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## **DRFM: A New Package for the Evaluation of Gas-Phase-Transport Properties**

Phillip H. Paul

Prepared by  
Sandia National Laboratories  
Albuquerque, New Mexico 87185 and Livermore, California 94550

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OF GAS-PHASE TRANSPORT PROPERTIES.**

**Phillip H. Paul, 8351**  
**Sandia National Laboratories**  
**Livermore CA**

**Abstract** This report describes a complete and modernized procedure to evaluate pure species, binary and mixture transport properties of gases in the low density limit. This includes a description of the relationships used to calculate these quantities and the means used to obtain the necessary input data. The purpose of this work is to rectify certain limitations of previous transport packages, specifically: to employ collision integrals suitable for high temperatures, to modernize the mixture formula, and to modernize the input data base. This report includes a set of input parameters for: the species involved in H<sub>2</sub> -, CO - air combustion, the noble gases, methane and the oxides of nitrogen.

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**DRFM: A NEW PACKAGE FOR THE EVALUATION  
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**Introduction** This work is directed at updating the current transport packages (e.g. MIXRUN [1], CHEMKIN's TRANLIB [2] and EGLIB[3]) as used for calculation of the transport properties of pure species and mixtures. This work grew out of a growing awareness that the previous package gave predicted values that were well outside of the acceptable range of tolerable error. The result of this work is a complete replacement of the old packages. The new package incorporates a number of advances including a more physically realistic molecular potential as based on the recent works of Mason and co-workers, a modernized data base including a self consistent set of parameters for radical species (albeit some are calculated but at least none are guessed), and a modernization of the means of computing mixture properties as based on the recent works of Ern and Giovangigli [4]. The current transport package in CHEMKIN was released in 1986 and is largely based on the works of Mason and co-workers (early 60's), the basic structure employed and much of the data base comes from the works of Warnatz [1,5]. This was and remains a solid tool for gas-phase simulations and by its existence has provided one of the fundamental supports for research into reacting flows.

A test was performed by using the existing CHEMKIN package to predict pure species viscosity and thermal conductivity and equimolar thermal diffusion factors, for stable species, as functions of temperature. The results were then compared to the values tabulated by Bzowski *et al.* [6] and by Uribe *et al.* [7]. In general the predicted thermal conductivity compared poorly (for some of the stable species deviations exceeded 20%). Predictions for viscosity were somewhat better with the worst case being H<sub>2</sub> which was predicted 15% low of the experimental value at 2000K when compared to the data tabulated by Assael *et al.* [8]. The predictions for the thermal diffusion factor were quite poor with differences exceeding 100% for mixtures with disparate molecular weights.

The following presents a complete and updated set of procedures for the calculation of pure species and mixture transport properties, including: thermal conductivity, binary diffusivity, thermal diffusion factor and shear viscosity. These procedures have been implemented in a new transport code (named DRFM for 'dipole reduced formalism') which as of this writing has little resemblance to existing transport packages and is thus not (repeat not) plug compatible with application programs that employ these packages. This is due in part to the need to transfer more information between the preprocessor and

the actual property functions used in the application codes, and the desire to make the new transport code suitable for use with parallelized codes.

**Collision Integrals** The transport properties are expressed in terms of the collision integrals  $\Omega_{ij}^{(1,1)*}$  and  $\Omega_{ij}^{(2,2)*}$  and the higher order functionals  $A_{ij}^*$ ,  $B_{ij}^*$ ,  $C_{ij}^*$  and  $E_{ij}^*$  which are functions of temperature and normalized molecular parameters for the collision partners (here indicated by the subscripts). In the previous implementations (e.g. MIXRUN, CHEMKIN's TRANLIB and EGLIB) the collision integrals were developed from a Stockmayer 12-6-3 potential which reduces to the more common Lenard-Jones 12-6 potential for all but polar-polar molecule interactions. One of the input parameters for every pure species is the Lenard-Jones (LJ) well depth,  $\epsilon$ , which is an energy usually expressed in Kelvins. As part of the calculation of transport properties it is necessary to employ a set of combination rules which provide the well depth (and other molecular parameters) for non-identical collision partners. The simplest combination rule for well depth gives  $\epsilon_{ij} \approx \sqrt{\epsilon_i \epsilon_j}$ . More accurate combination rules are given below. It is well known that the LJ inverse 12<sup>th</sup> power repulsive component becomes too stiff or hard for  $k_B T > 10\epsilon$ . An exponential repulsive component is required to accurately calculate transport properties at higher collision energies hence at higher temperatures. This is particularly important for combustion applications in which case species with relatively small well depths, like H and H<sub>2</sub>, are important at high temperatures. For H, H<sub>2</sub> and N<sub>2</sub> the well depths are of order 5, 25 and 98 K, respectively. Thus an exponential repulsive potential is required to accurately calculate diffusion of H into N<sub>2</sub> or viscosity of pure H<sub>2</sub> for temperatures above of order 250 K. It is completely possible to apply the LJ-based collision integrals for  $k_B T > 10\epsilon$  however this amounts to a curve fit in which case molecular parameters obtained, by fitting H<sub>2</sub> viscosity data (say), cannot be used beyond the curve fit. Formally, parameters obtained outside the range of valid application of the potential cannot be subsequently used in accordance with the principle of corresponding states to derive binary diffusion coefficients or mixture properties.

Following the prescription of Bzowski *et al.* [6] the collision integrals in the new package are broken into two ranges, a Lenard-Jones 12-6 for  $k_B T < 10\epsilon$  and an exponential repulsive for  $k_B T > 10\epsilon$ . Polynomial expressions for the collision integrals are given by Bzowski *et al.* [6] which are appropriately spliced together over the full range of temperatures. These polynomials (reproduced here in Appendix F for completeness) have been analytically combined to obtain the higher order collision functions. The non polar-polar collision integrals are thus functions of three molecular parameters (in CHEMKIN they are a function of a single parameter, the reduced temperature  $T^* = k_B T / \epsilon$ ), being  $T^*$  and the normalized energy  $V^* = V / \epsilon$  and radius  $\rho^* = \rho / \sigma$  for the exponential potential. It is important to note that the relations used in the new package, as given by Bzowski *et al.* [6], apply for  $T^*$  greater than unity. They make this restriction in that at lower reduced temperatures quantum effects become important. They do provide expressions for collision integrals for the noble gases applicable for  $T^* < 1$ .

**Quantum effects** Quantum effects become important when the size parameter,  $\sigma$ , approaches the de Broglie wavelength. In kinetic theory it is common practice to define a reduced deBoer parameter

$$\Lambda_{ij}^* = \frac{h}{\sigma_{ij} (m_{ij} k_B \varepsilon_{ij})^{1/2}} \quad (1)$$

which is the ratio of the de Broglie wavelength to the size parameter for a kinetic energy equal to the well depth. The gas behaves classically at all temperatures in the limit that  $\Lambda_{ij}^*$  goes to zero. Whereas quantum effects becomes significant for large values of  $\Lambda_{ij}^*$  as  $T_{ij}^*$  gets small. For example, quantum effects can be safely ignored for Ne-Ar mixtures ( $\Lambda^* = 0.34$ ,  $\varepsilon = 64\text{K}$ ) for temperatures above 30K or  $T^* > 1/2$ , whereas quantum effects become important for  $^3\text{He}$ - $^4\text{He}$  mixtures ( $\Lambda^* = 2.81$ ,  $\varepsilon = 10.4\text{K}$ ) for temperatures below 20 to 30 K or  $T^* = 2$  to 3. At present there is no consistent means of treating the collision integrals for other than the noble gases below  $T^* = 1$ .

In the new package we have introduced polynomial extensions of the representations for the classical collision integrals covering the range  $0.2 \leq T^* < 1.0$  which are analytic to second order with the representations given by Bzowski *et al* [6] through  $T^* = 1$ . This is done to be able to call into the code and get an appropriate values for species like  $\text{H}_2\text{O}$  ( $\Lambda^* = 0.2$ ,  $\varepsilon = 535\text{K}$ ) at ambient temperature.

**Exponential repulsive potentials, a case in point: Normal Hydrogen** Assael *et al.* [8] applied LJ based collision integrals to fit  $\text{H}_2$  viscosity data over the range  $20 < T < 2200\text{K}$ , to find  $\varepsilon_{\text{H}_2} = 33.3 \text{ K}$  and  $\sigma_{\text{H}_2} = 2.968\text{\AA}$ . However their fit shows strong systematic departures from the measurements at both low and high temperatures. Whereas restricting the fit to  $1 \leq T^* \leq 10$  we find  $\varepsilon_{\text{H}_2} = 23.957 \text{ K}$  and  $\sigma_{\text{H}_2} = 3.063\text{\AA}$ . From these parameters and the potential of Partridge *et al.* [9] we obtain  $\rho_{\text{H}_2}^* = 0.103$  and  $V_{\text{H}_2}^* = 1.14 \times 10^5$ . With this new parameter set, the deviations in the calculated values are less than the scatter in the experimental data over the entire range of temperatures.

