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The Correlation and Prediction of Thermal Conductivity and Other Properties of Gases at Zero Density[1]

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This paper presents a comparative study of the correlation of thermal conductivities in the limit of zero density for dilute gases including nitrogen, carbon monoxide, carbon dioxide, methane, and tetrafluoromethane. A theoretically based correlation scheme employing independent experimental information has been examined and found to be useful for the correlation of thermal conductivity data as well as for the evaluation of related quantities, e.g., effective collision cross sections. The latter provide the basis for further studies concerning the anisotropy of the intermolecular pair potential. The paper includes results regarding the simplified expression for the thermal conductivity proposed by Thijsse et al., which has been found to be especially useful for practical purposes.

KEY WORDS: carbon dioxide; carbon monoxide; effective collision cross sections; methane; nitrogen; polyatomic gas; thermal conductivity of gases; tetrafluoromethane; transport properties.

1. INTRODUCTION

Modern computer codes which suit the needs of the chemical and other industries should include powerful data bases which allow accurate and reliable numerical data to be calculated over the widest possible range of thermodynamic states. Concerning transport properties it has been widely agreed that it is possible to apply the so-called residual concept in order to

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represent these properties; i.e., the density- and temperature-dependent value of the transport property as a whole is thought to be the sum of a zero-density contribution, an excess value, and of the critical enhancement. The zero-density values are of dual importance in this context because they are also of considerable interest for the generation of sophisticated potential surfaces by multiproperty analyses.

This paper deals with the correlation of thermal conductivity in the limit of zero density. Its starting point is the well-known fact that whereas correlation schemes for the viscosity in the same limit are well developed [1–3], this is not true for the thermal conductivity. Therefore, the paper presents a comparative study of a theoretically based correlation of this quantity for dilute polyatomic gases including nitrogen, carbon monoxide, carbon dioxide, methane, and tetrafluoromethane. Conclusions for related properties, especially effective collision cross sections, are also shown.

2. DATA SELECTION

Modern computer facilities provide a sufficient basis for even complicated correlation and prediction schemes. In contrast, the experimental data available from the literature are often *not* sufficient either with respect to the range of thermodynamic states or with respect to their quality. Therefore, a careful—whenever possible—theoretically based data selection must be the important prerequisite for all data compilations. This point has been discussed elsewhere, both in general [4] and for the gases studied here [5–7]. Consequently, the following analysis is based on the selected primary data give in detail in Refs. 5–7.

3. THEORETICAL BACKGROUND

3.1. Viehland–Mason–Sandler Formalism

According to the kinetic theory the thermal conductivity (λ_0) of a polyatomic gas in the limit of zero density may be written as the sum of translational (λ_{tr}) and internal (λ_{int}) contributions,

$$\lambda_0 = \lambda_{\mathrm{tr}} + \lambda_{\mathrm{int}} \tag{1}$$

in which

$$\lambda_{\mathrm{tr}} = \frac{5k^2T}{2m\langle v\rangle_0}\left[\frac{\mathfrak{S}(1001)+r\mathfrak{S}\begin{pmatrix}1010\\1001\end{pmatrix}}{\mathfrak{S}(1010)\,\mathfrak{S}(1001)-\mathfrak{S}^2\begin{pmatrix}1010\\1001\end{pmatrix}}\right] \tag{2}$$

and

$$\lambda_{\text{int}} = \frac{5k^2T}{2m\langle v\rangle_0}\left[\frac{r\mathfrak{S}\begin{pmatrix}1010\\1001\end{pmatrix} + r^2\mathfrak{S}(1010)}{\mathfrak{S}(1010)\,\mathfrak{S}(1001) - \mathfrak{S}^2\begin{pmatrix}1010\\1001\end{pmatrix}}\right]S \tag{3}$$

Here T represents the temperature, m is the molecular mass, and k is Boltzmann's constant.

