**Transport Properties of Binary and Ternary Mixtures**

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Abstract

The paper develops a mathematical model for computing the binary diffusion coefficient, thermal diffusion factor, thermal diffusivity, viscosity and thermal conductivity in the real gas region with nonequilibrium statistical mechanics. For the analytical calculation of transport properties, we have used models of Kihara and Chapman-Cowling (up to the third order). In this paper, we have calculated transport properties for mixtures involving carbon monoxide, helium, argon, xenon and krypton. New mixing rules for the calculation of transport properties for mixtures are developed. The analytical results obtained by statistical mechanics are compared with experimental data and they show relatively good agreement. New developments regarding these transport properties for mixtures involving carbon monoxide and inert gases are discussed.

KEY WORDS: chain theory; fuel cell technology, hydrocarbons; isobutane; n-butane; mixtures; propane; refrigerant; thermodynamic properties
I. INTRODUCTION

Accurate calculations of diffusion coefficients are essential in numerous technological applications, such as the effective design of fuel cells. For example, performance of a solid oxide fuel cell (SOFC) depends on oxygen diffusion into the catalyst layer, between the cathode and electrolyte. The half-cell chemical reactions produce negative ions, which migrate across the electrolyte in an opposite direction (from the cathode to the anode). In addition to oxygen diffusion, hydrogen molecules diffuse through the anode to the same catalyst layer, where they combine with the oxygen ions and liberate electrons, while producing H2O and heat. Similar processes occur in a proton exchange membrane fuel cell (PEMFC), except that hydrogen ions flow to the cathode, where water molecules are produced. In these cases, accurate modelling of mass diffusion and diffusion coefficients are needed to determine voltage losses within the fuel cell.

More specifically, diffusion coefficients are needed to predict the rates of concentration polarization, namely voltage drops or entropy production arising from diffusive mass transfer. These voltage losses occur from diffusion of fuel / oxidant gases through the porous electrodes and mass transfer to the reaction sites. The partial pressure at the catalyst layer reaction site is less than the gas stream bulk pressure, thereby leading to concentration polarization, when the electrical current flows through the electrode. Chemical reactions in the catalytic layer deplete the molecular fuel faster than its replacement by gas diffusing through the electrodes. Accurate calculations of the diffusion coefficient are needed, in order to predict these rates of diffusion through the electrodes.
Within the porous electrode of a fuel cell, ordinary diffusion occurs when the diameter of a pore is large compared with the mean free path of the molecule. In contrast, Knudsen diffusion occurs when the diameter of the pore is small, relative to the molecular mean free path. Molecules collide more frequently with the pore walls than other molecules. The pore wall absorbs and then diffusively de-absorbs the molecules during these collisions. This article applies statistical methods to accommodate collisions between molecules, particularly the resulting effects of intermolecular interactions on the mass diffusivity.

Past studies have determined the diffusion coefficient from kinetic theory, after associating the gas molecule mean free path with the pore diameter and molecular velocity. The gas binary diffusion coefficient can be approximated from Chapman-Eskog theory, in terms of the total pressure, average collision diameter and the Lennard-Jones potential based on the collision integral. Within the electrodes, the effective ordinary diffusion coefficient depends on the porosity of the electrodes. Both ordinary and Knudsen diffusion may occur simultaneously within these electrodes. Mass transfer mechanisms of both counter-current diffusion and self-diffusion occur within either the cathode or anode of the fuel cell. In past studies of diffusivity calculations within the electrodes, it has been often assumed that different sized pores are highly inter-connected and randomly distributed, so the path of any molecule has nearly equivalent resistance through the porous electrode. This article develops a detailed formulation with statistical modeling of intermolecular collisions, thereby allowing interactions between molecules to be incorporated into calculations of the diffusion coefficient.
II. THERMOPHYSICAL PROPERTIES OF FLUIDS

Gases and liquids are very important substances in our lives. Knowing exact values of transport properties of gases and liquids is crucial for optimization of various technological systems and machines. It is estimated that around 50 million pure substances are known today, with only some 20,000 substances being recorded in journals and manuals. There are approximately 30 thermo-mechanical properties for each pure substance, essential to engineering practice, with some 12 among them being dependent on pressure and temperature. If every pure substance was to be measured at ten different temperatures and ten different pressures, 600 measurements should be made for each pure substance. We would need 100 trillion years of work to carry out measurement of properties for every pure substance and for known mixtures. In view of these challenges, other effective alternatives are needed to evaluate thermophysical properties of substances.

A combination of measurement techniques and analytical procedures has actually proved to be an effective way of determining thermo-mechanical properties of substances. Various past methods have been developed for accurately measuring properties of liquids and gases. Thermal conductivities of gaseous ammonia between 293 K and 450 K and pressures up to 500 atm were determined with a novel co-axial cylinder apparatus by Needham and Ziebland. Certain anomalies of thermal conductivity near the critical point were explained based on energy transport mechanisms involving clusters of molecules. Sources of errors in the analysis were assessed and the authors reported uncertainties of $\pm 2\%$ for the thermal conductivity variations. Lahoucine et al. developed a thermistor for simultaneously measuring thermal conductivity and thermal diffusivity of liquids. The method was tested with ethanol, toluene, water and mercury and an accuracy of $\pm 2\%$ was reported for the measured thermal conductivities. Kosky et al.
developed a method involving a sinusoidally varying heat flux for measurement of thermal diffusivity. A measured phase lag between the incident and transmitted waves through the test specimen was successfully correlated to thermophysical properties of the specimen.