**Exponential repulsive potentials, a case in point: Atomic Hydrogen** To obtain input data for atomic hydrogen, Dixon-Lewis [10] made use of the LJ radius estimated by Svehla [11]  $\sigma_{\text{H}} = 2.07 \text{ \AA}$ , and applied LJ based collision integrals to fit the diffusion coefficient measured by Clifford *et al.* [12] (i.e.  $D_{\text{H-N}_2} = 1.35 \pm 0.3 \text{ cm}^2/\text{s}$  at one atm. and 300K) to find  $\varepsilon_{\text{H}} = 37.0\text{K}$ . The well depth was revised upward in CHEMKIN to a value of  $\varepsilon_{\text{H}} = 145.0\text{K}$  (the result of assuming  $\sigma_{\text{H}} = 2.07 \text{ \AA}$  and fitting to H- $\text{H}_2$  data at 300K). Wang and Law [13] have observed that these input data for H atom are not consistent with results obtained from other experiments and calculations, and have suggested values of  $\sigma_{\text{H}} = 3.52 \text{ \AA}$  and  $\varepsilon_{\text{H}} = 9.1 \text{ K}$ . In using these new values they calculated (again using transport properties based on LJ collision integrals) a net reduction in laminar flame speeds for  $\text{H}_2$ -air mixtures as compared to those predicted using the original parameter values in the CHEMKIN transport data base. This decrease in flame speed is a direct result of the modified parameters for H atom which yield a decrease in H atom diffusion rates.

Using recent beam data and more complete combination rules (than those employed by Wang and Law [13] ) we find values of  $\sigma_{\text{H}} = 3.288 \text{ \AA}$  and  $\varepsilon_{\text{H}} = 5.417 \text{ K}$  which if applied in the same fashion as Wang and Law [13] would yield a further a further reduction in the

H atom diffusion rates and hence a further reduction in the predicted flame speeds. However the *ab initio* calculations of transport properties by Stallcop *et al.* [14] for H-N<sub>2</sub> mixtures and by Clark and McCourt [15] for H-H<sub>2</sub> mixtures suggest quite the opposite, the H atom diffusion rates should be higher than predicted by CHEMKIN. The root of this discrepancy is the inadequacy of the LJ based collision cross sections to predict transport properties for  $T > 10\epsilon$ . Binary diffusion coefficients as calculated using collision integrals derived from an exponential repulsive potential and using input parameters obtained solely from beam data, are found to be in good agreement with the predictions of the *ab initio* calculations and with the reported diffusion coefficients measured for H into H<sub>2</sub>, N<sub>2</sub> and Ar at 300K.

**Polar-Polar Collision Integrals** The existing transport libraries employ a Stockmeyer potential specifically to handle polar-polar interactions. Essentially all of the molecular combustion radicals are strongly polar as is water. It is interesting to note that in the CHEMKIN data base only water, methanol, ammonia and CH<sub>3</sub>O are given as polar. As a result of having left most the dipole moment entries at zero, the use of this same data base with the more simple 12-6 potential would have achieved essentially the same result as the 12-6-3 potential with much less computational effort.

The Stockmeyer potential is not isotropic (i.e. it depends on relative molecular orientation) and is written in the form

$$\varphi_{ij}(r, \omega) = 4\epsilon \left( \left( \frac{\sigma}{r} \right)^{12} - \left( 1 + \xi_{ij}^* \zeta_{d-id}(\omega_{ij}) \right) \left( \frac{\sigma}{r} \right)^6 - \delta_{ij}^* \zeta_{d-d}(\omega_{ij}) \left( \frac{\sigma}{r} \right)^3 \right) \quad (2)$$

where the  $\zeta(\omega)$  represent the relative angle dependence in the dipole-induced dipole (d-id) and dipole-dipole (d-d) attractive terms. Monchick and Mason [16] evaluated collision integrals for all possible orientations and then by geometrically averaging the results over all angles obtained a new set of collision integrals as a function of two reduced parameters;  $T^* = T/\epsilon$  and  $\delta^* = \mu^2/2\epsilon\sigma^3$ . There was a great deal of discussion in the literature regarding the theoretical basis for this approach but the method has survived in essence because it appeared to work reasonably well for viscosity and binary diffusion of polar species. This approach could be extended to include the exponential repulsive potential, however this would require a massive tabulation of collision integrals as functions of 5 dimensionless parameters.

A number of simplifying alternatives to the formalism of Monchick and Mason [16] have been attempted. One is to take the values of  $\zeta_{d-d}(\omega)$  and  $\zeta_{d-id}(\omega)$  as constants. Another is to use a thermally orientation-averaged potential of the form

$$\langle \varphi(r) \rangle = \frac{\iiint \varphi(r, \omega) \exp(-\varphi(r, \omega)/k_B T) d\omega}{\iiint \exp(-\varphi(r, \omega)/k_B T) d\omega} \quad (3a)$$

This ‘central’ or ‘spherical’ potential can be expanded in a series which leaves to low order

$$\langle \varphi_{ij}(r) \rangle = 4\epsilon_{ij} \left( \left( \frac{\sigma_{ij}}{r} \right)^{12} - \left( \frac{\sigma_{ij}}{r} \right)^6 \left( 1 + \xi_{ij}^* + \frac{2\gamma}{3} \frac{\epsilon_{ij} \delta_{ij}^{*2}}{T} \right) \right) \quad (3b)$$

Formally the expansion provides a value of  $\gamma = 1$ . These alternatives turned out to work poorly because they strongly under- and over-estimated the dipole-dipole contributions. Similar results were observed by Singh and Das Gupta [17] who evaluated the viability of a like series expanded central potential for evaluating transport properties for collision pairs subject to strong dipole-quadrapole interactions.

Gray and Gubbins [18] observe that the low order terms in an expansion for an effective central potential should match those in an expansion for the thermodynamic properties and the centers pair correlation function of a system actually having a pure central potential. Taking this into account requires a value of  $\frac{1}{4} \leq \gamma \leq \frac{1}{2}$  which has the effect of mediating the strength of the dipole-dipole term. We have tested the ability of this formalism to fit experimental viscosity data for some 20 strongly polar molecules and find excellent results for a fixed value of  $\gamma = \frac{1}{4}$ . The LJ parameters recovered from the new fits for species with  $\delta^*$  less than of order unity are in reasonable agreement with those recovered by re-fitting the same data with a Stockmeyer potential. In every case tested the quality of the new fits (as evidenced by the residuals and confidence intervals for the fit parameters) were superior using the effective central potential with  $\gamma = \frac{1}{4}$  than those obtained using the Stockmeyer potential. It is interesting to note that in applying the Stockmeyer potential, Monchick and Mason [16] did not report fits for molecules having values of  $\delta^*$  greater than of order unity. The Stockmeyer fits for  $\delta^*$  greater than unity are found to be poor (for reference  $\delta^* = 2.1, 2.1, 2, 1.6, 1.2,$  and  $0.7$  for  $\text{CH}_3\text{F}, \text{HCN}, \text{CH}_3\text{CN}, \text{HF}, \text{H}_2\text{O},$  and  $\text{NH}_3$ , respectively). In contrast the fits using the effective central potential with  $\gamma = \frac{1}{4}$  work uniformly well for all of the polar species tested (over the range  $0.03 < \delta^* < 2.4$ ).

The important advantage gained in using the effective central potential is that the dipole-dipole and dipole-induced dipole terms can be incorporated directly into the collision integrals for non polar-polar interactions by defining effective LJ and exponential repulsive parameters. First, define the quantity

$$\chi_{ij} \equiv \frac{\alpha_i \mu_j^2 + \alpha_j \mu_i^2}{4\epsilon_{ij} \sigma_{ij}^6} \quad (4a)$$

which is dimensionless and is zero only if both species are non-polar. Then define

$$\Delta_{ij} \equiv \frac{\mu_i^2 \mu_j^2}{24\epsilon_{ij} \sigma_{ij}^6} \quad (4b)$$

which has units of energy (e.g. Kelvin) and is zero unless both species are polar. Then the effective parameters become

$$\varepsilon'_{ij} = \varepsilon_{ij} \left(1 + \chi_{ij} + \Delta_{ij}/T\right)^2 \quad (5a)$$

$$\sigma'_{ij} = \sigma_{ij} \left(1 + \chi_{ij} + \Delta_{ij}/T\right)^{-1/6} \quad (5b)$$

$$V'_{ij} = V_{ij}^* \left(1 + \chi_{ij} + \Delta_{ij}/T\right)^{-2} \quad (5c)$$

$$\rho'_{ij} = \rho_{ij}^* \left(1 + \chi_{ij} + \Delta_{ij}/T\right)^{1/6} \quad (5d)$$

As such the transport property calculation is in terms of 6 reduced parameters for every collision pair:  $\varepsilon_{ij}$ ,  $\sigma_{ij}$ ,  $V_{ij}^*$ ,  $\rho_{ij}^*$ ,  $\chi_{ij}$  and  $\Delta_{ij}$ .