The quantities $\mathfrak{S}\left(\begin{smallmatrix}p & q & r & s\\ p' & q' & r' & s'\end{smallmatrix}\right)$ are effective collision cross sections [8] that incorporate all of the information about binary collisions and hence the intermolecular pair potential. [If $pqrs = p'q'r's'$ we adopt the usual notation $\mathfrak{S}\left(\begin{smallmatrix}p & q & r & s\\ p' & q' & r' & s'\end{smallmatrix}\right) = \mathfrak{S}(pqrs)$]. The additional symbols introduced in Eqs. (2) and (3) are

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

$$r = (2c_{\text{int}}/5k)^{1/2} \tag{5}$$

and

$$S \approx 1 - (5/3)(1 + \lambda_{\text{tr}}/\lambda_{\text{int}})(\Delta\lambda_{\parallel}/\lambda)_{\text{sat}} \tag{6}$$

where c_{int} is the internal heat capacity of the gas. Finally, S is the correction factor [9] to the semiclassical Wang Chang–Uhlenbeck theory that accounts for spin polarization effects. From Eqs. (1)–(6) and the exact relationships [10]

$$\mathfrak{S}\begin{pmatrix}1010\\1001\end{pmatrix} = (5r/6)\,\mathfrak{S}(0001) \tag{7}$$

and

$$\mathfrak{S}(1010) = (2/3)\,\mathfrak{S}(2000) + (25r^2/18)\,\mathfrak{S}(0001) \tag{8}$$

it becomes obvious that λ_0 is related to just three effective cross sections: $\mathfrak{S}(2000)$, $\mathfrak{S}(0001)$, and $\mathfrak{S}(1001)$.

The cross section $\mathfrak{S}(2000)$ is related to the viscosity (η_0) according to

$$\eta_0(T) = \frac{kT}{\langle v\rangle_0}\,\mathfrak{S}(2000)^{-1} \tag{9}$$

For the (hypothetical) coefficient of self-diffusion (D) we have

$$D = \frac{kT}{nm\langle v\rangle_0}\,\mathfrak{S}(1000)^{-1} \tag{10}$$

and for the Herzfeld–Litovitz [11] collision number for internal energy relaxation (ζ_{coll})

$$\zeta_{\text{coll}} = \frac{4kT}{\pi\eta\langle v\rangle_0}\,\mathfrak{S}(0001)^{-1} \tag{11}$$

The remaining quantity is the diffusion coefficient for internal energy (D_{int}) that has been defined as [9]

$$D_{\text{int}} = \frac{kT}{nm\langle v\rangle_0}\left[\mathfrak{S}(1001) - \frac{1}{2}\,\mathfrak{S}(0001)\right]^{-1} \tag{12}$$

It is, therefore, only this property that cannot be deduced from independent measurements.

3.2. Thijsse Formula

Starting from the first-order expression for the thermal conductivity, neglecting the effect of spin polarization, and using an alternative set of trial functions and hence related effective cross sections, Thijsse et al. [12] derived the expression

$$\lambda_0 = \frac{5k^2T(1+r^2)}{2m\langle v\rangle_0\,\mathfrak{S}(10E)}\left[1 - \frac{\mathfrak{S}^2\begin{pmatrix}10E\\10D\end{pmatrix}}{\mathfrak{S}(10E)\,\mathfrak{S}(10D)}\right]^{-1} \tag{13}$$

By making use of exact relationships among the various cross sections, it has been found [12, 13] that for N_2, CO, CO_2, CH_4, and CF_4 the correction factor on the right-hand side departs from 1.0 by no more than 0.9% for N_2 and CO, 0.4% for CO_2, and 0.1% for CH_4 and CF_4 in the temperature range above 300 K [13], so that the simpler formula

$$\lambda_0 = \frac{5k^2T}{2m\langle v\rangle_0}\,\frac{(1+r^2)}{\mathfrak{S}_T(10E)} \tag{14}$$

represents a useful approximation. Consequently, a simple means of representing the thermal conductivity data, analogously to the relation used for the viscosity, is afforded by defining a reduced cross section by

$$\mathfrak{S}_T^*(10E) = \mathfrak{S}_T(10E)/\pi\sigma^2 \tag{15}$$

and correlating values of $\mathfrak{S}_T^*(10E)$ as a function of T^* using the scaling parameters ε/k and σ derived from the viscosity correlation [1–3].

4. THE CORRELATION SCHEME

The starting point of our procedure consists of correlations for $\mathfrak{S}(2000)$ [1–3] and $\mathfrak{S}(0001)$ [14–16] via Eqs. (9) and (11). $C^0_{\mathrm{int}}(T)$ has been derived from the literature [5–7], whereas $(\Delta\lambda''/\lambda)_{\mathrm{sat}}$ has been taken from the measurements of Hermans et al. [17] and assumed to be a constant [18].

