AIAA Journal
Vol. 41, No. 3, March 2003

New Approximate Formulas for Viscosity and Thermal Conductivity of Dilute Gas Mixtures

Drew A. Copeland*
The Boeing Company, Canoga Park, California 91309-7922

New approximate formulas are developed for accurately estimating the viscosity and thermal conductivity of dilute, polyatomic gas mixtures, which may include polar and nonpolar species. For the viscosity and the translational energy contribution to the thermal conductivity, the new formulas use well-known approximations for the required collision integrals in an analytic formula obtained from a single iteration of the preconditioned conjugate-gradient method for solving the linear transport equations. Unlike many approximate formulas, they are derived from a manifestly multicomponent solution of the transport equations and include, to lowest order, contributions from the off-diagonal elements of the transport property matrix. For polyatomic mixtures, the internal energy contribution to the thermal conductivity is obtained using the Hirschfelder–Eucken formalism or the Thijsse total-energy formalism. The new rules require the pure species viscosity, conductivity, molecular weight, specific heats, and the Lennard–Jones or Stockmayer potential parameters and are easy to numerically evaluate. By the use of a large experimental viscosity and conductivity database covering a broad range of molecular weights, gas temperatures, and molar compositions, these rules were tested, and their predictions compared with those of the Wilke and Brokaw rules for viscosity and conductivity and the Mason–Saxena rule for conductivity. The new rules perform better than the Wilke rules, have comparable performance to the Brokaw rules and Mason–Saxena conductivity rule for binary mixture data, and outperform the Wilke, Brokaw, and Mason–Saxena rules for multicomponent mixture data.

I. Introduction

To be useful, computational fluid dynamic (CFD) simulations of complex, multicomponent, reacting flows require accurate estimates of the mass diffusion, viscosity, and thermal conductivity coefficients to describe correctly mass, momentum, and energy transport within the flow. With the increased importance of including nonequilibrium reactive chemical kinetics to obtain realistic laser, propulsion, combustion, and biochemical models, it is important to simulate dynamically the transport properties that change as the fluid composition changes rather than use static or fixed transport properties. However, for many gas mixtures of practical interest, extensive measurements of the transport properties over a broad range of conditions with the required accuracy to validate and/or justify evaluation of the exact kinetic theory expressions are unavailable. Furthermore, for some applications, currently used approximate expressions may lead to large errors for some operating conditions of interest. For example, in a recent assessment of physical properties and chemical kinetic modeling methodologies for the chemical oxygen iodine laser (COIL), Paschkewitz et al.[1] point out that, because of the large disparity in molecular masses of a typical COIL mixture containing light diluent gases, such as helium, and the heavy iodine atoms, which lase, the often used Wilke[2] rule can lead to large errors in the predicted mixture viscosity. In practice, the accuracy required for a particular application must be balanced with the computational costs, including the complexity of initial programming and the execution speed of the resulting computer program. Thus, the need for approximate expressions for these transport properties, which are accurate but computationally efficient, remains a subject of interest.

Rigorous kinetic theory expressions for the viscosity of dilute gas mixtures and the thermal conductivity of monatomic, dilute gas mixtures,[3,4] as well as the Hirschfelder–Eucken correction to the monatomic conductivity to account for the internal degrees of freedom of polyatomic gas mixtures, have been known for over 50 years. However, because of their complexity and evaluation costs, many approximate formulas or rules have been developed to estimate the viscosity and conductivity of a dilute gas mixture. More than 50 years ago, Wilke[2] empirically derived a simple rule for the viscosity of a gas mixture that is still widely used today in CFD simulations.[1,5] Mason and Saxena,[6] using a more formal approach based on kinetic theory, derived a similar empirical rule for thermal conductivity, applicable to both monatomic and polyatomic mixtures, which is also often used in CFD simulations. Brokaw,[7−10] based on exact expressions for binary mixtures, devised more complex, but more accurate, approximate rules that are less known than the Wilke[2] and Mason–Saxena[6] rules. Whereas Brokaw[7−11] tested and compared the predictions of his viscosity rule with an extensive experimental database, and performed similar although less extensive, testing of his conductivity rule, he did not make extensive comparisons of the predictions of his rules with those of Wilke[2] or Mason and Saxena.[6] More recently, Schreiber et al.[12] employed the Thijsse et al.[13] total-energy formalism and assumed that the molecular interaction potential is spherically symmetric to obtain an approximate expression for the thermal conductivity of polyatomic gas mixtures that is analogous to that for monatomic gas mixtures. Also, Ern and Giovangigli (EG)[14] provide numerical algorithms to evaluate the kinetic theory expressions for mixture viscosity and conductivity, but the emphasis of their work is on rapid and accurate evaluation of the exact expressions, not on obtaining approximate rules. In the present work, new approximate formulas are developed for accurately estimating the viscosity and thermal conductivity of dilute, polyatomic gas mixtures, which may include both polar and nonpolar species.

To determine the transport properties of a gas mixture there are three steps: 1) Determine the transport property of each pure species component. 2) Evaluate the coefficient matrix of the linear equation describing the transport property. 3) Solve the linear equations for the mixture property. In general, at each step, various approximations are employed to simplify the determination of the transport properties of the mixture. Assuming that the pure species viscosity, conductivity, molecular weight, specific heats, and the Lennard–Jones potential parameters for nonpolar molecules or the Stockmayer potential parameters for polar molecules are available from either experimental or theoretical considerations, the focus

---

Presented as Paper 2002-0914 at the 40th Aerospace Sciences Meeting, Reno, NV, 14–17 January 2002; received 15 February 2002; revision received 17 July 2002; accepted for publication 4 November 2002.

*Member of Technical Staff, Rocketdyne Propulsion and Power, 6633 Canoga Avenue; currently Senior Scientist/Engineer, Schafer Corporation, 26565 Agoura Road, Calabasas, CA 91302. Member AIAA.

of the present work is on steps 2 and 3. The new formulas for the mixture viscosity and conductivity are the result of using the Brokaw[9,10] approximations for the collision integrals in the analytic formula obtained from a single iteration of the EG[14] solution of the linear transport equations. This formula includes, to lowest order, contributions from the off-diagonal elements of the transport matrix. For polyatomic mixtures the well-known Hirschfelder–Eucken formalism (see Refs. 15 and 16) or the Thijsse et al.[13] total-energy formalism (see Refs. 12 and 17) is used to obtain the mixture thermal conductivity. These rules are then tested using a large experimental viscosity and conductivity database that covers a large number of gas mixtures with a broad range of molar composition and species molecular weights ranging from about 2 to 150 g/mol. Although the temperature range of the database extends from about 90 to 800 K, most of the data employed were for temperatures near 300 K. Also, when the same database is used, the predictions of these new rules are compared with those using the well-known approximation formulas of Wilke[2] for viscosity and conductivity, Mason–Saxena[6] for conductivity, and the less known Brokaw rules for viscosity and conductivity. Unlike the Wilke,[2] Mason–Saxena,[6] and Brokaw[9,10] rules, which, although based on kinetic theory, are empirically derived and employ the Sutherland–Wassiljewa functional form, the new rules are derived from a manifestly multicomponent solution of the linear transport equations and include contributions from the off-diagonal elements of the transport matrix. Because of this, the experimental database used to test and compare rules is partitioned into binary and multicomponent mixtures and the various approximate rules tested on each database separately. The new viscosity/conductivity rules are found to perform better than the Wilke[2] rules, have comparable performance to the Brokaw[9,10] rules and Mason–Saxena[6] conductivity rules for binary mixture data, and to outperform the Wilke,[2] Brokaw,[9,10] and Mason–Saxena[6] rules for multicomponent data.

This paper is organized as follows. In Sec. II, the EG[14] solution of the linear transport equations for the viscosity and monatomic thermal conductivity of dilute gas mixtures is briefly reviewed. In Sec. III, approximate expressions for the required matrix elements for the viscosity of a gas mixture are developed. Then, in Sec. IV, approximate expressions for the required matrix elements for the thermal conductivity of a monatomic gas mixture are developed, after which the rule for conductivity is extended to treat polyatomic gas mixtures using the Hirschfelder–Eucken formalism (see Refs. 15 and 16) and the Thijsse et al.[13] total-energy formalism (see Refs. 12 and 17). Following this, in Sec. V, the Wilke,[2] Mason–Saxena,[6] and Brokaw[9,10] rules are reviewed. Finally, in Sec. VI, all of these rules are tested and compared and the results summarized. An Appendix summarizes an alternative, simpler derivation of the single-iteration EG solution of the linear transport equations.

II. EG[14] Solution for the Viscosity and Conductivity of a Gas Mixture

According to the Chapman–Enskog theory of transport processes in dilute gases, the viscosity of a mixture of gases and the thermal conductivity of a mixture of monatomic gases can be expressed as (see Refs. 3 and 4)

$$P = \sum_i \tilde{P}_i = \sum_i \tilde{p}_i x_i = \tilde{p}^T x \tag{1a}$$

where P is the viscosity or conductivity of the gas mixture, $x = \{x_i \,|\, i = 1, \ldots, N_S\}$ is the column vector of mole fractions, N_S is the number of species, and $\tilde{\boldsymbol{p}} = \{\tilde{p}_i \,|\, i = 1, \ldots, N_S\}$ is a column vector that satisfies the linear equation

$$H\tilde{\boldsymbol{p}} = \boldsymbol{x} \tag{1b}$$

where $H = H(T, x, p, W, \Omega)$ is an $N_S \times N_S$ symmetric, positive definite matrix that is, in general, a function of the gas temperature T, the species mole fractions x, the viscosity or conductivity of the pure species $p = \{p_i \,|\, i = 1, \ldots, N_S\}$, the molecular weights of the species $W = \{W_i \,|\, i = 1, \ldots, N_S\}$, and Ω is collectively the dependence of H on several reduced molecular collision integrals, $\Omega_{ij}^{(l,s)^*}$, which are functions of various species molecular collision parameters σ, ε, and μ (following section). Throughout this work, all vectors are real, and the superscript T indicates the transpose operator so that $x^T y$ denotes the matrix product of the row vector x^T with the column vector y. $\tilde{P}_i$ may be thought of as a partial viscosity or conductivity due to species i, analogous to a partial pressure. Similarly, $\tilde{p}_i$ may be thought of as a partial viscosity or conductivity per unit mole fraction of species i, which is similar, although not identical, to the molecular weight of a species.

The specific form of the matrix H for the viscosity of a gas mixture and the thermal conductivity of a monatomic gas mixture will be given later. The physical interpretation of the diagonal and off-diagonal elements of the matrix H, applicable to either viscosity or thermal conductivity, has been discussed by Cowling et al.[18] They differentiate between two mechanisms of momentum or heat transport through a dilute gas mixture. The first, larger effect is that molecules of one species interfere with or impede the transport of momentum or heat by collisions with themselves or other species in the mixture. This interference with transport is accounted for by the diagonal elements of H. The second, smaller effect is the transfer of momentum or heat from one species to another by collisions among different species. This transfer of transport is accounted for by the off-diagonal elements of H.