In most cases, numerous independent experiments are needed to evaluate thermophysical properties of substances over a range of temperatures and pressures. Dowding et al.\textsuperscript{5} have reported that temperature dependent variations of thermal properties can be determined from sequential analysis of parameter estimation. The sequential analysis combines multiple experiments, while using regularization and prior information from a previous experiment. The authors reported that the sequential method shows excellent agreement with previous techniques considering the experiments independently.

Measurements of thermophysical properties are generally very time-consuming and large amounts of funding are typically needed to purchase the measurement equipment. This has resulted in a growing need to predict thermophysical properties of existing and new substances, without measurements. For example, an unsteady method of line heat impulses was developed by Kolyshkin and co-workers\textsuperscript{6} to predict thermal properties of various gases. Furukawa\textsuperscript{7} has developed useful expressions for evaluating property dependencies on both temperature and pressure for a variety of common working fluids. Temperature dependent variations of thermal conductivity of hydrogen were predicted based on lattice theory by Jones\textsuperscript{8}. Calculations were performed for temperatures between 78 K and 300 K, as well as conditions between the triple point and 80 K.

Various other prediction methods for gases have been developed. Properties of argon have been evaluated by iterative solutions of the integrated momentum equations by Bahadori and Soo\textsuperscript{9}. The authors considered relaxation of electrons along a cooled surface in the
calculations. The atom and ion temperatures decreased near the surface, while the thermal and electrical conductivities stayed higher than values based on equilibrium electron configurations. The transport properties of other noble gases have been calculated based on modified Enskog and statistical perturbation theories by Mehdipour and Eslami. The temperature-dependent parameters were determined from the intermolecular pair potential and a Lennard-Jones (12-6) potential. For helium gas calculations, the method was reported to be accurate within 2.66% for thermal conductivity and 3.03% for viscosity. Semi-empirical methods were used by Zoby et al. to evaluate mixture properties involving helium over a wide range of temperatures. Correlations were developed for the thermal conductivity and viscosity at equilibrium conditions. The predicted variations of thermophysical properties were motivated by applications to spacecraft design.

The choice of method for evaluating thermophysical properties has significance on the accuracy of heat transfer correlations. For example, it affects the onset of convection (characterized by a critical Rayleigh number) in heated fluid layers. Cordoba reported that linear variations of thermal conductivity and specific heat yield first-order corrections to the critical value of the Rayleigh number. However, linear variations of the thermal expansion coefficient lead to second-order corrections to the critical Rayleigh number. Numerous other examples in past literature have shown that thermophysical property evaluation has significance in predictions of the thermo-fluid transport phenomena.

This article considers new predictive models of transport properties in binary and ternary gas mixtures. In particular, diffusion coefficients, thermal conductivity and viscosity are predicted with methods based on statistical thermodynamics and nonequilibrium mechanics. These predictions have important practical applications in complex thermo-fluid systems involving gas
mixtures. For example, varying diffusion coefficients have important effects on counter-diffusing gases in chemical reactions. This article outlines a new analytical method for predicting changes of these coefficients at varying pressure and temperature.

III. NONEQUILIBRIUM MECHANICS

Accurate knowledge of nonequilibrium or transport properties of pure gases and liquids is essential for the optimum design of various technological processes, i.e., chemical process plants, determination of intermolecular potential energy functions, development of accurate theories of transport properties in dense fluids, etc. Transport coefficients describe the process of relaxation to equilibrium from a state perturbed by temperature, pressure, density, velocity or composition gradients. The theoretical description of these phenomena constitutes that part of nonequilibrium statistical mechanics that is known as kinetic theory. From the semi-classical kinetic theory for polyatomic fluids, we can express the coefficient of thermal conductivity, shear viscosity and bulk viscosity as follows:

\[
\lambda = \frac{2k^2T}{3m}[A, A], \quad \eta = \frac{1}{10}kT[B, B], \quad \kappa_s = kT[\Gamma, \Gamma]
\]

where \(A\), \(B\) and \(\Gamma\) are complex vector, tensor and scalar functions \(^{13-16}\). The detailed description of the physical origin of bulk viscosity is explained in past literature\(^{14}\). It arises in dense polyatomic gases and liquids.

Past literature\(^{30}\) indicates that in collisions between rotating molecules, generally only one or a few quanta of rotational energy are exchanged. Since the rotational quantum for fluids at ordinary temperatures is much smaller than the relative kinetic energy of a colliding pair, the assumption of very small influences of rotational energy is accurate. Furthermore, for the
vibrational degrees of freedom, we note that at normal temperatures, only the lowest vibrational energy states are occupied. This is the reason that in our model, inelastic scattering will be neglected and the cross section is independent of the internal states of the molecules. In such a case, the original bracket integral equations are reduced to those in a monatomic gas.

The kinetic theory of dilute gases assumes a macroscopic system at densities low enough so that molecules most of the time move freely and interact through binary encounters only. Nevertheless, the densities are high enough to ensure that the effects of molecule-wall collisions can be neglected, compared to those from molecule-molecule encounters. It is worth noting in this paper that the terms “dilute” or “low-density gas” represent a real physical situation, whereas the frequently used expression “zero-density limit” is related to results of a mathematical extrapolation of a density series of a particular transport property at constant temperature to zero density. This paper is predominantly concerned with the transport properties of fluids of practical significance. This means that attention is concentrated upon systems containing polyatomic molecules and upon the traditional transport properties, such as the viscosity and thermal conductivity. The ease of practical evaluation of the transport properties of a dilute gas, by means of these relationships, decreases as the complexity of the molecules increases. For a pure monatomic gas, with no internal degrees of freedom, the calculations are trivial, consuming minutes on a personal computer. But for systems involving atoms and rigid rotors, the computations are almost routine and take hours on workstations. For systems that involve molecules other than rigid rotors, the theory is still approximate and calculations are heuristic.