The primary data for λ_0 enable $\mathfrak{S}(1001)$ to be evaluated for certain temperatures using Eqs. (1)–(8) and correlated for the range of measurements. The final result is a consistent set of the effective cross sections appearing in the Viehland–Mason–Sandler formalism that is useful to interpolate λ_0 within the range of measurements and to predict values within certain limits [4]. For practical purposes this method is rather cumbersome. Therefore, the simplified Thijsse formula of Eqs. (15) and (16) has been adopted in order to evaluate a "practical correlation." This was found quite useful for all gases studied here [5–7].

Finally, it is also possible to deduce values for the ratio D_{int}/D that has been widely used in the literature. But it must be stressed that this is not an essential part of the original correlation procedure.

5. RESULTS

5.1. Thermal Conductivity in the Limit of Zero Density

The results of our analyses have been expressed via $\mathfrak{S}^*_T(10E)$ using

$$\ln \mathfrak{S}^*_T(10E) = \sum_{i=0}^{7} a_i (\ln T^*)^i \tag{16a}$$

or

$$\mathfrak{S}^*_T(10E) = \sum_{i=0}^{7} a_i / T^{*i} \tag{16b}$$

The coefficients a_i are given in Table I. The associated uncertainty is ±0.5% near 300 K, rising to ±1% at 1000 K and to ±2.5% at either extreme of the temperature range for the linear molecules, similarly for methane, and ±0.5% in the range 300–450 K for CF_4, rising to ±2% at 1000 K.

These results have been compared to other recent correlations in Refs. 4–7. Here, we additionally analyzed deviations of this correlation from results computed using the modified EUCKEN formula

$$\lambda_0 = (k\eta_0/m)[(15/4) + (\rho D/\eta_0)(c_{\mathrm{int}}/k)] \tag{17}$$

Table I. Coefficients a_i for the Representation of λ_0 in Terms of $\mathfrak{S}^*_T(10E)$ According to Eqs. (15) and (16)

a_i	N_2[a]	CO[a]	CO_2[b]	CH_4[b]	CF_4[b]
a_0	4.5384086	4.6027178	42.26159	39.7099037	39.71382904
a_1	−0.71858394	−0.46386818	62.80115	58.8572159	110.213585
a_2	0.74042225	0.096315989	−53.87661	−12.38833904	−282.287323
a_3	−0.91728276	−0.27186355	67.35941	1.003322363	790.6494
a_4	0.68036729	0.26415878	0.0	−0.0352643132	−1317.7395
a_5	−0.27205905	−0.091615525	0.0	0.000454049819	1204.5525
a_6	0.055323448	0.010736359	−43.62677	0.0	−465.494293
a_7	−0.0045342078	0.0	22.55388	0.0	0.0
T (K) range	$120 < T < 2100$	$120 < T < 2100$	$220 < T < 1500$	$300 < T < 1000$	$300 < T < 1000$
ε/k, K	104.2	104.2	251.196	163.558	156.5
$\mathfrak{S}$, nm	0.3632	0.3632	0.3751	0.3709	0.4579

[a] $\ln \mathfrak{S}^*_T(10E) = \sum_{i=0}^{7} a_i (\ln T^*)^i$.

[b] $\mathfrak{S}^*_T(10E) = \sum_{i=0}^{7} b_i / T^{*i}$.

This has been done because it has been widely assumed that this relation may be a good representation for the thermal conductivity of dilute gases at high temperatures. Since this formula has been derived neglecting relaxation effects and the spin polarization correction as well as assuming $D_{\text{int}} = D$, this must not be true. Indeed, remarkable deviations are evident in Fig. 1 even at high temperatures, especially for methane, and also in preliminary results for other gases with many vibrational degrees of freedom [19].

5.2. EUCKEN Factors

Another quantity that is often used to represent the temperature dependence of thermal conductivities is the so-called EUCKEN factor

$$f_{\mathrm{E}} = m\lambda_0/(\eta_0 c_v^0) \tag{18}$$

A comparison of these factors for N_2, CO, CO_2, CH_4, and CF_4 as a function of temperature is shown in Fig. 2. Among other interesting features it demonstrates the remarkable result that for nitrogen and carbon