**Combination Rules** The new transport data base includes 7 molecular parameters for each pure species. There are:

$\varepsilon$	Lenard-Jones well depth (K)
$\sigma$	Lenard-Jones radius (Å)
$V^* \equiv V/\varepsilon$	exponential (Born-Mayer) potential energy
$\rho^* \equiv \rho/\sigma$	exponential (Born-Mayer) potential radius
$\alpha$	molecular static polarizability (Å <sup>3</sup> )
$\mu$	molecular dipole moment (Debye)
$C_{6,i}^* \equiv C_6/\varepsilon\sigma^6$	normalized dispersion energy

A data base containing sets of parameters for a number of the species of interest in combustion and aerothermodynamic flows is given in Appendix B.

Following the prescriptions of Bzowski *et al.*, [6,19] and Tang and Toennies [20] the molecular parameters are combined according to the following rules:

- 1) Let  $a_i = \sigma_i(1 - (C_{6,i}^*/2.2)^{1/6})$  for all  $C_{6,i}^* < 2.2$  and  $a_i = 0$  otherwise
- 2) Determine  $\sigma_{ij} = (\sigma_i + \sigma_j)/2$
- 3) Let

$$X_{ij} = \frac{\alpha_i}{\alpha_j} \left( \frac{C_{6,j}}{C_{6,i}} \right)^{1/2} \quad (6a)$$

and then determine

$$\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j} \left( \frac{(\sigma_i - a_i)^3 (\sigma_j - a_j)^3}{(\sigma_{ij} - (a_i + a_j)/2)^6} \right)^{\frac{2}{\sqrt{X_{ij} + 1/X_{ij}}}} \quad (6b)$$

4) Determine

$$\rho_{ij}^* = \frac{\rho_i^* \sigma_i + \rho_j^* \sigma_j}{2\sigma_{ij}} \quad (6c)$$

5) Finally determine

$$V_{ij}^* = \frac{\rho_{ij}^*}{\varepsilon_{ij}} \left[ \frac{V_i}{\rho_i} \right]^{2\rho_{ij}^*} \left[ \frac{V_j}{\rho_j} \right]^{2\rho_{ij}^*} \quad (6d)$$

Note that in these combination rules, the ‘ \* ‘ superscript refers to normalized quantities whereas the absence of this superscript refers to a dimensioned quantity (e.g.  $\rho = \rho^* \sigma$  or  $C_6 = C_6^* \varepsilon \sigma^6$ ). Bzowski *et al.* [6,19] give a more sophisticated combination rule for  $\sigma_{ij}$  but the correction appears as less than 1% and is thus ignored here.

**Binary Diffusion** The binary diffusion coefficients,  $D_{ij}$ , are given by

$$nD_{ij} = \frac{3}{8} \sqrt{\frac{k_B T}{2\pi m_{ij}}} \frac{1 + d_{ij}}{\sigma_{ij}^2 \Omega_{ij}^{(1,1)*}} \quad (7)$$

here  $m_{ij} \equiv m_i m_j / (m_i + m_j)$  and  $n$  is the total number density. The higher order correction is in terms of the factor  $d_{ij}$  which depends on the mixture composition and has the form

$$d_{ij} = 1.3(6C_{ij}^* - 5)^2 \frac{c_i \alpha}{1 - c_i + c_i \alpha \beta} \quad (8a)$$

where  $c_i = x_i / (x_i + x_j)$  and

$$\alpha = \frac{\sqrt{2}}{8(1 + 1.8m_j/m_i)^2} \frac{\Omega_{ij}^{(1,1)*}}{\Omega_{ii}^{(2,2)*}} \quad (8b)$$

$$\beta = 10 \left( 1 + 1.8m_j/m_i + 3(m_j/m_i)^2 \right) \quad (8c)$$

The convention for evaluation of  $d_{ij}$  is to re-order  $i$  and  $j$  such that  $m_j \leq m_i$  (note that this reordering is only for the computation of  $d_{ij}$  and as such the  $D_{ij}$  remain symmetric under exchange of  $i$  and  $j$ ).

For the self diffusion coefficient (i.e. the case of  $i = j$ ) the correction is obtained by taking  $c_i = 1$  and  $m_i = m_j$ . The higher order correction is in general small being most important for the diffusion of a trace light species into a heavy partner. For a trace heavy or a trace slightly heavy species (e.g.  $x_i \ll x_j$  and  $m_j \ll m_i$  or  $m_j \approx m_i$ , respectively) then  $d_{ij}$  goes to zero. In contrast, for a trace slightly light or a trace light species (e.g.  $x_j \ll x_i$  and  $m_j \approx m_i$  or  $m_j \ll m_i$ , respectively) then  $d_{ij} \approx 1.3(6C_{ij}^* - 5)/58$  or  $d_{ij} \approx 1.3(6C_{ij}^* - 5)/10$ , respectively. The later case may amount to as much as a 10 percent increase in the binary diffusion coefficient.

**Shear Viscosity** The pure component shear viscosity is given by

$$\eta_i = \frac{5}{16} \sqrt{\frac{m_i k_B T}{\pi}} \frac{1 + h_i}{\sigma_{ii}^2 \Omega_{ii}^{(2,2)*}} \quad (9a)$$

with the correction term

$$h_i = \frac{3}{196} (8E_{ii}^* - 7)^2 \quad (9b)$$

To calculate mixture viscosity (discussed below) it is necessary to define a fictitious binary viscosity of the form

$$\eta_{ij} = \frac{5}{16} \sqrt{\frac{m_{ij} k_B T}{\pi}} \frac{1}{\sigma_{ij}^2 \Omega_{ij}^{(2,2)*}} \quad (10)$$

**Thermal Conductivity** Prior methods for calculating pure species thermal conductivity,  $\lambda$ , have been based upon: 1) kinetic theory which predicts that  $\lambda$  is closely related to the shear viscosity, and 2) the works of Eucken [21] who suggested that the persistence of transitional energy did not hold for energy carried by the molecular internal degrees of freedom, and thus that external and internal degrees of freedom could be treated separately. With these assumptions

$$\frac{m\lambda}{\eta} = \frac{5}{2} c_{v,tran} + f_{int} c_{int} \quad (11)$$

where  $c_v = c_{v,tran} + c_{int}$  is the heat capacity of the molecule, and  $f_{int}$  is the persistence-length ratio for internal energy. The common expressions for  $f_{int}$  are based on a first order theory which contains a number of approximations and omissions, such as the neglect of spin polarization, ‘complex’ collisions and certain correlations between internal energy states and relative transitional energy. With these simplifications the expression for  $\lambda$  and the mixture formulas contain a number of inelastic cross sections and relaxation times that are poorly or completely unknown.

Uribe *et. al.* [7] have proposed a correlation for pure species thermal conductivity and have applied it successfully to calculations for N<sub>2</sub>, CO, CO<sub>2</sub>, O<sub>2</sub>, NO, CH<sub>4</sub>, CF<sub>4</sub> and SF<sub>6</sub>. They note that the correlation cannot be applied to species like C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> which

have multiple coupled internal modes, beyond rotation, that can be excited in thermal collisions. A consideration of each internal mode requires a separate diffusion factor and a correction for mode-mode coupling. They observe that modes with long lifetimes can be considered independent (e.g.  $\tau_{\text{vib}} \gg \tau_{\text{rot}}$  in linear diatomic molecules). In NO an electronic mode is active but contributes only a small fraction to  $C_p$  and  $\tau_{\text{elec}} > 10\tau_{\text{rot}}$ , thus treating this mode as independent provides a reasonable approximation. The correlation for  $\lambda$  proposed by Uribe *et al.* [7] requires as input: 1) a knowledge of  $\eta(T)$ ,  $D_{ii}(T)$  and  $C_p(T)$ ; 2) molecular dipole and quadrupole moments; 3) molecular rotational constants; 4) LJ well depth; 5) a rotational collision number,  $Z_{\text{rot}}$ , at some temperature; and, 6) a spin-polarization parameter. They achieve reasonable success in predicting  $\lambda$  for HCl but note that the expression used for  $Z_{\text{rot}}(T)$  is based on a theory for homonuclear diatomics and thus may not extend well to polar species.