The transport properties for pure gases are represented as sums of terms for the temperature-dependent dilute-gas contributions and terms for the temperature and density-
dependent residual contributions. Contributions for the critical enhancement are not included in these background functions. For the Lennard-Jones intermolecular potential, it is almost impossible to obtain the collision integrals analytically. Because of the difficulty of calculating these integrals, their values are usually taken from published tables. To make computerized calculations more convenient and to improve on the accuracy obtained by linear interpolation of tables, we used the following formulation of Neufeld\textsuperscript{17} et al., which is obtained on the basis of numerical simulations and interpolation procedures.

\[ \Omega^{(L)} = \frac{A}{T^B} + \frac{C}{\exp(D T^*)} + \frac{E}{\exp(F T^*)} + \frac{G}{\exp(H T^*)} + R T^B \sin(S T^W - P) \] (2)

This equation contains 12 adjustable parameters and it is developed for 16 collision integrals.

For the calculation of transport properties for polyatomic molecules, a quantum mechanical treatment of processes is necessary to account for the changes of internal state. The fully quantum mechanical kinetic theory of polyatomic gases is based on the Waldman-Snider\textsuperscript{15,16} equation and summarized by McCourt and co-workers\textsuperscript{15}. Wang-Chang, Uhlenbeck and de Boer (WCUB) formulated a semi-classical kinetic theory. The quantum mechanical theory has the advantage that it can treat the degeneracy of rotational energy states. Therefore, it is able to describe the effect of magnetic and electric fields on the transport properties. The disadvantage of this theory for practical applications is that it is only formally established for gases with rotational degrees of freedom. On the other hand, the semi-classical theory has the advantages that it treats all forms of internal energy and it is the semi-classical limit of the quantum mechanical approach. In this paper, we used simple expressions for taking into account rotational contributions. Internal modes have, at relatively low temperatures, almost no influence on viscosity and relatively high influence on thermal conductivity.
The dilute gas viscosity is obtained from kinetic theory assuming that a Lennard-Jones (LJ) potential applies and the expression is written as:

\[ \eta_0(T) = \frac{5}{16} \frac{\sqrt{\pi M k T}}{\pi \Omega^{\frac{3}{2}}} \sigma^2 F_c \]  

(3)

In this paper, we have calculated the correction factor, \( F_c \), with help of the following equations outlined previously by Kihara\textsuperscript{24} and Chapman and Cowling\textsuperscript{25}.

a) Kihara model (K)

The factor \( F_c \) has been theoretically found to be:\textsuperscript{26}

\[ F_c^K = 1 + \frac{(H_{01})^2}{H_{00}H_{11}} + \left( \frac{\left(\frac{(H_{01})^2}{H_{00}H_{11}}\right)^2}{H_{00}H_{11}} + \frac{\left(H_{01}H_{12} - H_{11}H_{02}\right)^2}{H_{00}H_{11}H_{22}} \right) \]  

(4)

b) Chapman-Cowling model (K)

\[ F_c^{CC} = 1 + \frac{(H_{01})^2}{H_{00}H_{11}} + \left[ \frac{H_{00}H_{11}H_{22} + 2H_{01}H_{02}H_{12} - H_{00}H_{11}^2 - H_{00}H_{02}^2}{H_{00}H_{11}H_{22} + 2H_{01}H_{02}H_{12} - H_{00}H_{11}^2 - H_{00}H_{02}^2} \right] \]  

(5)

The constants \( H^{pq} \) satisfy the symmetry relation. With the help of K and CC solutions and the Sonine expansion, we can express the coefficients \( H^{pq} \) as:

\[ H_{00} = \frac{2}{5kT} - 4\Omega^{(2,2)} \]
where $\Omega$ represents the collision integral. The thermal conductivity, $\lambda$, for a dilute gas is written as

$$\lambda_0 = \frac{25}{32} \frac{\pi \text{MkT}^{1/2}}{\eta \rho \Omega^{(2,2)}} \psi \chi_{c1} \psi$$

(7)

where $c_v$ is the specific isochoric heat capacity and $F_{c1}$ is the higher order analytical correction. The term $\psi$ represents the influence of polyatomic energy contributions to the thermal conductivity. For the calculation of the polyatomic influence, we used the Thijsse theory.35

The final expression for the influence of internal degrees of freedom is represented as:34

$$\psi = \frac{\left(1 + r^2\right)^2 \left(1 + \Delta_{SPN}\right)}{1 + r^2 \left(\frac{1}{3} \rho D_{int} / \eta + \frac{4}{3} \pi Z_{int} \right) \left(1 - \alpha\right)}$$

(8)

where $r^2$ is given as the ratio of the internal molar heat capacity $C_{INT}$ to the molar heat capacity of an ideal monatomic species at constant pressure, i.e.,

$$r^2 = \frac{C_{INT}}{C_p^{trans}} = \frac{2C_p}{5R} - 1$$

(9)
In Eq. (8) $D_{\text{int}}$ and $Z_{\text{INT}}$ represent the diffusion coefficients and collision number. Also, $\Delta_{\text{SPN}}$ and $\alpha$ are the small spin-polarization correction factor and correction factor, respectively. In the model, the spin polarization factor neglected due to the small influence on transport properties. The correction factor has a small value, except for strongly polar molecules in which near-resonant rotational exchange collisions are important.

