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Prediction of the Thermal Conductivity of Gas Mixtures at Low Pressures

V. Vesovic[1]

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Three methods, namely, Mason–Saxena–Wassiljewa (MSW), Hirschfelder–Eucken (HE), and Schreiber–Vesovic–Wakeham (SVW), for predicting the thermal conductivity of nonpolar, multicomponent, molecular mixtures in the dilute-gas limit were tested against the available experimental data. Overall, the accuracy of the MSW method is judged to be of the order of ±6 to 8% while that of HE and SVW is ±2 to 3%. For the latter two methods this is a remarkably good agreement, considering the approximations made in deriving the prediction scheme from the kinetic theory results. The agreement achieved indicates that the HE and SVW methods can form the basis of accurate engineering estimation techniques for the thermal conductivity of gaseous mixtures at low pressures.

KEY WORDS: kinetic theory; mixtures; prediction; thermal conductivity.

1. INTRODUCTION

An accurate knowledge of thermophysical properties of fluids and fluid mixtures is required in a number of branches of engineering for successful and optimal design purposes. This demand has led to the development of prediction schemes, since the versatility of chemical mixtures and operating conditions precludes a completely experimental approach. Historically, the lack of sufficient computing power introduced severe constraints on the form of the practicable prediction schemes. Thus, simplicity and readily available input data were of paramount importance, sometimes even to the detriment of reduced accuracy and certainly lack of transferability to different fluids. Nowadays, the tremendous advances in computational speed

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[1] T. H. Huxley School of Environment, Earth Sciences and Engineering, Imperial College of Science, Technology and Medicine, London SW7 2BP, United Kingdom. E-mail: v.vesovic@ic.ac.uk

and memory storage capacity have greatly relaxed the need for simple schemes requiring rudimentary input data. Instead, the accuracy and the reliability of the estimated values have become the most important issue. Modern trends in the prediction of thermophysical properties are to base the schemes on the best available theory sufficiently simplified to allow for practical usage and to validate the predictions against a critical set of primary experimental data of proven accuracy. Certainly for pure fluids, this has led to a plethora of reliable correlations of thermophysical properties whose accuracy is commensurate with the best available experimental data. For mixtures, the trend has been to exploit the developments of correlations for pure fluids and incorporate this knowledge into prediction schemes for the mixtures.

For the thermal conductivity of gaseous multicomponent mixtures at low pressures, this trend has resulted in prediction methods that can be classified into two general groups. The first has its origins in the kinetic theory of dilute gases, and the resulting prediction schemes make some use of the results of the kinetic theory, albeit with an additional set of approximations. The second has its origins in the corresponding states principle, which states that, in general, the thermophysical behavior of any fluid can, by appropriate choice of scaling parameters, be reduced to that of a universal reference fluid. The development of corresponding-states prediction schemes has been driven primarily by the need to predict accurately the behavior of fluid mixtures at high pressures. As such, their accuracy at low pressures is not very high and is often lower than what can be achieved by prediction schemes based on kinetic theory. In this work, only the prediction schemes belonging to the first category, based on kinetic theory, have been examined.

Until very recently, predictions of thermal conductivity were hampered by a lack of suitable, practical expressions based on the underlying kinetic theory of dilute, polyatomic mixtures. One of the reasons for this is that although the development of formal kinetic theory culminated in the early sixties with the derivation of expressions for thermal conductivity [1], the resulting expressions were too complex to be of immediate practical use. Nevertheless, by making use of a number of reasonable physical approximations, simplifications of the formal expressions can be made, leading to the development of theoretically based prediction schemes.

In the late 1950s, Hirschfelder [2] generalized the Eucken approximation to mixtures based on heuristic arguments and proposed a relatively straightforward method of estimating the thermal conductivity of polyatomic mixtures, which subsequently was rederived from formal expressions by means of a spherical approximation [1]. More recently, Schreiber, Vesovic, and Wakeham (SVW) [3] proposed a different way of estimating thermal conductivity based on the use of different basis expansion vectors in the formal expressions. Historically, both of these methods were preceded by the work of Wassiljewa [4], who introduced a set of more stringent approximations to derive a very simple expression for the thermal conductivity of monatomic mixtures, which Mason and Saxena [5] extended to polyatomic mixtures.

Although different researchers have used both the Hirschfelder–Eucken (HE) and the Mason–Saxena–Wassiljewa (MSW) methods to analyze their experimental thermal conductivity measurements, the engineering design is performed primarily by means of the MSW scheme. The current consensus is that the MSW scheme can predict thermal conductivity to within ±5 to 10%, and even these results are based on validation against data of a lower accuracy than are currently available. The recent developments and validation tests of the SVW scheme [6] indicate that a much higher accuracy of the order of ±2 to 3% is achievable. These encouraging results led us to perform more comprehensive tests of the three schemes by comparing their predictions with experimental thermal conductivity data for binary and multicomponent molecular mixtures. The present paper reports on the results of such investigations for a number of molecular mixtures for which accurate experimental data are available.

It is worth noting that the emphasis of this work is on the accuracy of the theoretical approximations made to obtain practicable methods of estimating thermal conductivity, rather than on the numerical techniques used in solving for thermal conductivity. Thus, no discussion is presented of the iterative, variational techniques which have recently been proposed [7] as a computationally cheaper method of evaluating the thermal conductivity of multicomponent mixtures.

2. THEORY

The experimental measurement of the thermal conductivity of gas mixtures is always carried out under the condition of zero net diffusive flux, and as a consequence the expression for the experimental thermal conductivity, λ^{∞}, contains only the contributions due to thermal diffusion and pure conduction [8, 9]. Thus, the thermal conductivity of a multicomponent, polyatomic gas mixture at zero density can be expressed in a formal way as [8, 10]

$$\lambda^{\infty} = \frac{1}{3} k_B [\mathbf{A} . \mathfrak{R}(\mathbf{A})] + \frac{1}{3} \frac{k_B}{\nabla \ln T} \sum_{q'} [\mathbf{A} . \mathfrak{R}(\mathbf{F}^{q'})] \, \mathbf{d}_{q'} \tag{1}$$

where T and $\mathbf{d}_{q'}$ are the temperature and diffusion driving force for species q', respectively, k_B is the Boltzmann constant, $\mathfrak{R}$ is the Wang-Chang–

Uhlenbeck operator [11, 12], and the brackets indicate the kinetic theory equilibrium average summed over all components [10]. Symbols $\mathbf{A}$ and $\mathbf{F}^{q'}$, inside the brackets, indicate that the summations over all components are performed using vectors $\mathbf{A}_q$ and $\mathbf{F}_q^{q'}$, respectively. Vectors $\mathbf{A}_q$ and $\mathbf{F}_q^{q'}$ are unknown functions that relate the magnitude of the temperature and diffusion perturbation, respectively, to the perturbation in the molecular velocity distribution. To relate the expression for the thermal conductivity, Eq. (1), to microscopic observables, vectors $\mathbf{A}_q$ and $\mathbf{F}_q^{q'}$ are expanded in terms of orthogonal polynomials. Presently, for thermal conductivity, there are two approaches [10, 12] in choosing the polynomials, resulting in different first-order kinetic theory expressions for the thermal conductivity.

2.1. Hirschfelder–Eucken Expression

Traditionally, in the Wang-Chang–Uhlenbeck approach [11, 12], vectors $\mathbf{A}_q$ and $\mathbf{F}_q^{q'}$ were expanded in terms of a double series of basis vectors, $\mathbf{\Phi}^{10sr\,|\,q}$,

$$\mathbf{A}_q = \sum_s \sum_r a_{qsr} \mathbf{\Phi}^{10sr\,|\,q} \tag{2}$$

$$\mathbf{F}_q^{q'} = \sum_s \sum_r f_{qsr}^{q'} \mathbf{\Phi}^{10sr\,|\,q} \tag{3}$$