The previous means of calculating pure component thermal conductivity rely on the first approximation for the diffusion coefficient and ignore or use simple models for inelastic exchange and spin collisions. Exchange collisions being particularly important for polar molecules (e.g. for HCl, a 15 % error in predicted thermal conductivity at 300 K is incurred without explicit consideration of exchange collisions). Some transport packages do include an *ad hoc* but somewhat hidden correction for exchange effects in polar-polar collisions for particular species. It has become apparent that there is no general means to calculate thermal conductivity of pure species even given much more input data than supplied in the previous or new data bases. However both CHEMKIN and EGLIB require the capability to calculate thermal conductivity in order to calculate the multicomponent thermal conductivity of a mixture.

Hirschfelder *et al.* [22] give a relation for the thermal conductivity of a multicomponent mixture of monatomic gases in terms of a four-block L matrix. Subsequently Monchick, Pereira and Mason [23] extended this definition to employ a 9-block L matrix as a means of incorporating polyatomic species. This *Monchick, Pereira and Mason* formalism was adopted by Dixon-Lewis [10] and is the means employed to calculate multicomponent thermal conductivity in CHEMKIN and in EGLIB. The additional components of the 9-block L-matrix have an explicit dependence on the specific heats and diffusion coefficients of molecular internal modes, inelastic cross sections and relaxation times which describe both the pure species thermal conductivities and the interactions with unlike collision partners.

Muckenfuss and Curtiss [24] observed that the conductivity of a mixture of monatomic species as given by the 4-block L-matrix was obtained by mixing terms in the first and second approximation. They find a considerably simpler representation (solely in terms of the  $L^{11}$  block) for mixture thermal conductivity as a consequence of carrying the expansion to completion in the second approximation. Hirschfelder *et al.* [22, see notes added in 2<sup>nd</sup> printing] recommended adopting this representation. Hirschfelder [25] further recommended that the thermal conductivity of a multicomponent mixture containing polyatomic gases be expressed as a linear sum of the thermal conductivity of the mixture as if all the components were monatomic and the thermal conductivity due to internal degrees of freedom, in what is termed the *Hirschfelder-Eucken* formalism.

Uribe *et al.* [26] invoke three recent developments to obtain a predictive algorithm for mixture thermal conductivity:

- 1) The use of experimental or accurately calculated values for the pure species transport properties and dropping all other explicit dependencies on inelastic cross sections. This is in essence a return to the *Hirschfelder-Eucken* formalism. The diffusion coefficients for internal energy are replaced by ratios of ordinary mass diffusion coefficients. The use of this interpolation scheme corrects most of the deficiencies in the first order theory except for mixtures in which the masses of the components are very different.
- 2) Najafi *et al.* [27] investigated the properties of mixtures of noble gases. They suggest that the problem with disparate mass ratios can be largely corrected by using the proper diffusion coefficient rather than its first approximation.
- 3) Reliance on accurate data for binary diffusion coefficients, pure component viscosity and thermal conductivity.

Based on these, Uribe *et al.* [26] give a working formula for a mixture of N components

$$\lambda_{mix} = \lambda_{mix}^{(m)} + \sum_{i=1}^N \left( \frac{\lambda_i}{\lambda_i^{(m)}} - 1 \right) \frac{15k_B}{4m_i} \eta_i x_i \left[ x_i + \sum_{j=1, \neq i}^N x_j \frac{D_{ii}}{D_{ij}} \right]^{-1} \quad (12)$$

which is the relation proposed by Hirschfelder [25]. Here the  $x_i$  are the mole fractions of the constituents and the superscript (m) refers to a hypothetical thermal conductivity as if the molecule behaved like a monatomic gas, that is

$$\lambda_i^{(m)} \equiv 15k_B \eta_i / 4m_i \quad (13)$$

One result of using equation 12 for the mixture thermal conductivity is that it is no longer necessary to be able to decompose the pure species thermal conductivity into internal and external components for the purpose of calculating mixture properties. In the new package, the only requirement for pure species thermal conductivity is of the form

$$P_i \equiv \lambda_i / \lambda_i^{(m)} \quad (14)$$

We have adopted the procedure of supplying the function  $P_i(T)$  in the form of a polynomial curve fit as a part of the transport data base (see Appendix A). This data can be obtained by fitting to experimental data or to accurate calculations performed off-line, or in a pinch by assuming some simplified relation for the Prandtl number (see appendix A). Two of the input parameters required in the existing CHEMKIN transport data base,  $Z_{rot}$  and LIN, are thus no longer required having been replaced by the input curve fit for  $P_i$ .

**Thermal Diffusion Factors** The binary thermal diffusion factor,  $\alpha_{Tij}$ , contains a complicated dependence on composition, molecular mass and collision integrals. It is useful to define a reduced thermal diffusion factor,  $\alpha_R$ , via

$$\alpha_{Tij} \equiv \alpha_{Rij} \left( \frac{x_i S_1 - x_j S_2}{x_i^2 Q_1 + x_j^2 Q_2 + x_i x_j Q_{12}} \right) \quad (15)$$

where the functionals  $S$  and  $Q$  depend on collision integrals and the molecular masses of both species (the expression for these functions are given by Bzowski *et al.* [6] and are reproduced in Appendix E for completeness). In equation 15 the terms containing the  $S$  and  $Q$  carry the major dependencies on composition, molecular mass and the collision integrals that represent the interactions of like molecules. The reduced factor can be approximated by

$$\alpha_{Rij} \approx (6C_{ij}^* - 5)(1 + \kappa_{Tij}) \quad (16)$$

The quantity  $\kappa_T$  is described as small and is generally neglected in calculations [6]. The approximation for the reduced diffusion factor is then the difference between two numbers of similar magnitude and demonstrates the extreme sensitivity in  $\alpha_T$  to effects that occur in the interaction of unlike molecules. That the thermal diffusion factor is a second order transport property is best seen via the relation given by Marreno and Mason [28]

$$\alpha_{R,ij} \cong 4 - 2 \left( \frac{\partial \ln(D_{ij}^{(1)})}{\partial \ln(T)} \right)_P \quad (17)$$

where  $D_{ij}^{(1)}$  represents the binary diffusion coefficient in the first approximation. As a result of this sensitivity, Bzowski *et al.* [6] find that calculated values of  $\alpha_T$  may involve uncertainties that are an order of magnitude greater than the uncertainties in calculated values for viscosity or binary diffusion coefficients. They also note that errors in the experimental data for the thermal diffusion factor involve uncertainties of similar magnitude.

Unlike the other transport properties the thermal diffusion factor retains a strong dependence on both composition and temperature and thus must be evaluated ‘on-line’ in a reacting flow simulation. Paul and Warnatz [29] have expanded the thermal diffusion factor for large values of the ratio  $m_i/m_j$  and give a simplified relationship suitable for use in reacting flow simulation codes (see Appendix D).

**Calculation of Mixture Properties** The calculation of multicomponent diffusion coefficients (i.e.  $D_{i,j}^{(m)}$  the binary diffusion coefficient of the  $i$ ’th and  $j$ ’th species pair within a multicomponent mixture) requires the solution of a constrained, possibly singular, set of linear equations. As of this writing, only mixture-averaged diffusion coefficients are implemented in the new package, given by

$$D_{i,mix} = \frac{\sum_{j \neq i} x_j M_j}{\sum_j x_j M_j \sum_{j \neq i} x_j / D_{ij}} \quad (18)$$

Ern and Giovangigli [4] have investigated various means to implement the calculation of mixture properties, and they give an optimized algorithm for multicomponent diffusion coefficients.

Calculation of multicomponent viscosity and thermal conductivity also require the solution of systems of equations. However Ern and Giovangigli [4] give an analytical expression for the first iterate in a conjugate gradient solution

$$\eta_{mix} \cong \frac{\left( \sum_i x_i^2 / H_{ii} \right)^2}{\sum_i \sum_j \frac{x_i x_j}{H_{ii} H_{jj}} H_{ij}} \quad (19)$$

where the matrix elements are given by [6]

$$H_{ii} = \frac{x_i^2}{\eta_i} + \sum_{j=1 \neq i}^N \frac{2x_i x_j}{\eta_{ij}} \frac{m_i m_j}{(m_i + m_j)^2} \left( \frac{5}{3A_{ij}^*} + \frac{m_j}{m_i} \right) \quad (20a)$$

$$H_{ij} = \frac{-2x_i x_j}{\eta_{ij}} \frac{m_i m_j}{(m_i + m_j)^2} \left( \frac{5}{3A_{ij}^*} - 1 \right) \quad (20b)$$

There are several approximations which can be used for mixture viscosity. First Wilke '49 which is of the form [30]

$$\eta_{mix} = \sum_{i=1}^N x_i \eta_i \left( x_i + 1.385 \sum_{j \neq i} x_j \eta_j / m_j n D_{ij} \right)^{-1} \quad (21)$$

which is found to work reasonably well giving values within 5% of the full solution, albeit systematically high. The more common approximation is Wilke '50, which is used in CHEMKIN and is of the form [31]

$$\eta_{mix} = \sum_{i=1}^N x_i \eta_i \left( x_i + \sum_{j \neq i} x_j \Phi_{ij} \right)^{-1} \quad (22a)$$

with

$$\Phi_{ij} = \left( 1 + \left( \frac{m_j}{m_i} \right)^{1/4} \left( \frac{\eta_i}{\eta_j} \right)^{1/2} \right)^2 \left( 8 \left( 1 + \frac{m_i}{m_j} \right) \right)^{-1/2} \quad (22b)$$

This relation has been found to work as well as Wilke '49.

