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Composition Dependence of the Thermal Conductivity of Low-Density Polyatomic Gas Mixtures

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We present a predictive scheme for the composition dependence of the thermal conductivity of mixtures containing polyatomic gases at zero density. This supplements earlier work which developed a method to interpolate for the composition dependence of dense gas mixtures, as well as an earlier procedure to calculate the thermal conductivity of mixtures of monatomic gases. In all cases, the algorithm makes use of accurately measured values of the thermal conductivity of pure gases and is validated with the aid of almost equal accurately measured values of selected binary mixtures. Such accurate data have been obtained mostly in transient hot-wire instruments. The formulae proposed for the calculations use the Monchick–Pereira–Mason kinetic-theory analysis as a starting point but contain a number of detailed improvements. The present algorithm is tested by comparison with measurements on 22 mixtures, which show absolute average deviations from the predictions ranging from 0.7 to 2.7%, with one unexplained case, that of CF_4–He mixtures, which show deviations reaching as much as 7%. We estimate that the algorithm predicts the zero-density thermal conductivity of binary mixtures, containing at least one polyatomic component, with a probable error in the order of 2%.

KEY WORDS: binary mixtures; kinetic theory; polyatomic gas mixtures; thermal conductivity.

1. INTRODUCTION

Over about the past 20 years the transient hot-wire method for the measurement of the thermal conductivity of gases has been developed into the most accurate technique available. The modern version of the method was pioneered by Haarman [1] and further refined and developed by Kestin, Wakeham, and their co-workers [2–6]. A very substantial body of

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accurate data has by now been assembled, and in particular, many carefully selected mixtures have been studied over the past 10 years, mostly near room temperature [7–18]. A leading motive for these mixture studies has been the hope of developing a reliable calculation procedure for the prediction of mixture thermal conductivities, since it is obviously a practical impossibility to carry out direct measurements on all mixtures that might be of interest. Only limited success has so far been achieved in the search for a predictive algorithm, as discussed in a review by Kestin and Wakeham [19]. They concluded that the main difficulty lay in the description of the limit of zero density, since an interpolation scheme [20] for the composition dependence of dense gas mixtures seemed to work well in most cases.

The purpose of this paper is to present a predictive scheme for the composition dependence of the thermal conductivity of mixtures containing polyatomic gases in the limit of low density. It starts from the same kinetic-theory basis that previous attempts have used [19], but a careful analysis of the major sources of error allows us to produce several improvements that yield predictions whose accuracy is of the order of 2%. While not as good as the experimental precision of about 0.3%, this result should prove satisfactory for many purposes.

2. THEORY

The starting point is the kinetic-theory analysis of Monchick et al. [21], which is a first-order solution of the semiclassical extension of the Boltzmann equation given by Wang Chang et al. [22]. As a first-order theory it contains a number of omissions and approximations, such as neglect of spin polarization, of "complex" collisions involving more than a single quantum jump, and of certain correlations between internal energy states and relative translational velocities. In addition, only first approximations for the constituent transport coefficients in terms of average cross sections are obtained. Even with these simplifications, the mixture formulas contain a large number of inelastic cross sections and relaxation times, which are known only poorly, if at all. There are three essential developments that enable us to obtain an accurate predictive algorithm from this approximate theory.

(1) Use of the Monchick–Pereira–Mason Expressions as Interpolation Formulas Only. In particular, this means using the experimental values (or accurately calculated ones) of the thermal conductivities and viscosities of the pure components and dropping all the other explicit inelastic cross-section terms. The result is called the Hirschfelder–Eucken formula [21];

the additional approximation is also made of replacing diffusion coefficients for internal energy by ordinary mass diffusion coefficients (only ratios of such diffusion coefficients occur). A great deal of testing and numerical experimentation has shown that the Hirschfelder–Eucken formula usually gives results very close to those of the full inelastic formulas, provided that both sets of formulas are forced to produce the same values for the pure components [7–19, 21]. In other words, the inelastic-collision terms do not change the *shape* of the curve of thermal conductivity as a function of composition very much; they only move it up or down [21].