To solve Eq. (1) numerically, EG[14] suggested using the well-known preconditioned conjugate-gradient method for solving symmetric, positive definite, linear systems of equations.[19–21] The theoretical basis and implementation of this numerical method is thoroughly discussed by Golub and van Loan[19] and Stoer and Bulirsch,[20] whereas a more practical summary of the algorithm is given by Datta.[21] Although the method can be used to obtain an exact numerical solution of the linear system, it is often thought of as an iterative method. Here only a summary of the algorithm, suitable for the numerical solution of the present problem, is provided. For the preconditioning matrix, we take the diagonal of the matrix H. For an initial guess of the solution $\tilde{p}$, with which to start the iteration process, we take $\tilde{p}_0 = 0$, where the subscript is the iteration, not species, index. When the convergence tolerance requirement is denoted by ε, the iteration index by k, and the maximum number of iterations by M, the algorithm may be written[21,22] as follows:

```
$d_0 = 0$
$\tilde{p}_0 = 0$
$r_0 = x - H\tilde{p}_0 \equiv x$
$y_0 = r_0/D$
$\beta = 0$
Do $k = 0, 1, 2, \ldots M$
    (a) $d_{k+1} = y_k + \beta d_k$
    (b) $w = Hd_{k+1}$
    (c) $\alpha = y_k^T r_k \big/ d_{k+1}^T w$
    (d) $\tilde{p}_{k+1} = \tilde{p}_k + \alpha d_{k+1}$
        $P_{k+1} = \tilde{p}_{k+1}^T x$                                        (A)
    (e) $r_{k+1} = r_k - \alpha w$
    (f) $y_{k+1} = r_{k+1}/D$
    (g) If $\left(y_{k+1}^T r_{k+1} \geq \varepsilon$ and $r_{k+1}^T r_{k+1} \geq \varepsilon\right)$
        Then Continue Else Exit
    (h) $\beta = y_{k+1}^T r_{k+1} \big/ y_k^T r_k$
End
```

Here α and β are scalars; x, D, d_k, $\tilde{p}_k$, r_k, y_k, and w are vectors of length N_S; and the subscript k denotes the iteration index. D is a vector that is the diagonal of the matrix H. The notation Hd_k is the ordinary matrix product of H with d_k, whereas the notation r_k/D indicates that the division is element by element. At step (d) $\tilde{p}_{k+1}$ is the $(k+1)$ iterate for the partial transport property per unit mole fraction of the species and P_{k+1} is the corresponding estimate of the transport property of the mixture. If the mixture consists of only a single species, some additional care must be taken to ensure that the algorithm terminates correctly after a single iteration. In particular, in the steps $y_k = r_k/D$, $k = 0, 1, 2, \ldots$, an element of the vector y_k is set to zero if the corresponding element of the vector r_k is zero, and otherwise it is set to the corresponding element of the vector r_k/D. In addition, following step (f), if $y_{k+1}^T r_{k+1} \equiv 0$, then the iteration is terminated. The preconditioned conjugate-gradient algorithm (A) is efficient and yields with exact arithmetic an exact solution of Eq. (2) if N_S iterations are taken. Moreover, it can be shown from the properties of the algorithm that the transport property P can be expressed as a convergent series,[22] which, if truncated, provides an explicit approximation for P. This yields a sequence of convergent iterates that may be expressed as

$$P_k = \sum_{j=1}^{k} \frac{\left(d_j^T x\right)^2}{d_j^T H d_j} \tag{B}$$

where the vector d_j is obtained from algorithm (A). The sequence of iterates P_k are positive and satisfy $P_{k+1} \geq P_k \geq \cdots \geq P_1$ for $k \geq 1$ and converge to P in at most N_S iterations.[22] In practice, usually only a few iterations, or possibly a single iteration, are required to obtain convergence to a specified tolerance.

Although the preceding algorithm is intended to provide an exact numerical solution, if we take a single iteration, as was suggested by EG,[14] a useful, accurate, analytical formula for either the viscosity or monatomic conductivity of the gas mixture is obtained. Dropping the iteration index for clarity, we find

$$\tilde{p} \equiv \alpha y = (y^T x / y^T H y) y \tag{2a}$$

$$P \equiv \tilde{p}^T x = (y^T x)^2 / y^T H y \tag{2b}$$

where $y = x/D$ and D is the diagonal of H. If the matrix H is known or a suitable approximation to it is available, it is apparent that Eqs. (2) are very easy to evaluate, whereas numerical results, discussed later, show that this provides a very good estimate for P. Equally important, unlike some approximation schemes for estimating P, the present approximation is derived from a manifestly multicomponent solution of the transport equations. Note that if the matrix H were, in fact, diagonal, then the solution to Eq. (1) would be exactly $y = x/D$, and, in this case, $\alpha \equiv 1$, so that

$$\tilde{p} \equiv y = x/D \tag{3a}$$

$$P \equiv \tilde{p}^T x = y^T x \tag{3b}$$

which is the approximation obtained by Hirschfelder et al. (HCB)[3] by expanding the determinants in Cramer's rule and assuming that the off-diagonal elements of H are small compared to the diagonal elements of H. Further simplification of approximation (3) has been discussed by HCB,[3] but we shall not be further concerned with this approximation. The EG approximation (2b), unlike the HCB approximation (3b), depends on the off-diagonal, as well as the diagonal elements of H, and so, physically, it includes the effect of the transfer of transport, as well as the effect of interference with transport. An alternative derivation of the EG approximation (2b) is given in the Appendix.

III. Viscosity of Gas Mixtures

In this section, two approximations for the matrix H describing the viscosity of gas mixtures are discussed. Substitution of either of these approximations into the analytical formula (2) of EG[14] provides a simple analytical approximation for the viscosity of the mixture. For viscosity, the matrix elements of H are[3,4]

$$H_{ii} = \frac{x_i^2}{\eta_i} + \sum_{j \neq i} \frac{2 x_i x_j}{\eta_{ij}} \frac{W_i W_j}{(W_i + W_j)^2} \left(\frac{5}{3A_{ij}^*} + \frac{W_j}{W_i} \right) \tag{4a}$$

$$H_{ij} = -\frac{2 x_i x_j}{\eta_{ij}} \frac{W_i W_j}{(W_i + W_j)^2} \left(\frac{5}{3A_{ij}^*} - 1 \right) = H_{ji} \tag{4b}$$

Note that H_{ii} is not simply H_{ij} with $j \equiv i$. Here x_i is the mole fraction of species i, W_i is the molecular weight of species i, η_i is the viscosity of pure species i, which, if not available experimentally, is

$$\eta_i = \frac{5}{16} \frac{1}{N_A} \frac{(\pi W_i R T)^{\frac{1}{2}}}{\pi \sigma_i^2 \Omega_i^{(2,2)^*}} \tag{5a}$$

and η_{ij} is a fictitious viscosity, which is

$$\eta_{ij} = \frac{5}{16} \frac{1}{N_A} \frac{(2\pi W_{ij} R T)^{\frac{1}{2}}}{\pi \sigma_{ij}^2 \Omega_{ij}^{(2,2)^*}} \tag{5b}$$

where

$$W_{ij} = W_i W_j / (W_i + W_j) \tag{5c}$$

is the reduced molecular weight of species i and j, T is the gas temperature, σ_i and σ_{ij} are distances characterizing the size of the collision complex, $\Omega_i^{(l,s)^*}$ and $\Omega_{ij}^{(l,s)^*}$ are reduced collision integrals, $A_{ij}^* \equiv \Omega_{ij}^{(2,2)^*} / \Omega_{ij}^{(1,1)^*}$ is a ratio of reduced collision integrals that is very nearly unity, R is the universal gas constant, and N_A is Avogadro's number. For nonpolar molecules, the reduced collision integrals are a function of the reduced temperature $T^* \equiv k_B T/\varepsilon$, whereas for polar molecules they are functions of the reduced temperature and a polarity parameter $\delta \equiv \mu^2 / 2\varepsilon\sigma^3$, which characterizes the strength of the repulsive dipole interaction energy relative to the attractive well-depth energy. Here ε is the characteristic well-depth of the collision complex, σ is the characteristic size of the collision complex, μ is the dipole moment of the colliding molecules, and k_B is the Boltzmann constant. Here, η_{ij} may be regarded[3] as the viscosity of a hypothetical pure species, whose molecular weight is $2W_{ij}$ and molecular potential parameters are σ_{ij}, ε_{ij}, and μ_{ij} [see Eq. (11)]. Observe that $\eta_{ii} \equiv \eta_i$ because $2W_{ii} \equiv W_i$. When only a single species is present, for example, $i = K$, then $x_i = \delta_{iK}$, and it is not difficult to show that Eqs. (4) reduce to $H_{ii} = \delta_{iK}/\eta_K$ and $H_{ij} \equiv 0$ and Eqs. (2) become $\tilde{p}_i = \delta_{iK}\eta_K$ and $P = \eta_K$, the viscosity of the pure Kth component, as expected.

It can be shown, on substituting the expressions (5) for η_i and η_{ij} into Eq. (4) and rearranging, that

$$H_{ii} = \frac{x_i^2}{\eta_i} - \sum_{j \neq i} H_{ij} \frac{\left(5/3A_{ij}^* + W_j/W_i\right)}{\left(5/3A_{ij}^* - 1\right)} \tag{6a}$$

$$H_{ij} = -\frac{x_i x_j}{(\eta_i \eta_j)^{\frac{1}{2}}} \gamma_{ij} = H_{ji} \tag{6b}$$

$$\gamma_{ij} = \frac{1}{2} S_{ij} M_{ij}^3 \left(\frac{5}{3A_{ij}^*} - 1 \right) = \gamma_{ji} \tag{6c}$$

$$S_{ij} = \frac{\sigma_{ij}^2 \Omega_{ij}^{(2,2)^*}}{\left(\sigma_i^2 \Omega_i^{(2,2)^*} \sigma_j^2 \Omega_j^{(2,2)^*}\right)^{\frac{1}{2}}} = S_{ji} \tag{6d}$$

$$M_{ij} = \left[\frac{4 W_i W_j}{(W_i + W_j)^2} \right]^{\frac{1}{4}} \tag{6e}$$

The matrices γ, S, and M are symmetric and dimensionless. The γ matrix characterizes the interaction between unlike molecules, and because the S matrix is a ratio of cross sections, we shall refer to it as the scattering matrix. Because the variation of A_{ij}^* with temperature is relatively weak, the primary temperature and molecular collision dynamics dependence enters through the S matrix. The expression (6) for the matrix H is exact.

The next step in deriving an approximate expression for H is to recognize that for realistic intermolecular potentials $A_{ij}^* \cong 10/9$ (Refs. 9 and 10). With this additional approximation, Eqs. (6) for the matrix elements of H become

$$H_{ii} = \frac{x_i^2}{\eta_i} - \sum_{j \neq i} H_{ij} \left[1 + 2 \left(\frac{W_i + W_j}{W_i} \right) \right] \tag{7a}$$

$$H_{ij} = -\frac{x_i x_j}{(\eta_i \eta_j)^{\frac{1}{2}}} \gamma_{ij} = H_{ji} \tag{7b}$$

$$\gamma_{ij} = \frac{1}{4} S_{ij} M_{ij}^3 \tag{7c}$$

where the matrices S and M are given by Eqs. (6d) and (6e), respectively. When Eq. (7) is implemented, the factors involving the species molecular weights can be precomputed and stored.

The final step in deriving an approximate expression for H is to obtain an estimate of the scattering matrix. At least two simple approximations for the S matrix suggest themselves. In the first approach, we assume a hard sphere collision model, for which $\Omega_{ij}^{(l,s)^*} \equiv 1$ and then estimate the required collision cross sections $\pi\sigma_i^2$ from the species viscosity η_i. After some algebra, this yields

$$S_{ij}^{(H)} = S_{ji}^{(H)} \cong \frac{\sigma_{ij}^2}{\sigma_i\sigma_j} = \frac{\left[\frac{1}{2}(\sigma_i + \sigma_j)\right]^2}{\sigma_i\sigma_j}$$

$$= \frac{1}{4}\left(\frac{\eta_j}{\eta_i}\right)^{\frac{1}{2}}\left(\frac{W_i}{W_j}\right)^{\frac{1}{4}}\left[1 + \left(\frac{\eta_i}{\eta_j}\right)^{\frac{1}{2}}\left(\frac{W_j}{W_i}\right)^{\frac{1}{4}}\right]^2 \tag{8}$$

As expected $S_{ii}^{(H)} = 1$. Although several different derivations are possible, the Wilke[2] rule for viscosity can be obtained by assuming $A_{ij}^* \approx 5/3$, substituting the hard sphere scattering matrix (8) into Eq. (6a), and the result for the matrix elements H_{ii} into the approximation (3). The Wilke formula is based solely on the diagonal elements of the transport matrix and so includes only the effects of impeding transport not the transfer of transport between species. Although the success of the Wilke rule might suggest that the hard sphere collision model would be an adequate approximation, the comparisons with experimental data, summarized later, show the resulting rules give deviations larger than the Wilke rule.