We have used the common assumption of mechanically independent modes of internal motion, thereby yielding\textsuperscript{34}

\begin{equation}
\frac{C_{\text{INT}}}{Z_{\text{INT}}} = \frac{C_{\text{ROT}}}{Z_{\text{ROT}}} + \frac{C_{\text{VIB}}}{Z_{\text{VIB}}} + \frac{C_{\text{EL}}}{Z_{\text{EL}}}
\end{equation}

\begin{equation}
\frac{C_{\text{INT}}}{D_{\text{INT}}} = \frac{C_{\text{ROT}}}{D_{\text{ROT}}} + \frac{C_{\text{VIB}}}{D_{\text{VIB}}} + \frac{C_{\text{EL}}}{D_{\text{EL}}}
\end{equation}

The heat capacities of ideal gases are calculated by statistical thermodynamics. This paper features all important contributions (translation, rotation, internal rotation, vibration, intermolecular potential energy and influence of electron and nuclei excitation). Collision numbers for vibrational energy relaxation are on the order of $10^4$ or greater, as rotational collision numbers and also electronic energy relaxation are expected to be quite large, i.e.,

\begin{equation}
Z_{\text{ROT}} \ll Z_{\text{VIB}}, Z_{\text{EL}} \rightarrow \frac{C_{\text{INT}}}{Z_{\text{INT}}} = \frac{C_{\text{ROT}}}{Z_{\text{ROT}}}
\end{equation}

Furthermore, when $Z_{\text{INT}}$ is large and the resonant exchange of internal energy is negligible, it is reasonable to approximate the internal energy diffusion coefficient by the mass self-diffusion coefficient, denoted here by $D$. For the vibration and electronic degrees of freedom, it is assumed that the diffusion coefficients are given by:

\begin{equation}
\frac{\rho D_{\text{VIB}}}{\eta} = \frac{\rho D_{\text{EL}}}{\eta} = \frac{\rho D}{\eta} = \frac{6}{5} A^*\text{.}
\end{equation}
For rotational collision numbers, we have used the following relationship given by Brau and Jonkman:

$$Z_{\text{ROT}} = \left( 1 + \frac{\pi^{1.5}}{2T^*} \right)^{\pi^2/4 + 2} \left( \frac{1}{T^*} + \frac{\pi^{1.5}}{T^{*1.5}} \right)$$  \hspace{1cm} (14)

where $Z_{\text{ROT}}^\infty$ denotes the rotational collision number in the high temperature limit.

Similarly, to estimate the rotational energy diffusion coefficient, we proceed in a manner similar to that used by the Uribe-Mason-Kestin (UMK) correlation for the rotational collision number.

$$\frac{\rho D_{\text{rot}}}{\eta} = \begin{cases} 
\left( Z_{\text{ROT}}^\infty \right) \left( 1.122 + \frac{4.522}{T^*} \right) \frac{Z_{\text{ROT}}}{Z_{\text{ROT}}^\infty} & T^* < T_{\text{crs}}^* \\
\frac{6}{5} \left[ 1 + \frac{0.27}{Z_{\text{ROT}}} - \frac{0.44}{Z_{\text{ROT}}^2} - \frac{0.90}{Z_{\text{ROT}}^3} \right] & T^* \geq T_{\text{crs}}^* 
\end{cases}$$  \hspace{1cm} (15)

In our model, we have also taken into account near-resonant rotational exchange interactions as dipole-dipole, dipole-quadrupole and quadrupole-quadrupole interactions:

$$D_{\text{ROT}} = \frac{D_{\text{rot}}}{1 + \Delta} = \frac{D_{\text{rot}}}{1 + \Delta_{\mu \mu} + \Delta_{\mu \phi} + \Delta_{\phi \phi}}$$  \hspace{1cm} (16)

For linear molecules the exchange correction terms for multipole interactions are:

$$\Delta_{\mu \mu} = 0.44 \cdot \exp \left( -\frac{2\theta}{3T} \right) \left( 1 - \frac{\theta}{3T} \right) \left( \frac{3\pi^2}{2} \right)^{\pi^2/2} \frac{\mu^2}{\eta} \frac{\eta}{\rho D_{\text{rot}}} \left( \frac{0_R}{T} \right)^{1.5}$$  \hspace{1cm} (17)

$$\Delta_{\mu \phi} = 0.51 \cdot \exp \left( -\frac{170\theta}{12T} \right) \left( 1 - \frac{50\theta}{6T} \right) \left( \frac{56\pi^2}{45} \right)^{\pi^2/5} \left( \frac{3}{5} \right)^{1/2} \left( \frac{\mu^2}{h} \right)^{1/3} \left( \frac{R_m T}{M} \right)^{1/6} \frac{\eta}{\rho D_{\text{rot}}} \left( \frac{0_R}{T} \right)^{1.5}$$  \hspace{1cm} (18)

