.0	28.34	15.07		610.0	92.77
260.0	29.01	15.34		620.0	94.88
265.0	29.69	15.61		630.0	96.99
270.0	30.37	15.88		640.0	99.12
275.0	31.07	16.15		650.0	101.25
280.0	31.77	16.42	14.52	660.0	103.40
285.0	32.48	16.68	14.89	670.0	105.55
290.0	33.20	16.94	15.27	680.0	107.72
295.0	33.94	17.21	15.66	<b>69</b> 0.0	109.89
300.0	34.68	17.47	16.04	700.0	112.07
305.0	35.43	17.72	16.43	710.0	114.27

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Tetrafluoromethane

Thermal

conductivity (mW m<sup>-1</sup> K<sup>-1</sup>)

16.82

17.21

17.61

18.00

18.40

18.80

19.20

19.60

20.01

20.41

20.82

21.23

21.63

22.04

22.45

22.86

23.27

23.68

24.09

24.50

24.91

25.32

25.73

26.14

26.55 26.96

27.37

27.77

28.18

28.59 28.99

29.40

29.80

30.21

30.61

31.01

31.41

31.81

32.21

33.01

33.80

34.59

35.37

36.14

36.92

37.68

38.44

39.20

39:95

40.69

41.43

42.17

42.90

43.62

44.34

45.05

45.76

46.46

47.16

47.85

Viscosity

(µPa s)

17.98

18.24

18.49

18.74

18.99

19.24

19.49

19.73

19.98

20.22

20.46

20.70

20.94

21.18

21.41

21.64

21.87

22.10

22.33

22.56

22.78

23.01

23.23

23.45

23.67

23.89 24.10

24.32

24.53

24.74

24.95

25.16 25.37

25.58

25.78

25.99

26.19

26.39

26.59

26.99

27.38

27.77

28.15

28.53

28.91

29.28

29.65

30.01

30.37

30.73

31.08

31.43

31.78

32.12

32.46

32.80

33.13

33.46

33.79

34.12

TABLE 6. The thermal conductivity of methane and the thermal conductivity and viscosity of tetrafluoromethane — Continued

	Methane	Tetraf	luoromethane
T	Thermal	Viscosity	Thermal
(K)	conductivity	(µPa s)	conductivity
	$(mW m^{-1} K^{-1})$	•	$(mW m^{-1} K^{-1})$
720.0	116.47	34.45	48.53
730.0	118.67	34.77	49.21
740.0	120.89	35.09	49.89
750.0	123.12	35.41	50.56
760.0	125.35	35.73	
770.0	127.58	36.04	
780.0	129.82	36.36	
790.0	132.07	36.67	
800.0	134.32	36.98	
810.0	136.57	37.29	
820.0	138.82	37.60	
830.0	141.07	37.90	
840.0	143.31	38.21	
850.0	145.55	38.51	
860.0	147.78	38.81	
870.0	150.00	39.12	
880.0	152.21	39.42	
890.0	154.41	39.72	
900.0	156.58	40.02	
910.0	158.74	40.31	
920.0	160.87	40.61	
930.0	162.97	40.91	
940.0	165.04	41.21	
950.0	167.08	41.50	
960.0	169.07	41.80	
970.0	171.03	42.09	
980.0	172.93	42.39	
990.0	174.78	42.68	
1000.0	176.56	42.98	

## 6. Conclusions

A concise representation of the thermal conductivity of methane and tetrafluoromethane in the limit of zerodensity, based upon a limited set of accurate experimental data and the kinetic theory, has been presented. For methane the accuracy of the correlation of the thermal conductivity and the associated tabulations is estimated as one of  $\pm 2\%$  in the temperature range 300-500 K, rising to  $\pm 2.5\%$  at low and  $\pm 4.0\%$  at high extremes of the temperature range. For tetrafluoromethane the accuracy of the correlation of the thermal conductivity and the associated tabulations is estimated as one of  $\pm 1\%$  in the temperature range 280-450 K rising to  $\pm 5\%$  at high temperature.

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