Alternatively, a second approach is to estimate the required collision integrals using an approximation suggested by Brokaw.[9,10] Monchick and Mason[23] present numerical values of the reduced orientation-averaged collision integral $\Omega^{(2,2)^*}(T^*, \delta)$ for the Stockmayer potential that describes collisions of polar molecules and reduces to the Lennard–Jones potential for nonpolar molecules. Brokaw[10] provides the following approximation:

$$\Omega^{(2,2)^*}(T^*, \delta) = \Omega_{LJ}^{(2,2)^*}(T^*) + \tfrac{1}{5}(\delta^2/T^*) \tag{9}$$

where $\Omega_{LJ}^{(2,2)^*}$ is the corresponding reduced collision integral for the Lennard–Jones potential. Brokaw[9] also provides an additional, somewhat more drastic, approximation valid over the temperature range, where dipole forces are important, or

$$\Omega^{(2,2)^*}(T^*, \delta) \approx \tfrac{4}{5}(1 + 1/T^* + \delta^2/4T^*) \tag{10}$$

which reproduces the tabulations of Monchick and Mason[23] within 8% for $\delta = 0$ to 1 over a reduced temperature range of $T^* = 0.5$–10 and within 14% for reduced temperatures up to $T^* = 20$. Brokaw[9,10] also suggests approximating the characteristic distance, potential well-depth energy, and dipole moment for unlike molecules by

$$\sigma_{ij} = \sqrt{\sigma_i\sigma_j} \tag{11a}$$

$$\varepsilon_{ij} = \sqrt{\varepsilon_i\varepsilon_j} \tag{11b}$$

$$\mu_{ij} = \sqrt{\mu_i\mu_j} \tag{11c}$$

from which it follows that

$$T_{ij}^* \equiv k_B T/\varepsilon_{ij} = \sqrt{T_i^* T_j^*} \tag{12a}$$

$$\delta_{ij} \equiv \mu_{ij}^2 \big/ 2\varepsilon_{ij}\sigma_{ij}^3 = \sqrt{\delta_i\delta_j} \tag{12b}$$

Adding indices to correspond to interactions between like (i or j) or unlike (ij) molecules and inserting Eqs. (10–12) into Eq. (6d) yields

$$S_{ij}^{(B)} = S_{ji}^{(B)} \cong \frac{\left[1 + \left(T_i^* T_j^*\right)^{\frac{1}{2}} + \delta_i\delta_j/4\right]}{\left(1 + T_i^* + \delta_i^2\big/4\right)^{\frac{1}{2}}\left(1 + T_j^* + \delta_j^2\big/4\right)^{\frac{1}{2}}} \tag{13}$$

As expected $S_{ii}^{(B)} = 1$. In mixtures of nonpolar gases S_{ij} can be taken to be unity. However, in mixtures of polar and nonpolar gases, the interactions are essentially nonpolar, and hence, the unlike cross sections are smaller than a simple averaging of the pure component cross sections would suggest, that is, the S_{ij} are less than unity. Unfortunately, for nonpolar gases, $\delta_i = \delta_j \equiv 0$, S_{ij} does not reduce to unity. For these reasons Brokaw[9,10] recommends when computing mixture viscosities (but not mixture conductivities) that Eq. (13) be used if either δ_i or δ_j is greater than 0.1, whereas S_{ij} should be taken to be unity if both δ_i and δ_j are less than 0.1. We follow his recommendations.

To summarize, two different approximations were tried for the elements of the scattering matrix S and, hence, for the matrix H, which, in either case, is given by Eq. (7). In the first, the hard sphere collision model is used and S is computed using Eq. (8), whereas in the second the Monchik–Mason[23]–Brokaw[9,10] collision model is used, and S is computed using Eq. (13). Substituting either approximation into the EG[14] solution (2) yields a simple analytical approximation for the mixture viscosity. The resulting viscosity mixtures rules are designated EG–H or EG–B, depending on which approximation for S is employed.

IV. Thermal Conductivity of Gas Mixtures

A. Monatomic Gases

Two approximations for the matrix describing the thermal conductivity of a mixture of monatomic gases are discussed. Here this matrix is denoted by F to avoid confusion; the matrix F is related to the matrix L of HCB (Ref. 3, p. 538) by $F = -L^{11}/4$. As for viscosity, substitution of either approximation into the analytical formula (2) provides a simple analytical approximation for the mixture conductivity. For thermal conductivity, the matrix elements of F are[3]

$$F_{ii} = \frac{x_i^2}{\lambda_i} + \sum_{j \neq i} \frac{x_i x_j}{2A_{ij}^*\lambda_{ij}}$$

$$\times \frac{\left[(15/2)W_i^2 + (25/4)W_j^2 - 3W_j^2 B_{ij}^* + 4W_i W_j A_{ij}^*\right]}{(W_i + W_j)^2} \tag{14a}$$

$$F_{ij} = -\frac{x_i x_j}{2A_{ij}^*\lambda_{ij}}\frac{W_i W_j}{(W_i + W_j)^2}\left(\frac{55}{4} - 3B_{ij}^* - 4A_{ij}^*\right) = F_{ji} \tag{14b}$$

Again F_{ii} is not simply F_{ij} with $j \equiv i$. Here λ_i is the conductivity of pure species i, which, if not available experimentally, is

$$\lambda_i = \frac{25}{8}\frac{P}{T}\frac{D_i}{A_i^*} = \frac{25}{32}\frac{\frac{3}{2}R}{W_i}\frac{1}{N_A}\frac{(\pi W_i RT)^{\frac{1}{2}}}{\pi\sigma_i^2\Omega_i^{(2,2)^*}} \equiv \frac{15}{4}\frac{R}{W_i}\eta_i \tag{15a}$$

where the second equality results by substituting for the binary mass self-diffusion coefficient for species i and the third equality results from using Eq. (5a). Here λ_{ij} is a fictitious thermal conductivity given by

$$\lambda_{ij} = \frac{25}{8}\frac{P}{T}\frac{D_{ij}}{A_{ij}^*} = \frac{25}{32}\frac{\frac{3}{2}R}{2W_{ij}}\frac{1}{N_A}\frac{(2\pi W_{ij} RT)^{\frac{1}{2}}}{\pi\sigma_{ij}^2\Omega_{ij}^{(2,2)^*}} \equiv \frac{15}{4}\frac{R}{2W_{ij}}\eta_{ij} \tag{15b}$$

which, analogous to η_{ij}, may be thought of as the thermal conductivity of a hypothetical pure species with molecular weight $2W_{ij}$ and potential parameters σ_{ij}, ε_{ij}, and μ_{ij}; the second equality results by substituting for the binary mass diffusion coefficient for species i in species j, and the third equality results from using Eq. (5b). The binary mass diffusion coefficient D_{ij} is

$$D_{ij} = \frac{3}{8}\frac{RT}{PN_A}\frac{(\pi RT/2W_{ij})^{\frac{1}{2}}}{\pi\sigma_{ij}^2\Omega_{ij}^{(1,1)^*}} \tag{15c}$$

where P is the gas pressure, $B_{ij}^* \equiv (5\Omega_{ij}^{(1,2)^*} - 4\Omega_{ij}^{(1,3)^*})/\Omega_{ij}^{(1,1)^*}$ is another ratio of reduced collision integrals, which is very nearly unity, and the remaining notation is as in Sec. III. Because $2W_{ii} \equiv W_i$, observe that $\lambda_{ii} \equiv \lambda_i$ and that $D_{ii} \equiv D_i$, which is simply D_{ij} with $j \equiv i$, is the binary self-diffusion coefficient. As expected, when only a single species is present, for example, $i = K$, then the substitution of Eqs. (14) into Eqs. (2) reduces to $P = \lambda_K$, the conductivity of the Kth component.

To develop an approximation for the conductivity of a mixture of monatomic gases, one proceeds precisely as was done for viscosity. It is not difficult to show that substituting the expressions (15) for λ_i and λ_{ij} into Eqs. (14) and rearranging yields

$$F_{ii} = \frac{x_i^2}{\lambda_i} - \sum_{j \neq i} F_{ij} \left(\frac{15}{4} \frac{W_i^2}{A_{ij}^*} + \frac{25}{8} \frac{W_j^2}{A_{ij}^*} - \frac{3}{2} W_j^2 \frac{B_{ij}^*}{A_{ij}^*} + 2 W_i W_j \right) \Big/ \left(\frac{55}{8A_{ij}^*} - \frac{3}{2} \frac{B_{ij}^*}{A_{ij}^*} - 2 \right) W_i W_j \tag{16a}$$

$$F_{ij} = -\frac{x_i x_j}{(\lambda_i \lambda_j)^{\frac{1}{2}}} \xi_{ij} = F_{ji} \tag{16b}$$

$$\xi_{ij} = \frac{1}{4} S_{ij} M_{ij}^5 \left(\frac{55}{8A_{ij}^*} - \frac{3}{2} \frac{B_{ij}^*}{A_{ij}^*} - 2 \right) \tag{16c}$$

and S and M are the symmetric, dimensionless matrices given in Eqs. (6d) and (6e), respectively. The matrix ξ characterizes the interaction between unlike molecules. The expression (16) for the matrix F is exact.

To proceed, we again observe that for realistic intermolecular potentials $A_{ij}^* \cong 10/9$ and $B_{ij}^* \cong 10/9$ (Refs. 9 and 10), in which case Eqs. (16) become

$$F_{ii} = \frac{x_i^2}{\lambda_i} - \sum_{j \neq i} F_{ij} \frac{\left(54 W_i^2 + 21 W_j^2 + 32 W_i W_j\right)}{43 W_i W_j} \tag{17a}$$

$$F_{ij} = -\frac{x_i x_j}{(\lambda_i \lambda_j)^{\frac{1}{2}}} \xi_{ij} = F_{ji} \tag{17b}$$

$$\xi_{ij} = \frac{43}{64} S_{ij} M_{ij}^5 \tag{17c}$$

When Eqs. (17) are implemented, the factors involving the species molecular weights can be precomputed and stored. The scattering matrix S can be approximated using either the hard sphere collision model [Eq. (8)] or the Monchik–Mason[23]–Brokaw[9,10] collision model [Eq. (13)]. Substituting either approximation for S into the expression (17) for F and the result into Eq. (2) yields a simple analytical approximation for the thermal conductivity of a mixture of monatomic gases.

B. Polyatomic Gases: Hirschfelder–Eucken Formalism

Hirschfelder[15] recommended that the thermal conductivity of a multicomponent mixture containing polyatomic gases be expressed as a linear sum of a term describing the thermal conductivity as if all components were monatomic and a term describing the thermal conductivity of the internal degrees of freedom. This is called the Hirschfelder–Eucken formalism; for further discussion, see Uribe et al.[16] The first term describes the thermal conductivity of the translational degrees of freedom. When the translational and internal contributions to the thermal conductivity of the mixture are denoted $\Lambda^{(T)}$ and $\Lambda^{(I)}$, respectively, and the EG[14] solution (2) is employed for the translational contribution, the Hirschfelder–Eucken formalism becomes

$$\lambda = \Lambda^{(T)} + \Lambda^{(I)} = (z^T x)^2 \big/ z^T F^{(T)} z + \left(\lambda^{(I)} \big/ G^{(I)} x\right)^T x \tag{18a}$$

where $z = x/D^{(T)}$; x is the species mole fractions; $D^{(T)}$ is the vector consisting of the diagonal elements of the matrix $F^{(T)}$; $F^{(T)}$ is the matrix [Eq. (17)] evaluated using $\lambda^{(T)}$; $\lambda^{(T)}$ and $\lambda^{(I)}$ are the translational and internal contributions to the pure species thermal conductivity, respectively; and $G^{(I)}$ is a matrix describing the diffusion of internal energy whose elements are

$$\begin{aligned} G_{ij}^{(I)} &\equiv D_{ii}/D_{ij} = S_{ij} M_{ij} \left(A_i^* \big/ A_{ij}^*\right) \left(\lambda_i^{(T)} \big/ \lambda_j^{(T)}\right)^{\frac{1}{2}} \\ &\equiv \left(A_i^* \big/ A_j^*\right) \left(\lambda_i^{(T)} \big/ \lambda_j^{(T)}\right) G_{ji}^{(I)} \end{aligned} \tag{18b}$$

where D_{ii} and D_{ij} are the binary self-diffusion and binary mass diffusion coefficient, respectively, both of which are given by Eq. (15c). Although $G^{(I)}$ is not symmetric, it has a unity diagonal. Expressions for $\lambda^{(T)}$ and $\lambda^{(I)}$ will be given later.

