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Higher-Order Approximation to the Thermal Conductivity of Monatomic Gas Mixtures

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This paper presents expressions for the evaluation of the second- and third-order Chapman-Cowling approximation to the thermal conductivity of a multicomponent monatomic gas mixture in the limit of zero density. Calculation of these higher-order corrections have been carried out for some monatomic gas mixtures. The higher-order corrections contribute as much as 3% to the thermal conductivity of binary mixtures of gases with a large mass ratio. It is found that the higher-order kinetic theory formulae provide an adequate description of recent thermal conductivity data that have an associated uncertainty of ±0.2%. The results of this analysis are employed to demonstrate that these thermal conductivity data are entirely consistent with earlier viscosity data on the same systems.

KEY WORDS: gas mixtures; kinetic theory; thermal conductivity; transport theory.

1. INTRODUCTION

Recent developments in the measurement of the thermal conductivity of fluids have made it possible to determine the thermal conductivity of dilute gases and gas mixtures with an associated uncertainty of ±0.2% [1–3]. A prerequisite for the interpretation of such data is a kinetic theory expression for the thermal conductivity of the gas or gas mixture that relates the transport property to intermolecular pair potential energy functions, and which is at least as accurate as the experimental results. In the case of pure

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monatomic gases, such a relation has been available for a considerable time [4]. However, in the case of binary and multicomponent mixtures, no explicit formulae of equivalent accuracy are available. First, this is a consequence of the relatively poor precision of earlier thermal conductivity measurements, which did not justify a formula of high accuracy. Second, it is a result of the sheer algebraic complexity of the problem. In order to avoid these algebraic difficulties, simple modifications have sometimes been applied to the lowest-order formula for the thermal conductivity [5] in an attempt to improve its accuracy [6, 7]. In a recent publication [3] it has been shown that the available kinetic theory formulae for the thermal conductivity are incapable of describing very accurate data, and so in this paper we obtain rigorous formulae for high-order approximations to this transport property for multicomponent gas mixtures. We then employ them for the interpretation of the recent accurate experimental data.

2. THEORETICAL BACKGROUND

The thermal conductivity of a dilute gas mixture of ν components in the stationary state, when all diffusion fluxes are zero, is denoted by λ_∞ and may be written in the form [8]

$$\lambda_\infty = \lambda_0 - n\mathbf{k} \sum_{i=1}^{\nu} k_{Ti} D_{Ti} \tag{1}$$

where $\mathbf{k}$ is Boltzmann's constant. Here, λ_0 is the thermal conductivity of the mixture when it is of uniform composition, the k_{Ti} are the multicomponent thermal diffusion ratios for the mixtures, and the D_{Ti} are the multicomponent thermal diffusion coefficients.[3] The symbol n denotes the total number density of molecules in the gas. All experimental methods for the measurement of the thermal conductivity of a mixture, including the transient hot-wire technique, determine λ_∞ rather than λ_0 [10]. Consequently, in order to develop a useful theoretical expression for the mixture thermal conductivity, we must evaluate the individual transport coefficients λ_0, k_{Ti}, and D_{Ti}.

Each of these transport coefficients can be written, at least implicitly, in terms of the coefficients of Sonine polynomial series expansions, which occur in the Chapman-Enskog solution of the Boltzmann equations [8]. These expansion coefficients are themselves determined from sets of linear algebraic equations derived from various integral relations that arise in the solution. An

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[3] The multicomponent thermal diffusion coefficients we employ here are those defined by Waldmann [9].

exact solution for the transport coefficients can only be obtained if each of the Sonine polynomial expansions used in the Chapman-Enskog solution of the Boltzmann equation contains an infinite number of terms. Correspondingly, the required expansion coefficients are then to be obtained from the solution of an infinite set of linear algebraic equations. Chapman and Cowling [11] developed a scheme whereby successive approximations to the transport coefficients can be obtained by employing a finite Sonine polynomial expansion and a corresponding finite set of equations for the expansion coefficients. Thus, according to the Chapman-Cowling approximation scheme, an nth order approximation to the three transport coefficients of interest here can be derived from the equations [8]

$$[\lambda_0]_n = \frac{5}{4}\mathbf{k}\sum_{i=1}^{\nu}\left(\frac{n_i}{n}\right)a_{i,1}{}^{(n)} \tag{2}$$

$$[D_{Ti}]_n = -\frac{1}{2n}a_{i,0}{}^{(n)} \tag{3}$$

and

$$\sum_{j=1}^{\nu} d_{j,0}{}^{i(n+1)}[k_{Tj}]_n = -\frac{5}{2}\sum_{j=1}^{\nu}\left(\frac{n_j}{n}\right)d_{j,1}{}^{i(n+1)} \qquad (i = 1, \ldots, \nu) \tag{4a}$$

with

$$\sum_{i=1}^{\nu} k_{Ti} = 0 \tag{4b}$$

Here $a_{i,1}{}^{(n)}$, $a_{i,0}{}^{(n)}$, $d_{j,0}{}^{i(n)}$, and $d_{j,1}{}^{i(n)}$ are the coefficients of the Sonine polynomial expansions. The superscript (n) that is attached to each symbol indicates explicitly that the value of a particular coefficient depends upon the order of approximation and so upon the number of terms retained in the Sonine polynomial expansions. The symbol n_i denotes the number density of molecules of species i in the mixture.

The expansion coefficients $a_{i,q}{}^{(n)}$ are to be obtained from the set of equations [8]

$$\sum_{j=1}^{\nu}\sum_{q=0}^{n}\Lambda_{ij}{}^{pq}a_{j,q}{}^{(n)} = \frac{4}{5\mathbf{k}}\left(\frac{n_i}{n}\right)\delta_{p1} \qquad \begin{pmatrix} i = 1, \ldots, \nu \\ p = 0, \ldots, n \end{pmatrix} \tag{5a}$$

with

$$\sum_{i=1}^{\nu} \left(\frac{\rho_i}{\rho}\right) a_{i,0}{}^{(n)} = 0 \quad \text{for } p = 0 \tag{5b}$$

The coefficients $d_{j,q}{}^{i(n)}$ are obtained from the set of equations

$$\sum_{j=1}^{\nu} \sum_{q=0}^{n-1} \Lambda_{ij}^{pq} d_{j,q}{}^{k(n)} = \frac{8}{25\mathbf{k}} \left(\delta_{ik} - \frac{\rho_i}{\rho}\right) \delta_{p0} \qquad \begin{array}{l} (i = 1, \ldots, \nu \\ p = 0, \ldots, n-1) \end{array} \tag{6a}$$

with

$$\sum_{i=1}^{\nu} \left(\frac{\rho_i}{\rho}\right) d_{i,0}{}^{k(n)} = 0 \quad \text{for } p = 0 \tag{6b}$$

In these equations we have introduced the symbols ρ_i for the mass density of species i, ρ for the total mass density of the gas mixture and, in addition, δ_{ij} represents the Kronecker delta. The quantities Λ_{ij}^{pq} are related to certain so-called bracket integrals [8]. They include all the information about the collision dynamics of pairwise molecular encounters. They therefore depend upon the intermolecular pair potentials and will be defined later.