$$\Delta_{\phi \phi} = 1.31 \cdot \exp \left( -\frac{130\theta}{6T} \right) \left( 1 - \frac{40\theta}{3T} \right) \left( \frac{7}{4} \right)^{\pi^2/4} \left( \frac{R_m T}{M} \right)^{1/4} \frac{\eta}{\rho D_{\text{rot}}} \left( \frac{0_R}{T} \right)^{1.5}$$  \hspace{1cm} (19)
where $D_{\text{rot}}$ is the diffusion coefficient, uncorrected for the near-resonant rotational exchange interaction, while $\Delta_{\mu\mu}$, $\Delta_{\mu 0}$ and $\Delta_{00}$ are the exchange correction terms for dipole-dipole, dipole-quadrupole, and quadrupole-quadrupole interactions. With help of Eq. (14-19) we can express the collisions numbers and internal energy diffusion coefficient to give

$$Z_{\text{INT}} = \frac{C_{\text{INT}}}{C_{\text{ROT}}} \cdot Z_{\text{ROT}} = \frac{r^2}{s^2} Z_{\text{ROT}}$$

$$\frac{1}{D_{\text{INT}}} = \frac{(1 + \Delta)^{\frac{3}{2}}}{D_{\text{rot}}} \cdot \left(1 - \frac{s^2}{r^2} \right)$$

$$s^2 = \frac{C_{\text{ROT}}}{C_{\text{TRANS}} + R_m}$$

The correction factor $\alpha$ is expressed with the following relation:

$$\alpha = \frac{r^2 \left(1 + \frac{1}{2 \rho D_{\text{int}} / \eta} + \left(\frac{5}{3} r^2 + 1\right) \frac{2}{\pi Z_{\text{INT}}} \right)^2}{\left[1 + r^2 \left(\frac{1}{2 \rho D_{\text{int}} / \eta} + \frac{4}{3 \pi Z_{\text{INT}}}\right) + \frac{1}{2 \rho D_{\text{int}} / \eta} + r^2 + 3 \left(\frac{5}{3} r^2 + 1\right)^2 \frac{1}{\pi Z_{\text{INT}}} \right]}$$

a) Kihara model (K)

The factor $F_c$ has been theoretically found to be:
\[ F_{el}^K = 1 + \left( \frac{\Lambda^{12}}{\Lambda^1 \Lambda^{22}} \right)^2 + \left( \frac{\left( \Lambda^{12} \right)^2}{\Lambda^1 \Lambda^{22}} \right)^2 + \frac{\left( \Lambda^{12} \Lambda^{23} - \Lambda^{22} \Lambda^{13} \right)^2}{\Lambda^1 \left( \Lambda^{22} \right)^2 \Lambda^{33}} \]  

(24)

b) Chapman-Cowling model (CC)

\[ F_{el}^{CC} = 1 + \frac{\left( \Lambda^{12} \right)^2}{\Lambda^1 \Lambda^{22} - \left( \Lambda^{12} \right)^2} + \left( \frac{\Lambda^{11} \left( \Lambda^{12} \Lambda^{23} - \Lambda^{22} \Lambda^{13} \right)^2}{\Lambda^1 \Lambda^{22} \Lambda^{33} + 2\Lambda^{12} \Lambda^1 \Lambda^{23} - \Lambda^{11} \left( \Lambda^{23} \right)^2 - \Lambda^{22} \left( \Lambda^{13} \right)^2 - \Lambda^{33} \left( \Lambda^{12} \right)^2} \right) \]  

(25)

The constants \( \Lambda^{pq} \) satisfy the symmetry relation. With help of the Kihara solution and the Sonine expansion, we can express the coefficients \( \Lambda^{pq} \) as

\[
\Lambda^{11} = \frac{8M}{75k^2T} 4\Omega^{(2,2)}
\]

\[
\Lambda^{12} = \frac{8M}{75k^2T} \left[ \frac{77}{4} \Omega^{(2,2)} - 7\Omega^{(2,3)} + \Omega^{(2,4)} \right]
\]

\[
\Lambda^{22} = \frac{8M}{75k^2T} \left[ \frac{63}{8} \Omega^{(2,2)} - \frac{9}{2} \Omega^{(2,3)} + \frac{1}{2} \Omega^{(2,4)} \right]
\]

\[
\Lambda^{13} = \frac{8M}{75k^2T} \left[ \frac{945}{32} \Omega^{(2,2)} - \frac{261}{16} \Omega^{(2,3)} + \frac{25}{8} \Omega^{(2,4)} - \frac{1}{4} \Omega^{(2,5)} \right]
\]

\[
\Lambda^{23} = \frac{8M}{75k^2T} \left[ \frac{14553}{256} \Omega^{(2,2)} - \frac{1215}{32} \Omega^{(2,3)} + \frac{313}{32} \Omega^{(2,4)} - \frac{9}{8} \Omega^{(2,5)} + \frac{1}{16} \Omega^{(2,6)} + \frac{1}{2} \Omega^{(2,4)} \right]
\]

\[
\Lambda^{33} = \frac{8M}{75k^2T} \left[ \frac{14553}{256} \Omega^{(2,2)} - \frac{1215}{32} \Omega^{(2,3)} + \frac{313}{32} \Omega^{(2,4)} - \frac{9}{8} \Omega^{(2,5)} + \frac{1}{16} \Omega^{(2,6)} + \frac{1}{2} \Omega^{(2,4)} \right]
\]
IV. PREDICTION OF VISCOSITY AND THERMAL CONDUCTIVITY FOR MIXTURES