This interpolation ploy takes care of most, but not all, of the deficiencies of the original first-order theory. Unacceptably large errors can still appear when the masses of the components are very different. Correction for this effect constitutes the second development.

(2) Disparate Mass-Ratio Correction. The error that arises with disparate masses is a convergence error in the usual sequence of kinetic-theory approximations. It has nothing to do with polyatomic gases as such and occurs even with mixtures of noble gases. The major source of this convergence error was identified long ago by Mason and Saxena [23] as occurring in the diffusional transport of energy by the light molecules in the presence of the heavy ones. They suggested that most of the error could be compensated by using a correct diffusion coefficient instead of its first approximation. This suggestion has been tested on several noble-gas mixtures and found to work well [24]. Presumably the same correction should also be applied to the coefficient that describes the diffusional transport of internal energy of the light molecules.

(3) Availability of Accurate Input Data. These include the thermal conductivities, viscosities, and self-diffusion coefficients of the pure components, the binary diffusion coefficients of all the gas pairs, and three dimensionless ratios of collision integrals that characterize interactions between all the pairs (the quantities A^*_{12}, B^*_{12}, and C^*_{12}). Most of these are available from recent extensive sets of corresponding-states correlations [25–28], including predictive combination rules [29] and correlations for mixture quantities [30]. Accurate values of all these quantities are necessary in order to calculate mixture thermal conductivities.

As a result of these developments, the working formulas for the thermal conductivity of a mixture of N components are as follows:

$$\lambda_{\mathrm{mix}} = \lambda_{\mathrm{mix}}(\mathrm{mon}) + \sum_{i=1}^{N} [\lambda_i - \lambda_i(\mathrm{mon})] \left[1 + \sum_{\substack{j=1 \\ j \neq i}}^{N} \frac{x_j D_{ii}}{x_i D_{ij}} \right]^{-1} \tag{1}$$

in which the λ_i are the *experimental* (or accurately calculated) thermal conductivities of the pure components, the x's are mole fractions, and the D's are diffusion coefficients. The $\lambda_i(\text{mon})$ are hypothetical thermal conductivities that would be measured if the components behaved like monatomic gases. Thus $\lambda_{\text{mix}}(\text{mon})$ represents the translational contribution to the mixture conductivity and the second term (the sum) represents the contribution from the diffusive transport of internal energy. Notice that Eq. (1) automatically gives the correct limiting values; i.e., $\lambda_{\text{mix}} = \lambda_i$ if $x_i = 1$. The $\lambda_i(\text{mon})$ are to be calculated from *experimental* (or accurately calculated) values of viscosity η_i,

$$\lambda_i(\text{mon}) = \frac{15}{4}\frac{k}{m_i}\eta_i \tag{2}$$

where k is Boltzmann's constant and m_i is the molecular mass of component i. Although Eq. (2) is based on only first-order kinetic theory, no correction for this fact needs to be made. The reason is that if $\lambda_i(\text{mon})$ is slightly underestimated (say), then the internal contribution $[\lambda_i - \lambda_i(\text{mon})]$ will be correspondingly overestimated, and the errors will compensate.

The expression for $\lambda_{\text{mix}}(\text{mon})$ is rather complicated:

$$\lambda_{\text{mix}}(\text{mon}) = 4 \begin{vmatrix} L_{11} & \cdots & L_{1N} & x_1 \\ \vdots & & & \vdots \\ L_{N1} & \cdots & L_{NN} & x_N \\ x_1 & \cdots & x_N & 0 \end{vmatrix} \begin{vmatrix} L_{11} & \cdots & L_{1N} \\ \vdots & & \vdots \\ L_{N1} & \cdots & L_{NN} \end{vmatrix}^{-1} \tag{3}$$