The basis vectors, $\mathbf{\Phi}^{10sr\,|\,q}$, are expressed as a product of two orthonormal polynomials, one of which is a function of the translational energy only and the other a function of the internal energy only. Analogous to the monatomic case, Wang-Chang and Uhlenbeck, in their original derivation [11], used Sonine polynomials to account for the dependence on translational energy, while for the internal energy they introduced the so-called Wang-Chang and Uhlenbeck polynomial [11, 12]. Following this choice of basis vectors, it is possible to derive [1] the first-order kinetic theory result for the thermal conductivity of a multicomponent, polyatomic gas mixture at zero density,

$$\lambda^{\infty} = -\begin{vmatrix} L_{11,\,\text{mon.}} & \cdots & L_{1n,\,\text{mon.}} & x_1 \\ \vdots & & \vdots & \vdots \\ L_{n1,\,\text{mon.}} & \cdots & L_{nn,\,\text{mon.}} & x_n \\ x_1 & \cdots & x_n & 0 \end{vmatrix} \Bigg/ \begin{vmatrix} L_{11,\,\text{mon.}} & \cdots & L_{1n,\,\text{mon.}} \\ \vdots & & \vdots \\ L_{n1,\,\text{mon.}} & \cdots & L_{nn,\,\text{mon.}} \end{vmatrix} + \lambda_{\text{poly}} \tag{4}$$

where x_i is the mole fraction of species i and the subscript mon. indicates that the elements of the determinants are given by the expressions for the monatomic species, namely,

$$L_{qq,\,\text{mon.}} = \frac{x_q^2}{\lambda_q} + \sum_{\mu \neq q} \frac{25 x_q x_\mu}{8A^*_{q\mu}\lambda_{q\mu}} \left[\frac{25}{4}\, y^4_{\mu q} + \frac{15}{2}\, y^4_{q\mu} - 3y^4_{\mu q} B^*_{q\mu} + 4y^2_{q\mu}\, y^2_{\mu q} A^*_{q\mu} \right] \qquad (5)$$

$$L_{qq',\,\text{mon.}} = -\frac{25 x_q x_{q'}\, y^2_{qq'}\, y^2_{q'q}}{8A^*_{qq'}\lambda_{qq'}} \left[\frac{55}{4} - 3B^*_{qq'} - 4A^*_{qq'} \right] \qquad (6)$$

where λ_q is the thermal conductivity of pure molecular species q, $\lambda_{qq'}$ is the interaction thermal conductivity, R is the gas constant, and the quantities $A^*_{qq'}$ and $B^*_{qq'}$ are ratios of effective cross sections [3, 6, 12]. The effective cross sections incorporate all of the information about the binary molecular interactions for a particular coupling between the relative velocity and the angular momentum of colliding species [12]. In addition, $y_{qq'}$ is the mass ratio of species q, given by

$$y^2_{qq'} = \frac{M_q}{(M_q + M_{q'})} \qquad (7)$$

where M_q and $M_{q'}$ are the relative molecular weights of species q and q', respectively.

The expression for $\lambda_{\text{poly.}}$ contains all the information on the polyatomic quantities entering the expression for the thermal conductivity [1]. It is a lengthy and complicated function of a number of inelastic cross sections, namely, those relating to the diffusion and relaxation of internal energy, for different species. Currently, there are no readily available calculations or even estimates of these quantities, and in some cases it is even impossible to obtain them by experimental means. Thus, to get a practical expression for the evaluation of the thermal conductivity, traditionally a set of approximations is introduced that greatly simplifies the expressions for $\lambda_{\text{poly.}}$. The assumption is made that the molecules of different species in the mixture interact through an effective spherical intermolecular potential. In this case, the expression for $\lambda_{\text{poly.}}$ reduces to [1]

$$\lambda_{\text{poly.}} = \sum_q x_q(\lambda_q - \lambda_{qq}) \left[x_q + \sum_{\mu \neq q} x_\mu \frac{A^*_{q\mu}\lambda_{q\mu}}{A^*_{qq}\lambda_{qq}} \right]^{-1} \qquad (8)$$

Thus, the expressions given by Eqs. (4)–(6) and (8) allow for a computationally easy evaluation of the thermal conductivity of a multicomponent, polyatomic gas mixture providing a number of input parameters are known. The expressions, Eqs. (4)–(6) and (8), are known as the HE expressions, and were derived in the late 1950s [2] following heuristic arguments.

2.2. Schreiber–Vesovic–Wakeham Expression

A second approach in choosing the basis vectors, due originally to Thijsse et al. [13], is to perform the expansion in terms of two orthonormal polynomials that are functions of the sum of the translational and internal energy and the difference of the translational and internal energy, respectively. If these basis vectors are used for the expansion, the first-order kinetic theory result for the thermal conductivity of a multicomponent, polyatomic gas mixture at zero density can be expressed in a form analogous to that for a mixture consisting of monatomic species, namely [3],

$$\lambda^{\infty} = -\begin{vmatrix} L_{11} & \cdots & L_{1n} & x_1 \\ \vdots & & \vdots & \vdots \\ L_{n1} & \cdots & L_{nn} & x_n \\ x_1 & \cdots & x_n & 0 \end{vmatrix} \Bigg/ \begin{vmatrix} L_{11} & \cdots & L_{1n} \\ \vdots & & \vdots \\ L_{n1} & \cdots & L_{nn} \end{vmatrix} \tag{9}$$

The resulting expressions for the elements of the determinants, L_{ij}, are complicated functions of the effective cross sections [10] and, at present, are of little value for practical evaluation of thermal conductivity. It has been shown for pure polyatomic gases [13, 14] and atom–molecule mixtures [15] that accurate and relatively simple expressions can be obtained by means of the Thijsse approximation, which identifies total energy as the dominant factor in determining thermal conductivity. The Thijsse approximation has been applied to polyatomic systems [3], and the resulting expressions for elements L_{ij} have been written in terms of, at least in principle, measurable quantities rather than in terms of effective cross sections. Nevertheless, a further set of approximations had to be made to provide a practical means of calculating thermal conductivity. Hence, all of the quantities that enter the expressions for the elements, L_{ij}, have been replaced by their spherical limits [3]. Following the application of Thijsse and spherical approximations to the full results, the relevant determinant elements, L_{ij}, are given by

$$\begin{aligned} L_{qq} = {} & \frac{x_q^2}{\lambda_q} + \sum_{\mu \neq q} \frac{25 x_q x_\mu}{8 A^*_{q\mu} \lambda_{q\mu}} \left(\frac{R}{C^0_{Pq}}\right)^2 \\ & \times \left[\frac{25}{4}\, y^4_{\mu q} + \frac{15}{2}\, y^4_{q\mu} - 3 y^4_{\mu q} B^*_{q\mu} + 4 y^2_{q\mu}\, y^2_{\mu q} A^*_{q\mu} + \left(\frac{C^0_{Pq}}{R} - 2.5\right)\right] \end{aligned} \tag{10}$$

$$L_{qq'} = -\frac{25 x_q x_{q'}\, y^2_{qq'}\, y^2_{q'q}}{8 A^*_{qq'} \lambda_{qq'}} \left(\frac{R}{C^0_{Pq}}\right)\left(\frac{R}{C^0_{Pq'}}\right)\left[\frac{55}{4} - 3 B^*_{qq'} - 4 A^*_{qq'}\right] \tag{11}$$

where C^0_{Pq} is the ideal gas, isobaric heat capacity of species q.

Expressions given by Eqs. (9)–(11), constitute the SVW scheme for calculating thermal conductivity of mixtures. Analogous to the HE expressions, these allow for a computationally easy evaluation of the thermal conductivity of a multicomponent, polyatomic gas mixture provided that a number of input parameters are known.

2.3. Mason–Saxena–Wassiljewa Expression

Most of the current engineering predictions [16] do not make use of either the HE or the SVW expressions, but rely on empirical expressions that are all essentially based on the Wassiljewa equation. In its original derivation, Wassiljewa showed [4], on the basis of mean-free path theory, that the thermal conductivity of a multicomponent monatomic mixture can be expressed very simply as

$$\lambda^{\infty} = \sum_{q} x_q \lambda_q \left[x_q + \sum_{\mu \neq q} x_\mu G_{q\mu} \right]^{-1} \tag{12}$$

The same result can be derived [5, 8] from the first-order kinetic theory for monatomic mixtures by assuming that the off-diagonal interaction elements L_{ij} in the determinant, Eq. (4), are negligibly small compared to the diagonal determinant elements L_{ii}. Such a derivation also establishes the form of the functions $G_{qq'}$,

$$G_{qq'} = \varepsilon \frac{y_{q'q}}{\sqrt{8}} \left[1 + (y_{qq'} \lambda_{qq} / y_{q'q} \lambda_{q'q'})^{1/2}\right]^2 \tag{13}$$

as originally derived by Mason and Saxena [5]. The parameter ε is a ratio, near unity, of functions of molecular masses and interaction parameters $A^*_{qq'}$ and $B^*_{qq'}$, whose exact value depends on the particular approximations used to derive the expression given by Eq. (13). It is common practice to treat it as an adjustable parameter, and on the basis of experimental thermal conductivity of binary inert gas mixtures available at the time, Mason and Saxena [5] assigned it a value of $\varepsilon = 1.065$. Although Eqs. (12) and (13) were originally derived for monatomic mixtures, it can be shown [5] that a similar set of approximations, when applied to the HE expression for thermal conductivity of mixtures, Eqs. (4)–(6) and (8), would yield the same results as given by Eqs. (12) and (13). Therefore, Eqs. (12) and (13) can be used to calculate the thermal conductivity of polyatomic gas mixtures and, as such, constitute the MSW scheme.