As noted above the calculation of multicomponent thermal conductivity is reduced in part to a calculation for a fictitious mixture of monatomic species. Thus the 1<sup>st</sup> iterate solution of Ern and Giovangigli [4] for mixture viscosity can be adapted to yield

$$\lambda_{mix}^{(m)} \cong \frac{-4 \left( \sum_i x_i^2 / L_{ii} \right)^2}{\sum_i \sum_j \frac{x_i x_j}{L_{ii} L_{jj}} L_{ij}} \quad (23a)$$

where the matrix elements are given by [26]

$$L_{ii} = \frac{-16m_i x_i^2}{15k_B \eta_i} - \frac{16x_i}{25k_B} \sum_{j=1 \neq i}^N \frac{x_j}{nD_{ij}} \frac{\frac{15}{2}m_i^2 + \frac{25}{4}m_j^2 - 3m_j^2 B_{ij}^* + 4m_i m_j A_{ij}^*}{(m_i + m_j)^2} \quad (23b)$$

$$L_{ij} = \frac{16x_i x_j}{25k_B nD_{ij}} \frac{m_i m_j}{(m_i + m_j)^2} \left( \frac{55}{4} - 3B_{ij}^* - 4A_{ij}^* \right) \quad (23c)$$

There are several mixture averaged or combination averaging formulations for thermal conductivity. Of these the one proposed by Mason and Saxena [32] is found to work reasonably well. They give the mixture thermal conductivity as

$$\lambda_{mix} = \sum_i x_i \lambda_i \left( x_i + 1.065 \sum_{j \neq i} x_j \Phi_{ij} \right)^{-1} \quad (24)$$

where the function  $\Phi_{ij}$  is the same as that given in Equation 22b.

The order 1/4 relation given by Ern and Giovangigli [4] also appears to work reasonably well,

$$\lambda_{mix} \cong \left( \sum_k x_k \lambda_k^{1/4} \right)^4 \quad (25)$$

The often used (1,-1) rules for computing mixture viscosity and thermal conductivity are found to work poorly. These are of the form

$$\lambda_{mix} = \frac{1}{2} \sum_j x_j \lambda_j + \frac{1}{2} \left( \sum_j x_j / \lambda_j \right)^{-1} \quad (26)$$

a similar (-1,1) relation can be written for  $\eta_{mix}$ .

While it is possible to calculate full multicomponent thermal diffusion coefficients using the methods given by Hirschfelder *et al.* [22] or by Ern and Giovangigli [4], the complexity and extra computational load may not be warranted given the inherent uncertainties in the thermal diffusion factors. Chapman and Cowling [33] give the mixture-averaged thermal diffusion ratio of the  $i$ 'th species into the mixture as

$$k_{Ti} = x_i \sum_{k=1}^N x_k \alpha_{ik} \quad (27)$$

where the sum of the  $k_{Ti}$  over the mixture is identically zero.

**Input Data Base** The data base for each pure species is composed of two parts; 1) a set of seven parameters to describe the molecular potential, and 2) a fit for the ratio  $\lambda / \lambda^{(m)}$ . Also required are the molecular weights. Note that the specific heats, which are required in the previous packages, are not required in the new package.

Bzowski *et al.* [6] report full parameter sets for N<sub>2</sub>, O<sub>2</sub>, NO, CO, CO<sub>2</sub>, CH<sub>4</sub>, CF<sub>4</sub>, SF<sub>6</sub> and the noble gases. They also give a partial parameter set (lacking  $V^*$  and  $\rho^*$ ) for C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub>. The beam data summarized by Tang & Toonies [20] has been used to provide a full parameter set for H. The beam data of Aquilanti *et al.* [34] has been similarly used to extract a full parameter set for O. A full parameter set for N was obtained from the beam data of Pirani and co-workers [35] and the *ab initio* potentials employed by Stallcop *et al.* [36]. A full set of parameters for H<sub>2</sub> was obtained by fitting viscosity data as tabulated and referenced by Assael *et al.* [8] and from the *ab initio* potentials given by Partridge *et al.* [9].

For almost any stable species and for a number of the combustion radicals, values for the polarizability and dipole moment can be found in the literature. To some extent values for C<sub>6</sub> are also available. Such information is available for a number of strongly polar molecules including H<sub>2</sub>O, NH<sub>3</sub>, NO<sub>2</sub>, HCN, SO<sub>2</sub>, OCS, H<sub>2</sub>S, C<sub>2</sub>H<sub>5</sub>OH, CH<sub>3</sub>OH, (CH<sub>3</sub>)<sub>2</sub>CO, (CH<sub>3</sub>)<sub>2</sub>O, HBr, HCl, HF, CH<sub>3</sub>CN and many fluoro-chloro-carbons. The available experimental viscosity data for all of these polar species has been refit using the new potential described above (where necessary, the data has been selected to limit the fits to  $1 \leq k_B T / \epsilon \leq 10$ ). Given  $\epsilon$ ,  $\sigma$ ,  $\alpha$ ,  $\mu$  and  $C_6^*$  a consistent set of  $V^*$  and  $\rho^*$  parameters has been obtained using the prescriptions of Tang and Toonies [37]. Their method requires higher order dispersion parameters which were obtained using the correlations  $C_8^* = (4/3)C_6^*(\alpha/\sigma^3)^{1/3}$  and  $C_{10}^* = (5/4)C_8^{*2}/C_6^*$ . This leaves a large number of species of interest for which there is no experimental transport data (e.g. OH, CH<sub>3</sub>, CH<sub>2</sub>O) and a good number of these for which even the polarizability and dipole moments are unknown.

We have performed a self-consistent fields (SCF) simulation using GAUSSIAN '92 [38] for the full set of species included in GRI mech 2.1 [39] which includes the standard set of species considered in  $C_{(1)}$  and  $C_{(2)}$  hydrocarbon combustion chemistry as well as a set of species associated with  $NO_x$  formation. The purpose of the simulation was to obtain dipole moments and polarizabilities for the entire set. Species with known values were carried as a test of the SCF simulation. Values for  $\epsilon$ ,  $\sigma$  and  $C_6^*$  were then calculated, given a polarizability and an equivalent oscillator number, following the prescriptions of Cambi *et al.* [40] Again species with known values were carried as a test. Finally values for  $V^*$  and  $\rho^*$  were calculated as described above and species with known values were carried as a test.

The data used for the polynomial fits for the ratio  $\lambda / \lambda^{(m)}$  were obtained from a number of sources including: For  $H_2O$  the data for viscosity and thermal conductivity were taken from the compilation by Matsunaga and Nagashima [41]. For  $H_2$  the data for viscosity and thermal conductivity were taken from the compilation of Assael *et al.* [8]. For many of the stable non-polar species the data was obtained from the tabulations of Bzowski *et al.* [6] and Uribe *et al.* [7] which were supplemented by the studies by Wakeman and co-workers [42]. Additional data was taken from the compilations by Beaton and Hewitt [43] and Touloukian and co-workers [44]. Fits for OH and  $H_2O_2$  are based on the application of the correlation model of Uribe *et al.* [7].

**Additions to the Data Base** For the parameter set: The preferable means is to begin by getting polarizability and dipole moment data from the literature, followed by fitting experimental viscosity data, restricted to  $1 < T^* < 10$ , to obtain the LJ parameters. Then determine a value for  $C_6^*$  from the fit parameters and a literature value for  $C_6$ . Finally, since beam data for the repulsive parameters or high temperature viscosity data to fit the repulsive parameters are very scarce, obtain  $V^*$  and  $\rho^*$  using the procedure described above. In the absence of any experimental data then the starting point must be an SCF calculation for the polarizability and dipole moment, and  $C_6$  if possible. Followed by the full procedures outlined above.