where the matrix elements are

$$L_{ii} = -\frac{4x_i^2}{\lambda_i(\text{mon})} - \frac{16x_i}{25k}\sum_{\substack{k=1\\k\neq i}}^{N}\frac{x_k}{nD_{ik}} \times \frac{\left(\frac{15}{2}m_i^2 + \frac{25}{4}m_k^2 - 3m_k^2 B_{ik}^* + 4m_i m_k A_{ik}^*\right)}{(m_i + m_k)^2} \tag{4}$$

$$L_{ij}(i \neq j) = \frac{16x_i}{25k}\frac{x_j}{nD_{ij}}\frac{m_i m_j}{(m_i + m_j)^2}\left(\frac{55}{4} - 3B_{ij}^* - 4A_{ij}^*\right) \tag{5}$$

in which A_{ij}^* and B_{ij}^* are the dimensionless ratios already mentioned. They are to be calculated from the available correlation results [25, 30], if possible. The crucial factor related to the disparate-mass correction is the diffusion coefficient D_{ik} for $m_i \ll m_k$ that appears in L_{ii}.

The remaining quantities needed are the diffusion coefficients D_{ij}. It is expected that they, too, will be calculated from the correlation results [25, 26, 30], according to the formula

$$nD_{ij}=\frac{3}{8}\left(\frac{kT}{\pi m_{ij}}\right)^{1/2}\frac{f_{ij}}{\sigma_{ij}^{2}\Omega_{ij}^{(1,1)*}} \tag{6}$$

where n is the total number density of the gas mixture (the results are actually independent of the value used for n), and m_{ij} is twice the reduced mass of the ij pair,

$$m_{ij}=2m_i m_j/(m_i+m_j) \tag{7}$$

The quantities σ_{ij} and $\Omega_{ij}^{(1,1)*}$ are given in the correlations. The higher-order correction factor f_{ij} depends on the mixture composition and is the source of the disparate-mass correction. It can be calculated with adequate accuracy from the semiempirical expression [24]

$$f_{ij}=1+1.3(6C_{ij}^{*}-5)^{2}\left(\frac{ax_i}{x_i+x_j+bx_i}\right) \tag{8}$$

$$a=\frac{2^{1/2}}{8[1+1.8(m_j/m_i)]^{2}}\,\frac{\Omega_{ij}^{(1,1)*}}{\Omega_{jj}^{(2,2)*}} \tag{9}$$

$$b=10a[1+1.8(m_j/m_i)+3(m_j/m_i)^{2}]-1 \tag{10}$$

where C_{ij}^{*} and $\Omega_{jj}^{(2,2)*}$ are given in the correlations. At first glance it appears that D_{ij} in Eq. (6) is not symmetric on interchange of the labels i and j because f_{ij} is not symmetric. Symmetry is not necessary in this case because the convention of $m_j \leqslant m_i$ biases the definition of f_{ij}. The magnitude of f_{ij} for the self-diffusion coefficient D_{ii} can be obtained with sufficient accuracy by setting $x_i=1$, $x_j=0$, and $m_j=m_i$ in Eq. (8), although the correlations give a slightly more accurate formula if needed. This completes the specifications for the calculation of λ_{mix}.

3. COMPARISON WITH EXPERIMENT

The available accurate experimental data are contained in Refs. 7 through 18. All the measurements were made near room temperature with the sole exception of a few on N_2–CO_2, which extend to 470 K [18]. We omit the mixtures containing H_2, because H_2 has not yet been included in the recent correlation schemes and we therefore lack accurate input data for this gas. There remain 21 binary mixtures, in 6 of which both components are polyatomic. No accurate data on multicomponent mixtures are available at present.

The results are shown in Figs. 1–4 as deviation plots: $(\lambda_{\mathrm{expt}} - \lambda_{\mathrm{calc}})/\lambda_{\mathrm{calc}}$ as a function of the mole fraction of the first-named component.