When the same approximations by which Eqs. (17) were obtained from Eqs. (16) are used, the elements of the matrices $F^{(T)}$ and $G^{(I)}$ are

$$F_{ii}^{(T)} = \frac{x_i^2}{\lambda_i^{(T)}} - \sum_{j \neq i} F_{ij}^{(T)} \frac{\left(54 W_i^2 + 21 W_j^2 + 32 W_i W_j\right)}{43 W_i W_j} \tag{19a}$$

$$F_{ij}^{(T)} = -\frac{x_i x_j}{\left(\lambda_i^{(T)} \lambda_j^{(T)}\right)^{\frac{1}{2}}} \xi_{ij} = F_{ji}^{(T)} \tag{19b}$$

$$\xi_{ij} = \frac{43}{64} S_{ij} M_{ij}^5 \tag{19c}$$

$$G_{ij}^{(I)} = S_{ij} M_{ij} \left(\frac{\lambda_i^{(T)}}{\lambda_j^{(T)}} \right)^{\frac{1}{2}} \tag{19d}$$

The matrix M is given by Eq. (6e), and the scattering matrix S is given by either the hard sphere approximation [Eq. (8)], or the Monchick–Mason[23]–Brokaw[9,10] approximation [Eq. (13)], and again, the resulting rules are designated EG–HEH or EG–HEB, respectively.

To use expression (18) for the mixture thermal conductivity, it is necessary to partition the total, pure species thermal conductivity λ into its translational $\lambda^{(T)}$ and internal $\lambda^{(I)}$ contributions. This would be straightforward if all of the species conductivities were computed a priori using an appropriately detailed theory or consisted of only translational contributions, as for the rare gases; however, in practice, the species conductivities are often obtained from experimental or theoretical tabulations that do not distinguish between these contributions. Whereas several approaches are possible,[7,10,16,24] the most straightforward is simply to estimate the translational contribution to the thermal conductivity as if the species were monatomic. In this case, dropping the species index for clarity,

$$\lambda^{(T)} = \frac{15}{4} \frac{R}{W} \eta \tag{20a}$$

$$\lambda^{(I)} = \lambda - \lambda^{(T)} \tag{20b}$$

In this approach, we simply define the translational portion of the conductivity to be given by the equivalent (but fictitious) monatomic conductivity for the species, $\lambda^{(T)}$, and then subtract it from the given species conductivity λ to obtain the internal conductivity $\lambda^{(I)}$. This method is recommended by Uribe et al.,[16] and it is appealing in its theoretical and computational simplicity, requires only the pure species molecular weight W and viscosity η, which are often available, is exact for ideal monatomic species, and is the easiest for polyatomic species. For polyatomics, although the translational contribution, $\lambda^{(T)}$, is only correct to lowest order, if $\lambda^{(T)}$ is somewhat underestimated (for example) then the internal contribution, $\lambda^{(I)}$, is correspondingly overestimated and the errors tend to compensate.[16]

C. Polyatomic Gases: Thijsse Total Energy Formalism

An objection to the Hirschfelder–Eucken formalism for the conductivity of polyatomic mixtures is the necessity of partitioning the total species thermal conductivity into its translational and internal contributions. Although theoretical models[7,10,16,24] may provide insight into and expressions for these contributions, in practice, such models often require estimate of ancillary parameters, for example, internal energy diffusion coefficients, as well as rotational and vibrational collision numbers, which are difficult to obtain experimentally or theoretically. From a formal point of view this partitioning arises in the semiclassical theory of Wang–Chang et al.[25] for dilute polyatomic gases because the solution to the generalized Boltzmann equation is expanded in two expansion vectors, one proportional to the translational energy and the other proportional to the internal (rotational and vibrational) energy. In the late 1970s Thijsse et al.[13] obtained expressions for the thermal conductivity of a pure species by expanding the solution in terms of two different basis vectors, one proportional to the total translational and internal energy and the other proportional to the difference between the translational and internal energy. It was then shown that greatly simplified expressions for the conductivity could be obtained by retaining only the basis vector proportional to the total energy. Subsequent work by van der Oord and Korving[26] and Millat et al.[27] confirmed the applicability of this approximation for pure gases. Recent work by Ross et al.[17] and Ern and Giovangigli[28] extended the Thijsse et al.[13] total-energy formalism to obtain expressions for the thermal conductivity of dilute polyatomic gas mixtures that can be cast in a form analogous to that for the thermal conductivity of a monatomic gas mixture. Unfortunately, although important in the development of the formalism, these expressions still contain a number of collision integrals that make their exact evaluation difficult. Recent work by Vesovic and Wakeham[29] and Schreiber et al.[12] suggests that assuming the molecular interaction potential is spherically symmetric and approximating several of the required collision integrals by their equivalent spherical limit leads to a simple, but accurate, expression for the thermal conductivity of a dilute polyatomic gas mixture. In this limit, which we refer to as the Thijsse et al.[13] spherical approximation, the diffusion coefficients for internal energy relaxation tend to the binary mass diffusion coefficients, and the collision numbers for internal energy relaxation tend to infinity because for a spherical potential there is no possibility of internal energy exchange, and hence, in principle, it would take an infinite number of collisions to relax the molecule. For further details, as well as a brief but interesting history of the development of expressions for thermal conductivity, see Schreiber et al.[12]

In the Thijsse et al.[13] spherical potential approximation, the matrix elements of F may be written as[12]

$$F_{ii} = \frac{x_i^2}{\lambda_i} + \sum_{j \neq i} \frac{x_i x_j}{2A_{ij}^* \lambda_{ij}} \frac{1}{\left(1+r_i^2\right)^2} \left[\frac{15}{2}W_i^2 + \frac{25}{4}W_j^2 - 3W_j^2 B_{ij}^* + 4W_i W_j A_{ij}^* + \frac{5}{2}(W_i+W_j)^2 r_i^2\right] \bigg/ (W_i+W_j)^2 \tag{21a}$$

$$F_{ij} = -\frac{x_i x_j}{2A_{ij}^* \lambda_{ij}} \frac{W_i W_j}{(W_i+W_j)^2} \frac{1}{\left(1+r_i^2\right)\left(1+r_j^2\right)} \times \left[\frac{55}{4} - 3B_{ij}^* - 4A_{ij}^*\right] = F_{ji} \tag{21b}$$

$$r_i^2 \equiv \frac{C_i^{(I)}}{C_P^{(M)}} = \frac{2}{5}\frac{C_i^{(I)}}{R} = \frac{2}{5}\frac{C_{Pi}}{R} - 1 \tag{21c}$$

where $C_i^{(I)}$ is the total internal molar specific heat capacity, $C_P^{(M)} \equiv (5/2)R$ is the molar specific heat capacity at constant pressure for an ideal monatomic species, and $C_{Pi} = (5/2)R + C_i^{(I)}$ is the molar specific heat capacity at constant pressure, and the remaining notation is as defined earlier. Here r_i^2 is the ratio of the internal heat capacity of species i to the heat capacity of an ideal monatomic species at constant pressure and, thus, measures the deviation of the heat capacity of species i from that of an ideal monatomic species. It is apparent that if all species were monatomic, then $r_i^2 \equiv 0$ for all i and Eqs. (21) reduce to Eqs. (14), which are the matrix elements for a pure monatomic gas mixture. Whereas Eqs. (21) require the pure species molar heat capacities at constant pressure, other than the simple, well-known, partitioning of the heat capacity into its translational and internal contributions, there is no need to partition the pure species thermal conductivity into its translational and internal contributions.

Using the same approximations by which Eqs. (17) were obtained from Eqs. (14), we obtain the required matrix elements for the thermal conductivity of a mixture of polyatomic gases or

$$F_{ii} = \frac{x_i^2}{\lambda_i} - \sum_{j \neq i} F_{ij} \frac{\left(1+r_j^2\right)}{\left(1+r_i^2\right)} \times \frac{\left[54W_i^2 + 21W_i W_j + 32W_j^2 + 18(W_i+W_j)^2 r_i^2\right]}{43 W_i W_j} \tag{22a}$$

$$F_{ij} = -\frac{x_i x_j}{(\lambda_i \lambda_j)^{\frac{1}{2}}} \chi_{ij} = F_{ji} \tag{22b}$$

$$\chi_{ij} = \frac{43}{64} S_{ij} M_{ij}^5 \frac{1}{\left(1+r_i^2\right)\left(1+r_j^2\right)} \tag{22c}$$

Once again the scattering matrix can be obtained using either the hard sphere or Monchick–Mason[23]–Brokaw[9,10] collision models [Eqs. (8) and (13)], respectively. Substituting either approximation for S into Eqs. (22) and the result into Eqs. (2) yields a simple analytic approximation for the thermal conductivity of a mixture of polyatomic gases. The resulting rules will be designated EG–TSH and EG–TSB, respectively.

V. Other Rules for the Viscosity and Thermal Conductivity of a Gas Mixture

Many approximate expressions have been derived either from simple mean-free-path arguments, empirical fitting, and/or simplification of the rigorous theory with suitable approximations. Recent surveys of the methods used to estimate the mixture viscosity or conductivity, given the pure species viscosities or conductivities, as well as other molecular properties of the individual gas species comprising the mixture, have been given by Poling et al.[30] and Touloukian et al.[31,32] Many, although not all such approximations, lead to expressions having the Sutherland–Wassiljewa form (see Refs. 8 and 30–32)

$$P = \tilde{p}^T x = (p/Vx)^T x \tag{23}$$

where P is the transport property of gas mixture, $\tilde{p}$ is the partial transport property per unit mole fraction, p is the pure species transport property, x is species mole fraction, and the matrix $V = V(T, p, W, \Omega)$ is required to have unity diagonal elements and be independent of the species mole fractions x but may be dependent on the gas temperature T, the viscosity or conductivity of the pure species p, various molecular properties such as the species molecular weights W, and the reduced collision integrals Ω. Although the matrix V may be derived from or related in some manner to the transport property matrices H or F, the matrix V should not be confused with these matrices.

For mixture viscosity η, one of the simplest and most popular such rules is Wilke's,[2] in which the elements of the Wilke matrix $V^{(W)}$ are

$$V_{ij}^{(W)} = \frac{\left[1 + (\eta_i/\eta_j)^{\frac{1}{2}} (W_j/W_i)^{\frac{1}{4}}\right]^2}{[8(1+W_i/W_j)]^{\frac{1}{2}}} \equiv \frac{\eta_i}{\eta_j}\frac{W_j}{W_i} V_{ji}^{(W)} \tag{24}$$

from which it is apparent that $V_{ii}^{(W)} = 1$ and that the Wilke matrix is not symmetric. Wilke[2] originally derived this approximation from an earlier, empirical approximation developed by Buddenberg and Wilke[33] for binary mixtures. An alternative derivation was described following Eq. (8), which makes it clear that the Wilke[2] approximation does not depend upon the off-diagonal elements of the transport matrix H. Many researchers have tested this method, although often only for nonpolar gas mixtures, and have obtained reasonable results.[2,30,31] However, Poling et al.[30] have noted that for some systems containing H_2 less satisfactory agreement is obtained and that the principal reservation with Wilke's[2] rule appears to be for cases in which $W_i \gg W_j$ and $\eta_i \gg \eta_j$.

Mason and Saxena[6] have derived a similar rule to determine the mixture thermal conductivity λ. The off-diagonal elements of the Mason–Saxena matrix $V^{(\mathrm{MS})}$ are

$$V_{ij}^{(\mathrm{MS})} = \alpha \frac{\left[1 + \left(\lambda_i^{(T)}/\lambda_j^{(T)}\right)^{\frac{1}{2}} (W_i/W_j)^{\frac{1}{4}}\right]^2}{[8(1+W_i/W_j)]^{\frac{1}{2}}} \equiv \frac{\lambda_i^{(T)}}{\lambda_j^{(T)}} V_{ji}^{(\mathrm{MS})} \tag{25a}$$

whereas the diagonal elements are

$$V_{ii}^{(\mathrm{MS})} = 1 \tag{25b}$$

where α is a numerical constant that is near one. In application, it is almost universal to estimate the translational contribution to the thermal conductivity using Eq. (20a) so that, except for the factor α, the Mason–Saxena matrix is identical to the Wilke[2] matrix. Mason and Saxena[6] originally recommended $\alpha = 1.065$ but later suggested that $\alpha = 1$, reducing the Mason–Saxena matrix $V^{(\mathrm{MS})}$ to the Wilke[2] matrix $V^{(\mathrm{W})}$ (see Ref. 8). The Mason–Saxena[6] rule with $\alpha = 1$ will be called the Wilke[2] rule for thermal conductivity. Other researchers have proposed different values for α (Ref. 32). It appears that this rule for conductivity has not been as well tested as the Wilke[2] rule for viscosity.