A number of other workers have proposed empirical modifications [8, 17] to the above expressions, resulting in more input requirements but not in significant improvements in thermal conductivity predictions [16]. Since these improved correlations were based on fitting to data of a lower accuracy than is currently available, it was decided to test only the MSW scheme as a representative of the currently recommended methods [16] of evaluating thermal conductivity for engineering purposes.

2.4. Input Parameters

To calculate the thermal conductivity of a multicomponent gas mixture by any of the schemes outlined above, one requires, at the temperature of interest, knowledge of both a number of pure species properties and some binary interaction parameters. In this respect, the MSW scheme is the least demanding, since for a given mixture it requires only knowledge of the thermal conductivity of the pure species, λ_q. The HE scheme, in addition, requires knowledge of three binary interaction parameters, namely, the interaction thermal conductivity, $\lambda_{qq'}$, and the ratios $A^*_{qq'}$ and $B^*_{qq'}$ for each binary pair. The SVW scheme requires the largest number of input parameters, since, in addition to the properties already mentioned, it requires knowledge of the ideal-gas, isobaric heat capacity, C^0_{pq}, of each pure species.

Information on the thermal conductivity and the isobaric heat capacity of pure species is readily available for a large number of fluids as a function of temperature, either in terms of correlations or directly from experimental information. In this work, where possible, properties of each pure component have been calculated from the recommended correlations that are based on the best available experimental data. For the following fluids, used in this work, such correlations exist for thermal conductivity: H_2 [18], N_2 [19], O_2 [20], CO [19], CO_2 [21], CH_4 [22], C_2H_6 [23], C_3H_8 [24], and C_4H_{10} [24]; and for heat capacity: H_2 [25], N_2 [26], O_2 [27], CO [28], CO_2 [29], CH_4 [30], C_2H_6 [31], C_3H_8 [24], and C_4H_{10} [24]. The thermal conductivity of inert gases has been obtained from a universal correlation [32] based on the corresponding-states principle.

The interaction parameters required for the HE and SVW schemes were estimated from empirical correlations. These correlations are, in general, based on a corresponding-states principle, and the binary data for a relevant interaction are usually obtained by the critical examination of the experimental mixture viscosity and the binary diffusion data. To make use of these expressions, one needs to define the interaction thermal conductivity, $\lambda_{qq'}$, in terms of the interaction viscosity, $\eta_{qq'}$, which in turn can be related to the reduced viscosity collision integral, Ω_η^*, through the following expressions:

$$\lambda_{qq'} = \frac{15}{8} R \frac{(M_q + M_{q'})}{M_q M_{q'}} \eta_{qq'} = 0.4675 \frac{R^{3/2}\sqrt{T}}{\sigma_{qq'}^2 \Omega_\eta^*} \tag{14}$$

where $\sigma_{qq'}$ is the distance scaling parameter.

For the purposes of this work, simple forms of the universal functions for Ω_η^*, $A_{qq'}^*$, and $B_{qq'}^*$ were used [33] and are summarized below.

$$\ln \Omega_\eta^* = \sum_{i=0}^{4} \omega_i (\ln T^*)^i \tag{15}$$

$$\ln A_{qq'}^* = \sum_{i=0}^{4} a_i (\ln T^*)^i \tag{16}$$

$$\ln B_{qq'}^* = \sum_{i=0}^{3} b_i (\ln T^*)^j \tag{17}$$

$$T^* = T/\varepsilon_{qq'} \tag{18}$$

where the coefficients ω_i, a_i, and b_i are given, for completeness, in Table I. The energy and distance scaling parameters, $\varepsilon_{qq'}$ and $\sigma_{qq'}$, are provided for most binary interactions [33], and where the data were not available, notably for H_2 mixtures, the traditional mixing rules,

$$\varepsilon_{qq'} = \sqrt{\varepsilon_q \varepsilon_{q'}} \tag{19}$$

$$\sigma_{qq'} = \tfrac{1}{2}(\sigma_q + \sigma_{q'}) \tag{20}$$

were used to obtain the relevant scaling parameters from their pure-species counterparts.

Table I. Coefficients for the Corresponding-States Expressions, Eqs. (15)–(17)

n	ω_i Eq. (15)	a_i Eq. (16)	b_i Eq. (17)
0	0.46649	0.1281	0.1789
1	−0.57015	−0.1108	−0.1233
2	0.19164	0.0962	0.0558
3	−0.03708	−0.0271	−0.0074
4	0.00241	0.0024	—

Some more recent work [34], based on a more comprehensive examination of the available experimental data, has produced more accurate universal correlations for Ω_η^*, $A_{qq'}^*$, and $B_{qq'}^*$. Nevertheless, the increase in accuracy, at least above $T^* = 1$, did not warrant its use for the purposes of estimating the thermal conductivity of mixtures, as discussed in Section 3.2.

3. COMPARISON WITH EXPERIMENTAL DATA

To make a sensible comparison of the predictions of the three methods with the experimental data, it is imperative that the data used are of the highest possible accuracy. Thus, a critical analysis of the available data has initially been performed with the emphasis on the type of instrument used and the claimed accuracy and the agreement, with other workers, of the pure thermal conductivity data obtained in the same apparatus. Ideally, the primary data set would comprise those measurements performed in instruments for which a full working equation exists and for which a high precision in measuring thermal conductivity has been achieved. For the purposes of the present work, these constraints would severely limit the available data. Hence other data with well-defined uncertainty levels have been included in the analysis, to cover as much as possible of the temperature range and examine a wide variety of different mixtures. To make the discussion easier, the data were divided into three categories based on the type of molecules present in the mixture and the number of components. The accuracy quoted by the authors varied between ±0.3 and 2%, although when a critical examination of the data of a number of workers for the same systems is carried out, quoted uncertainty figures are generally found to err on the optimistic side.

The comparison was limited to mixtures consisting of nonpolar species. The reason for this choice is twofold. First, the interaction parameters necessary for the HE and SVW methods are evaluated from the corresponding-states correlations, Eqs. (15)–(18). In general, such two-parameter correlations would not adequately represent the interaction between polar molecules, and as yet there are no equivalent expressions which take into account the polarity of the molecules. Second, the accuracy of the thermal conductivity of pure polar species is, with a few exceptions, still low, and only for a few species are recommended correlations as a function of temperature available.

3.1. Binary Atom–Molecule Mixtures

A binary atom–molecule system represents the simplest polyatomic mixture, and for a number of such mixtures the thermal conductivity has been measured by different investigators by means of various experimental techniques. Thus, the data on binary atom–molecule mixtures provide a natural starting point for testing the accuracy of the three predictive methods. A literature search and critical assessment of the available data indicated that data from four laboratories would provide a sufficient data bank for a stringent test of the predictive methods to be carried out.

In the early 1980s Kestin and his collaborators undertook an extensive experimental study of inert gas (He, Ne, Ar, Kr, Xe)–molecule (H_2, N_2, CO_2, CH_4) systems [35–39]. The measurements were performed by means of the transient hot-wire technique with a claimed accuracy of $\pm 0.3\,\%$ or better. Recent analysis of the thermal conductivity of pure gases and comparison with data of other investigators indicate that the accuracy of these data is slightly lower, of the order of $\pm 0.5\,\%$. Wakeham and his collaborators extended this study using the same type of instrument, with commensurate accuracy, to inert gas–H_2 and inert gas–CO systems [40, 41]. Although a large number of mixtures was measured, the measurements were performed at a single temperature only, either 300 or 308 K. Nevertheless, the resulting high-precision data bank, which consists of 47 experimental data points, is extremely useful as the primary data set. To help the discussion, the experimental data set was divided into two parts. The first part consisted of systems where the mass ratio of the two species was less than 3, while the second part consisted of He–molecule and inert gas–H_2 mixtures.