We note here that we have adopted the convention of Ferziger and Kaper [8] for the nomenclature of the various orders of approximation to the transport coefficients. Thus an nth order approximation to *any* transport coefficient is obtained by employing the appropriate value of n in Eqs. (2)–(6). This implies that the first-order approximation to any transport coefficient is the first nonvanishing approximation.[4] The nth order approximation to the stationary state thermal conductivity λ_∞ is, therefore, given by the expression [8]

$$[\lambda_\infty]_n = [\lambda_0]_n - n\mathbf{k} \sum_{i=1}^{\nu} [k_{Ti}]_n [D_{Ti}]_n \tag{7}$$

Equations (2)–(7) together form a consistent scheme for the evaluation of the thermal conductivity $[\lambda_\infty]_n$ for a multicomponent mixture to any order

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[4] This convention is different from that employed by Muckenfuss and Curtiss [5], who defined the order of approximation as the number of terms occuring in the Sonine polynomial expansion. Thus, with the present nomenclature their expression for the thermal conductivity of a multicomponent mixture is a first-order approximation.

of approximation given only values for the quantities Λ_{ij}^{pq}. Indeed, the advent of high speed digital computers may make this implicit formulation the most convenient, since the sets of linear algebraic equations (4)–(6) can be readily solved numerically to yield $a_{i,1}^{(n)}$, $d_{j,0}^{i(n+1)}$, $d_{j,0}^{i(n+1)}$ and $[k_{Tj}]_n$. We note that in order to evaluate $[k_{Tj}]_n$, it is necessary to determine $d_{j,0}^{i}$ and $d_{j,1}^{i}$ to the $(n+1)$th order. There are some advantages to be gained from an explicit algebraic solution of the foregoing equations and these solutions are presented in the subsequent section.

3. EXPLICIT FORMULAS

A. First-Order Approximation

A consistent, first-order approximation for the thermal conductivity of a multicomponent gas mixture has already been given by Muckenfuss and Curtiss [5]. In this order the result is comparatively simple and may be written in terms of the single determinant ratio:

$$[\lambda_\infty]_1 = -\begin{vmatrix} L_{11}^{11} & \cdots & L_{1\nu}^{11} & x_1 \\ \vdots & & \vdots & \vdots \\ L_{\nu 1}^{11} & \cdots & L_{\nu\nu}^{11} & x_\nu \\ \vdots & & & \\ x_1 & \cdots & x_\nu & 0 \end{vmatrix} \Bigg/ \begin{vmatrix} L_{11}^{11} & \cdots & L_{1\nu}^{11} \\ \vdots & & \vdots \\ L_{\nu 1}^{11} & \cdots & L_{\nu\nu}^{11} \end{vmatrix} \tag{8}$$

Here we have employed a notation such that

$$L_{ij}^{11} = \Lambda_{ij}^{11} \tag{9}$$

which we shall find useful for the higher-order approximations.[5] The elements L_{ij}^{11} are defined in terms of reduced collision integrals in the Appendix.

B. The *n*th Order Approximation

In approximations of higher order than the first, the two terms of the right-hand side of Eq. (7) are not easily combined. Consequently, it is preferable to give general expressions for each of the individual transport coefficients $[\lambda_0]_n$, $[D_{Ti}]_n$, and $[k_{Ti}]_n$ for use in Eq. (7). Algebraic solutions of

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[5] The L_{ij}^{pq} defined here are not those employed by Hirschfelder et al. [4] and Muckenfuss and Curtiss [5]. The two sets of quantities are related by the identity $L_{ij}^{pq} = -\frac{1}{4}\,(L_{ij}^{pq})_{HCB}$.

Eqs. (4)–(6), when employed in Eqs. (2) and (3), yield the following results:

$$[\lambda_0]_n = - \frac{\left|\begin{array}{c|c|c|c|c|c} L^{00} & L^{01} & L^{02} & \cdots\cdots & L^{0n} & \mathcal{O} \\ \hline L^{10} & L^{11} & L^{12} & \cdots\cdots & L^{1n} & X \\ \hline L^{20} & L^{21} & L^{22} & \cdots\cdots & L^{2n} & \mathcal{O} \\ \hline \vdots & \vdots & \vdots & & \vdots & \vdots \\ \hline L^{n0} & L^{n1} & L^{n2} & \cdots\cdots & L^{nn} & \mathcal{O} \\ \hline \mathcal{O} & X & \mathcal{O} & \cdots\cdots & \mathcal{O} & 0 \end{array}\right|}{D} \tag{10}$$

where

$$D = \left|\begin{array}{c|c|c|c|c} L^{00} & L^{01} & L^{02} & \cdots\cdots & L^{0n} \\ \hline L^{10} & L^{11} & L^{12} & \cdots\cdots & L^{1n} \\ \hline L^{20} & L^{21} & L^{22} & \cdots\cdots & L^{2n} \\ \hline \vdots & \vdots & \vdots & & \vdots \\ \hline L^{n0} & L^{n1} & L^{n2} & \cdots\cdots & L^{nn} \end{array}\right| \tag{11}$$

In these determinants L^{pq} represents the array

$$L^{pq} \equiv \begin{array}{cccc} L_{11}{}^{pq} & L_{12}{}^{pq} & \cdots\cdots & L_{1\nu}{}^{pq} \\ L_{21}{}^{pq} & L_{22}{}^{pq} & \cdots\cdots & L_{2\nu}{}^{pq} \\ \vdots & \vdots & & \vdots \\ L_{\nu 1}{}^{pq} & L_{\nu 2}{}^{pq} & \cdots\cdots & L_{\nu\nu}{}^{pq} \end{array} \tag{12}$$

where in terms of the quantities Λ_{ij}^{pq}

$$L_{ij}^{pq} = (1 - \delta_{ij}\delta_{p0}\delta_{q0})\left[\Lambda_{ij}^{pq} - \delta_{p0}\delta_{q0}\frac{M_j}{M_i}\frac{x_j}{x_i}\Lambda_{ii}^{00}\right] \qquad \begin{array}{l}(i, j = 1, 2, \ldots \nu \\ p, q = 0, 1 \ldots n)\end{array} \tag{13}$$

Here δ_{kl} represents the Kronecker delta, and M_i the molecular weight of species i. In addition, in Eq. (10), X represents the horizontal or vertical array

$$X = x_1 x_2 x_3 \ldots x_\nu \tag{14}$$

where x_i is the mole fraction of the ith component in the mixture. The symbol $\mathcal{O}$ represents a horizontal or vertical array of ν zeros.

The multicomponent diffusion coefficients $[D_{Ti}]_n$ can be written in a similar notation as

$$[D_{Ti}]_n = \frac{2}{5\mathbf{k}n}\;\frac{\left|\begin{array}{c|c|cc|c|c|c}
L^{00} & L^{01} & L^{02} & \cdots & \cdots & L^{0n} & \mathcal{O} \\ \hline
L^{10} & L^{11} & L^{12} & \cdots & \cdots & L^{1n} & X \\ \hline
L^{20} & L^{21} & L^{22} & \cdots & \cdots & L^{2n} & \mathcal{O} \\ \hline
\cdot & \cdot & \cdot & & & \cdot & \\
\cdot & \cdot & \cdot & & & \cdot & \\
\cdot & \cdot & \cdot & & & \cdot & \\ \hline
L^{n0} & L^{n1} & L^{n2} & \cdots & \cdots & L^{nn} & \mathcal{O} \\ \hline
\delta_i & \mathcal{O} & \mathcal{O} & \cdots & \cdots & \mathcal{O} & 0
\end{array}\right|}{D} \tag{15}$$

Here, the symbol δ_i denotes the horizontal array of Kronecker deltas,

$$\delta_i = \delta_{i1}\delta_{i2} \cdot \cdot \cdot \cdot \delta_{i\nu} \tag{16}$$