Brokaw[7–10] in a series of papers spanning a decade devised several approximations of the form (23) for both viscosity and monatomic thermal conductivity. To derive his approximation, Brokaw first considered the exact form of the viscosity and monatomic conductivity expressions for binary mixtures and manipulated them into the form (23), where the matrix was dependent on the species mole fractions. Next, by evaluating the result at some intermediate composition, he derived a matrix which is independent of composition. Finally, he employed approximate expressions for the Monchick and Mason[23] averaged collision integrals $\Omega^{(l,s)^*}$, the approximations $A^*_{ij} \cong B^*_{ij} \cong 10/9$, and the correlation $\eta_i \propto W_i^{0.1}$ (Ref. 9). Assuming that the gas is sufficiently dilute so that three-body interactions can be neglected, he then generalized and applied his binary mixture expressions to multicomponent mixtures. Brokaw extended his monatomic conductivity results to polyatomic mixtures using the Hirschfelder–Eucken formalism. Although their derivation and form are much more complex than either the Wilke[2] or Mason–Saxena[6] approximations and require the species molecular potential parameters, in addition to the species molecular weights and viscosities or conductivities, Brokaw's expressions[7–10] for viscosity and thermal conductivity are, generally speaking, more accurate but, in practice, are not particularly more difficult to use than the Wilke[2] or Mason–Saxena[6] expressions. Furthermore, because Brokaw's expression[7–10] for thermal conductivity employs the Hirschfelder–Eucken formalism, it accounts, at least approximately, for the contributions of both the translational and internal degrees of freedom.

In Brokaw's approximation[9,10] for the viscosity of a gas mixture, the elements of the Brokaw matrix $V^{(B)}$ are

$$V^{(B)}_{ij} = S_{ij}\beta_{ij}(\eta_i/\eta_j)^{\frac{1}{2}} \tag{26a}$$

$$\beta_{ij} = M_{ij}(W_j/W_i)^{\frac{1}{2}} \times\left\{1 + \frac{(W_i/W_j) - (W_i/W_j)^{0.45}}{2(1 + W_i/W_j) + \left[\left(1 + (W_i/W_j)^{0.45}\right)\big/(1 + M_{ij})\right]M_{ij}}\right\} \tag{26b}$$

where the S and M matrices are given by Eqs. (13) and (6e), respectively. Although its diagonal is unity as required, the Brokaw matrix $V^{(B)}$ does not satisfy any obvious symmetry property like the Wilke[2] matrix $V^{(W)}$ does. Because the matrix β is dependent only on the species molecular weights, it can be precomputed and stored.

Brokaw's approximation[10] for the thermal conductivity of a gas mixture λ employs the Hirschfeld–Eucken formalism with

$$\lambda = \Lambda^{(T)} + \Lambda^{(I)} = \left(\lambda^{(T)}\big/V^{(T)}x\right)^T x + \left(\lambda^{(I)}\big/V^{(I)}x\right)^T x \tag{27a}$$

where $\lambda^{(T)}$ and $\lambda^{(I)}$ are the translational and internal contributions to the pure species thermal conductivity, which are given by Eqs. (20). The elements of the Brokaw[10] translational, $V^{(T)}$, and internal, $V^{(I)}$, matrices are

$$V^{(T)}_{ij} = \zeta_{ij}V^{(I)}_{ij} \tag{27b}$$

$$\zeta_{ij} = K_{ij}\left(1 + \left\{\left[K_{ij}^{-1} - \left(\frac{W_i}{W_j}\right)^{0.45}(K_{ij}K_{ji})^{-\frac{1}{2}}\right]\Big/ \left[\frac{64}{43}M_{ij}^{-4} + \frac{(W_i/W_j)^{0.45} + (K_{ij}/K_{ji})^{\frac{1}{2}}}{1 + M_{ij}(K_{ij}K_{ji})^{\frac{1}{2}}}M_{ij}\right]\right\}\right) \tag{27c}$$

$$K_{ij} = 1 + \frac{(W_i - W_j)}{(W_i + W_j)^2}\left[\frac{19}{8}W_i - \frac{5}{16}W_j\right] \tag{27d}$$

$$V^{(I)}_{ij} = S_{ij}M_{ij}\left(\lambda_i^{(T)}\big/\lambda_j^{(T)}\right)^{\frac{1}{2}} \tag{27e}$$

where the S and M matrices are given by Eqs. (13) and (6e), respectively. As required, the diagonal elements of both $V^{(T)}$ and $V^{(I)}$ are unity. Although the matrix $V^{(I)} \equiv G^{(I)}$ satisfies the symmetry property (18b), the matrices ζ, K, and $V^{(T)}$ have no obvious symmetry properties. The matrices ζ and M can be precomputed and stored.

VI. Results and Summary

To validate the new approximate expressions or rules for the viscosity and conductivity of gas mixtures, extensive comparisons of their predictions with experimental viscosity and thermal conductivity data are summarized. In addition, predictions using the rules of Wilke[2] and Brokaw[9,10] for mixture viscosity and the expressions of Wilke,[2] Mason–Saxena,[6] and Brokaw[10] for mixture conductivity are compared with the same experimental data.

Table 1 Viscosity database

Reference	Table	Gas system	Temperature, K	Number of data points
Brokaw[7]	I	H_2–Ar	293.15	3
Brokaw[8]	I, II	He–Ne, He–Ar, Ne–Ar, He–Ne–Ar	293.15	18, 8[a]
Brokaw[9]	I, II	He–Ne, He–Ar, He–Kr, Ne–Ar, He–N_2, Ne–CO_2, Ar–CO_2, N_2–CO_2, NH_3–Ar	293.15, 303.15	102
		He–Xe	291.15	10
		He–H_2	293.15	3
		H_2–N_2	292.15	4
		NH_3–H_2, NH_3–N_2, NH_3–C_2H_4	293.15, 523.15	33
		NH_3–O_2	293.15, 473.15	10
		SO_2–H_2	290.15, 472.15	9
		HCl–H_2	294.15, 523.15	8
		CH_2Cl_2–CCl_4	293.15, 413.15	10
	III	H_2O–CH_3OH, H_2O–$(CH_3)_2O$	373.15	15
		CH_3Cl–SO_2, CH_3Cl–$(CH_3)_2O$, SO_2–$(CH_3)_2O$, CH_3Cl–SO_2–$(CH_3)_2O$	308.15, 353.15	52, 8[a]
Brokaw[11]	I	$(C_2H_5)_2O$–NH_3	299, 331, 373	15
		$(C_2H_5)_2O$–H_2S	298, 331, 373	15
Buddenberg and Wilke[33]	II	CO_2–CCl_2F_2, N_2–O_2, H_2–CCl_2F_2, H_2–C_3H_8, H_2–CO, He–Ar, N_2–CCl_2F_2, Ne–H_2–CO_2, H_2–N_2–CCl_2F_2, N_2–CO_2–CCl_2F_2, Ne–H_2–CO_2–CCl_2F_2, H_2–N_2–CO_2–CCl_2F_2	298.15	30, 5[a]
Wilke[2]	III	CO_2–CO–H_2–N_2, CO_2–O_2–CO–H_2–CH_4–N_2–C_2H_6	293	5[a]
Touloukian et al.[31]	126GCE	N_2–O_2	300, 400, 500, 550	12
	164GCE	CO_2–O_2–N_2	293.2	3[a]
	182GCE	CO_2–CO–H_2–CH_4–N_2	293.2	3[a]

[a] Multicomponent data points.

To test the viscosity expressions, experimental viscosity data reported by Wilke,[2] Brokaw,[7–11] Touloukian et al.,[31] and Buddenberg and Wilke[33] were used to make the comparisons. The viscosity database is summarized in Table 1. Touloukian et al.[31] report that the accuracy of their tabulated experimental viscosity data measurements is ±1%. The required species molecular weights W, collision diameters σ, potential well-depths ε/k_B, dipole moments μ, and polarity parameters δ are summarized in Table 2. With the units employed in Table 2,

$$\delta \equiv \mu^2/2\varepsilon\sigma^3 \cong 3621.6\left[\mu^2\big/(\varepsilon/k_B)\sigma^3\right] \qquad (28)$$

All potential parameters were taken from Monchick and Mason[23] or Svehla[34] and were determined from either a least-squares or graphical fit of experimental viscosity data; see Refs. 23 and 34 for further discussion of the fit methodology. The dipole moment of CO was obtained from Poling et al.[30] In all, 381 data points for 44 different gas mixtures, including both polar and nonpolar gas species, were used. Whereas the bulk of the database, 349 points, was for binary gas mixtures, 32 points were for multicomponent gas mixtures. The molecular weights of the pure species ranged from about 2 to 150 g/mol. The gas temperature of the mixtures ranged from about 290 to 550 K, although the temperature for the majority of the data was near 300 K. The four rules for the gas mixture viscosity which were tested are 1) Wilke,[2] Eqs. (23) and (24); 2) Brokaw, Eqs. (23), (26), and (13); 3) EG–H, EG[14] single-iteration solution with the hard sphere S matrix, Eqs. (2), (7), and (8); and 4) EG–B, EG[14] single-iteration solution with the Brokaw S matrix, Eqs. (2), (7), and (13). The designation EG–H or EG–B refers to the new rules developed in the present work. For each of the four approximations, the predicted value was compared to the reported experimental value, and the error relative to the experimental value was computed. The database was partitioned into binary and multicomponent mixtures, and the maximum, minimum, and average relative errors, as well as the standard deviation of the relative error, were then computed. Because the pure species data points are reproduced exactly by all of the approximations, these points were not included when tabulating the errors.

For binary mixtures, scatter plots of the relative error or deviation of the predictions of the Wilke,[2] Brokaw,[9,10] EG–H, and EG–B viscosity rules from the experimentally reported values are shown in Figs. 1, 2, 3, and 4, respectively. It is apparent that there is much less scatter in the deviation for the Brokaw[9,10] and EG–B rules than the Wilke[2] or EG–H rules. Although the scatter in the deviation for the EG–H rule is somewhat less than that for the Wilke[2] rule, it is clearly negatively biased, indicating that the EG–H rule tends to

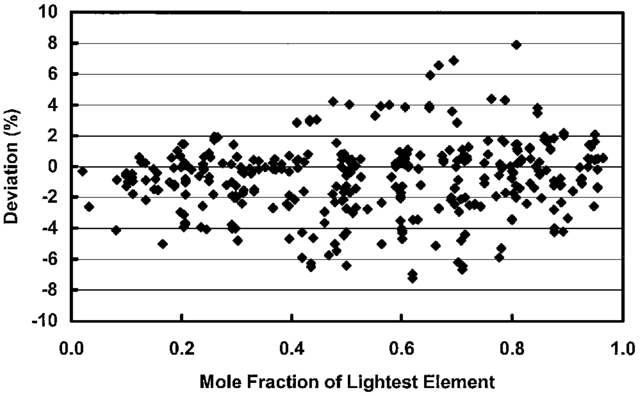

Fig. 1 Scatter plot of deviation for the Wilke[2] viscosity rule for binary mixture data.

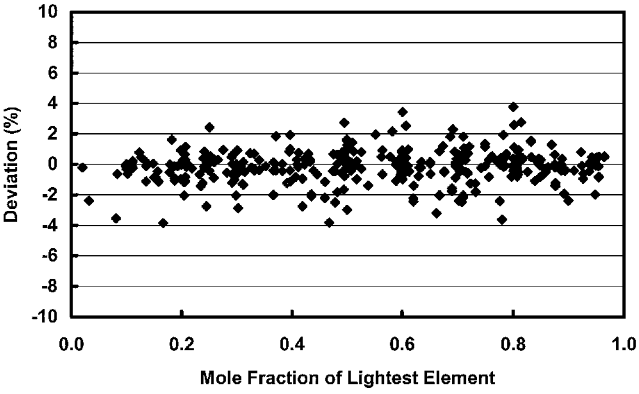

Fig. 2 Scatter plot of deviation for the Brokaw[9,10] viscosity rule for binary mixture data.