Figure 1 shows mixtures containing N_2 and CO but not containing He or CO_2. Of the eight mixtures, only three do not contain a monatomic gas as one component (N_2–CH_4, N_2–CO, and CO–CH_4). No deviation is as large as 2%, and the average absolute deviation of the points shown is 0.7%.

Figure 2 shows other mixtures not containing He. Of the seven mixtures, only two do not contain a monatomic gas (CO_2–CH_4 and N_2O–CO_2). Here the deviations are a little greater than in Fig. 1, but the worst point is off by only about 3%. The average absolute deviation of the points shown is 1.3%.

Figure 3 shows mixtures containing He, for which the disparate-mass effect is the largest. The system CF_4–He shows large deviations, up to about 7%, for which we can find no explanation. Perhaps they result from a fortuitous accumulation of errors, rather than a cancellation. Other than this system, the deviations are all smaller than 4%, with an average absolute deviation of 2.7%.

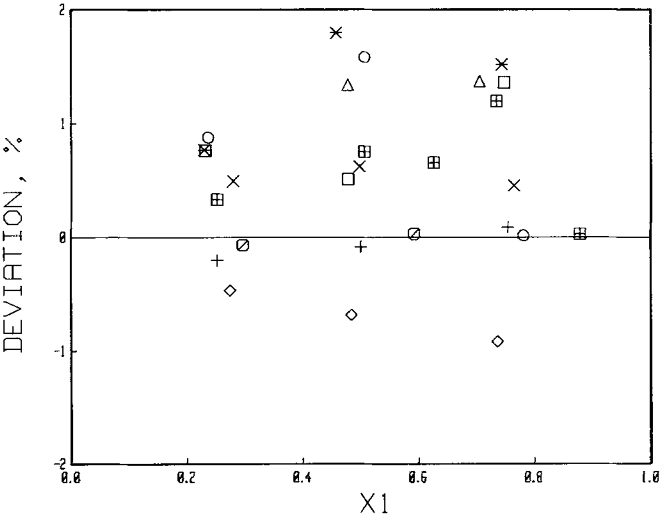

Fig. 1. Deviations of the experimental mixture thermal conductivities from the calculated values, at 27.5°C unless otherwise noted. The mole fraction of the first-named component is x_1. ○, N_2–Ne [8]; ×, N_2–Ar [8]; △, N_2–Kr [8]; ∗, N_2–CH_4 [12]; +, N_2–CO [15]; ◇, CO–Ne [16]; ⊞, CO–Ar [16]; ⊘, CO–Ar, 35°C [11]; □, CO–CH_4 [16].

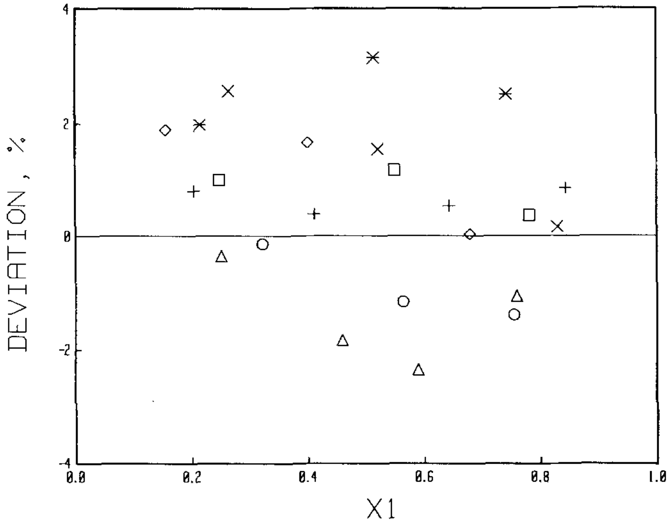

Fig. 2. Deviations of the experimental mixture thermal conductivities from the calculated values, at 27.5°C. The mole fraction of the first-named component is x_1. ○, CO_2–Ne [10]; ×, CO_2–Ar [10]; ∗, CO_2–CH_4 [13]; +, N_2O–CO_2 [15]; △, CH_4–Ne [9]; □, CH_4–Ar [9]; ◇, CF_4–Ar [17].