The multicomponent thermal diffusion ratios $[k_{Ti}]_n$ are given by the equation

$$[k_{Ti}]_n = - \frac{\begin{vmatrix} D_{11}^{\;1(n+1)} & D_{12}^{\;1(n+1)} & \cdots & D_{1n}^{\;1(n+1)} & S^{1(n+1)} \\ D_{21}^{\;2(n+1)} & D_{22}^{\;2(n+1)} & \cdots & D_{2\nu}^{\;2(n+1)} & S^{2(n+1)} \\ \vdots & \vdots & & \vdots & \vdots \\ D_{\nu 1}^{\;\nu(n+1)} & D_{\nu 2}^{\;\nu(n+1)} & \cdots & D_{\nu\nu}^{\;\nu(n+1)} & S^{\nu(n+1)} \\ \delta_{i1} & \delta_{i2} & \cdots & \delta_{i\nu} & 0 \end{vmatrix}}{\begin{vmatrix} D_{11}^{\;1(n+1)} & D_{12}^{\;1(n+1)} & \cdots & D_{1\nu}^{\;1(n+1)} \\ D_{21}^{\;2(n+1)} & D_{22}^{\;2(n+1)} & \cdots & D_{2\nu}^{\;2(n+1)} \\ \vdots & \vdots & & \vdots \\ D_{\nu 1}^{\;\nu(n+1)} & D_{\nu 2}^{\;\nu(n+1)} & \cdots & D_{\nu\nu}^{\;\nu(n+1)} \end{vmatrix}} \tag{17}$$

In this equation the elements $D_{m,l}^{\;k(n+1)}$ are defined by the relations

$$D_{mm}^{\;k(n+1)} = 0 \quad \text{for } m = 1, 2 \ldots \nu,\ k = 1, 2 \ldots \nu \tag{18}$$

$$D_{ml}^{\;k(n+1)} = d_{l,0}^{\;k(n+1)} - d_{m,0}^{\;k(n+1)} \qquad \begin{array}{r} l \neq m,\ k = 1, 2 \ldots \nu \\ l, m = 1, 2 \ldots \nu \end{array} \tag{19}$$

The quantities $d_{l,0}^{\;k(n+1)}$ are themselves given by the equation

$$d_{l,0}^{\;k(n+1)} = - \frac{8}{25\mathbf{k}} \; \frac{\left|\begin{array}{c|c|c|c|c|c} L^{00} & L^{01} & L^{02} & \cdots & L^{0n} & \Delta_k \\ \hline L^{10} & L^{11} & L^{12} & \cdots & L^{1n} & \mathcal{O} \\ \hline L^{20} & L^{21} & L^{22} & \cdots & L^{2n} & \mathcal{O} \\ \vdots & \vdots & \vdots & & \vdots & \vdots \\ \hline L^{n0} & L^{n1} & L^{n2} & \cdots & L^{nn} & \mathcal{O} \\ \hline \delta_l & \mathcal{O} & \mathcal{O} & \cdots & \mathcal{O} & 0 \end{array}\right|}{D},$$

$$(k, l = 1, 2 \ldots \nu) \tag{20}$$

where Δ_k is a vertical array of ν elements:

$$\Delta_k \equiv \left(\delta_{1k} - \frac{\rho_1}{\rho}\right)\left(\delta_{2k} - \frac{\rho_2}{\rho}\right) \cdots \left(\delta_{\nu k} - \frac{\rho_\nu}{\rho}\right) \qquad (k = 1, 2 \cdots \nu) \quad (21)$$

In addition, D is defined by Eq. (11) and δ_l by the correspondence of (16).

Finally, the elements $S^{j(n+1)}$ of Eq. (17) are defined as

$$S^{j(n+1)} = \frac{4}{5\mathbf{k}} \frac{\begin{vmatrix} L^{00} & L^{01} & L^{02} & \cdots\cdots & L^{0n} & \Delta_j \\ L^{10} & L^{11} & L^{12} & \cdots\cdots & L^{1n} & \mathcal{O} \\ L^{20} & L^{21} & L^{22} & \cdots\cdots & L^{2n} & \mathcal{O} \\ \vdots & \vdots & \vdots & & \vdots & \vdots \\ L^{n0} & L^{n1} & L^{n2} & \cdots\cdots & L^{nn} & \mathcal{O} \\ \mathcal{O} & X & \mathcal{O} & \cdots\cdots & \mathcal{O} & 0 \end{vmatrix}}{D} \qquad (22)$$

in which X is defined by the relation (14).

Equations (7) and (10)–(22) provide an explicit, consistent calculation scheme for the thermal conductivity of a dilute, multicomponent gas mixture of monatomic components of any order of approximation, which is readily coded for a digital computer once the elements L_{ij}^{pq} are defined. Further reduction of these formulae is therefore unnecessary.

3.1 The Elements L_{ij}^{pq}

The quantities L_{ij}^{pq} are defined by Eq. (13) in terms of the Λ_{ij}^{pq}, which themselves are given by the general expression [8]

$$\Lambda_{ij}^{pq} = \frac{8 m_i^{1/2} m_j^{1/2}}{75\,\mathbf{k}^2 T} \Bigg\{ \delta_{ij} \sum_k x_i x_k \, [S_{3/2}^{(p)}(C^2)\mathbf{C}, S_{3/2}^{(q)}(C^2)\mathbf{C}]'_{ik} + x_i x_j [S_{3/2}^{(p)}(C^2)\mathbf{C}, S_{3/2}^{(q)}(C^2)\mathbf{C}]''_{ij} \Bigg\} \qquad (23)$$

The terms in square brackets are the partial bracket integrals of kinetic theory defined in Ref. [8]. The symbol $S_{3/2}{}^{(p)}(C^2)$ represents a Sonine polynomial of order p, while $\mathbf{C}$ is the reduced molecular velocity and C its magnitude. Because of the symmetry properties of the partial bracket integrals, the $\Lambda_{ij}{}^{pq}$ satisfy the symmetry requirement [8]

$$\Lambda_{ij}{}^{pq} = \Lambda_{ji}{}^{qp} \qquad \begin{array}{l}(i, j = 1, 2 \cdots \nu;\\ p, q = 0, 1 \cdots n)\end{array} \tag{24}$$

In addition, they satisfy the two further conditions [8],

$$\sum_{i=1}^{\nu} \Lambda_{ij}{}^{p0} = 0, \qquad \sum_{i=1}^{\nu} \Lambda_{ij}{}^{0q} = 0 \qquad \begin{array}{r}(p, q = 0, 1 \cdots n;\\ j = 1, 2 \cdots \nu)\end{array} \tag{25}$$

It then follows from the definition of the quantities $L_{ij}{}^{pq}$ that they satisfy the conditions

$$L_{ij}{}^{pq} = L_{ji}{}^{qp} \qquad (p, q = 0, 1 \cdots n; i, j = 1, 2 \cdots \nu \text{ except} \left\{\begin{matrix} p = q = 0 \\ i \neq j \end{matrix}\right\} \tag{26}$$

$$\sum_{i=1}^{\nu} L_{ij}{}^{p0} = 0, \qquad \sum_{i=1}^{\nu} L_{ij}{}^{0q} = 0, \qquad (p, q = 0, 1 \cdots n; j = 1, 2 \cdots \nu) \tag{27}$$

Each of the partial bracket integrals of Eq. (23) can be reduced to a linear combination of the collision integrals characteristic of the interaction of species i and k according to the method described by Ferziger and Kaper [12]. Since we are ultimately interested here in the evaluation of the thermal conductivity to the third-order Chapman and Cowling approximation, it is necessary to evaluate the $L_{ij}{}^{pq}$ as far as $p = q = 3$. Ferziger and Kaper have provided a tabulation of expressions for the partial bracket integrals up to and including $p = q = 2$ as linear combination of collision integrals [8]. Here we employ their results, together with new results generated according to their procedure for higher-order bracket integrals, to construct expressions for the $L_{ij}{}^{pq}$ as far as $p = q = 3$.