Table 2 Species molecular weights W, collision diameters σ, potential well-depths ε, dipole moments μ, and polarity parameters δ

Species name	Formula	W, g/mol	σ, A	ε/k_B, K	μ, D	δ	Reference
Acetone	$(CH_3)_2CO$	58.08	4.600	560.2	2.88	0.551	34
Ammonia	NH_3	17.031	3.150	358.0	1.47	0.699	23
Argon	Ar	39.948	3.542	93.3	0	0	34
Benzene	C_6H_6	78.114	5.349	412.3	0	0	34
Carbon dioxide	CO_2	44.010	3.941	195.2	0	0	34
Carbon monoxide	CO	28.010	3.690	91.7	0.1	0.008	30
Carbon tetrachloride	CCl_4	153.840	5.881	327.0	0	0	23
Diethyl ether	$(C_2H_5)_2O$	74.123	5.490	362.0	1.15	0.080	23
Dimethyl ether	$(CH_3)_2O$	46.069	4.210	432.0	1.3	0.190	23
Ethane	C_2H_6	30.070	4.443	215.7	0	0	34
Ethanol	C_2H_5OH	46.069	4.310	431.0	1.69	0.300	23
Ethylene	C_2H_4	28.054	4.163	224.7	0	0	34
Freon	CCl_2F_2	120.914	5.250	253.0	0	0	34
Hydrogen	H_2	2.016	2.827	59.7	0	0	34
Hydrogen chloride	HCl	36.470	3.360	328.0	1.08	0.340	23
Hydrogen sulfide	H_2S	34.080	3.490	343.0	0.92	0.210	23
Helium	He	4.003	2.551	10.22	0	0	34
Krypton	Kr	83.300	3.655	178.9	0	0	34
Methane	CH_4	16.043	3.758	148.6	0	0	34
Methanol	CH_3OH	32.042	3.690	417.0	1.7	0.500	23
Methylene	CH_2Cl_2	84.933	4.520	483.0	1.57	0.200	23
Methyl chloride	CH_3Cl	50.488	3.940	414.0	1.87	0.500	23
Nitrogen	N_2	28.014	3.798	71.4	0	0	34
Neon	Ne	20.183	2.820	32.8	0	0	34
Oxygen	O_2	31.999	3.467	106.7	0	0	34
Propane	C_3H_8	44.094	5.061	254.0	0	0	23
Sulfur dioxide	SO_2	64.063	4.040	347.0	1.63	0.421	23
Water	H_2O	18.015	2.520	775.0	1.85	0.999	23
Xenon	Xe	131.30	4.047	231.0	0	0	34

Table 3 Error and standard deviation for the viscosity rules for the binary mixture data in Table 1 (349 points)

Rule	Maximum error, %	Minimum error, %	Average error, %	Standard deviation, %	Normalized
Wilke[2]	7.90	−7.23	1.76	1.68	1.00
Brokaw[9,10]	3.76	−3.85	0.81	0.79	0.47
EG–H	1.26	−9.86	2.48	2.13	1.27
EG–B	3.38	−4.48	0.89	0.88	0.53

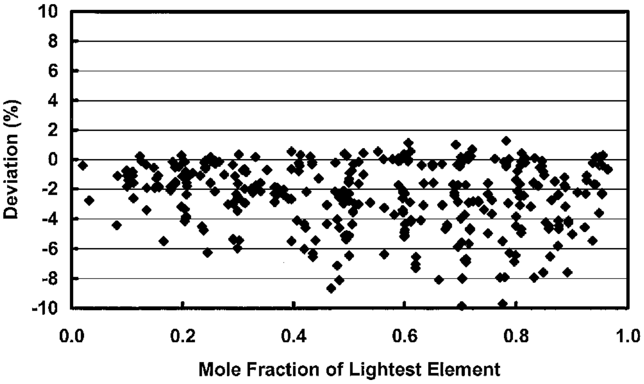

Fig. 3 Scatter plot of deviation for the EG–H viscosity rule for binary mixture data.

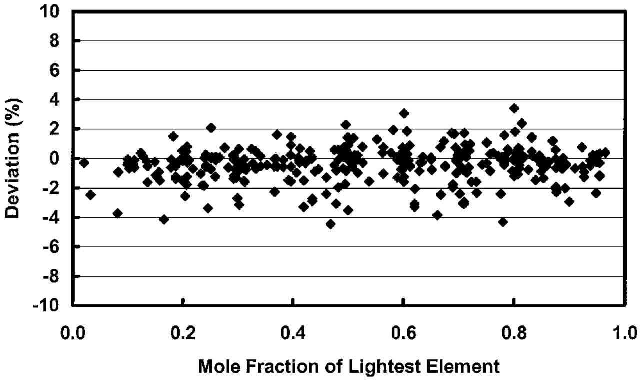

Fig. 4 Scatter plot of deviation for the EG–B viscosity rule for binary mixture data.

underpredict the mixture viscosity. For each of the four rules tested, the maximum, minimum, and average errors and the standard deviation of the relative error are summarized in Table 3. Also tabulated is the standard deviation normalized by the Wilke[2] value. The standard deviations of the Brokaw and EG–B rules are about 50% less than that of the Wilke[2] rule, whereas that of the EG–H rule is about 25% higher; the EG–H rule is less accurate than the other three rules. Correspondingly, the maximum error of the Wilke[2] rule is about twice that of either the EG–B or Brokaw rules. Interestingly, for this database, for each of the Wilke,[2] Brokaw, and EG–B rules, the magnitude of the maximum and minimum errors are approximately equal. Because the number of points with positive deviation approximately equals the number with negative deviation, each of these approximations is as likely to underpredict as to overpredict the value of the mixture viscosity. Both the Brokaw and the EG–B viscosity rules reduce the correlation error by about 50% compared to the Wilke[2] rule, but based on these results, neither the Brokaw or EG–B rule is to be preferred over the other.

To test the conductivity expressions, experimental conductivity data reported by Brokaw,[7,8] Touloukian et al.,[32] and Mathur et al.[35] was used to make the comparisons; the database is summarized in Table 4. Touloukian et al.[32] state that the accuracy of their tabulated experimental conductivity data measurements is ±2% or better with the exception of that for the He–N_2 mixtures, which was as low as ±5%. The required species data are tabulated in Table 2 with the exception of the required specific heat capacities, which were obtained from the polynomial fits given by Poling et al.[30] In all, 470 data points for 37 different nonpolar and polar gas mixtures were used. Whereas the bulk of the database, 374 points, was for binary gas mixtures, 96 points were for multicomponent gas mixtures. The molecular weights ranged from about 2 to 131 g/mol. The gas temperature ranged from about 90 to 810 K, although the temperature for the majority of the data was near 300 K. The seven rules for the gas mixture conductivity which were tested are 1) Wilke,[2] Eqs. (23) and (24); 2) MS,[6] Eqs. (23) and (25) with $\alpha = 1.065$; 3) Brokaw, Eqs. (27) and (13); 4) EG–HEH, EG[14] single-iteration solution with the hard sphere S matrix, Eqs. (18a), (19), and (8); 5) EG–HEB, EG[14] single-iteration solution with the Brokaw S matrix, Eqs. (18a), (19), and (13); 6) EG–TSH, EG[14] single-iteration solution with the Thijsse et al.[13] spherical approximation and the hard sphere S matrix, Eqs. (2), (22), and (8); and 7) EG–TSB, EB[14] single-iteration solution with the Thijsse et al.[13] spherical approximation and the Brokaw S matrix, Eqs. (2), (22), and (13). For each of the seven approximations, the predicted value was compared to the reported experimental value, the database partitioned, and the maximum, minimum, and average relative errors, as well as the standard deviation of the relative error, were computed. Again, the pure species data points were not included.

For binary mixtures, because the scatter plots of the deviation of the seven conductivity rules were similar to those obtained for the viscosity rules, shown in Figs. 1–4, these plots are not shown. Table 5 summarizes the results. Compared with viscosity, the larger relative errors associated with the thermal conductivities are due, at least in part, to the larger uncertainties in the experimental heat conductivity data. For binary mixtures, the MS,[6] Brokaw,[10] and EG–TSB rules reduce the correlation errors by about 20% compared to the Wilke[2] rule. The EG–HEB rule reduces the correlation error by about 25% compared to the Wilke[2] rule, although this is probably not statistically different from the reduction achieved by either the MS,[6] Brokaw, or EG–TSB rules. For this database, for each of the MS,[6] Brokaw, EG–HEB, and EG–TSB rules, the magnitudes of the maximum and minimum errors are approximately equal, and each of these rules is as likely to underpredict as overpredict the mixture conductivity. The Wilke[2] rule tends to slightly overpredict the mixture conductivity. Although the standard deviations of the EG–HEH and EG–TSH rules are comparable to that of the Wilke[2] rule, their minimum error is almost three times that of the Wilke rule as well as much worse than the remaining rules. Again, the rules employing the hard sphere scattering matrix, EG–HEH and EG–TSH, are less accurate than the other rules. The MS rule with $\alpha = 1.065$ and not $\alpha = 1$ appears preferred; at least for the database considered here. Other values of α were not tested.

For binary mixtures the preceding results demonstrate that, for viscosity, the Brokaw[9,10] and the new EG–B rule outperform the traditional Wilke[2] rules, whereas, for conductivity, the Brokaw, the MS,[6] EG–HEB, and EG–TSB conductivity rules also outperform the Wilke[2] rule. Because the EG rules are based on a manifestly multicomponent solution of the linear transport equations, whereas the other rules are either empirically derived and/or obtained from the binary rules by generalization, it is of interest to determine how well the multicomponent viscosity and conductivity data is predicted by each of these rules. For the multicomponent data, each of the four viscosity and the seven conductivity rules were tested, and the maximum, minimum, and average errors as well as the standard deviation are summarized in Tables 6 and 7, respectively. From Tables 6 and 7, it is apparent that the Brokaw[9,10] and new EG–B viscosity rules reduce the correlation errors by about 30 and 40%, respectively, compared to the Wilke[2] rule, whereas the Brokaw,[10] EG–HEB, and EG–TSB conductivity rules reduce the correlation errors by about 30, 40, and 40%, respectively, compared to the Wilke[2] rule. The standard deviation of the MS[6] rule is comparable to that of the Brokaw rule. For multicomponent data, the EG–B viscosity rule and the EG–HEB and EG–TSB conductivity rules clearly outperform the Wilke,[2] Brokaw[10] and MS[6] rules. Also, it is clear that the hardsphere rules, EG–H for viscosity and EG–HEH or EG–TSH for conductivity, perform worse than the Wilke[2] rules.

Table 4 Conductivity database

Reference	Table	Gas system	Temperature, K	Number of data points
Brokaw[7]	II	He–Ar, H_2–Ar, H_2–CO_2, C_6H_6–Ar	273.15	19
Brokaw[8]	IV, V	He–Kr, He–Xe, Kr–Xe, He–Kr–Xe	302.15	15, 20[a]
Mathur et al.[35]	2, 3	Ar–Ne, Kr–Ne, Xe–Kr,	313.15, 338.15, 363.15	36
	2	Xe–Ar	311.15, 366.15	8
	4	Xe–Kr–Ar–Ne	311.21, 366.74	6[a]
Touloukian et al.[32]	73a	Ar–N_2	90.2, 258.3, 273.2, 293.3, 311.2, 313.2, 338.2, 366.2, 393.2, 473.2	59
	74a	Ar–O_2	90.2, 258.3, 293.3, 311.2, 313.2, 338.2, 366.2, 393.2, 473.2	51
	85a	He–N_2	273.2, 303.2, 318.2, 377.2, 589.2	21
	86a	He–O_2	303.2, 318.2	12
	91a, 92a	Kr–N_2, Kr–O_2	303.2, 318.2	24
	96a, 97a	Ne–N_2, Ne–O_2	303.2, 313.2, 318.2, 338.2, 366.2, 368.2, 408.2, 448.2	56
	100a, 101a	Xe–N_2, Xe–O_2	303.2, 318.2	24
	121a	N_2–O_2	313.2, 338.2, 366.2, 368.2, 408.2, 448.2, 592.2	19
	122a	C_3H_8–N_2	591.2, 811.2	2
	123a	C_6H_6–$(CH_3)_2CO$	349.9, 376.0, 398.3	9
	125a	CO–NH_3	295.2	4
	126a	C_2H_4–NH_3	298.2	3
	129a	C_2H_5OH–Ar	369.2	3
	130a	C_3H_8–C_2H_5OH	368.2, 591.2	3
	131a	Ar–CH_3OH	351.2, 373.2	6
	140	Kr–Ar–Ne	311.2, 313.2, 338.2, 363.2	19[a]
	141	He–Ar–Xe	311.2	5[a]
	143	He–Ar–Kr	308.2, 323.2, 343.2, 363.2	16[a]
	144	He–Ne–Xe	303.2, 323.2, 343.2, 363.2	20[a]
	157	Ne–N_2–O_2	313.2, 338.2, 366.2, 368.2, 408.2, 448.2	9[a]
	159	N_2–O_2–CO_2	370.2	1[a]

[a] Multicomponent data points.