For the determination of viscosity of fluid mixtures, we have used a purely analytical model.\textsuperscript{14,25,30} According to this theory, the viscosity of dense fluid mixtures containing \(N\) components can be written in the following form:\textsuperscript{14}

\[
\eta = \frac{1}{\pi} \left( \sum_{i=1}^{N} \psi_i \eta_i + \sum_{i=1}^{N} \psi_i \eta_{ij} \right) + \sum_{i=1}^{N} \psi_i \psi_j \psi_{ij} \left( \frac{20}{3} + \frac{4M_i}{M_j} A_{ij}^* \right)
\]

where \(\rho\) is the molar density, \(\psi_i\) and \(\psi_j\) are mole fractions of species \(i\) and \(j\), and \(M_i\) and \(M_j\) are their molecular masses. \(A_{ij}^*\) is a weak function of intermolecular potential for \(i-j\) interactions. The symbol \(\eta_i\) represents the viscosity of pure component \(i\) and \(\eta_{ij}\) represents the viscosity of \(i-j\) interactions. We have developed the following new equation for \(\eta_{ij}\):

\[
\eta_{ij} = \left( \frac{\eta_i + \eta_j}{2} \right) \psi_{ij}
\]

For the determination of thermal conductivity of fluid mixtures, we have also used a purely analytical model.\textsuperscript{14,25,30} According to this theory, the thermal conductivity of dense gas mixtures containing \(N\) components can be written in the following form:\textsuperscript{14}
\[
\lambda = \begin{bmatrix}
\Lambda_{11} & \cdots & \Lambda_{1N} & \psi_1 \\
\vdots & \ddots & \vdots & \vdots \\
\Lambda_{N1} & \cdots & \Lambda_{NN} & \psi_N \\
\psi_1 & \cdots & \psi_N & 0
\end{bmatrix}
\]

For \( N=1 \), the expression in Eq. (19) reduces to the following one-component gas equation,

\[
\Lambda_{ii} = \frac{\psi_i^2}{\lambda_i} + \sum_{j \neq i}^N \psi_i \psi_j \frac{M_i M_j}{2 \lambda_{ij} A_{ij}^*} \left( \frac{15}{2} M_i^2 + \frac{25}{4} M_j^2 - \frac{3 M_i^2 B_{ij}^* + 4 M_i M_j A_{ij}^*}{(M_i + M_j)^2} \right)
\]

\[
\Lambda_{ij}(j \neq i) = -\frac{\psi_i \psi_j}{2 \lambda_{ij} A_{ij}^*} \frac{M_i M_j}{(M_i + M_j)^2} \left( -\frac{3}{4} B_{ij}^* - 4 A_{ij}^* \right)
\]

where \( \rho \) is the molar density, \( \psi_i \) and \( \psi_j \) are mole fractions of species \( i \) and \( j \), and \( M_i \) and \( M_j \) are their molecular masses. Also, \( A_{ij}^* \) and \( B_{ij}^* \) are weak functions of the intermolecular potential for \( i-j \) interactions. Both coefficients were calculated with the help of Neufeld et al.’s expression for the reduced collision integrals\(^{17} \).

\[
A_{ij}^* = \frac{\Omega_{ij}^{(2,2)*}}{\Omega_{ij}^{(1,1)*}}, \quad B_{ij}^* = \frac{\left( 5 \Omega_{ij}^{(1,2)*} - 4 \Omega_{ij}^{(1,3)*} \right)}{\Omega_{ij}^{(1,1)*}}
\]

The symbol \( \lambda_i \) represents the viscosity of a pure component \( i \) and \( \lambda_{ij} \) represents the viscosity of \( i-j \) interactions:

\[
\lambda_{ij} = \left( \frac{\lambda_i + \lambda_j}{2} \right) \xi_{ij}
\]
V. DIFFUSION COEFFICIENTS FOR BINARY MIXTURES

In the case of binary mixtures, there is only one independent diffusion coefficient. From kinetic theory and the Chapman-Cowling approximation, we have

$$D_{12}^{CC} = \frac{3}{16nM_{12}} \left( \frac{2\pi M_{12}kT}{\rho_{12}^{1/2}} \right)^{1/2} (1 - \Delta)^{-1}$$  \hspace{1cm} (36)

$$\Delta = \frac{1}{10} \left( 6C_{12}^* - 5 \right)^2 \left( \frac{P_1\psi_1^* + P_2\psi_2^* + P_{12}\psi_1\psi_2}{Q_1\psi_1^* + Q_2\psi_2^* + Q_{12}\psi_1\psi_2} \right)$$  \hspace{1cm} (37)

$$P_1 = \frac{2M_2^2}{M_2(M_1 + M_2)} \frac{2M_2}{M_1 + M_2} \frac{\Omega_{11}^{(2,2)*}}{\Omega_{12}^{(1,1)*}} \frac{\sigma_{11}}{\sigma_{12}}$$  \hspace{1cm} (38)

$$P_{12} = 15 \left( \frac{M_1 - M_2}{M_1 + M_2} \right)^2 + \frac{8M_1M_2}{(M_1 + M_2)^2} \left( \frac{\sigma_{11}}{\sigma_{12}} \right)^2$$  \hspace{1cm} (39)

$$Q_1^{CC} = \frac{2}{M_2(M_1 + M_2)} \left( \frac{2M_2}{M_1 + M_2} \right)^{1/2} \frac{\sigma_{11}}{\sigma_{12}} \frac{\Omega_{11}^{(2,2)*}}{\Omega_{12}^{(1,1)*}} \left[ \frac{5}{2} - \frac{6B_{12}^*}{5M_1^2} + 3M_2^2 + \frac{8}{5}M_1M_2A_{12}^* \right]$$  \hspace{1cm} (40)