For the polynomial fits: For a monatomic species the answer is unity. For molecules again the best place to start is the literature. Failing this a high quality calculation can be used, of the form described by Uribe *et al.* [7]. For stable species a literature search is warranted. There is an extensive line of new studies into the properties of pure species which follow the works of Wakeham and co-workers [42]. These studies fit experimental transport data to what are termed Thijssen cross sections (which are denoted by a symbol like  $\mathfrak{D}$ ) which are related to but not the same as the transport cross sections described above.

**Accuracy** It is useful to consider the accuracy of the transport properties as predicted by the new package. The best predictions are for the properties of  $N_2$ ,  $O_2$ ,  $NO$ ,  $CO$ ,  $CO_2$ ,  $CH_4$ ,  $CF_4$ ,  $SF_6$  and the noble gases as based on the parameter sets, collision integrals and combination rules, given by Bzowski *et al.* [6]. They estimate accuracies of 1% for  $\eta_{mix}$ , 5% for  $D_{ij}$  and 25% for the thermal diffusion factor. For the viscosity of pure  $H_2$  the parameter set used in the new package gives values within 2% of the mean from 50 to

2200 K which is within the scatter in the experimental data. For the stable polar species, the fits for pure species viscosity are all within the experimental scatter which is less than 5% of the mean. For H-Ar, H-N<sub>2</sub>, H-H<sub>2</sub>, O-N<sub>2</sub> and O-Ar mixtures at 300 K, the predicted binary diffusion coefficients are within the experimental error bars, which are of order 25%.

For thermal conductivity, Uribe *et al.* [7] estimate an accuracy of 1.5% for 300-500K and 3% for lower/higher temperatures for N<sub>2</sub>, CO, CO<sub>2</sub>, N<sub>2</sub>O, CH<sub>4</sub>, CF<sub>4</sub> and SF<sub>6</sub>. For O<sub>2</sub> and NO they estimate accuracies of 3% for 300-500K and 5% for lower/higher temperatures

**Summary and *Caveat Emptor*** A complete and updated algorithm for calculating pure species and mixture transport properties has been described. The procedures used to obtain from the literature or to estimate the required input data (where not available in the literature) have also been described. The input data base will evolve as better experimental data becomes available and as the capability of SCF calculations evolves to provide better predictions of molecular parameters. To quote the CHEMKIN transport manual, with reference to the new data base, ‘This data base should not be viewed as the last word in transport properties. Instead, it is a good starting point from which the user will provide the best available data for his particular application.’ Having said this a useful lesson can be learned through an examination of a collection of CHEMKIN transport data bases as obtained from sources around the world. These reveal that the original data base parameters remain largely unchanged. These data bases appear to have been modified but only to introduce new species. In which case the new parameters were largely obtained by copying those for some other species that was thought to be ‘similar’. There are a number of examples of entries for silicon, sulfur and gallium bearing compounds with non-physical LJ well depths in excess of several thousands of Kelvins. Finally there is one entry for something with the name ‘E’ which is listed as a monatomic species with a LJ well depth of 850 K and a radius of 425.0 Å. Whatever it is, ‘E’ is certainly not any known atomic species and is simply too large to be a sub-atomic particle (also charged particles like electrons are completely outside of the realm of validity of the transport model), possibly an antibody.

One is left with a philosophical question: If the inclusion of terms for the Soret and Dufort effects are essential to accurately model flames and CVD processes (as some believe) and these effects are related to derivatives of diffusion coefficients, then, is it important to get the diffusion coefficients right? If so then this requires accurate input data, use of an appropriate potential and the possible use of higher order approximations to the transport properties. Otherwise, for reacting flow computations, it may be better and even closer to the correct answer to simply drop Soret and Dufort and even assume mixture properties equal to- and binary diffusion into-the largest component. The current work is an effort to address these issues. One must assume that given another 10 years or less this new package will be found lacking and need to be replaced.

**Future Developments** The only plans (by the author) for further work on this package are: 1) the refinement and testing of the development code and the application of this code to particular flow calculations as a means of investigating the impact of changes in the computation of the transport properties; and 2) the completion of the data base to

include species relevant in  $C_1$  and  $C_2$  hydrocarbon-air and  $NO_x$  chemistry as well as a number of other stable species of interest. As of this writing and as noted in the introduction, there are no formal plans in place to make this work a plug-compatible replacement for existing transport codes.

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## Appendix A: Thermal Conductivity Data Base

The polynomial representing the ratio  $\lambda/\lambda^{(m)}$  has the form

$$P(T) = \frac{C_1 + C_3 y + C_5 y^2}{1 + C_2 y + C_4 y^2 + C_6 y^3} \quad (\text{A1})$$

where  $y \equiv \ln(T)$  with  $T$  in Kelvins. The exact form of this polynomial was selected as the most compact form which adequately fit all the data for the species considered, and which displayed reasonable high and low temperature behavior outside of the range of available data. Coefficients are given in Table A1 as restricted to  $250 \text{ K} < T$ .

Table A1: Fit coefficient for the polynomial  $P_i$

	$C_1$	$C_2$	$C_3$	$C_4$	$C_5$	$C_6$
CH <sub>4</sub>	1.0124190	-.35704300	-.31147680	.04240417	.02568945	-.00160871
CO	0.9133026	-.3384788	-.26450910	.03584491	.01961665	-.00108565
CO <sub>2</sub>	1.5518010	-.2911856	-.54380010	.02452900	.05427209	0.0
H <sub>2</sub>	0.6123433	-.4207392	-.20620020	.05689904	.01770746	-.00238307
H <sub>2</sub> O	0.5931511	-.1095666	-.03359944	0.0	0.0	0.0
H <sub>2</sub> O <sub>2</sub>	0.0243916	-.2087738	0.07258789	.01300192	0.0	0.0
HO <sub>2</sub>	-0.422988	-.1763043	0.16050169	0.0113138	0.0	0.0
O <sub>2</sub>	0.7759023	-.3787674	-.23802530	.04579047	.01837284	-.00170918
OH	0.7319990	-.3669068	-.21580729	.04311154	.01598934	-.00157644
NO	0.9576946	-.3496382	-.28842830	.03810040	.02220485	-.00117394
NO <sub>2</sub>	3.6188066	-.1954056	-.65721492	0.0	0.0	0.0
N <sub>2</sub> O	1.6153915	-.2973629	-.55752424	.02503407	.05408830	0.0
N <sub>2</sub>	1.0367960	-.3182594	-.29313580	.03122558	.02160071	-.00079964

Monatomic species (e.g. H, O, N, He, Ne, Ar, Kr and Xe) have the value,  $P \equiv 1.0$ .

Hirschfelder [1] gives a simple relation for the Prandtl number in terms of the Eucken factor

$$\text{Pr} \cong (C_p/R) \left( 3.75 + f_{\text{int}} (C_p/R - 2.5) \right)^{-1} \quad (\text{A2})$$

and gives a value of  $f_{\text{int}} = 1.27$  for non-polar species. Which then gives

$$P \equiv \frac{4}{15} \frac{C_p}{R} \frac{1}{\text{Pr}} \cong 1 + \frac{2f_{\text{int}}}{3} \left( \frac{2}{5} \frac{C_p}{R} - 1 \right) \quad (\text{A3})$$

This type of expression can be used to constrain the behavior at high temperatures.

Recent studies by van den Oord and Korving [2] and by Wakeman and co-workers [3] have employed the set of collision integrals developed by Thijsse *et al.* [4] to quantify the various elastic and inelastic cross sections involved in transport processes. They have begun the process of re-evaluating single species transport data in terms of the Thijsse cross sections. Recently Schreiber *et al.* [5] have detailed expressions for mixture properties in terms of the Thijsse cross sections. However at the present time, there is inadequate cross section data to implement these new relationships.

Van den Oord and Korving [2] give a remarkably simple correlation for the Prandtl number given by which is applicable in the limit that the collision numbers for relaxation of internal modes are ordered such that  $Z_{\text{elec}}, Z_{\text{vib}} \gg Z_{\text{rot}}$ , then

$$\text{Pr} \cong \frac{2}{3} \left( 1 + \frac{4}{3\pi} \frac{c_{\text{rot}}}{Z_{\text{rot}}(T^*)} \frac{1}{R} \right) \quad (\text{A4})$$

In the limit that  $T^*$  is of order or greater than unity, the rotational internal energy has reached a high temperature limiting behavior in which case  $c_{\text{rot}}/R \approx 1$  and  $3/2$  for linear and nonlinear molecules, respectively. The temperature dependence in the rotational collision number can be expressed in terms of the correlation [6,3]

$$Z_{\text{rot}}(T^*) = Z_{\text{rot}}^{\infty} \left( 1 + \frac{\pi^{3/2}}{2T^{*1/2}} + \frac{2 + \pi^2/4}{T^*} + \frac{\pi^{3/2}}{2T^{*3/2}} \right)^{-1} \quad (\text{A5})$$

Thus the high temperature behavior of the Prandtl number can be estimated in terms of the species specific constant  $Z_{\text{rot}}^{\infty}$  (here the superscript refers to a temperature). Note that the previous CHEMKIN transport package required as input (to be used in thermal conductivity calculations) the parameter  $Z_{\text{rot}}^{300}$  which is directly related to  $Z_{\text{rot}}^{\infty}$  by this correlation given a value for the LJ well depth,  $\epsilon$ . Values for  $Z_{\text{rot}}^{\infty}$  can be obtained from the literature, or by analysis of experimental thermal conductivity data [e.g. 1,3,6], or possibly from spectroscopic measurements of rotational relaxation rates. This correlation also provides a means to constrain the high temperature range of the fits to physically meaningful values.