We have formulated the results in terms of the commonly employed reduced collision integrals $\Omega_{ij}{}^{(l,s)*}$ for the interaction of species i and j defined by Hirschfelder et al. [4] and Ferziger and Kaper [8]. In addition, we have introduced a number of symbols for commonly occurring combinations of reduced collision integrals. Where there is an overlap with the results of Hirschfelder et al. [4] and Ferziger and Kaper [8] an identical notation for these combinations has been adopted. The expressions for the L_{ij}^{pq} are collected in the Appendix, and they show that, given reduced collision integrals characteristic of every pair interaction, the evaluation of the third-order approximation to the thermal conductivity of a multicomponent mixture is straightforward, if tedious. The reduced collision integrals themselves may be calculated by standard techniques, given a knowledge of the various intermolecular pair potential energy functions.

4. THE HIGHER-ORDER APPROXIMATIONS FOR BINARY MIXTURES

In the case of pure monatomic gases, the nth order approximation to the thermal conductivity can be written in the form [4]

$$[\lambda_i] = [\lambda_i]_1 f_\lambda^{(n)} \tag{28}$$

where $f_\lambda^{(n)}$ is a factor that accounts for approximations higher than the first, and $[\lambda_i]_1$ is the first-order approximation given by eq. (A.24); see the Appendix. Within the Chapman and Cowling approximation scheme, $f_\lambda^{(n)}$ takes the following forms for $n = 2$ and $n = 3$

$$f_\lambda^{(2)} = 1 + \frac{(L^{12})^2}{L^{11}L^{22} - (L^{12})^2} \tag{29}$$

$$\begin{aligned} f_\lambda^{(3)} = f_\lambda^{(2)} &+ L^{11}(L^{12}L^{23} - L^{22}L^{13})^2/\{[L^{11}L^{22} - (L^{12})^2] \\ &\times [L^{11}L^{22}L^{33} + 2L^{12}L^{13}L^{23} - L^{11}(L^{23})^2 - L^{22}(L^{13})^2 - L^{33}(L^{12})^2]\} \end{aligned} \tag{30}$$

Here we have omitted the subscripts from the L's since it is understood that they refer only to the single pure component i; that is, they can be derived from the L_{ij}^{pq} of the Appendix by setting $x_i = 1$ and $x_j = 0$ (for $j \neq i$).

In the case of multicomponent mixtures of gases, it is not generally possible to write the higher-order approximations as perturbations upon the first-order result. However, in two special cases such a procedure is possible, and they provide a means of checking our algebraic results for the mixture thermal conductivity. In one case we have derived the third-order approximation to the thermal conductivity of a mixture in the limit of one component mole fraction being unity. In the second case we have derived the third-order approximation to the thermal conductivity of a mixture of a gas with itself. The results of both calculations for $n = 2$ and $n = 3$ are identical with those given by Eqs. (28), (29), and (30), as they should be.

We can, of course, always define a function $f_{\text{mix}}^{(n)}$, which relates the first-order thermal conductivity of a mixture to the *n*th order approximation, by the equation

$$[\lambda_\infty]_n = [\lambda_\infty]_1 f_{\text{mix}}^{(n)} \tag{31}$$

The algebraic difficulties mentioned earlier prevent us from writing down an explicit formulation for $f_{\text{mix}}^{(n)}$. Nevertheless, for specific systems, $f_{\text{mix}}^{(n)}$ can be evaluated numerically by computing the mixture thermal conductivity in the first-, second-, and third-order approximations according to the equations given here. In order to illustrate the magnitude of the effects of higher-order approximations, we have carried out such calculations for three representative binary gaseous systems of monatomic species.

We have chosen for our examples the binary systems neon-argon, helium-argon, and helium-xenon. The mass ratios of the species in these three systems are 2, 10, and 33, respectively, so that they span the entire range of mass ratios for the monatomic species. In order to compute the reduced collision integrals for the various pair interactions we have employed an intermolecular pair potential determined from the functionals of the extended law of corresponding states [13, 14]; that is, we assume for the purposes of these sample calculations, that the intermolecular pair potentials for interactions among all the monatomic species can be rendered conformal by the choice of an energy scaling parameter ϵ_{ij} and a distance scaling parameter σ_{ij}. It follows from this hypothesis that the reduced collision integrals $\Omega^{(l,s)*}$ for all monatomic gas interactions are universal functions of the reduced temperature ($T_{ij}^* = \mathbf{k}\mathbf{T}/\epsilon_{ij}$), and this has then been shown to be obeyed to a high degree of accuracy by the collision integrals $\Omega^{(2,2)*}$ and $\Omega^{(1,1)*}$, determined from viscosity and diffusion coefficient measurements [13–15]. Boushehri et al. [16] have employed the universal correlation of the collision integral Ω_{22} [13–15] to obtain the universal intermolecular pair potential directly by means of the inversion procedure of Smith and coworkers [17, 18]. Maitland and Wakeham [19] have repeated this calculation and have shown that although there are deviations from conformality of the intermolecular pair potentials of the various pair interactions, these are generally small. Consequently, for the present purposes, the universal intermolecular potential energy function obtained in this way provides a convenient and useful approximation to the true pair potential function for each interaction.

Accordingly, we have employed the method of Smith and his coworkers [17, 18] to invert the universal functional Ω_{22} of the extended law of corresponding states [13–15]. We have then computed from the inverted potential the collision integrals up to $\Omega^{(4,4)*}$, which are required for the third-order approximation to the mixture thermal conductivity with the aid of the algorithm of Barker et al. [20]. When combined with the scaling parameters ϵ_{ij} and σ_{ij} of the extended law of corresponding states for each interaction [15], these collision integrals provide all that is required for the calculation of the mixture thermal conductivity up to the third order, and hence $f_{\mathrm{mix}}^{(2)}$ and $f_{\mathrm{mix}}^{(3)}$. In performing these calculations, we have confirmed that for a mixture of a gas with itself our computer program yields identically the correction factor $f_\lambda^{(n)}$ for the pure gas independent of mole fraction, as it should.

Figures 1–3 display the results of these calculations for the systems Ar-Ne, Ar-He, and Xe-He, respectively. We have plotted in these figures the correction factors $f_{\mathrm{mix}}^{(2)}$ and $f_{\mathrm{mix}}^{(3)}$ for several absolute temperatures as a function of the mixture composition. Taking the three figures together, it is clear that the magnitude of the correction factor for either order of approximation increases as the mass ratio of the two species is increased. In the case of Ar-Ne, the second-order correction factor $f_{\mathrm{mix}}^{(2)}$ contributes as much as 1.2% to the mixture thermal conductivity, and increases with temperature. This represents only a small enhancement of the correction factor for the pure gases. The inclusion of the third-order correction factor would increase the thermal conductivity of the mixture only by a further 0.1% at most, so that convergence is rapid. For experimental thermal conductivity data with an accuracy of ±0.2%, the second-order approximation is sufficient for argon-neon.

For argon-helium the correction factors $f_{\mathrm{mix}}^{(2)}$ and $f_{\mathrm{mix}}^{(3)}$ show a pronounced maximum at all temperatures. In this case the second-order

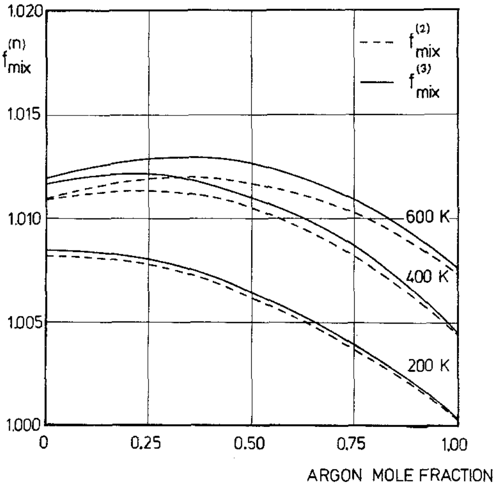

Fig. 1. The higher-order correction factor for the thermal conductivity of mixtures of argon and neon.