Figure 1 illustrates the deviations of the thermal conductivity predicted by the three methods from the experimental data for atom–molecule mixtures for the following systems: Ne,Ar,Kr–N_2 [37], Ne,Ar–CH_4 [38], Ne,Ar–CO_2 [39], Ar–CO [41], and He–H_2 [35]. Not surprisingly, no method reproduces the available data within its accuracy of $\pm 0.5\,\%$. Nevertheless, the HE and SVW methods do remarkably well by reproducing the experimental data with an rms deviation of 0.8 and 1.0 %, respectively. The maximum deviation observed was 2 % for HE and 2.4 % for SVW. The deviations shown in Fig. 1 are in agreement with preliminary findings [6] which indicated that the SVW scheme has an accuracy of $\pm 2.5\,\%$; a similar precision has been observed for the HE method [6]. In fact both the HE and the SVW methods reproduce all the data within the combined uncertainty, of the method and the experimental data, of $\pm 3.0\,\%$, as indicated by the two dashed lines in Fig. 1. The MSW method, in general, underestimates the data with an rms deviation of 2.9 % and a maximum deviation of $-7.5\,\%$.

It is interesting to make use of this high-precision data set to ascertain if improvements in the accuracy of the interaction parameters, $\eta_{qq'}$, $A^*_{qq'}$, and $B^*_{qq'}$ will improve the accuracy of the HE and SVW methods. To examine this, the deviations, illustrated in Fig. 1, were compared with

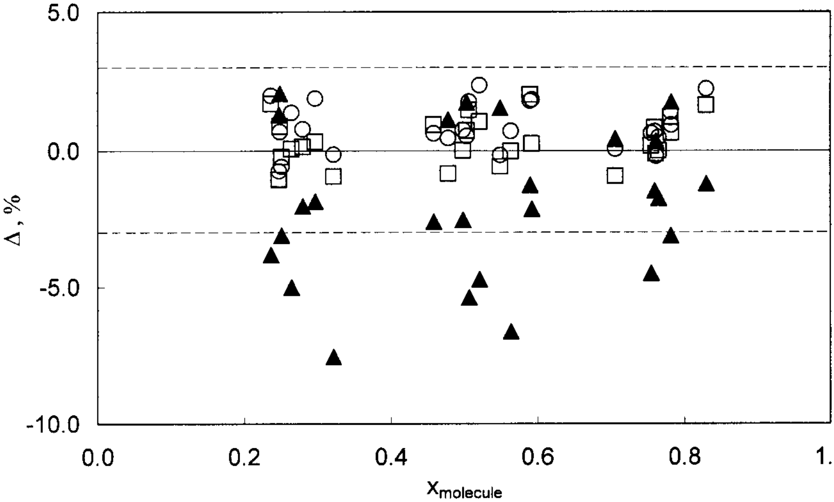

Fig. 1. Deviations, $\Delta = 100(\lambda_{pred.} - \lambda_{exp.})/\lambda_{exp.}$, of the predicted values of thermal conductivity from the experimental data [35, 37–39, 41] for atom–molecule mixtures. (□) HE method; (○) SVW method; (▲) MSW method.

those obtained by Schreiber and co-workers [6]. They have studied the same atom–molecule systems, with the exception of Ar–CO and He–H_2, but have employed more recent and more accurate expressions for the interaction parameters, as indicated in Section 2.4. Although for some individual atom–molecule systems the deviations were found to be different, the overall rms deviation for both the HE and the SVW methods remained the same. This gives further credence to the belief that the accuracy of both methods is limited by the approximations made in their derivation. It seems that no further increase in accuracy, below ±2.5%, is possible by increasing the accuracy of input quantities.

Figure 2 illustrates the deviations of the thermal conductivity predicted by the three methods from the experimental data for atom–molecule mixtures for the following systems: He–CH_4,N_2,CO,CO_2 [35–39, 41] and Ne,Ar,Kr–H_2 [40]. All these atom–molecule systems are characterized by the fact that one of the species is much lighter than the other, leading to a high mass ratio of the two species. It is known from studies on monatomic systems [8, 33] that the prediction of the thermal conductivity of such mixtures is less accurate than that of mixtures where the mass ratio is near unity. The reasons are twofold: first, the ratio of the thermal conductivity of the two pure species also tends to be large, making it difficult for any interpolation-like scheme to display a high accuracy; and second, the high mass ratio entering expressions for L_{ij}, Eqs. (5) and (6) or Eqs. (10)

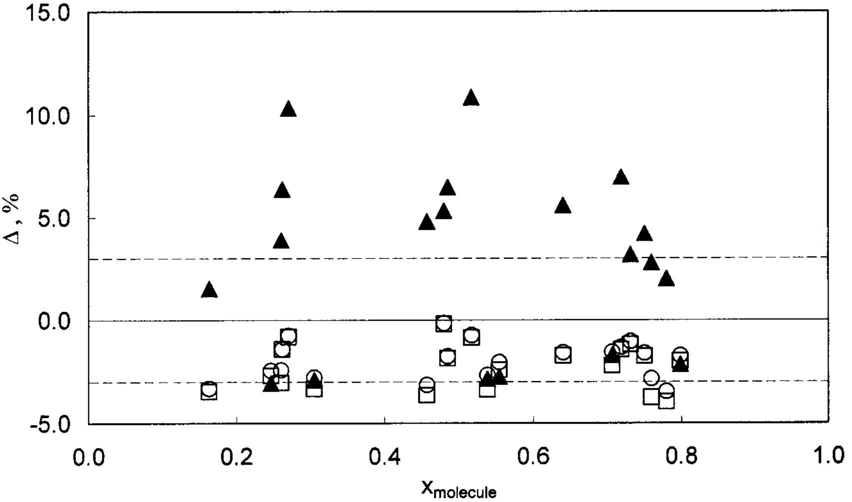

Fig. 2. Deviations, $\Delta = 100(\lambda_{pred.} - \lambda_{exp.})/\lambda_{exp.}$, of the predicted values of thermal conductivity from the experimental data [35–41] for atom–molecule mixtures. (□) HE method; (○) SVW method; (▲) MSW method.

and (11), tends to increase the contribution of interaction parameters to the overall thermal conductivity.

The deviations for all three methods, illustrated in Fig. 2, are in general larger than those observed in Fig. 1. Both the HE and the SVW methods produce very similar deviations, but both underestimate the experimental thermal conductivity. The HE and SVW rms deviations, for this set of 20 experimental data points, are 2.6 and 2.2%, respectively, while the maximum deviations are −4.0 and −3.4%, respectively. The MSW method in general overpredicts the experimental data, with an rms deviation of 5.3% and a maximum deviation of 10.9%. Although the decrease in accuracy of the MSW scheme can be attributed to the mass ratio effect, closer inspection of the deviations of the HE and SVW schemes indicates some unusual features. Namely, for Ne, Ar, Kr–H_2 [40] mixtures, which have a mass ratio in the range 10 to 40, both the HE and the SVW methods predict the experimental thermal conductivity with an rms deviation of 1.3% and a maximum deviation of −1.9%. These deviations are commensurate with those displayed for mixtures where the mass ratio is near unity as illustrated in Fig. 1. For He–CH_4, N_2, CO, CO_2 [35–39, 41], which have a mass ratio in the range 4 to 11, the HE method underpredicts the experimental thermal conductivity values by 2 to 4%, while the SVW method performs marginally better, underpredicting by 1 to 3%. Similar trends were observed for He–CH_4,N_2,CO_2 mixtures by Schreiber and co-workers [6] when using the more accurate interaction parameters.

Saxena and co-workers have also performed extensive experimental studies of the thermal conductivity of polyatomic mixtures. The measurements were performed in a thick hot wire cell, with a claimed accuracy of ±1 to 2%. The accuracy is lower than that of Kestin and co-workers, but these data have the advantage that the mixture thermal conductivity has been measured as a function of temperature. Although only a few atom–molecule systems were studied, the 33 experimental points available for Ne,Kr,Xe–H_2 [42] mixtures form a good data set to investigate the predictions of the three methods at temperatures other than room temperature. The experimental data presented in the literature [42] are smoothed data, so it is prudent to lower the accuracy of these data to ±2%.