In terms of Thijsen cross sections the Prandtl number is given by [2]

$$\text{Pr} = \mathfrak{D}_{10E} / \mathfrak{D}_{20} = 2/3 (1 + \mathfrak{D}_{0010} / 2\mathfrak{D}_{20}) \quad (\text{A6})$$

where  $\mathfrak{D}_{0010}$  is an inelastic cross section describing the collision-induced interchange between translation and internal modes. The quantity  $Z_{\text{rot}} = 4 \mathfrak{D}_{20} / \pi \mathfrak{D}_{0001}$  where  $\mathfrak{D}_{0001}$  is a cross section for rotationally inelastic effects. Thus

$$\text{Pr} = (2/3)(1 + 2\mathfrak{D}_{0010} / (\pi \mathfrak{D}_{0001} Z_{\text{rot}})) \quad (\text{A7})$$

In the limit that  $Z_{\text{rot}} \ll Z_{\text{vib}}, Z_{\text{elec}}$  then  $\mathfrak{D}_{0010} / \mathfrak{D}_{0001} = 2c_{\text{rot}}/3k_B$ , which then yields equation A4 above.

## References

- 1) J. O. Hirschfelder, in *The 6<sup>th</sup> Symposium (International) on Combustion*, (Reinhold, NY, 1957), pp. 351-366.
- 2) R. J. van den Oord and J. Korving, *J. Chem. Phys.* **89**, 4333-4338 (1988).
- 3) V. Vesovic, W. A. Wakeham, G. A. Olchoway, J. V. Seugers, J. T. R. Watson and J. Millat, *J. Phys. Chem. Ref. Data* **19**, 763-808 (1990). J. Millat and W. A. Wakeham, *J. Phys. Chem. Ref. Data* **18**, 565-581 (1989). A. Fenghour, W. A. Wakeham, V. Vesovic, J. T. R. Watson, J. Millat and E. Vogel, *J. Phys. Chem. Ref. Data* **24**, 1649-1667 (1995).
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- 6) F. J. Uribe, E. A. Mason and J. Kestin, *Physica A* **156**, 467-491 (1989). F. J. Uribe, E. A. Mason and J. Kestin, *J. Phys. Chem. Ref. Data* **19**, 1123-1136 (1990).

## Appendix B: Molecular Potential Data Base

Table B1: Molecular potential parameters

species	$\epsilon$ (K)	$\sigma$ (Å)	$\mu$ (Debye)	$\alpha$ (Å <sup>3</sup> )	$V^*$	$\rho^*$	$C_6^*$
CH <sub>4</sub>	161.40	3.721	0	2.60	3.07E06	0.0698	2.100
CO	98.40	3.652	0.1098	1.95	5.31E04	0.1080	2.630
CO <sub>2</sub>	245.30	3.769	0	2.65	2.80E06	0.0720	1.860
H	5.42	3.288	0	0.667	3.70E04	0.1010	6.586
H <sub>2</sub>	23.96	3.063	0	0.803	1.14E05	0.1030	4.245
H <sub>2</sub> O	535.21	2.673	1.847	1.450	3.50E07	0.0640	1.612
H <sub>2</sub> O <sub>2</sub>	368.11	3.499	1.573	2.230	8.23E05	0.0830	2.322
HO <sub>2</sub>	365.56	3.433	2.09	1.950	5.30E05	0.0860	2.450
O	57.91	3.064	0	0.802	5.06E05	0.0840	2.740
O <sub>2</sub>	121.10	3.407	0	1.600	1.32E06	0.0745	2.270
OH	281.27	3.111	1.655	0.980	7.73E04	0.1010	3.226
He	10.40	2.610	0	0.200	8.50E05	0.0797	3.090
Ne	42.00	2.755	0	0.400	1.11E06	0.0784	2.594
Ar	143.20	3.350	0	1.642	5.12E05	0.0836	2.210
Kr	197.80	3.571	0	2.490	4.49E05	0.0831	2.164
Xe	274.00	3.885	0	4.040	3.90E05	0.0854	2.162
NO	125.00	3.474	0.1578	1.740	2.15E05	0.0883	2.200
N <sub>2</sub> O	266.80	3.703	0.1687	3.00	2.60E06	0.0730	1.890
NO <sub>2</sub>	204.88	3.922	0.32	3.00	3.97E06	0.0740	2.062
N	74.50	3.360	0	1.110	1.17E06	0.0810	1.600
N <sub>2</sub>	98.40	3.652	0	1.750	5.31E04	0.1080	2.180

## Appendix C: Extracting potential parameters from polar-polar viscosity data

To fit experimental viscosity data for polar species it is useful to first rescale the data according to

$$f(T) = \eta(T)(16/5)(\mu^2/2T)^{2/3}(\pi/mk_B T)^{1/2} \quad (\text{C1})$$

and then fit the function

$$f(T) = \left(\frac{\varepsilon\delta}{T}\right)^{2/3} \frac{(1 + \alpha\varepsilon\delta^2/\mu^2 + \varepsilon\delta^2/6T)^{1/3}}{\Omega^{(22)}\left(T/\varepsilon(1 + \alpha\varepsilon\delta^2/\mu^2 + \varepsilon\delta^2/6T)^2\right)} \quad (\text{C2})$$

for the parameters  $\varepsilon$  and  $\delta$ , where  $\alpha$  and  $\mu$  are the molecular polarizability and dipole moment. The value of  $\sigma$  is obtained from the fit parameters via  $\sigma = (\mu^2/2\varepsilon\delta)^{1/3}$ . The fit should be restricted to  $1 \leq T^* \leq 10$ .

## Appendix D: A simplified relationship for the thermal diffusion factor

In reacting flow simulations thermal diffusion is most important for light-heavy species interactions, specifically H and H<sub>2</sub> collisions with all other species. The thermal diffusion ratio may be approximated as in the ‘light species limit’ where  $\alpha_{Tij}$  is taken as nonzero for binary pairs with  $m_j$  less than some small value (e.g.  $m_j < 5$ ) and for large values of  $m_i/m_j$ . Paul and Warnatz [1] have expanded the thermal diffusion factor for large values of the ratio  $m_i/m_j$  and give the approximation

$$\alpha_{T,ij} \cong \frac{\xi_{ij} (1 - F(\xi_{ij})) (6C_{ij}^* - 5)}{(5 - 12B_{ij}^*/5)c_i + (4\xi_{ij}/3)(m_j n D_{ij} / \eta_j) c_j} \quad (D1)$$

where  $c_i \equiv x_i/(x_i + x_j)$  and  $\xi_{ij} \equiv (m_j/(m_i + m_j))^{1/2}$ . The function  $F(\xi)$  is an empirical correction which makes the approximation reasonably accurate for values of  $m_j/m_i$  up to of order 1/2 and is given as

$$F(\xi) = 7.99027 (1 - \xi)^2 + 76.0603 (1 - \xi)^4 \quad (D2)$$

In equations D1 and D2 the indices are ordered such that  $m_j \leq m_i$  which is consistent with the normal sign convention for the thermal diffusion factor (i.e. above the inversion temperature  $\alpha_{Tij}$  is a positive number thus the thermal diffusion of heavy species will be towards a cooler region, and  $\alpha_{Tji} \equiv -\alpha_{Tij}$  with  $i$  and  $j$  such that  $m_j \leq m_i$ ).