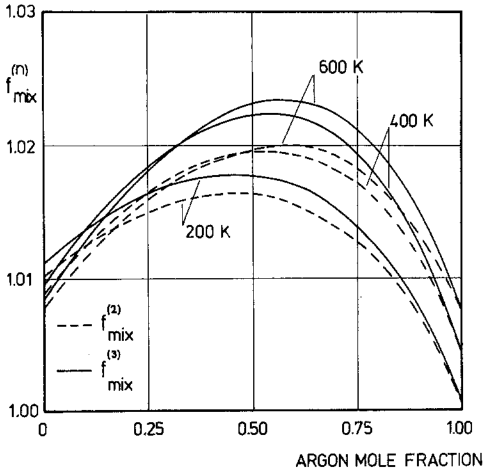

Fig. 2. The higher-order correction factor for the thermal conductivity of mixtures of argon and helium.

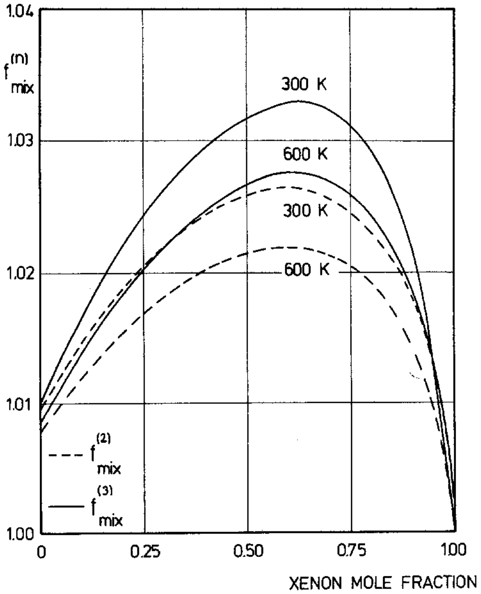

Fig. 3. The higher-order correction factor for the thermal conductivity of mixtures of xenon and helium.

correction contributes as much as 2% to the thermal conductivity of the mixture, but only about 1% to the thermal conductivity of the pure gases. The third-order correction factor contributes a further 0.3% to the thermal conductivity, so that convergence for this system is less rapid than for argon-neon, owing to the higher mass ratio. A second-order approximation is therefore barely adequate for argon-helium.

In the extreme case of xenon-helium, the higher-order correction factors for the mixtures decrease with increasing temperature, in contrast to the general behavior for the other systems. The second-order correction factor contributes as much as 2.6% to the mixture thermal conductivity, whereas the third-order correction adds a further 0.7% in the worst case. A third-order approximation is therefore essential for the description of the thermal conductivity of xenon-helium mixtures.

5. APPLICATION TO EXPERIMENTAL DATA

Measurements of the thermal conductivity of argon-neon and argon-helium mixtures in the limit of zero density at 27.5°C have recently been reported [3]. The experimental data have an accuracy of ±0.2%, and only for the argon-neon system could the results be adequately described by the first-order kinetic theory formulae. The earlier discussion indicates that this is, at least in part, because of the significant contribution to the mixture thermal conductivity from higher-order approximations. In this section we examine whether the same experimental data are consistent with the third-order kinetic theory formulae presented here.

An *ab initio* calculation of the third-order approximation to the thermal conductivity of binary mixtures of argon-neon and argon-helium requires accurate intermolecular pair potential energy functions for each pair interaction. Although reasonable estimates for these potential energy functions are available [19], they would not necessarily reproduce exactly even the thermal conductivity of the pure components. Since we are primarily interested here in the composition dependence of the mixture thermal conductivity, we therefore adopt a procedure which automatically ensures that the experimental pure component thermal conductivities are reproduced.

We first identify the experimental thermal conductivity data for a mixture with the third-order Chapman-Cowling approximation to it. Subsequently, we derive the first-order Chapman-Cowling approximation values from the experimental data by means of the equation

$$[\lambda_\infty]_1 = \frac{[\lambda_\infty]_3}{f_{\text{mix}}^{(3)}} = \frac{\lambda_{\text{expt}}}{f_{\text{mix}}^{(3)}} \tag{32}$$

In the calculations we have employed the values of $f_{\text{mix}}^{(3)}$ for each system generated by the procedure described earlier and based on the extended law of corresponding states. In the first-order approximation, the thermal conductivity of a binary mixture depends only on the elements L_{11}^{11}, L_{12}^{11}, L_{22}^{11} defined in the Appendix. Thus the only quantities, characteristic of the unlike interaction, which enter the expression for the thermal conductivity of the gas mixture are A_{12}^*, B_{12}^*, and $[\lambda_{12}]_1$, the "interaction" thermal conductivity [4]. Of these quantities, A_{12}^* B_{12}^* are relatively insensitive to the nature of the unlike pair potential energy function and can be estimated from the correlations of the extended law of corresponding states [14, 16]. Furthermore, the first-order approximations to the pure component thermal conductivities $[\lambda_1]_1$ and $[\lambda_2]_1$ can be obtained from the experimental data through Eq. (31). Consequently, we may first use the experimental data for the mixture thermal conductivity at each composition for each system to obtain the interaction thermal conductivity $[\lambda_{12}]_1$.

The results of such calculations, based on the experimental results of Ref. [3], are given in Table I. The definition of $[\lambda_{12}]_1$ given in Eq. (A.25) of the Appendix shows that it should be a composition independent quantity. For argon-neon, the mean value of the interaction thermal conductivity is

$$[\lambda_{\text{ar-Ne}}]_1 = 31.04 \text{ mW m}^{-1}\text{K}^{-1} \tag{33}$$

with a maximum deviation from the mean value of ±0.5%. When account is taken of the uncertainty in the experimental thermal conductivity data for the

Table I. The Interaction Thermal Conductivity $[\lambda_{12}]_1$

X_{Ar}	$[\lambda_\infty]_{\text{expt}} = [\lambda_\infty]_3$ (mW m^{-1} K^{-1})	$[\lambda_\infty]_1$ (mW m^{-1} K^{-1})	$[\lambda_{12}]_1$ (mW m^{-1} K^{-1})
	Argon-Neon		
0.0	49.45	48.92	
0.3675	33.81	33.46	30.97
0.5276	28.78	28.52	30.96
0.7377	23.36	23.20	31.20
1.0	17.74	17.70	
	Argon-Helium		
0.0	155.9	154.3	
0.2238	95.26	93.64	72.00
0.3453	74.95	73.51	72.65
0.6403	41.04	40.24	71.00
0.8105	28.80	28.35	72.65
1.0	17.74	17.70	

pure gases and the mixtures (±0.2%), the overall uncertainty in the calculated value of $[\lambda_{12}]_1$ for the system is estimated to be ±0.6%. Within the uncertainty bound then, the results for $[\lambda_{12}]_1$ are independent of composition, as they should be.

For argon-helium the mean value of the interaction thermal conductivity is

$$[\lambda_{\text{ar-He}}]_1 = 72.08 \text{ mW m}^{-1}\text{K}^{-1} \tag{34}$$

with a maximum deviation of 1.5%. For this system the uncertainty bound associated with the calculation of $[\lambda_{12}]_1$ is rather wider than for argon-neon. This is because of the large mass ratio of the two species, which renders the calculation of $[\lambda_{12}]_1$ more sensitive to the values employed for A_{12}^* and B_{12}^* as well as to the composition of the mixture compared with the argon-neon system. We have confirmed by direct calculation that an error of only 0.0005 in the mole fraction of the mixture can contribute as much as ±0.5% to the uncertainty in the calculated value of $[\lambda_{12}]_1$. In addition, errors of ±0.2% in the collision integral ratios A_{12}^* and B_{12}^* each contribute ±0.2% to the error in $[\lambda_{12}]_1$. When account is taken of these uncertainties, together with the errors in the thermal conductivity data themselves, the overall uncertainty in the calculated value of $[\lambda_{12}]_1$ is estimated to be one of ±2%. Within this, somewhat larger, uncertainty bound the composition independence of $[\lambda_{12}]_1$ for this system too is confirmed by the results of Table I.