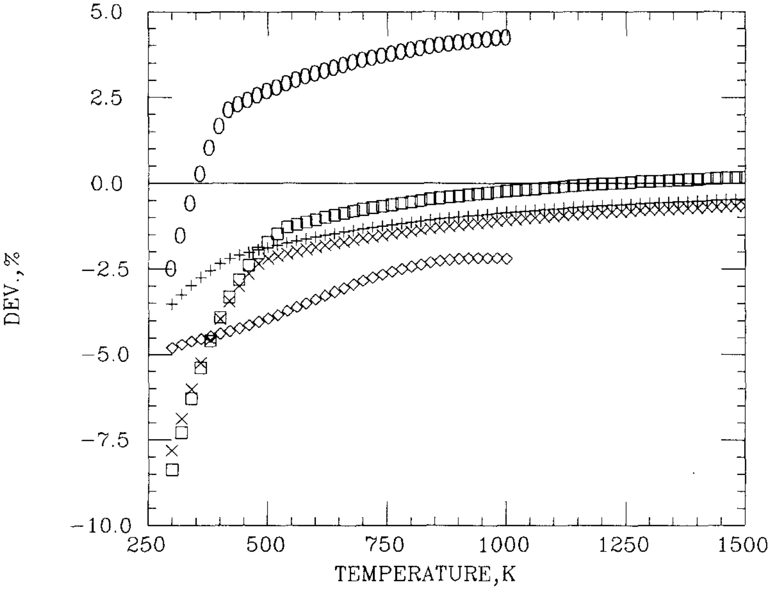

Fig. 1. Deviation plot (in percent) for λ_{E} according to the extended EUCKEN formula [dev. = $100*(\lambda_{\mathrm{E}} - \lambda_{\text{corr}})/\lambda_{\text{corr}}$]. (+) N_2; (×) CO; (□) CO_2; (○) CH_4; (◇) CF_4.

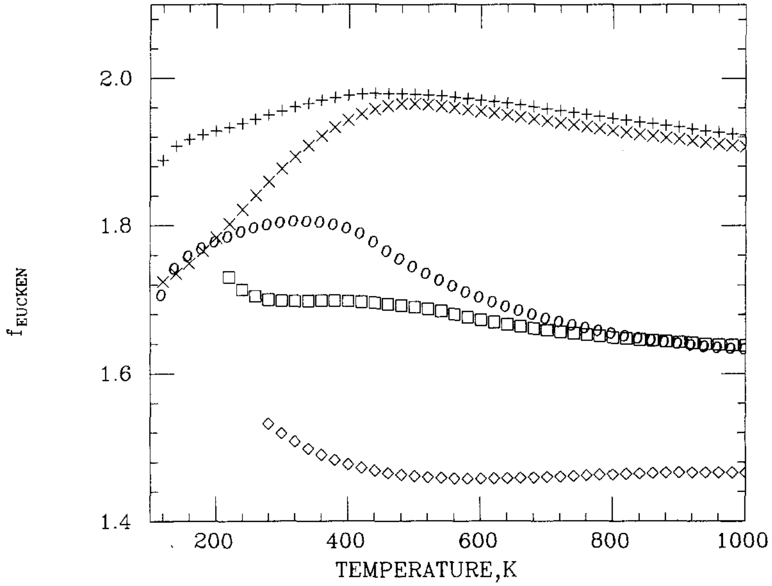

Fig. 2. The temperature dependence of EUCKEN factors. (+) N_2; (×) CO; (□) CO_2; (○) CH_4; (◇) CF_4.

monoxide, the thermal conductivity seems to be significantly different, especially at low temperatures, whereas the molecular mass and the viscosity are nearly identical [5].

5.3. The Effective Cross Section $\mathfrak{S}(1001)$

The effective collision cross sections $\mathfrak{S}(2000)$ and $\mathfrak{S}(0001)$ can be deduced from the viscosity and the collision number for internal energy relaxation (or bulk viscosity), respectively. The only source for $\mathfrak{S}(1001)$ is an analysis as carried out in this study. Therefore, this quantity and its comparison with other cross sections are of considerable interest, too.

Such a comparison is given for methane in Table II. This result is also typical of the other gases. It is possible to draw the following conclusions from this table.

(i) We find the diagonal cross sections $\mathfrak{S}(2000)$, $\mathfrak{S}(1001)$, and $\mathfrak{S}(1010)$ to be of the same order of magnitude.

(ii) It is obvious that the other diagonal cross section $\mathfrak{S}(0001)$ is remarkably smaller than the former and, according to Eq. (8), comparable to the coupling cross section $\mathfrak{S}\left({1010 \atop 1001}\right)$.

(iii) All effective cross-sections decrease with increasing temperature.