Figure 3 illustrates the deviations of the thermal conductivity predicted by the three methods from the experimental data for Ne,Kr,Xe–H_2 [42] systems as a function of the mole fraction of hydrogen present over a range of temperature extending from 313 to 448 K. The predictions of the HE and SVW methods are nearly identical, the largest difference being of the order of ±0.3%. The agreement with the experimental data is not as good; the rms deviation of both methods is 3.6%, while the maximum deviation is 8.9%. The MSW method in general overpredicts the experimental data, with an rms deviation of 8.7% and a maximum deviation of 15.8%. More

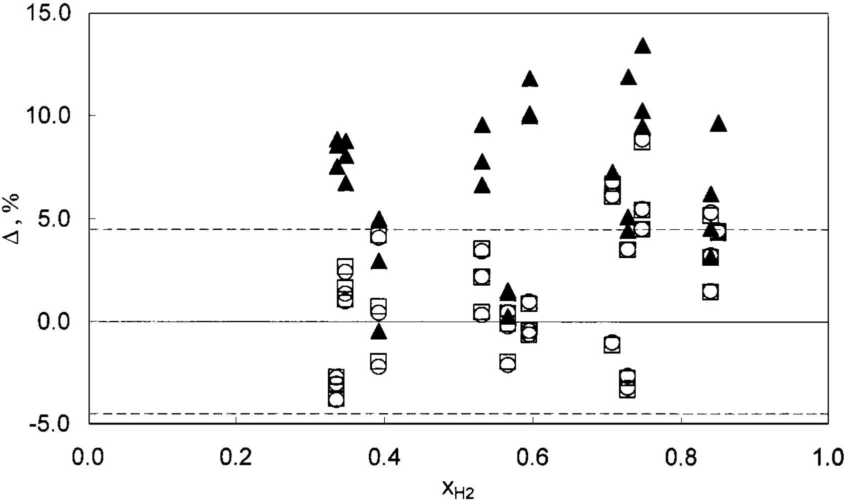

Fig. 3. Deviations, $\Delta = 100(\lambda_{\text{pred.}} - \lambda_{\text{exp.}})/\lambda_{\text{exp.}}$, of the predicted values of thermal conductivity from the experimental data [42] for atom–hydrogen mixtures. (□) HE method; (○) SVW method; (▲) MSW method.

surprisingly, the data indicate that the HE and SVW predictions deteriorate as the mole fraction of hydrogen in the mixture increases.

The cause of this behavior could be attributed to the larger-than-expected experimental uncertainty in the thermal conductivity of hydrogen-rich mixtures. In conjunction with work on mixtures, Saxena and co-workers have measured the thermal conductivity of a number of pure gases in the same apparatus over the same temperature range [42]. Their experimental data for Ne, Kr, Xe, and N_2 agree within ±1 to 2% with the current recommended values [19, 32] based on critical analysis of all the available measurements. For H_2 this is not the case, and the data of Saxena and co-workers are on average 4–5% below the currently recommended values [18]. It would thus seem plausible that the accuracy of the thermal conductivity of mixtures containing hydrogen might be lower than originally anticipated. To test this possibility, the hydrogen thermal conductivity as measured by Saxena, rather than the recommended one, was used as an input parameter in the HE, SVW, and MSW methods, keeping all the other input parameters unchanged. The resulting predictions in terms of deviations from the experimental data are illustrated in Fig. 4, where, for clarity, only the predictions of the HE and SVW methods are displayed. No trend with the hydrogen mole fraction is evident any longer. The SVW method now predicts the experimental data within the combined uncertainty of the method and experimental data, as indicated by the dashed

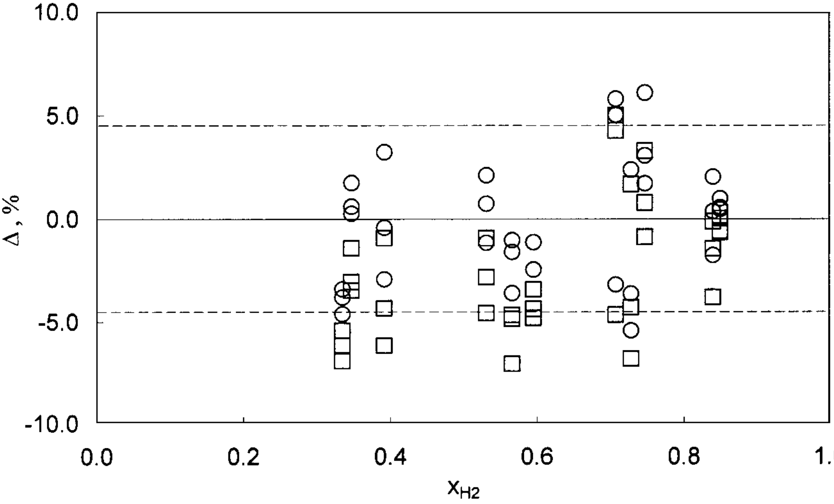

Fig. 4. Deviations, $\Delta = 100(\lambda_{\text{pred.}} - \lambda_{\text{exp.}})/\lambda_{\text{exp.}}$, of the predicted values of thermal conductivity from the experimental data [42] for atom–hydrogen mixtures. (□) HE method; (○) SVW method; (▲) MSW method.

lines in Fig. 4, and with an improved rms deviation of 3.0% and a lower maximum deviation of 6.1%. The HE method predicts the data slightly worse than before, with an rms deviation of 4.1%, but with a maximum deviation of -6.9%, compared with 8.9% in Fig. 3. The deterioration in the HE predictions is due to the structure of the expression for $\lambda_{\text{poly.}}$, Eq. (8), which is, in this case, dominated by the value of the thermal conductivity of hydrogen. This results in the high sensitivity of the mixture thermal conductivity to the value of λ_{H_2}, which persists to very low mole fractions of hydrogen. Thus, decreasing λ_{H_2} by 4.8% at 313 K would result, for the Xe–H_2 system, in a decrease in the mixture thermal conductivity of 5.3% at $x_{H_2}=0.84$, while at $x_{H_2}=0.4$ the mixture thermal conductivity would decrease by as much as 5.1%. This should be compared to the response of the SVW method, where the same change in the thermal conductivity of hydrogen would result in a change in the mixture thermal conductivity of 3.3% at $x_{H_2}=0.84$ and 0.9% at $x_{H_2}=0.4$. The predictions of the MSW method are also in slightly better agreement, with the maximum deviation being 14.1%.

Schramm and Schafer have also reported experimental thermal conductivity data for atom–molecule mixtures [43]. They have performed extensive measurements, by means of a steady-state hot-wire technique, of the thermal conductivity of binary mixtures of Ar and the first four unsaturated hydrocarbons in the temperature range extending from room temperature to 1000 K. No actual experimental data are available [43], but rather a table of interpolated, smoothed values as a function of mole fraction and temperature is presented, making assessment of the accuracy difficult. Comparison of their results for pure species with the currently recommended values indicates very good agreement for argon over the whole temperature range but poor agreement for the four hydrocarbons at temperatures above room temperature. For instance, the thermal conductivity of methane and ethane is low [22, 23], by 4 to 6% in the temperature range 370 to 680 K and by up to 15% at the highest temperature measured. There is no reason to believe that the thermal conductivity of the hydrocarbon-rich mixtures is any more accurate than that of their pure counterparts. To alleviate this problem of low accuracy of the hydrocarbon-rich mixtures, to a certain extent, the values quoted by Schramm and Schafer for the pure hydrocarbon species [43] have been used as the input to the three predictive methods. It was also felt prudent to restrict the comparison to a temperature range up to 700 K. These data, for the reasons outlined above, cannot be considered primary but are, nevertheless, useful to examine trends with temperature and with increasing carbon number.

Surprisingly, all three methods reproduce the data remarkably well, although the MSW method in general underpredicts the data. The rms

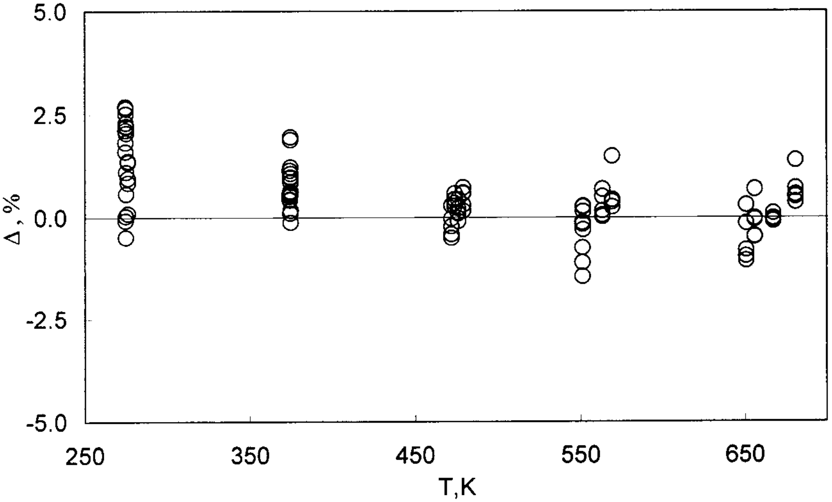

Fig. 5. Deviations, $\Delta = 100(\lambda_{\text{pred.}} - \lambda_{\text{exp.}})/\lambda_{\text{exp.}}$, of the predicted values of thermal conductivity from the experimental data [43] as a function of temperature for argon–molecule mixtures. (○) SVW method.

deviations range from 0.7% for HE, to 1.0% for SVW, to 1.9% for MSW, while the maximum deviations are 1.9, 2.6, and −4.3%, respectively. For clarity, Fig. 5 illustrates only the deviations of the thermal conductivity predicted by the SVW method from the experimental data as a function of temperature. No discernible temperature dependence of the deviations is observed for any method. Examination of the different deviation plots indicates that the data for all four Ar–C_nH_{n+2} systems are reproduced equally well. For instance, the equimolar binary mixture, which is usually the most difficult to predict accurately, is reproduced within the same rms deviations as the whole data set by all three methods.