Using the mean values of $[\lambda_{12}]_1$ given by Eqs. (33) and (34), we have

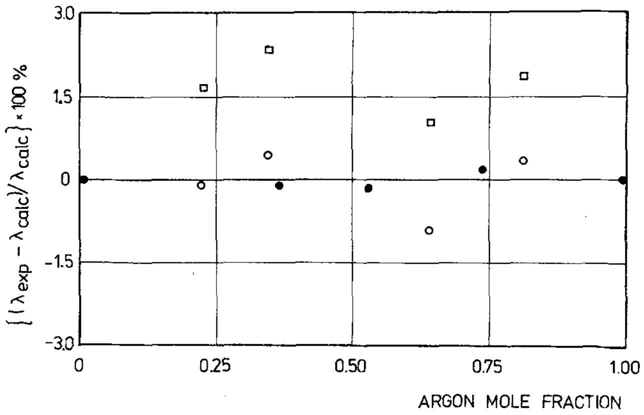

Fig. 4. Deviations of experimental thermal conductivity [3] from the calculated values at 27.5°C. ●, Ar-Ne third-order approximation calculation; ○, Ar-He third-order approximation calculation; □, Ar-He first-order approximation calculation.

computed the third-order approximation to the mixture thermal conductivity of the two systems Ar-Ne and Ar-He. In these calculations we have again employed the correction factor $f_{\mathrm{mix}}^{(3)}$ and A_{12}^* and B_{12}^* computed from the extended law of corresponding states as well as the experimental pure gas thermal conductivities [2, 3]. Figure 4 contains a plot of the deviations of the experimental data for these systems from the calculated values. In the case of argon-neon the deviation does not exceed ±0.2%, which is commensurate with the experimental error. For argon-helium the maximum deviation in the thermal conductivity amounts to 0.9% for one mixture but is considerably lower for the remainder. For the purpose of comparison, Fig. 4 also contains the deviations of the experimental data from a first-order calculation of the mixture thermal conductivity for argon-helium. For this calculation the experimental pure gas thermal conductivities have again been employed, together with the interaction thermal conductivity of Eq. (34). Here the deviations amount to as much as 2.4%. Thus the need for an approximation of higher order than the first in order to calculate adequately the thermal conductivity of binary mixtures with a large mass ratio is emphasized.

6. THE EUCKEN FACTOR

It is a result of the kinetic theory of gases that the interaction thermal conductivity $[\lambda_{12}]_1$ and the corresponding quantity for viscosity $[\mu_{12}]_1$ are related by the generalized Eucken equation [8, 21],

$$\mathrm{Eu}_{12} = \frac{[\lambda_{12}]_1 \, 8M_1M_2}{[\mu_{12}]_1 \, 15\mathbf{R}(M_1 + M_2)} = 1 \tag{35}$$

The present results, together with earlier viscosity data for argon-neon and argon-helium, afford the opportunity to assess the consistency of the two sets of experimental data. We have, therefore, employed the viscosity data of Refs. [22] and [23] to deduce the interaction viscosity of Ar-Ne and Ar-He at 27.5°C. For this purpose we have employed the second-order analysis described by Kestin et al. [15]. The mean values of the interaction viscosity obtained in this way are

$$[\mu_{\mathrm{Ar\text{-}Ne}}]_1 = 26.56 \pm 0.2 \ \mu\mathrm{Pa\ s} \tag{36}$$

and

$$[\mu_{\mathrm{Ar\text{-}He}}]_1 = 16.19 \pm 0.3 \ \mu\mathrm{Pa\ s} \tag{37}$$

In the case of argon-neon the uncertainty in the interaction viscosity is estimated to be one of ±1%, whereas for argon-helium the uncertainty is somewhat higher at about 2% for reasons similar to those cited for the thermal conductivity above.

When these values for the interaction viscosity are combined with the values for $[\lambda_{12}]_1$ given in Eqs. (32) and (33), we obtain the following results for the Eucken factors:

$$\mathrm{Eu}_{\mathrm{Ar\text{-}Ne}} = 1.004 \pm 0.016 \tag{38}$$

$$\mathrm{Eu}_{\mathrm{Ar\text{-}He}} = 1.04 \pm 0.04 \tag{39}$$

Thus for argon-neon and argon-helium we confirm the consistency of the viscosity and thermal conductivity of binary mixtures within the limits of experimental error. It is worthwhile pointing out here that the uncertainty bounds associated with the Eucken factors for the unlike interactions are unavoidably larger than those characteristic of pure gases. This is because, even when experimental data with an accuracy of ±0.2% are employed in a third-order approximation analysis, the determination of both $[\lambda_{12}]_1$ and $[\mu_{12}]_1$ from experimental data is necessarily deficient and subject to large uncertainties.

7. CONCLUSIONS

Second- and third-order Chapman-Cowling approximations to the thermal conductivity of a multicomponent mixture of monatomic gases have been derived. It has been shown that for gas mixtures containing species with a large mass ratio, the convergence of the theoretical expressions is slow. A third-order approximation to the thermal conductivity is essential for an accurate calculation for mass ratios exceeding about 10. With the aid of the equations developed here it has been possible to demonstrate the consistency of accurate viscosity and thermal conductivity measurements on binary mixtures.

A computer program for the evaluation of the higher-order correction factors for the thermal conductivity of gas mixtures, according to the scheme outlined here, can be obtained by writing to one of the authors (W.A.W.) of this paper.

APPENDIX

Expressions for the elements L_{ij}^{pq}, required for the calculation of the third-order approximation to the thermal conductivity of a multicomponent mixture of monatomic gases are listed below.

$$L_{ii}^{00} = 0 \tag{A.1}$$

$$L_{ij}^{00} = \frac{-x_i x_j}{2A^*_{ij}[\lambda_{ij}]_1} - \sum_{\substack{k=1\\k\neq i}}^{\nu} \frac{x_i x_k M_j}{2M_i A^*_{ik}[\lambda_{ik}]_1} \quad (i \neq j) \tag{A.2}$$

$$L_{ii}^{01} = \sum_{\substack{k=1\\k\neq i}}^{\nu} \frac{x_i x_k}{4A^*_{ik}[\lambda_{ik}]_1} \frac{M_k}{(M_i + M_k)} (6C^*_{ik} - 5) \tag{A.3}$$

$$= L_{ii}^{10} \tag{A.4}$$

$$L_{ij}^{01} = \frac{x_i x_j M_i}{4A^*_{ij}[\lambda_{ij}]_1 (M_i + M_j)} (6C^*_{ij} - 5) \quad (i \neq j) \tag{A.5}$$

$$= L_{ji}^{10} \tag{A.6}$$

$$L_{ii}^{11} = \frac{x_i^2}{[\lambda_i]_1} + \sum_{\substack{k=1\\k\neq i}}^{\nu} \frac{x_i x_k}{2A^*_{ik}[\lambda_{ik}]_1} \times \left\{ \frac{{}^{15}\!/_{2}\, M_i^2 + {}^{25}\!/_{4}\, M_k^2 - 3M_k^2 B^*_{ik} + 4M_i M_k A^*_{ik}}{(M_i + M_k)^2} \right\} \tag{A.7}$$