Table II. Comparison of Different Effective Collision Cross Sections for Methane

T(K)	$\mathfrak{S}(2000)$	$\mathfrak{S}(1001)$	$\mathfrak{S}(0001)$	$\mathfrak{S}(1010)$	$\mathfrak{S}\binom{1010}{1001}$
120.	62.33	66.91	22.05	59.96	14.25
200.	49.39	46.49	9.95	41.39	6.49
300.	41.62	34.87	5.42	33.17	3.83
400.	37.68	28.69	3.24	29.41	2.64
500.	35.40	26.28	2.16	27.32	2.01
600.	33.92	24.85	1.60	25.99	1.64
700.	32.86	23.84	1.26	25.07	1.41
800.	32.04	23.07	1.05	24.36	1.26
900.	31.34	22.44	0.91	23.78	1.15
1000.	30.72	21.89	0.82	23.26	1.07

It is worth noting that these conclusions for a large temperature range confirm results which have been found by Beenakker et al. [17] for the temperature range 77–300 K.

[It is necessary to mention here that the results for $\mathfrak{S}(1001)$ naturally depend on the input data. Since the collision number for internal energy relaxation usually has an uncertainty of ±15...±25%, the uncertainty of the related cross section is not comparable to that of $\mathfrak{S}(2000)$. The same must be true for $\mathfrak{S}(1001)$. This fact indicates that it is necessary to develop new experimental methods for the determination of bulk viscosities with a higher accuracy!]

5.4. The Ratio D_{int}/D

Since the ratio D_{int}/D has often been discussed in the literature, we include an analysis of this quantity as well. The values for D_{int} have been calculated using Eq. (12). The calculation of D_{int}/D then followed the standard procedure to express D in terms of the collision integral ratio A^* [22]:

$$D_{\text{int}}/D = \frac{5D_{\text{int}}nm}{6\eta A^*} \qquad (19)$$

The results of our calculations are shown in Fig. 3. As discussed in Ref. 4 the behavior of D_{int}/D for N_2, CO, and CO_2 is in agreement with theoretical results for linear molecules. That means, the ratio reaches $D_{\text{int}}/D = 1.0$ from below at a certain temperature. Equivalent theoretical predictions for spherical top molecules are not available. Thus, we have to conclude from

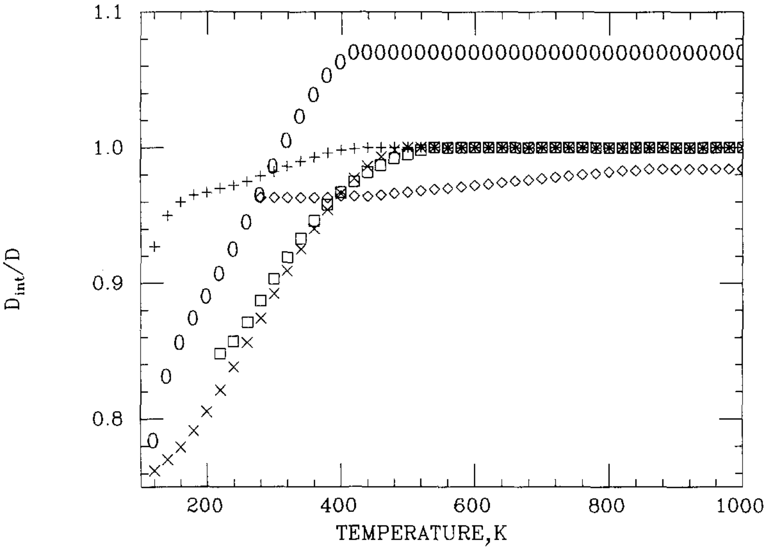

Fig. 3. The temperature dependence of D_{int}/D. (+) N_2; (×) CO; (□) CO_2; (○) CH_4; (◇) CF_4.

the result for methane (as well as from preliminary results for ethane and ethylene [19]) that values greater than 1.0 seem to be possible. One could assume that such results are caused by the uncertainties in $\mathfrak{S}(0001)$ or A^*. But we have found that this is *not* true. Therefore, our result necessitates additional high-precision measurements and further theoretical work in this field.

6. CONCLUSIONS

Results of a comprehensive study about the correlation of thermal conductivity of polyatomic gases in the limit of zero density have been summarized. Starting from carefully selected data sets we were able to carry out a theoretically based correlation scheme. For practical purposes the results have been correlated using the simplified Thijsse formula. The analysis of quantities which are related to the thermal conductivity shows the necessity of additional high-precision measurements, especially at low and high temperatures, as well as of further theoretical work in order to improve the kinetic theory of dilute polyatomic gases.

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