$$Q_{12}^{CC} = 15 \left( \frac{M_1 - M_2}{M_1 + M_2} \right)^2 \left( \frac{5}{2} - \frac{6B_{12}^*}{5M_1^2} \right) + 4 \frac{M_1M_2A_{12}^*}{(M_1 + M_2)^2} \left( \frac{11}{5} - \frac{12B_{12}^*}{5M_1^2} \right) + \frac{8}{5} \left( \frac{M_1 + M_2}{M_1M_2} \right)^{1/2} \frac{\sigma_{11}}{\sigma_{12}} \frac{\Omega_{11}^{(2,2)*}}{\Omega_{12}^{(1,1)*}} \frac{\sigma_{22}}{\sigma_{12}} \frac{\Omega_{22}^{(2,2)*}}{\Omega_{12}^{(1,1)*}}$$  \hspace{1cm} (41)

The expressions $P_2$ and $Q_2$ are obtained from $P_1$ and $Q_1$ by an interchange of subscripts.

b) Kihara model

$$D_{12}^K = \frac{3}{16nM_{12}} \left( \frac{2\pi M_{12}kT}{\rho_{12}^{1/2}} \right)^{1/2} \left( 1 + \frac{6C_{12}^* - 5}{16A_{12} + 40} \right)$$  \hspace{1cm} (42)

The coefficient $C_{12}$ is expressed as:
\[ C_{12} = \frac{\Omega_{12}^{(1,2)*}}{\Omega_{12}^{(0,0)*}} \]  

(43)

VI. THERMAL DIFFUSION FACTOR

In a binary mixture, there is only one independent thermal diffusion ratio. With the help of the first-order Chapman-Cowling approximation, we can express the thermal diffusion ratio \( k_t \) as:

\[
[k_t] = [\alpha_t] \psi_1 \psi_2
\]  

(44)

In Eq. (32), \( \alpha_t \) represents the thermal diffusion factor. An expression for the thermal diffusion factor of a binary mixture is obtained with help of the Chapman-Cowling solution as follows:

\[
\alpha_t^{CC} = \left( 6C_{12}^* - 5 \right) \frac{\psi_1 S_1 - \psi_2 S_2}{\psi_1^2 Q_1 + \psi_2 Q_2 + \psi_1 \psi_2 Q_{12}}
\]  

(44)

\[
S_1^{CC} = \frac{M_1}{M_2} \left( \frac{2M_2}{M_1 + M_2} \right)^{1/2} \frac{\sigma_{11}^2 \Omega_{11}^{(2,2)*}}{\sigma_{12}^2 \Omega_{12}^{(0,0)*}} - 4 \frac{M_1 M_2 A_{12}^*}{(M_1 + M_2)^2} + 15 \frac{M_2 (M_1 - M_2)}{2(M_1 + M_2)^2}
\]  

(45)

\[
Q_1^{CC} = \frac{2}{M_2 (M_1 + M_2)} \left( \frac{2M_2}{M_1 + M_2} \right)^{1/2} \frac{\sigma_{11}^2 \Omega_{11}^{(2,2)*}}{\sigma_{12}^2 \Omega_{12}^{(0,0)*}} \left[ \frac{5}{2} - \frac{6}{5} B_{12} \right] M_1^2 + 3M_2^2 + \frac{8}{5} M_1 M_2 A_{12}^* \]

(46)

\[
Q_{12}^{CC} = \frac{15}{(M_1 + M_2)^2} \left( \frac{5}{2} - \frac{6}{5} B_{12} \right) + 4 \frac{M_1 M_2 A_{12}^*}{(M_1 + M_2)^2} \left( \frac{11}{2} - \frac{12}{5} B_{12} \right) + \frac{8}{5} M_1 M_2 \frac{\sigma_{11}^2 \Omega_{11}^{(2,2)*}}{\sigma_{12}^2 \Omega_{12}^{(0,0)*}} \frac{\sigma_{22}^2 \Omega_{22}^{(2,2)*}}{\sigma_{12}^2 \Omega_{12}^{(0,0)*}}
\]  

(47)

b) Kihara model

\[
\alpha_t^K = \left( 6C_{12}^* - 5 \right) \frac{\psi_1 S_1 - \psi_2 S_2}{\psi_1^2 Q_1 + \psi_2 Q_2 + \psi_1 \psi_2 Q_{12}}
\]  

(48)
The expressions for $S_2$ and $Q_2$ are obtained from those of $S_1$ and $Q_1$ by interchanging subscripts 1 and 2. The thermal diffusion ratio is a very complex function of temperature, concentration and molecular masses. It depends parametrically on the force law of molecules. The primary concentration dependence is given by $\psi_1\psi_2$ and the function $S_1\psi_1 - S_2\psi_2$. The main dependence on the masses of molecules is given by $S_1$ and $S_2$. The thermal diffusion ratio could be positive or negative. If $k_t$ is positive, then component 1 tends to move into the cooler region and component 3 into the warmer region. The temperature at which $k_t$ is equal to zero is called the inversion temperature.

VII. RESULTS AND COMPARISON WITH EXPERIMENTAL DATA

In this section, we have calculated the transport properties for the mixtures CO-He, CO-Ar, and CO-Kr. The results for all transport properties obtained by CC and K models show relatively good agreement with experimental data. Due to almost identical results between CC and K models, we have decided to show in this paper only results for the K model. The difference between the CC model and K model was for all points less than 0.5%.