$$L_{ij}^{11} = \frac{-x_i x_j M_i M_j}{2A^*_{ij}[\lambda_{ij}]_1 (M_i + M_j)^2} \left\{ \frac{55}{4} - 3B^*_{ij} - 4A^*_{ij} \right\} \quad (i \neq j) \tag{A.8}$$

$$= L_{ji}^{11}$$

$$L_{ii}^{02} = \sum_{\substack{k=1\\k\neq i}}^{\nu} \frac{x_i x_k M_k^2}{4A^*_{ik}[\lambda_{ik}]_1 (M_i + M_k)^2} \left\{ \frac{35}{4} - 3B^*_{ik} - 6C^*_{ik} \right\} \tag{A.9}$$

$$= L_{ii}^{20}$$

$$L_{ij}^{02} = -\frac{x_i x_j M_i^2}{4A^*_{ij}[\lambda_{ij}]_1 (M_i + M_j)^2} \left\{ \frac{35}{4} - 3B^*_{ij} - 6C^*_{ij} \right\} \quad (i \neq j) \tag{A.10}$$

$$= L_{ji}^{20}$$

$$
\begin{aligned}
L_{ii}^{12} = {} & \frac{x_i^2[7 - 8E_{ii}^*]}{4[\lambda_i]_1} + \sum_{\substack{k=1 \\ k \neq i}}^{\nu} \frac{M_k x_i x_k}{2[\lambda_{ik}]_1 A_{ik}^*(M_i + M_k)^3} \\
& \times \left\{ M_i^2 \left(\frac{105}{4} - \frac{63}{2} C_{ik}^* \right) \right. \\
& + M_k^2 \left(\frac{175}{16} + \frac{255}{8} C_{ik}^* - \frac{57}{4} B_{ik}^* - 30 G_{ik}^* \right) \\
& \left. + 2 M_i M_k (7 - 8E_{ik}^*) A_{ik}^* \right\} \\
= {} & L_{ii}^{21}
\end{aligned}
\tag{A.11}
$$

$$
\begin{aligned}
L_{ij}^{12} = {} & - \frac{M_i^2 M_j x_i x_j}{2[\lambda_{ij}]_1 A_{ij}^* (M_i + M_j)^3} \\
& \times \left\{ \frac{595}{16} + \frac{3}{8} C_{ij}^* - \frac{57}{4} B_{ij}^* - 30 G_{ij}^* - 2(7 - 8E_{ij}^*) A_{ij}^* \right\} \\
& \qquad (i \neq j) \\
= {} & L_{ji}^{21}
\end{aligned}
\tag{A.12}
$$

$$
\begin{aligned}
L_{ii}^{22} = {} & \frac{x_i^2}{[\lambda_i]_1} \left[\frac{77}{16} - 7E_{ii}^* + 5H_{ii}^* \right] \\
& + \sum_{\substack{k=1 \\ k \neq i}}^{\nu} \frac{x_i x_k}{2[\lambda_{ik}]_1 A_{ik}^* (M_i + M_k)^4} \\
& \times \left\{ \frac{175}{8} M_i^4 + M_k^4 \left(\frac{1225}{64} + \frac{315}{2} C_{ik}^* - \frac{399}{8} B_{ik}^* \right. \right. \\
& \left. - 210 G_{ik}^* + 90 I_{ik}^* \right) + M_i^2 M_k^2 \left(\frac{735}{8} - 18 C_{ik}^* - \frac{81}{2} B_{ik}^* + 24 F_{ik}^* \right) \\
& \left. + 28 M_i^3 M_k A_{ik}^* + M_i M_k^3 (49 - 112 E_{ik}^* + 80 H_{ij}^*) A_{ik}^* \right\}
\end{aligned}
\tag{A.13}
$$

$$
\begin{aligned}
L_{ij}^{22} = {} & - \frac{x_i x_j M_i^2 M_j^2}{2[\lambda_{ij}]_1 A_{ij}^* (M_i + M_j)^4} \left\{ \frac{8505}{64} + \frac{558}{4} C_{ij}^* - \frac{723}{8} B_{ij}^* - 210 G_{ij}^* \right. \\
& \left. + 90 I_{ij}^* + 24 F_{ij}^* - (77 - 112 E_{ij}^* + 80 H_{ij}^*) A_{ij}^* \right\} \quad (i \neq j)
\end{aligned}
\tag{A.14}
$$

$$L_{ii}^{03} = \sum_{\substack{k=1 \\ k\neq i}}^{\nu} \frac{x_i x_k M_k^3}{2[\lambda_{ik}]_1 A^*_{ik}(M_i + M_k)^3} \left\{ \frac{315}{48} + \frac{81}{8} C^*_{ik} - \frac{27}{4} B^*_{ik} - 10G^*_{ik} \right\} \tag{A.15}$$
$$= L_{ii}^{30}$$

$$L_{ij}^{03} = \frac{x_i x_j M_i^3}{2[\lambda_{ij}]_1 A^*_{ij}(M_i + M_j)^3} \times \left\{ \frac{315}{48} + \frac{81}{8} C^*_{ij} - \frac{27}{4} B^*_{ij} - 10G^*_{ij} \right\} \quad (i \neq j) \tag{A.16}$$
$$= L_{ji}^{30}$$

$$\begin{aligned} L_{ii}^{13} = {} & \frac{x_i^2}{4[\lambda_i]_1} \left\{ \frac{63}{8} - 18E^*_{ii} + 10H^*_{ii} \right\} \\ & + \sum_{\substack{k=1 \\ k\neq i}}^{\nu} \frac{x_i x_k M_k^2}{2[\lambda_{ik}]_1 A^*_{ik}(M_i + M_k)^4} \\ & \times \left\{ \left[\frac{525}{32} + \frac{495}{4} C^*_{ik} - \frac{81}{2} B^*_{ik} - 160G^*_{ik} + 60I^*_{ik} \right] M_k^2 \right. \\ & + \left(\frac{945}{16} + \frac{243}{4} C^*_{ik} - \frac{81}{2} B^*_{ik} \right) M_i^2 \\ & \left. + \left(\frac{63}{2} - 72E^*_{ik} + 40H^*_{ik} \right) A^*_{ik} M_i M_k \right\} \\ = {} & L_{ii}^{31} \end{aligned} \tag{A.17}$$

$$\begin{aligned} L_{ij}^{13} = {} & - \frac{x_i x_j M_i^3 M_j}{2[\lambda_{ij}]_1 A^*_{ij}(M_i + M_j)^4} \\ & \times \left\{ \frac{2415}{32} + \frac{333}{4} C^*_{ij} - \frac{243}{4} B^*_{ij} - 160G^*_{ij} + 60I^*_{ij} \right. \\ & \left. - \left(\frac{63}{2} - 72E^*_{ij} + 40H^*_{ij} \right) A^*_{ij} \right\} \quad (i \neq j) \\ = {} & L_{ji}^{31} \end{aligned} \tag{A.18}$$

$$
\begin{aligned}
L_{ii}^{23} &= \frac{x_i^2}{4[\lambda_i]_1}\left[\frac{945}{32} - \frac{261}{4}E^*_{ii} + \frac{125}{2}H^*_{ii} - 30J^*_{ii}\right] \\
&\quad + \sum_{\substack{k=1\\k\neq i}}^{\nu} \frac{x_i x_k M_k}{2[\lambda_{ik}]_1 A^*_{ik}(M_i + M_k)^5}\Bigg\{M_i^4\left(\frac{1575}{16} - \frac{945}{8}C^*_{ik}\right) \\
&\quad + M_k^4\bigg[\frac{3675}{128} + \frac{28035}{64}C^*_{ik} - \frac{1953}{16}B^*_{ik} \\
&\quad - \frac{1505}{2}G^*_{ik} + 615I^*_{ik} - 210K^*_{ik}\bigg] \\
&\quad + M_i^2 M_k^2\bigg[\frac{6615}{32} + \frac{8343}{16}C^*_{ik} - \frac{2025}{8}B^*_{ik} \\
&\quad - 495G^*_{ik} + 108F^*_{ik} - 120Q^*_{ik}\bigg] \\
&\quad + M_i M_k^3\left[\frac{441}{4} - 378E^*_{ik} + 500H^*_{ik} - 240J^*_{ik}\right]A^*_{ik} \\
&\quad + M_i^3 M_k[126 - 144E^*_{ik}]A^*_{ik}\Bigg\} \\
&= L_{ii}^{32}
\end{aligned}
\tag{A.19}
$$