A further test was performed, whereby the thermal conductivity of pure hydrocarbon species was evaluated by means of the recommended correlations, as described in Section 2.4. Not surprisingly, larger deviations were observed, with the magnitude increasing toward the pure hydrocarbon end.

Parkinson and co-workers [44, 45] have also studied the thermal conductivity of binary argon–hydrocarbon mixtures. The measurements were performed in a two-wire cell at 50 and 100°C with a claimed accuracy of ±2%. For the purposes of the present analysis, the experimental data consisted of 54 thermal conductivity data points for the systems Ar–nC_4H_{10}, Ar–iC_4H_{10}, and Ar–nC_5H_{12}. For these systems, both the thermal conductivity of the pure species and the corresponding-states interaction parameters

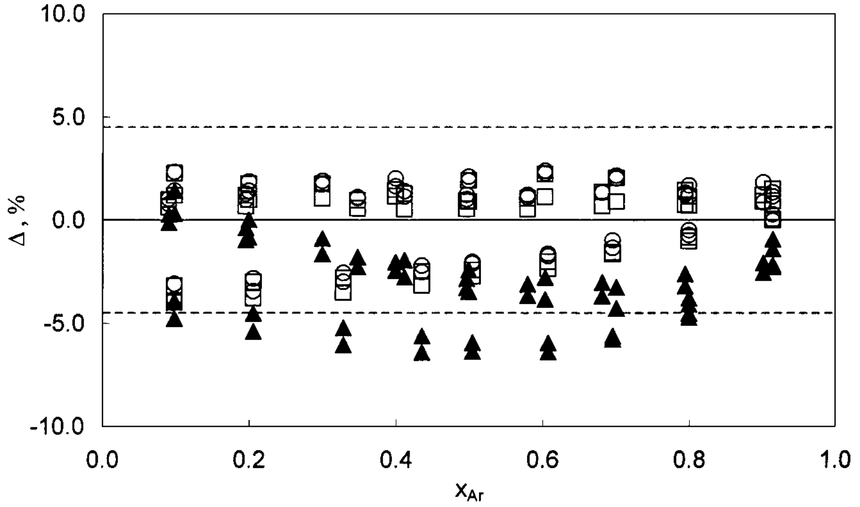

Fig. 6. Deviations, $\Delta = 100(\lambda_{\text{pred.}} - \lambda_{\text{exp.}})/\lambda_{\text{exp.}}$, of the predicted values of thermal conductivity from the experimental data [44, 45] for argon–molecule mixtures. (□) HE method; (○) SVW method; (▲) MSW method.

are available. Figure 6 illustrates the deviations of the thermal conductivity predicted by the three methods from the experimental data as a function of the mole fraction of argon. Both the HE and the SVW methods predict the experimental data with the same rms deviation of 1.8% and maximum deviations of −4.0 and −3.8%, respectively. Thus, all the experimental points are reproduced within a combined uncertainty of ±4.5% as indicated in Fig. 6 by the dashed lines. The MSW method also predicts the data very well, with an rms deviation of 3.7% and a maximum deviation of −6.4%. No temperature trends are observed for any of the three methods.

Parkinson and co-workers have also reported [44, 45] thermal conductivity data for binary mixtures consisting of Ar and cyclopropane, propene, butene, and isopentane. For the pure hydrocarbon components of these mixtures, there are no available corresponding-states scaling parameters, nor are there any recommended correlations of the thermal conductivity. In principle the scaling parameters for the hydrocarbons can be estimated from the Lennard–Jones 12–6 scaling parameters [45] or, if available, from the viscosity measurements over a range of temperatures. It was felt that this procedure is not entirely satisfactory and is bound to lead to a deterioration of the overall accuracy of both the HE and the SVW methods. Thus, these data were not used to compare the predictions of the three methods.

3.2. Binary Molecular Mixtures

The thermal conductivity data on binary molecular mixtures are less plentiful than those for atom–molecule mixtures, but at least for simple gas mixtures there exist a number of reliable and accurate measurements. A literature search indicated that the data from five laboratories, consisting of 102 data points, can be used for the purposes of testing the accuracy of the three prediction methods.

Kestin and his collaborators and Wakeham and his co-workers measured the thermal conductivity of binary mixtures of H_2–N_2,CO,CO_2,CH_4 [41, 46, 47], CH_4–N_2,CO,CO_2 [48–50], and N_2–CO [51] by means of the transient hot-wire technique under near-room temperature conditions. The resulting data set, consisting of 27 data points, with an assigned accuracy of ±0.5%, represents high-precision primary data. Figure 7 illustrates the deviations of the thermal conductivity predicted by the three methods from the experimental data as a function of the mole fraction of the lighter component in the binary mixture. The HE and SVW methods do remarkably well, reproducing the experimental data with an rms deviation of 1.7 and 1.5%, respectively; the maximum deviation observed is −3.1% for HE and 3.0% for SVW. In fact both the HE and the SVW methods reproduce all the data within a combined uncertainty of ±3%, as indicated by the two dashed lines in Fig. 7. The MSW method reproduces

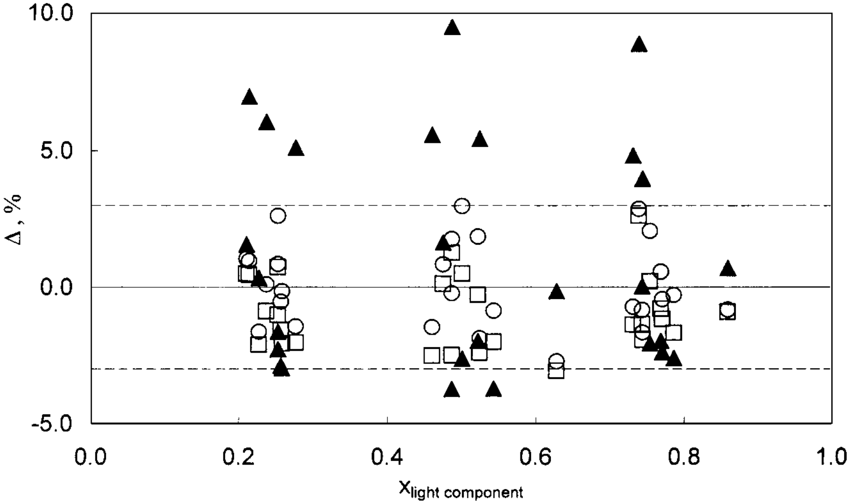

Fig. 7. Deviations, $\Delta = 100(\lambda_{\text{pred.}} - \lambda_{\text{exp.}})/\lambda_{\text{exp.}}$, of the predicted values of thermal conductivity from the experimental data [41, 46–51] for molecule–molecule mixtures. (□) HE method; (○) SVW method; (▲) MSW method.

the experimental data with an rms deviation of 4.5% and a maximum deviation of 9.5%. In fact for nonhydrogen mixtures, the MSW method does reasonably well, underestimating the experimental data by ±2 to 3%, while for hydrogen mixtures the deviations increase up to ±8 to 9%.

Saxena and co-workers have also performed measurements on molecular mixtures [52]. They have measured the thermal conductivity of 15 binary mixtures of H_2, N_2, and O_2 in the temperature range 313 to 418 K, producing 45 data points to which we have ascribed an accuracy of ±2%, following the discussion in Section 3.1. To minimize the uncertainty associated with hydrogen-rich mixtures, as described in Section 3.1, the values of the thermal conductivity of pure hydrogen as quoted by Saxena and co-workers [42] have been used in all three prediction methods.