Table 5 Error and standard deviation for the conductivity rules for the binary data in Table 4 (374 points)

Rule	Maximum error, %	Minimum error, %	Average error, %	Standard deviation, %	Normalized
Wilke[2]	12.51	−7.59	3.56	2.94	1.00
MS[6]	9.77	−10.52	3.23	2.31	0.78
Brokaw[10]	13.81	−11.52	2.42	2.44	0.83
EG–HEH	11.98	−19.18	3.40	2.94	1.00
EG–HEB	12.00	−12.33	2.38	2.23	0.76
EG–TSH	13.00	−19.18	3.07	2.92	0.99
EG–TSB	13.02	−12.33	2.40	2.35	0.80

Table 6 Error and standard deviation for the viscosity rules for the multicomponent mixture data in Table 1 (32 points)

Rule	Maximum error, %	Minimum error, %	Average error, %	Standard deviation, %	Normalized
Wilke[2]	5.34	−4.97	1.24	1.26	1.00
Brokaw[9,10]	4.79	−3.06	1.15	0.91	0.73
EG–H	0.28	−7.02	2.12	1.40	1.11
EG–B	4.17	−3.29	1.28	0.80	0.64

Table 7 Error and standard deviation for the conductivity rules for the multicomponent data in Table 4 (96 points)

Rule	Maximum error, %	Minimum error, %	Average error, %	Standard deviation, %	Normalized
Wilke[2]	10.85	−3.16	3.22	2.64	1.00
MS[6]	6.45	−7.46	2.88	1.92	0.73
Brokaw[10]	8.17	−3.34	1.95	1.82	0.69
EG–HEH	6.63	−18.55	8.38	4.65	1.76
EG–HEB	7.47	−3.87	1.79	1.55	0.59
EG–TSH	6.30	−18.55	8.36	4.68	1.77
EG–TSB	7.15	−3.87	1.83	1.53	0.58

Table 8 Error and standard deviation for the viscosity rules for all data in Table 1 (381 points)

Rule	Maximum error, %	Minimum error, %	Average error, %	Standard deviation, %	Normalized
Wilke[2]	7.90	−7.23	1.72	1.65	1.00
Brokaw[9,10]	4.79	−3.85	0.84	0.80	0.49
EG–H	1.26	−9.86	2.45	2.08	1.26
EG–B	4.17	−4.48	0.92	0.88	0.53

Table 9 Error and standard deviation for the conductivity rules for all the data in Table 4 (470 points)

Rule	Maximum error, %	Minimum error, %	Average error, %	Standard deviation, %	Normalized
Wilke[2]	12.51	−7.59	3.49	2.88	1.00
MS[6]	9.77	−10.52	3.16	2.24	0.78
Brokaw[10]	13.81	−11.52	2.32	2.33	0.81
EG–HEH	11.98	−19.18	4.41	3.91	1.36
EG–HEB	12.00	−12.33	2.26	2.12	0.73
EG–TSH	13.00	−19.18	4.15	3.97	1.38
EG–TSB	13.02	−12.33	2.28	2.21	0.77

Finally consider the predictions of the viscosity and conductivity rules when applied to the entire viscosity and conductivity databases, respectively. These results are given in Tables 8 and 9, respectively. Not surprisingly, the standard deviations for the entire database are simply those of the binary and multicomponent databases linearly weighted by the number of data points. For all of the data, the EG–B viscosity reduces the correlation errors by about 50%, whereas the EG–HEB or EG–TSB conductivity rules reduce the errors by about 30%. Brokaw[9] made extensive comparisons of the predictions of his approximate expression for viscosity with experimental data at several temperatures for 25 gas pairs comprising 280 mixtures and reports an average error of only 0.7% with a maximum error of 3.7%. These are comparable to the errors reported in Table 8 using the Brokaw expression. Brokaw[10] also made comparison of the predictions of his approximate expression for conductivity with experimental data for 19 gas pairs comprising 29 mixtures and reports an average error of only 2.1% and a maximum error of 6.7%. This average error is comparable with that determined here using the Brokaw expression; see Table 9.

For both viscosity and conductivity, the hard sphere rules, in which the Brokaw S matrix is replaced by the hard sphere S matrix, gave larger errors than the traditional Wilke[2] rule. Thus, the hardsphere rules, EG–H for viscosity and EG–HEH or EG–TSH for conductivity, are not recommended for applications. For binary mixtures, the new EG rules for viscosity and conductivity reduced the deviation by about 50 and 20%, respectively, in comparison to the classic Wilke rule.[2] Thus, for binary mixtures, the new EG rules performed comparably to the Brokaw[9,10] rules, or, for conductivity, to the MS[6] rule. For multicomponent mixtures, the EG–B viscosity rule and the EG–HEB and EG–TSB conductivity rules reduced the correlation errors by about 40% compared to the Wilke[2] rules, outperforming all of the other rules, Wilke,[2] Brokaw,[9,10] or MS,[6] that were tested. By way of comparison, for multicomponent data, the Brokaw rules reduced the correlation errors by about 30% compared to the Wilke[2] rules. For conductivity, the MS[6] rule performed better than the Wilke[2] rule when tested using either binary mixture or multicomponent mixture data. Thus, the EG rules are strongly recommended for practical applications. Less accurate, but probably acceptable for many applications, are the Wilke[2] rule for viscosity and the MS[6] rule with $\alpha = 1.065$ for conductivity.

An important distinction between the EG and Brokaw rules is that the EG rules were developed from a manifestly multicomponent theory whereas the Brokaw rules were developed from a generalization of a binary formalism. Because of this the EG rules have the potential for higher accuracy for a broad range of multicomponent mixtures, and so, from a purely theoretical view, the EG rules would be preferred. The present testing, although limited, bears this out and demonstrates that 1) the EG rules are as good as the Brokaw rules for binary mixtures and 2) the new EG rules outperform the Brokaw rules for the multicomponent mixtures considered. Nevertheless, as the bulk of the data used to test the rules was for binary mixtures, further testing using multicomponent gas mixture data is needed. For the present conductivity database, there was little practical difference in the correlation errors between the EG–HEB and EG–TSB conductivity rules. From a formal point of view, the EG–TSB rule may be preferred over the EG–HEB rule because 1) it formally reduces to the monatomic mixture rule if all species are monatomic; 2) it needs no partitioning of the pure species thermal conductivity, which, in practice, requires species parameters that are difficult to obtain; and 3) it requires fewer arithmetic operations to evaluate. However, from a practical point of view, the EG–HEB rule does not require the pure species specific heat capacities, unlike the EG–TSB rule, and more important, for the conductivity database used here, there was little difference between these rules.

The fact that the EG rules with the Brokaw S matrix (EG–B for viscosity and EG–HEB or EG–TSB for conductivity) outperform the Brokaw rules for multicomponent data, even though they use the same scattering matrix, indicates that, in a multicomponent mixture, the off-diagonal contributions of the transfer of transport between species is a significant correction to the diagonal terms accounting for the impedance of transport. However, the fact that the EG rules with the hardsphere S matrix (EG–H for viscosity and EG–HEH or EG–TSH for conductivity) rules do not perform as well as the Wilke[2] rules, whereas the EG rules with the Brokaw S matrix perform better than the Wilke[2] rules indicates that it is not merely the inclusion of the off-diagonal elements that yield a better approximation but that a good estimate of the scattering matrix is also necessary. In other words, accounting for the transfer of transport (off-diagonal terms) and using a realistic scattering matrix are important in obtaining accurate approximate formulas for the mixture viscosity and thermal conductivity of dilute gas mixtures.

In this work, the scattering matrix has been estimated using a simple temperature-dependent approximation [Eq. (10)] due to Brokaw[9] for the reduced orientation-averaged collision integral $\Omega^{(2,2)^*}(T^*, \delta)$ for the Stockmayer potential. It requires knowledge of the pure species molecular potential parameters σ, ε, and μ and $\delta \equiv \mu^2/2\varepsilon\sigma^3$. As already discussed, this approximation applies over the temperature range $T^* \approx 0.5$–10 for polarities of $\delta = 0$–1 with a relative error of less than 8%. Over this parameter range, the approximations $A^* \cong 10/9$ and $B^* \cong 10/9$ are also quite adequate. It is also fortunate that, because the scattering matrix is a ratio of collision integrals, small errors in the collision integrals tend to be somewhat compensated for, so that resulting error in the scattering matrix is less than would be expected on the basis of the error in the collision integrals. At low to intermediate temperatures, that is, those for which

$$T^* \leq 1 + \tfrac{1}{4}\delta^2 \tag{29}$$

the Brokaw scattering matrix accounts, albeit crudely, for the effective reduction in the scattering matrix from unity due to collisions between particles. At higher temperatures, that is, those temperatures for which

$$T^* \gg 1 + \tfrac{1}{4}\delta^2 \tag{30}$$

the Brokaw scattering matrix approaches unity. In this limit, the temperature dependence of the mixture viscosity or conductivity is determined (almost entirely) by the temperature dependence of the component viscosities and conductivities. Furthermore, because no approximations were made vis-à-vis the molecular weights of the component species, in the absence of chemical reaction and/or dissociation, the present approximation rules provide quite reliable estimates of the mixture viscosity and conductivity over a reduced temperatures range of $T^* = 0.5$–10 and somewhat less reliable estimates up to $T^* = 20$. Of course, the real justification for the approximations employed in the present model is a posteriori by comparison with experimental data. In this regard, because the bulk of the data used to test the rules, with the exception of the He data, was for $T^* < 10$, further testing using high-temperature data is needed.

With regard to the scattering matrix, note how to increase its accuracy over a broader temperature range, albeit at a cost of increasing the time needed to evaluate the matrix and/or requiring further molecular parameters for each pure species. Perhaps the simplest approach is simply to interpolate the tabulated orientation-averaged collision integrals $\Omega^{(2,2)^*}(T^*, \delta)$ of Monchick and Mason[23] to determine the value of the required collision integrals and scattering matrix. Although this requires no additional molecular parameters, it does increase the complexity and cost of the program. However, such an approach is outdated, especially in light of recent work by Bzowski et al.,[36] Paul,[37] and Paul and Warnatz.[5] It is well known that the Stockmayer or Lennard–Jones potential, which describes the repulsive component of the potential by an r^{-12} law, is too stiff at high temperatures and that an exponential repulsive component is required to compute transport properties accurately at high gas temperatures; see Paul[37] for further discussion. Based on an improved principle of corresponding states, Bzowski et al.[36] provide analytic functionals for the required collision integrals for both noble and molecular gases that are based on a nearly universal spherical potential. In addition to the molecular parameters σ and ε required to describe the potential for midtemperatures $1 \lesssim T^* \leq 10$, the reduced long-range dispersion constant $C_6^* \equiv C_6/\varepsilon\sigma^6$ is required at cryogenic temperatures $T^* \lesssim 1$, and the reduced repulsive potential strength $V^* \equiv V/\varepsilon$ and repulsive potential range $\rho^* \equiv \rho/\sigma$ are required at high temperatures $T^* > 10$. Extensive comparisons with data determine and validate both the functionals and the choice of the molecular parameters σ, ε, C_6^*, V^*, and ρ^* for the noble gases and many molecular species.[36] Paul[37] extends the work of Bzowski et al.[36] to obtain an improved treatment for polar molecules at the cost of requiring the reduced molecular polarizability, $\alpha^* = \alpha/\sigma^3$, and dipole polarity parameter, $\delta = \mu^2/2\varepsilon\sigma^3$. In either case, the resulting scattering matrix, combined with the approximations, $A^* \cong 10/9$ and $B^* \cong 10/9$, and the present analytic expressions for the viscosity and thermal conductivity can then be used to extend the present results over a broader range of temperatures. Whereas it is straightforward to program the required collision integrals, the resulting scattering matrix requires much more time to evaluate. More important, for species other than those whose parameters are tabulated by Bzowski et al.[36] or Paul,[37] considerable effort is required to derive and/or develop a consistent set of the required molecular parameters; for further discussion see Paul.[37]