$$
\begin{aligned}
L_{ij}^{23} &= \frac{x_i x_j}{2[\lambda_{ij}]_1 A^*_{ij}} \frac{M_i^3 M_j^2}{(M_i + M_j)^5} \\
&\quad \times \Bigg\{\frac{42735}{128} + \frac{53847}{64}C^*_{ij} - \frac{6003}{16}B^*_{ij} + 108F^*_{ij} - 120Q^*_{ij} \\
&\quad - \frac{2495}{2}G^*_{ij} + 615I^*_{ij} - 210\,K^*_{ij} \\
&\quad - \left(\frac{945}{4} - 522E^*_{ij} + 500H^*_{ij} - 240J^*_{ij}\right)A^*_{ij}\Bigg\} \quad (i \neq j) \\
&= L_{ji}^{32}
\end{aligned}
\tag{A.20}
$$

$$
\begin{aligned}
L_{ii}^{33} = {} & \frac{x_i^2}{4[\lambda_i]_1}\left[\frac{14553}{256} - \frac{1215}{8}E_{ii}^* + \frac{1565}{8}H_{ii}^* \right. \\
& \left. - 135J_{ii}^* + \frac{105}{2}S_{ii}^* + 4U_{ii}^*\right] \\
& + \sum_{\substack{k=1\\ k\neq i}}^{\nu} \frac{x_i x_k}{2[\lambda_{ik}]_1 A_{ik}^*(M_i + M_k)^6} \\
& \times \left\{ M_k^6 \left[\frac{99225}{2304} + \frac{25515}{24}C_{ik}^* - \frac{52731}{192}B_{ik}^* - \frac{4515}{2}G_{ik}^* \right.\right. \\
& \left. + \frac{5535}{2}I_{ik}^* - 1890K_{ik}^* + 560V_{ik}^*\right] + M_i^6\,\frac{6615}{144} \\
& + M_i^2 M_k^4 \left[\frac{178605}{384} + \frac{13851}{4}C_{ik}^* - \frac{18225}{16}B_{ik}^* \right. \\
& - 4455G_{ik}^* + 1755I_{ik}^* \\
& \left. + 486F_{ik}^* - 1080Q_{ik}^* + 720W_{ik}^*\right] \\
& + M_i^4 M_k^2 \left[\frac{14175}{32} - 135C_{ik}^* - \frac{1485}{8}B_{ik}^* + 180F_{ik}^*\right] \\
& + M_i^3 M_k^3 [567 - 1296E_{ik}^* + 880H_{ik}^* + 64U_{ik}^*]A_{ik}^* \\
& + \frac{M_i^5 M_k 189}{2}A_{ik}^* + M_i M_k^5 \left[\frac{3969}{16} - 1134E_{ik}^* \right. \\
& \left. + 2250H_{ik}^* - 2160J_{ik}^* + 840S_{ik}^*\right] \\
& \left. + 180M_i^4 M_k^2 F_{ik}^* \right\}
\end{aligned}
\tag{A.21}
$$

$$
\begin{aligned}
L_{ij}^{33} = {} & -\frac{x_i x_j M_i^3 M_j^3}{2[\lambda_{ij}]_1 A_{ij}^*(M_i + M_j)^6}\left\{\frac{255255}{256} + \frac{35127}{8}C_{ij}^* - \frac{102357}{64}B_{ij}^* \right. \\
& - \frac{13425}{2}G_{ij}^* + \frac{9045}{2}I_{ij}^* - 1890K_{ij}^* + 666F_{ij}^* - 1080Q_{ij}^* \\
& + 490V_{ij}^* + 720W_{ij}^* - \left(\frac{14553}{16} - 2430E_{ij}^* + 3130H_{ij}^* \right. \\
& \left.\left. - 2160J_{ij}^* + 840S_{ij}^* - 64U_{ij}^*\right)A_{ij}^*\right\} \quad (i \neq j) \\
= {} & L_{ji}^{33}
\end{aligned}
\tag{A.22}
$$

In these expressions we have employed the following definitions of collision integral ratios

$$\begin{array}{ll}
A_{ij}^{*} = \dfrac{\Omega^{(2,2)*}}{\Omega^{(1,1)*}} & B_{ij}^{*} = [5\Omega_{ij}^{(1,2)*} - 4\Omega_{ij}^{(1,3)*}]/\Omega_{ij}^{(1,1)*} \\[2ex]
C_{ij}^{*} = \dfrac{\Omega_{ij}^{(1,2)*}}{\Omega_{ij}^{(1,1)*}} & E_{ij}^{*} = \dfrac{\Omega_{ij}^{(2,3)*}}{\Omega_{ij}^{(2,2)*}} \\[2ex]
F_{ij}^{*} = \dfrac{\Omega^{(3,3)*}}{\Omega^{(1,1)*}} & G_{ij}^{*} = \dfrac{\Omega_{ij}^{(1,4)*}}{\Omega^{(1,1)*}} \\[2ex]
H_{ij}^{*} = \dfrac{\Omega^{(2,4)*}}{\Omega^{(2,2)*}} & I_{ij}^{*} = \dfrac{\Omega^{(1,5)*}}{\Omega^{(1,1)*}} \\[2ex]
J_{ij}^{*} = \dfrac{\Omega_{ij}^{(2,5)*}}{\Omega_{ij}^{(2,2)*}} & K_{ij}^{*} = \dfrac{\Omega_{ij}^{(1,6)*}}{\Omega_{ij}^{(1,1)*}} \\[2ex]
Q_{ij}^{*} = \dfrac{\Omega_{ij}^{(3,4)*}}{\Omega_{ij}^{(1,1)*}} & S_{ij}^{*} = \dfrac{\Omega_{ij}^{(2,6)*}}{\Omega_{ij}^{(2,2)*}} \\[2ex]
U_{ij}^{*} = \dfrac{\Omega_{ij}^{(4,4)*}}{\Omega_{ij}^{(2,2)*}} & V_{ij}^{*} = \dfrac{\Omega_{ij}^{(1,7)*}}{\Omega_{ij}^{(1,1)*}} \\[2ex]
W_{ij}^{*} = \dfrac{\Omega_{ij}^{(3,5)*}}{\Omega_{ij}^{(1,1)*}} &
\end{array} \tag{A.23}$$

In addition, we have used the first approximation to the thermal conductivity of pure gas i:

$$[\lambda_i]_1 = \frac{75}{64}\left(\frac{\mathrm{N}_A \cdot \mathrm{k}^3 T}{\pi M_i}\right)^{1/2} \frac{1}{\sigma_{ii}^{2}\Omega_{ii}^{(2,2)*}} \tag{A.24}$$

as well as the so-called interaction thermal conductivity

$$[\lambda_{ij}]_1 = \frac{75}{64}\left(\frac{\mathrm{N}_A\,\mathrm{k}^3 T(M_i + M_j)}{2\pi M_i M_j}\right)^{1/2} \frac{1}{\sigma_{ij}^{2}\Omega_{ij}^{(2,2)*}} \tag{A.25}$$

where N_A is Avogadro's constant.

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