Figure 8 illustrates the deviations of the thermal conductivity predicted by the three methods from the experimental data as a function of the mole fraction of the lighter component in the binary mixture. No systematic trends with increasing mole fraction are observed. The SVW method produces the best agreement with the experimental data. The rms deviation is 2.1%, while the maximum deviation is −4.9%. Furthermore, the whole set of data is reproduced within the combined uncertainty of the method and the experimental data, as indicated by the dashed lines. The HE method reproduces the experimental data with a higher rms deviation of

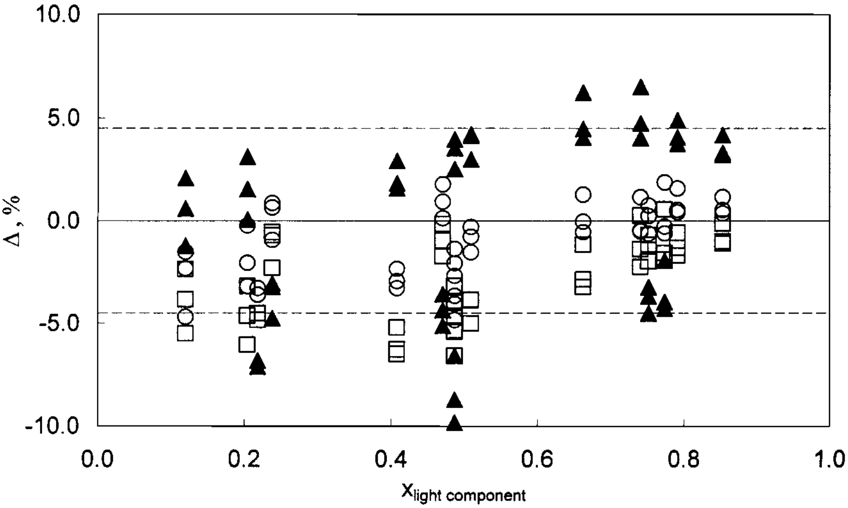

Fig. 8. Deviations, $\Delta = 100(\lambda_{\text{pred.}} - \lambda_{\text{exp.}})/\lambda_{\text{exp.}}$, of the predicted values of thermal conductivity from the experimental data [52] for molecule–molecule mixtures. (□) HE method; (○) SVW method; (▲) MSW method.

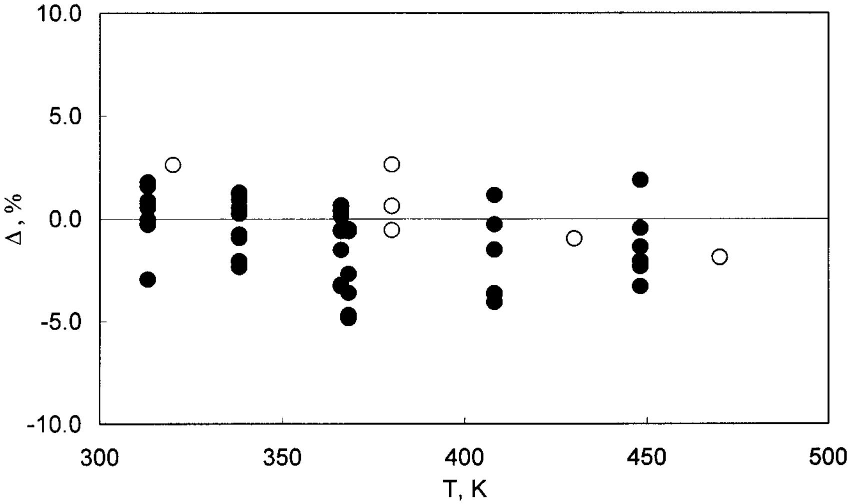

Fig. 9. Deviations, $\Delta = 100(\lambda_{\text{pred.}} - \lambda_{\text{exp.}})/\lambda_{\text{exp.}}$, of the predicted values of thermal conductivity from the experimental data [52, 53] as a function of temperature, for molecule–molecule mixtures. SVW method: (●) Ref. 52; (○) Ref. 53.

3.6% and a maximum deviation of −6.6%, marginally exceeding the combined uncertainty. The MSW method also produces reasonable agreement, with an rms deviation of 4.5% and a maximum deviation of −10%.

Deviations of the predicted thermal conductivity from the experimental data of Ref. 52 as a function of temperature are illustrated in Fig. 9; for clarity, only the trends for the SVW method are shown. No systematic trends are observed, and, as in the atom–molecule case, no deterioration of the SVW predictions with increasing temperature is evident. Both the HE and the MSW methods exhibit similar behavior, and their accuracy does not decrease when the predictions are made at temperatures other than room temperature.

Johns et al. [53] have also performed a series of measurements on molecular binary mixtures, namely, nitrogen–carbon dioxide. The measurements were performed in a hot-wire apparatus, capable of a claimed accuracy of ±1%, at 380 K as a function of mole fraction and at three other temperatures in the range 320 to 470 K at one mole fraction at each temperature. The HE and SVW schemes reproduce the data with an rms deviation of 2.0%, while MSW reproduces the data with an rms deviation of 5.4%. Figure 9 also illustrates the deviations of the thermal conductivity predicted by the SVW method from the experimental data of Johns et al. [53] as a function of temperature. All the experimental points are reproduced within the accuracy of the SVW scheme, and no deterioration in the predictions is observed with increasing temperature. Similar conclusions about the temperature trend can be drawn about the HE and MSW schemes.

Roder and Friend [54] have performed extensive measurements on the methane–ethane mixture by means of the transient hot-wire technique. The zero-density thermal conductivity data bank consists of 28 data points, pertaining to three binary mixtures, covering the temperature range $194 < T$ (K) < 325 with a claimed accuracy of ±1.6%. It is likely that the accuracy of these data is slightly lower than that claimed, and for the purposes of this work the data have been assigned an accuracy of ±2%. This conclusion is based on the examination of the data for pure ethane, obtained in the same apparatus [55], which exhibit a strong temperature trend, of the order of ±2.5%, compared with the recommended correlation for ethane [23]. In comparing the predictions of the three methods with the experimental data, a lower-limit temperature of 225 K has been set, which corresponds to the lower limit of validity of the recommended ethane correlation [23]. Thus, the data set used in comparison consisted of 24 data points. Figure 10 illustrates the deviations of the thermal conductivity predicted by the three methods from the experimental data as a function of temperature. The HE method does remarkably well, reproducing all the data with an rms deviation of 1.2% and a maximum deviation of 2.2%, well within the combined uncertainty, as indicated by the dashed

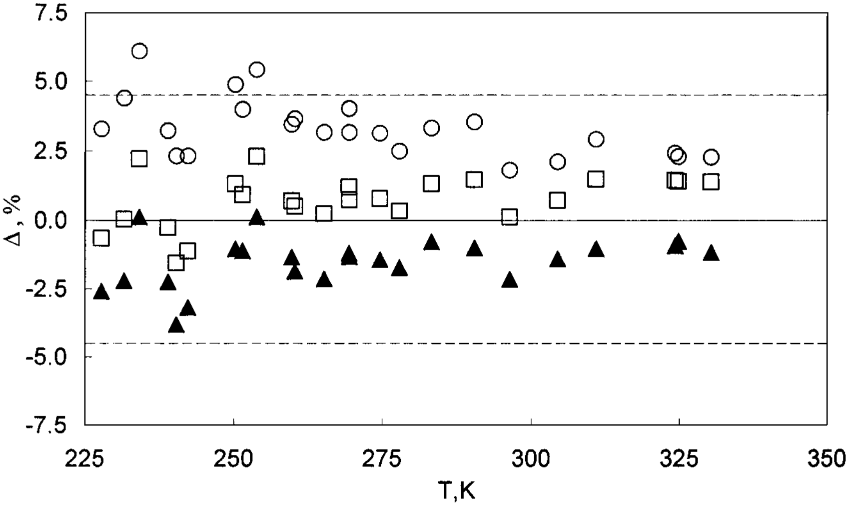

Fig. 10. Deviations, $\Delta = 100(\lambda_{\text{pred.}} - \lambda_{\text{exp.}})/\lambda_{\text{exp.}}$, of the predicted values of thermal conductivity from the experimental data [54] for methane–ethane mixtures. (□) HE method; (○) SVW method; (▲) MSW method.

lines in Fig. 10. The SVW method overpredicts the data by an average of 2 to 4%, with an rms deviation of 3.6% and a maximum deviation of 6.1%. Although, these deviations are still within the combined uncertainty, the relative failure of the SVW method compared with the HE method is surprising, especially in light of the very good agreement with the other data examined. The predictions of the MSW method show a very good agreement with the data, with an rms deviation of 1.8% and a maximum deviation of −3.8%, although the data are, in general, underpredicted.