VII. Conclusions

New rules for the viscosity and thermal conductivity of polyatomic, polar and nonpolar, dilute gas mixtures have been developed. To determine the viscosity of a dilute gas mixture, a single iteration of the preconditioned conjugate-gradient solution of the linear transport equations is employed together with the collision integral approximation $A_{ij}^* \cong 10/9$ and the Brokaw approximation for the scattering matrix. To determine the thermal conductivity of a dilute, polyatomic gas mixture, the translational energy contribution to the mixture conductivity is computed using a single iteration of the preconditioned conjugate-gradient solution with the collision integral approximations $A^*_{ij} \cong B^*_{ij} \cong 10/9$ and the Brokaw approximation for the scattering matrix, whereas the internal energy contribution to the mixture conductivity is computed using either the Hirschfelder–Eucken formalism and the usual approximation for the internal energy diffusion matrix or the Thijsse et al.[13] total-energy formalism and obtaining the required collision integrals in the spherical limit. These new rules are based on an approximate solution of the appropriate Chapman–Enskog transport equations, which is manifestly derived for multicomponent mixtures and includes, to lowest order, contributions from the off-diagonal elements of the transport matrix. The new rules require a reasonable minimum of information, that is, the pure species viscosity, conductivity, molecular weight, specific heat capacity, and potential parameters, which are available for a wide variety of molecules, and are easy to evaluate numerically. These rules have been extensively tested and compared to the Wilke[2] viscosity and conductivity rules, the MS[6] conductivity rule, and the Brokaw[9,10] viscosity and conductivity rules using appropriate experimental viscosity and conductivity data for both binary and multicomponent mixtures. For binary mixtures, the new rules perform better than the Wilke[2] rules, have comparable performance to the Brokaw[9,10] rules and the MS[6] conductivity rule, whereas for multicomponent mixtures, they outperform the Wilke,[2] Brokaw,[9,10] and MS[6] rules. The improvement is due to the retention, to lowest order, of the off-diagonal terms of the transport matrix, which account for the transfer of momentum or heat between species during collisions, and the use of a scattering matrix, which accounts, albeit approximately, for the temperature dependence of the potential interaction of the collision partners. On purely formal grounds, the approximate rule for the conductivity of a dilute polyatomic gas mixture obtained using the Thijsse et al.[13] total-energy formalism is preferred over that obtained using the Hirshfelder–Eucken formalism, but, practically speaking, for the conductivity database used here, there was little difference between these rules.

Appendix: Simple Derivation of Eqs. (2) and (3)

When the decomposition $H = D + R$ is introduced, where D is the diagonal and R the off-diagonal remainder of the symmetric matrix H, and $y = x/D$, the formal solution of $H\tilde{p} = x$ for $\tilde{p}$ can be written as

$$\tilde{p} = [1/(1 + R/D)]y \tag{A1}$$

Expanding the denominator in a power series yields

$$\tilde{p} = y - (R/D)y + (R/D)^2 y - (R/D)^3 y + \cdots \tag{A2}$$

The transport property $P \equiv \tilde{p}^T x$ is then given by

$$P = y^T x - y^T R y + y^T R(1/D)Ry - y^T R(1/D)R(1/D)Ry + \cdots \tag{A3}$$

which is identical with the expansion obtained from Cramer's rule as reported by HCB.[3] When $y^T x$ is factored out and the approximation that $1 - \delta \approx 1/(1 + \delta)$ is used, when $\delta \ll 1$, to unexpand Eq. (A3), expression (A3) may be rewritten as

$$P \approx (y^T x)^2/[y^T Dy + y^T Ry - y^T R(1/D)Ry + y^T R(1/D)R(1/D)Ry - \cdots] \tag{A4}$$

because $y^T Dy \equiv y^T x$. Thus, to zeroth order in the off-diagonal elements,

$$P^{(0)} = (y^T x)^2/y^T Dy \equiv y^T x \tag{A5}$$

which is the HCB[3] approximation (3b) and to first order in the off-diagonal elements

$$P^{(1)} = \frac{(y^T x)^2}{y^T Dy + y^T Ry} \equiv \frac{(y^T x)^2}{y^T Hy} \tag{A6}$$

which is the EG[14] approximation (2b). The advantage of the conjugate-gradient method is that it converges to the exact solution in a finite number of steps unlike the formal solution (A3), which is an infinite series.

Acknowledgments

The author thanks L. F. Moon, R. D. Quinnell, and T. T. Yang and the AIAA reviewers for their careful review and suggestions regarding this work.

References

[1] Paschkewitz, J., Shang, J., Miller, J., and Madden, T., "An Assessment of COIL Physical Property and Chemical Kinetic Modeling Methodologies," AIAA Paper 2000-2574, June 2000.

[2] Wilke, C. R., "A Viscosity Equation for Gas Mixtures," *Journal of Chemical Physics*, Vol. 18, No. 4, 1950, pp. 517–519.

[3] Hirschfelder, J. O., Curtiss, C. F., and Bird, R. B., *Molecular Theory of Gases and Liquids*, Corrected Printing with Notes Added, Wiley, New York, 1964.

[4] Ferziger, J. H., and Kaper, H. G., *Mathematical Theory of Transport Process in Gases*, North–Holland, Amsterdam, 1972.

[5] Paul, P. H., and Warnatz, J., "A Re–Evaluation of the Means used to Calculate Transport Properties of Reacting Flows," *Twenty-Seventh Symposium (International) on Combustion*, Combustion Inst., Pittsburgh, PA, 1998, pp. 495–504.

[6] Mason, E. A., and Saxena, S. C., "Approximate Formula for the Thermal Conductivity of Gas Mixtures," *Physics of Fluids*, Vol. 1, No. 5, 1958, pp. 361–369.

[7] Brokaw, R. S., "Approximate Formulas for the Viscosity and Thermal Conductivity of Gas Mixtures," *Journal of Chemical Physics*, Vol. 29, No. 2, 1958, pp. 391–397.

[8] Brokaw, R. S., "Approximate Formulas for the Viscosity and Thermal Conductivity of Gas Mixtures. II," *Journal of Chemical Physics*, Vol. 42, No. 4, 1965, pp. 1140–1146.

[9] Brokaw, R. S., "Viscosity of Gas Mixtures," NASA TN D-4496, April 1968.

[10] Brokaw, R. S., "Predicting Transport Properties of Dilute Gases," *I & EC Process Design and Development*, Vol. 8, No. 2, 1969, pp. 240–253.

[11] Brokaw, R. S., "Viscosity of Binary Polar-Gas Mixtures," *Journal of Chemical Physics*, Vol. 52, 1970, pp. 2796, 2797.

[12] Schreiber, M., Vesovic, V., and Wakeham, W. A., "Thermal Conductivity of Multicomponent Dilute Gas Mixtures," *International Journal of Thermophysics*, Vol. 18, No. 4, 1997, pp. 925–938.

[13] Thijsse, B. J., Hooft, G. W., Coombe, D. A., Knapp, H. F. P., and Beenakker, J. J. M., "Some Simplified Expressions for the Thermal Conductivity in an External Field," *Physica*, Vol. 98A, 1979, pp. 307–312.

[14] Ern, A., and Giovangigli, V., "Fast and Accurate Multicomponent Transport Property Evaluation," *Journal of Computational Physics*, Vol. 120, 1995, pp. 105–116.

[15] Hirschfelder, J. O., "Heat Conductivity in Polyatomic, Electronically Excited, or Chemically Reacting Mixtures, III," *Sixth Symposium (International) on Combustion*, Reinhold, New York, 1957, pp. 351–356.

[16] Uribe, F. J., Mason, E. A., and Kestin, J., "Composition Dependence of the Thermal Conductivity of Low-Density Polyatomic Gas Mixtures," *International Journal of Thermophysics*, Vol. 12, No. 1, 1991, pp. 43–51.

[17] Ross, M. J., Vesovic, V., and Wakeham, W. A., "Alternative Expressions for the Thermal Conductivity of Dilute Gas Mixtures," *Physica A*, Vol. 183, 1992, pp. 519–536.

[18] Cowling, T. G., Gray, P., and Wright, P. G., "The Physical Significance of Formulae for the Thermal Conductivity and Viscosity of Gaseous Mixtures," *Proceedings of the Royal Society of London, Series A: Mathematical and Physical Sciences*, Vol. A276, 1963, pp. 69–82.

[19] Golub, G. H., and van Loan, C. F., *Matrix Computations*, 3rd ed., Johns Hopkins Press, Baltimore, MD, 1996.

[20] Stoer, J., and Bulirsch, R., *Introduction to Numerical Analysis*, 2nd ed., Springer-Verlag, New York, 1993.

[21] Datta, B. N., *Numerical Linear Algebra and Applications*, Books/Cole, Pacific Grove, CA, 1995.

[22] Ern, A., and Giovangigli, V., "Projected Iterative Algorithms with Applications to Multicomponent Transport," *Linear Algebra and Its Application*, Vol. 250, 1997, pp. 289–315.

[23] Monchick, L., and Mason, E. A., "Transport Properties of Polar Gases," *Journal of Chemical Physics*, Vol. 35, No. 5, 1961, pp. 1676–1697.

[24] Fristrom, R. M., and Monchick, L., "Two Simple Approximations to the Thermal Diffusion Factor and Their Applications to Flame Studies," *Combustion and Flame*, Vol. 71, 1988, pp. 89–99.

[25] Wang-Chang, C. S., Uhlenbeck, G. E., and de Boer, J., "The Heat Conductivity and Viscosity of Polyatomic Gases," *Studies in Statistical Mechanics*, edited by J. de Boer and G. E. Uhlenbeck, Vol. 2, North–Holland, Amsterdam, 1964, pp. 241–268.

[26] van der Oord, R. J., and Korving, J., "The Thermal Conductivity of Polyatomic Molecules," *Journal of Chemical Physics*, Vol. 89, No. 7, 1988, pp. 4333–4338.

[27] Millat, J., Vesovic, V., and Wakeham, W. A., "On the Validity of the Simplified Expression for Thermal Conductivity of Thijsse et al.," *Physica*, Vol. 148A, 1988, pp. 153–164.

[28] Ern, A., and Giovangigli, V., "Thermal Conduction and Thermal Diffusion in Dilute Polyatomic Gas Mixtures," *Physica A*, Vol. 214, 1995, pp. 526–546.

[29] Vesovic, V., and Wakeham, W. A., "Practical Accurate Expressions for the Thermal Conductivity of Atom–Diatom Mixtures," *Physica A*, Vol. 201, 1993, pp. 501–514.

[30] Poling, B. E., Prausnitz, J. M., and O'Connell, J. P., *The Properties of Gases and Liquids*, 5th ed., McGraw–Hill, New York, 2001.

[31] Touloukian, Y. S., Saxena, S. C., and Hestermans, P., *Viscosity: Thermophysical Properties of Matter*, Vol. 11, Plenum, Washington, DC, 1975.

[32] Touloukian, Y. S., Liley, P. E., and Saxena, S. C., *Thermal Conductivity: Nonmetallic Liquids and Gases. Thermophysical Properties of Matter*, Vol. 3, Plenum, Washington, DC, 1970.

[33] Buddenberg, J. W., and Wilke, C. R., "Calculation of Gas Mixture Viscosities," *Industrial and Engineering Chemistry*, Vol. 41, No. 7, 1949, pp. 1345–1347.

[34] Svehla, R. A., "Estimated Viscosities and Thermal Conductivities of Gases at High Temperature," NASA TR R-132, 1962.

[35] Mathur, S., Tondon, P. K., and Saxena, S. C., "Thermal Conductivity of Binary, Ternary, and Quaternary Mixtures of Rare Gases," *Molecular Physics*, Vol. 12, No. 6, 1967, pp. 569–579.

[36] Bzowski, J., Kestin, J., Mason, E. A., and Uribe, F. J., "Equilibrium and Transport Properties of Gas Mixtures at Low Density: Eleven Polyatomic Gases and Five Noble Gases," *Journal of Physical Chemistry Reference Data*, Vol. 19, No. 5, 1990, pp. 1179–1232.

[37] Paul, P. H., "DRFM: A New Package for the Evaluation of Gas-Phase Transport Properties," Sandia National Labs., Rept. SAND98-8203, UC-1409, Albuquerque, NM, and Livermore, CA, Nov. 1997.

G. V. Candler
Associate Editor