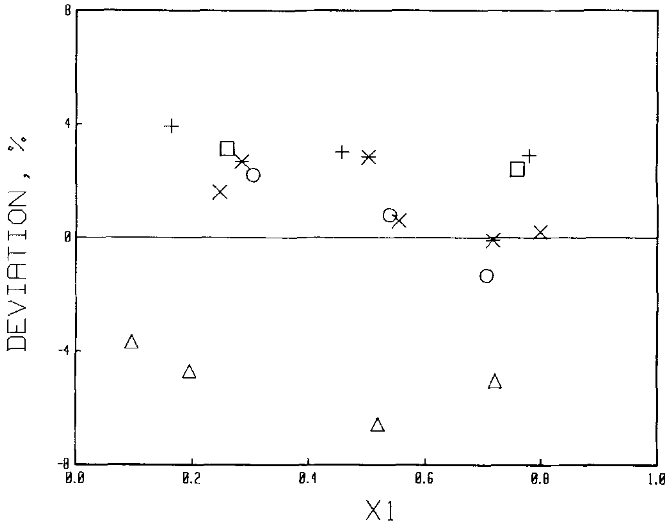

Fig. 3. Deviations of the experimental thermal conductivities from the calculated values for mixtures containing He, at 27.5°C unless otherwise noted. The mole fraction of the first-named component is x_1. +, N_2–He [8]; ∗, CO–He [16]; □, CO–He, 35°C [11]; ○, CO_2–He [10]; ×, CH_4–He [7]; △, CF_4–He [17].

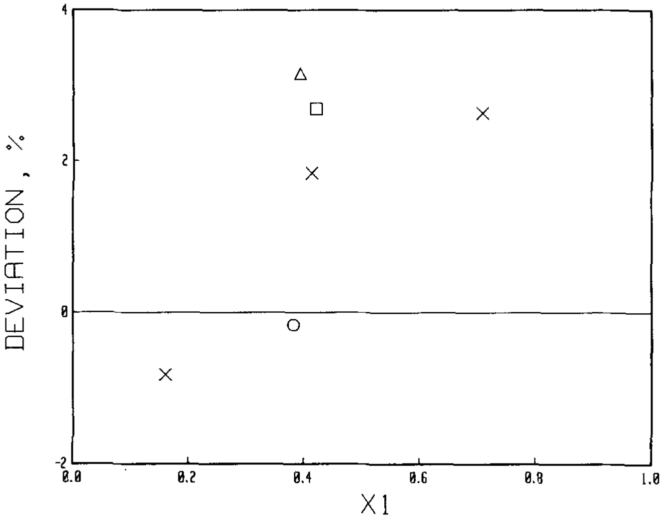

Fig. 4. Deviations of the experimental mixture thermal conductivities from the calculated values for N_2–CO_2 mixtures at higher temperatures [18]. The mole fraction of N_2 is x_1. ○, 320 K; ×, 380 K; △, 430 K; □, 470 K.

Figure 4 represents N_2–CO_2 mixtures at higher temperatures (and presumably somewhat lower accuracy). Use of correlation values [27, 28] for the thermal conductivities of the single components rather than directly measured values shifts the deviations by less than 1%. The overall deviations are comparable to those shown in Figs. 1 and 2, with the worst deviation being about 3% and the average absolute deviation being 2.0%.

4. CONCLUSIONS

The general level of accuracy of the mixture formula is about 2% but, generally, is somewhat worse for mixtures containing He. There are large deviations for CF_4–He, which are unexplained. Outside of this system, the deviations are not particularly systematic, indicating that no single large effect remains unaccounted for. Improvements will probably be difficult to achieve, requiring consideration of higher-order kinetic-theory approximations and more insight into the details and systematics of inelastic collisions, among other things. The present result should thus prove useful, and adequate for many purposes.

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