3.3. Multicomponent Mixtures

There are only a few measurements available for multicomponent mixtures, and they tend to involve primarily monatomic species. Therefore the testing of the present method had to be carried out with a very limited set of data, consisting of 36 data points covering three ternary and one quaternary systems, based on the measurements of Saxena and his collaborators. Saxena and Gupta [52] performed measurements on two ternary N_2–H_2–O_2 mixtures in the temperature range 313 to 366 K, while Tondon and Saxena [56] performed measurements on three N_2–H_2–Ne mixtures, two Ar–Kr–H_2 mixtures, and three O_2–N_2–Ne in the temperature range 313 to 448 K. Also, Tondon and Saxena [57] performed measurements on two quaternary N_2–H_2–Ne–Ar mixtures in the temperature range 313 to 366 K. As discussed in Section 3.1, the accuracy of the data is estimated to be ±2%. Figure 11 illustrates the deviations of the thermal conductivity predicted by the three methods from the experimental data as a function of the mole fraction of the lightest component in each mixture. All three methods reproduce the data reasonable well. The SVW method exhibits the smallest rms deviation, 3.6%, while the HE and MSW methods reproduce the data with rms deviations of 3.9 and 6.5%, respectively. Examination of the individual data sets relating to a particular mixture indicates no systematic trends, except in the case of the hydrogen-rich Ar–Kr–H_2 mixture. The three data points, as illustrated in Fig. 11 at $x_{H_2} = 0.57$, are overpredicted by the HE and SVW methods by 5 to 11% and by the MSW method by 11 to 19% as a function of increasing temperature. Such large deviations, especially for the SVW and HE methods, have not been observed for any other system, nor are they observed for the hydrogen-lean Ar–Kr–H_2 mixture. Furthermore, there is nothing exceptional about this mixture, so it seems likely that this particular data set is less accurate than the rest of the data. If this set of three data points were not used in the comparison, the rms deviations of the three methods, HE, SVW, and MSW, will decrease considerably, to 3.1, 2.6, and 4.4%, respectively. In this case, both the HE and the SVW methods reproduce the data within ±5.5%, which is marginally outside the combined uncertainty of

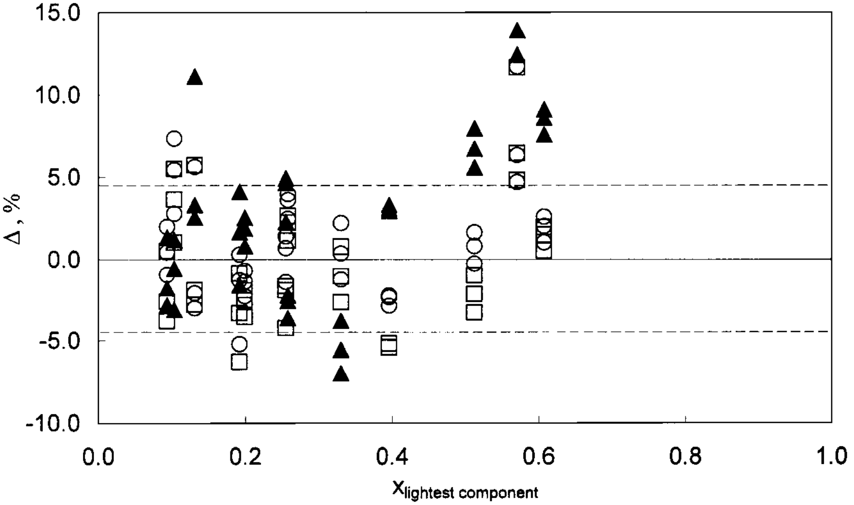

Fig. 11. Deviations, $\Delta = 100(\lambda_{\text{pred.}} - \lambda_{\text{exp.}})/\lambda_{\text{exp.}}$, of the predicted values of thermal conductivity from the experimental data [52, 56, 57] for multi-component mixtures. (□) HE method; (○) SVW method; (▲) MSW method.

the experimental data and the methods, as indicated by the dashed lines; the MSW method reproduces the data within ±8%.

3.4. Overall Agreement

Table II summarizes the overall predictions of the three methods, evaluated on the basis of comparison with 372 experimental data points, as described previously. Although the results presented in Table II indicate that the SVW method is more accurate than the HE method, the differences are marginal and it would be prudent to assign them the same accuracy. Thus, on the evidence presented in this paper, both methods are capable of predicting the thermal conductivity of mixtures within ±2 to 3%.

Table II. Comparison of the Overall Uncertainty of the Three Methods

	Deviation		Number of points	
Method	rms	Max.	5–10%	>10%
HE	2.3%	−6.6%	21	0
SVW	2.0%	6.1%	11	0
SW	4.3%	14.1%	51	4

The prediction power of the MSW is substantially worse than that of the other two methods, and the accuracy is estimated to be ±6 to 8%.

4. DISCUSSION

To appreciate fully the very good agreement obtained, primarily for the HE and SVW methods, it is useful to examine the accuracy of the simplifications made in deriving all three methods.

All three methods have been derived from the first-order kinetic theory expressions. As discussed for the SVW method [6], the neglect of the higher-order terms, for most systems, introduces an error of below 1%, although for some equimolar mixtures of a high mass ratio, a higher-order correction can contribute up to 3%. At present it is not practicable to incorporate, into the three methods, the spherical values of the higher-order correction factor because of the complexity of the expressions for mixtures [33]. Instead, it is expected that the use of experimental thermal conductivity values of pure species in Eqs. (5), (8), (10), and (12), rather than those in the first-order approximation, will produce a compensating effect.

The error introduced by invoking the spherical approximation is very difficult to estimate, since only a few, limited calculations are available for mixtures [58]. The calculations involved comparing the full thermal conductivity of inert gas–N_2 mixtures, obtained by the classical trajectory method [59–61], with that given by the SVW method. On the basis of those calculations, a ±2% error is introduced in mixture thermal conductivity, although it would not be surprising if, for some systems, the spherical approximation produces an error as large as 5%.

The errors associated with the approximations made in deriving the MSW method are difficult to quantify, but some analysis of the neglect of $L_{qq'}$ elements of the determinant indicate that errors of ±5% are not uncommon.

The sensitivity of the mixture thermal conductivity to the estimated uncertainty of the physical quantities used as input is better understood, at least for the SVW method [6]. On the basis of that analysis, for the mixtures considered in this work, the overall error in the mixture thermal conductivity, due to uncertainties in the ideal-gas, isobaric heat capacity, the thermal conductivity of the pure species, the interaction viscosity, and the ratios $A^*_{qq'}$ and $B^*_{qq'}$ can be as high as 6%.

There is therefore a wide scope for large, overall errors in thermal conductivity estimated by means of the HE and SVW methods and, especially, by the MSW method. Nevertheless, the very good accuracy obtained in examining a wide range of experimental data covering a variety of different mixtures indicates that the propagation of errors is minimized. In principle, all three methods rely on values of the pure thermal conductivity of the species present to predict the thermal conductivity of the mixture. Thus, in essence, they are interpolation methods that make use of different, theoretically based formulae to perform the calculations at specified mole fractions. It seems that the use of such interpolation schemes acts in a way that the uncertainties introduced by simplifications and input data compensate one another to a great extent.

5. CONCLUSIONS

Three prediction methods for evaluating the thermal conductivity of nonpolar, multicomponent molecular mixtures in the dilute-gas limit have been examined, namely, the Mason–Saxena–Wassiljewa (MSW), Hirschfelder–Eucken (HE), and Schreiber–Vesovic–Wakeham (SVW) methods. All the methods are based on formal kinetic theory, adequately simplified to allow for workable expressions, and thus, at least in principle, all should provide an accurate way of predicting thermal conductivity.

The predictions of all three methods have been tested against the available, accurate experimental data. The data consisted of 372 data points with a quoted accuracy ranging from ±0.5 to ±2.0%, covering 42 mixtures over a substantial temperature range. The maximum deviations observed between the predicted and the experimental thermal conductivity data for the HE and SVW methods are of the order of 6%, with rms deviations of the order of 2%. This is an excellent agreement, which, taking into account the accuracy of the experimental data, demonstrates that both the HE and the SVW methods are capable of generating thermal conductivity values with an uncertainty of ±2 to 3%.

The MSW method, which is currently the recommended method for engineering purposes, seems much worse. The maximum deviations observed are in excess of 10%, while the overall rms deviation is 4.3%. Based on the analysis carried out in this work, the accuracy of the MSW method is estimated to be of the order of ±6 to 8%.

The results obtained indicate that both the HE and the SVW prediction methods can form the basis of an accurate, general method suitable for engineering applications and, as such, replace the MSW method, at least for mixtures of simple molecules for which all the input parameters are known.

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