Many reacting flow simulation codes make use of a preprocessor which creates curve fits for transport properties as functions of temperature to speed up the calculations. These fits are often of the form

$$\ln(D_{ij}) = \sum_{k=0}^4 a_k^{(ij)} (\ln(T))^k \quad (D3)$$

and

$$\ln(\eta_j) = \sum_{k=0}^4 b_k^{(j)} (\ln(T))^k \quad (D4)$$

For such cases, Paul and Warnatz [1] observe that their approximate form for the thermal diffusion factor can be evaluated directly from these fits, via

$$n_j D_{ij} / \eta_j = (P_0 m_j / k_B T) \exp\left(\sum_{k=0}^4 (a_k^{(ij)} - b_k^j) (\ln(T))^k\right) \quad (D5)$$

$$C_{ij}^* = \frac{3}{2} - \frac{1}{3} \sum_{k=1}^4 a_k^{(ij)} (k) (\ln(T))^{k-1} \quad (D6)$$

$$B_{ij}^* = 4C_{ij}^* - 3(C_{ij}^*)^2 + \frac{1}{3} \sum_{k=2}^4 a_k^{(ij)} (k)(k-1)(\ln(T))^{k-2} \quad (\text{D7})$$

Note that in most transport codes the binary diffusion coefficient is calculated at a particular pressure (typically one atm. or one bar) and then rescaled for subsequent usage. The pressure  $P_0$  in equation D5 is the pressure at which the diffusion coefficients were calculated in the preprocessor. The formulation of Paul and Warnatz [1] provides a rapid and accurate means to obtain the thermal diffusion factors within a modern reacting flow simulation code.

## References

- 1) P. H. Paul and J. Warnatz, 'A re-evaluation of the means used to calculate transport properties of reacting flows,' (in preparation, 1997).

## Appendix E: Full expression for the thermal diffusion factor

The binary thermal diffusion factor (see Equations 15 and 16) is given by

$$\alpha_{Tij} \equiv \left(6C_{ij}^* - 5\right) \left( \frac{x_i S_1 - x_j S_2}{x_i^2 Q_1 + x_j^2 Q_2 + x_i x_j Q_{12}} \right) \quad (\text{E1})$$

where  $x_i + x_j = 1$ . The functionals  $S$  and  $Q$  are given by [1] and are reproduced here for completeness.

Order  $i$  and  $j$  such that  $m_j < m_i$  and define  $z \equiv m_i/m_j$ . Then

$$S_1 = z \left( \frac{2}{1+z} \right)^{1/2} \frac{\Omega_{ii}^{(22)*} \sigma_{ii}^2}{\Omega_{ij}^{(11)*} \sigma_{ij}^2} - \frac{4zA_{ij}^*}{(1+z)^2} + \frac{15(z-1)}{2(1+z)^2} \quad (\text{E2a})$$

$$S_2 = \left( \frac{2}{z+z^2} \right)^{1/2} \frac{\Omega_{jj}^{(22)*} \sigma_{jj}^2}{\Omega_{ij}^{(11)*} \sigma_{ij}^2} - \frac{4zA_{ij}^*}{(1+z)^2} + \frac{15z(1-z)}{2(1+z)^2} \quad (\text{E2b})$$

$$Q_1 = \left( \frac{2}{1+z} \right)^{1/2} \frac{\Omega_{ii}^{(22)*} \sigma_{ii}^2}{\Omega_{ij}^{(11)*} \sigma_{ij}^2} \frac{(2.5 - 1.2B_{ij}^*)z^2 + 3 + 1.2zA_{ij}^*}{1+z} \quad (\text{E2c})$$

$$Q_2 = \left( \frac{2z}{1+z} \right)^{1/2} \frac{\Omega_{jj}^{(22)*} \sigma_{jj}^2}{\Omega_{ij}^{(11)*} \sigma_{ij}^2} \frac{(2.5 - 1.2B_{ij}^*) + 3z^2 + 1.2zA_{ij}^*}{z+z^2} \quad (\text{E2d})$$

$$Q_{12} = \frac{8(1+z)}{5z^{1/2}} \frac{\Omega_{ii}^{(22)*} \sigma_{ii}^2}{\Omega_{ij}^{(11)*} \sigma_{ij}^2} \frac{\Omega_{jj}^{(22)*} \sigma_{jj}^2}{\Omega_{ij}^{(11)*} \sigma_{ij}^2} +$$

$$\frac{4zA_{ij}^*}{(1+z)^2} \left(11 - 2.4B_{ij}^*\right) + 15 \left( \frac{z-1}{z+1} \right)^2 \left(2.5 - 1.2B_{ij}^*\right) \quad (\text{E2e})$$

The binary thermal diffusion factor is asymmetric under exchange of indices, that is

$$\alpha_{Tij} = -\alpha_{Tji} \quad (\text{E3})$$

### References

- 1) J. Bzowski, J. Kestin, E. A. Mason and F. J. Uribe, J. Phys. Chem. Ref. Data **19**, 1179-1232 (1990).

## Appendix F: Relationships for the Collision Integrals

The expression for the collision integrals [1] are reproduced here for completeness.

For  $T^* \leq 10$ , let  $z \equiv \ln(T^*)$  then:

$$\Omega^{(11)*} = \exp\left(\sum_{i=0}^5 a_i z^i\right) \quad (\text{F1})$$

$$\Omega^{(22)*} = \exp\left(\sum_{i=0}^5 b_i z^i\right) \quad (\text{F2})$$

The coefficients  $a$  and  $b$  for the ranges  $0.2 \leq T^* < 1$  and  $1 \leq T^* \leq 10$  are given in Table F1.

$$A^* = \Omega^{(22)*} / \Omega^{(11)*} \quad (\text{F3})$$

$$C^* \equiv 1 + \frac{1}{3} \frac{d \ln \Omega^{(11)*}}{dz} = 1 + \frac{1}{3} \sum_{i=1}^5 i a_i z^{i-1} \quad (\text{F4})$$

$$E^* \equiv 1 + \frac{1}{4} \frac{d \ln \Omega^{(22)*}}{dz} = 1 + \frac{1}{4} \sum_{i=1}^5 i b_i z^{i-1} \quad (\text{F5})$$

$$B^* \equiv 4C^* - 3C^{*2} - \frac{1}{3} \frac{d^2 \ln \Omega^{(11)*}}{dz^2} = 4C^* - 3C^{*2} - \frac{1}{9} \sum_{i=2}^5 i(i-1) a_i z^{i-2} \quad (\text{F6})$$

Table F1

0.2 ≤ T* < 1	i = 0	1	2	3	4	5
a <sub>i</sub>	0.295402	-0.510069	0.189395	0.484463	0.417806	0.122148
b <sub>i</sub>	0.46641	-0.56991	0.19591	0.747363	0.662153	0.188447
1 ≤ T* ≤ 10	i=0	1	2	3	4	5
a <sub>i</sub>	0.295402	-0.510069	0.189395	-0.045427	0.0037928	0.0
b <sub>i</sub>	0.46641	-0.56991	0.19591	-0.03879	0.00259	0.0

For  $T^* > 10$ , define  $z \equiv \ln(T^*)$ ,  $\alpha \equiv \ln(V^*/T^*)$  and  $\alpha_{10} \equiv \ln(V^*/10)$ , then:

$$\Omega^{(11)*} = (\rho^* \alpha)^2 \left( 1.04 + \sum_{i=2}^4 g_i T^{*-i} \right) \quad (\text{F7a})$$

where

$$g_2 = -267.0 + \frac{201.670 + 174.672/\alpha_{10} + (7.36916/\alpha_{10})^2}{(\alpha_{10} \rho^*)^2} \quad (\text{F7b})$$

$$g_3 = 26700.0 - \frac{19.2265 + 27.6938/\alpha_{10} + (3.29559/\alpha_{10})^2}{(\alpha_{10} \rho^*)^2} \times 10^3 \quad (\text{F7c})$$

$$g_4 = -8.90 \times 10^5 + \frac{6.31013 + 10.2266/\alpha_{10} + (2.33033/\alpha_{10})^2}{(\alpha_{10} \rho^*)^2} \times 10^5 \quad (\text{F7d})$$

$$\Omega^{(22)*} = (\rho^* \alpha)^2 \left( 0.89 + \sum_{i=2}^4 f_i z^{-i} \right) \quad (\text{F8a})$$

where

$$f_2 = -33.0838 + \frac{20.0862 + 72.1059/\alpha_{10} + (8.27648/\alpha_{10})^2}{(\alpha_{10} \rho^*)^2} \quad (\text{F8b})$$

$$f_3 = 101.571 - \frac{56.4472 + 286.393/\alpha_{10} + (17.7610/\alpha_{10})^2}{(\alpha_{10} \rho^*)^2} \quad (\text{F8c})$$

$$f_4 = -87.7036 + \frac{46.3130 + 277.146/\alpha_{10} + (19.0573/\alpha_{10})^2}{(\alpha_{10} \rho^*)^2} \quad (\text{F8d})$$

For  $T^* > 10$  the remaining functionals are given by:

$$A^* = \Omega^{(22)^*} / \Omega^{(11)^*} \quad (\text{F9})$$

The expression for B\*, C\* and E\* can be derived using the definitions of Eqn.s F4, F5 and F6 and are left to the reader as an exercise.

## References

- 1) J. Bzowski, J. Kestin, E. A. Mason and F. J. Uribe, J. Phys. Chem. Ref. Data **19**, 1179-1232 (1990).

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