Figures 1 - 12 show comparisons of the binary diffusion coefficient, thermal diffusion factor, thermal conductivity and viscosity, between the analytical computations based on
nonequilibrium statistical mechanics (NSM), Haghighi et al.’s model (HFP)\textsuperscript{36} and experimental data (Exp.).\textsuperscript{36,37} Table 1 shows empirical constants used for the analytical calculations. In general, the results for all transport properties obtained by the newly developed NSM model, experimental data and past analytical models show relatively good agreement. In the results, the relative deviation (RD) is defined by the following expression:

$$RD(\text{model} - \text{REF}) = \frac{(\text{data}_{\text{model}} - \text{data}_{\text{REF}})}{\text{data}_{\text{REF}}}$$

In Fig. 1, the relative deviation between the predicted viscosities (using NSM and HFP models) for different gases remains below about 5% over a temperature range of about 1000 K. Similar trends are observed for the predicted deviation for thermal conductivity in Fig. 2. The closest agreement between both models occurs with Ar (monatomic gas), while the diatomic gas (CO) exhibits higher deviations.

In Figs. 3 (CO + Ar), 5 (CO + Kr) and 7 (CO + Kr + Ar), the relative deviations of HFP / K models with experimental data for viscosities are shown. These deviations were determined from the predicted trends of viscosity over a range of temperatures. Those results indicated that viscosity increases at higher temperatures (as expected). Unlike liquids with closely spaced molecules and strong intermolecular cohesive forces, molecules within the gases (Figs. 3, 5 and 7) are more widely spaced and intermolecular forces are negligible. As a result, resistance to relative motion across adjoining gas layers is more closely related to momentum exchange between the layers, rather than intermolecular forces. When molecules are transported randomly between regions of different velocity, this momentum exchange resists relative motion between the layers. Since the random molecular exchange between the layers increases when the energy level of molecules becomes larger, the gas viscosity increases at higher temperatures. The
current NSM / K model predicts these trends successfully, based on statistical modeling that incorporates the intermolecular exchange of momentum.

Corresponding results for thermal conductivity of the same gases (CO + Ar, CO + Kr, CO + Kr + Ar) are shown in Figs. 4, 6 and 8, respectively. In the previous case (viscosity), the K model generally exhibits smaller deviations from experimental data than the HFP model. This suggests slightly better accuracy of the NSM / K model. For thermal conductivity, the relative deviation rises initially for the K model (CO + Ar) at higher temperatures and reaches an asymptotic value of about 0.065 thereafter. In contrast, the deviations become smaller for the mixtures involving CO + Kr and CO + Ar + Kr. For example, the relative deviation falls below -0.003 for the latter mixture. These results suggest that the new mixture rules have been successfully implemented in the overall NSM model.

In past literature\textsuperscript{36}, accuracies of the HFP model for five mixtures were previously reported as ±1\% for viscosity, ±1\% for the binary diffusion coefficient and ±25\% for the thermal diffusion factor (\(\alpha T\)). The thermal diffusion factor includes the thermal diffusivity and the product of density and specific heat (called the volumetric heat capacity), which measures the substance’s ability to store thermal energy. Gases are poorly suited for thermal energy storage since their densities and volumetric heat capacity are much smaller than liquids and solids. In Fig. 9, the thermal diffusion factor increases with temperature. The results indicate the ability of CO + He to conduct thermal energy, relative to its ability to store internal energy, over a range of temperatures.

In order to understand these trends with thermal diffusion, it is useful to consider how thermal conductivity varies with temperature. The thermal conductivity depends on collisions between gas molecules and other intermolecular interactions documented by the NSM model in
this article. The thermal conductivity of monatomic gases generally depends on temperature alone. However, for low-pressure monatomic gases, the gas density depends on both pressure and temperature, from the ideal gas law. As a result, the thermal diffusivity exhibits a dependence on both temperature and pressure. Consequently, when this coupled dependence is considered in thermal conductivity models, the corresponding thermal diffusivity can be shown to typically increase more rapidly than thermal conductivity as the temperature increases.

The intermolecular spacing is much larger and intermolecular interactions are more random in gases, in comparison with solids. As a result, the internal energy transport becomes less effective in gases. This partly explains why solid materials usually have a higher thermal conductivity than gases. In previous sections, the NSM model has considered how intermolecular interactions are related to the mean free path of molecular motion, number of molecules per unit volume, \( n \), and the characteristics of molecular motion. The thermal conductivity is expected to be proportional to the rate of intermolecular collisions, so it typically increases with temperature, as the mean molecular speed and collision rates become larger. Since the velocity of sound in a gas varies with the square root of temperature, a simplified treatment can verify that the thermal conductivity varies in a similar fashion, since the speed of sound characterizes the mean speed of molecules.

Results are presented at varying temperatures in Fig. 9 - 11. The mean free path is inversely proportional and \( n \) is directly proportional to gas pressure, so the results are considered to be independent of pressure. If the gas pressure approaches the critical pressure, these observations cannot be assumed and other models must be developed. Furthermore, the situation becomes more complex near the saturation point and the liquid state. In those cases, the molecules become more closely packed and molecular force fields exert a strong influence on
the energy exchange during intermolecular collisions. Results in this article are limited to ideal gases, well above the saturation and critical points.

Additional results for the binary diffusion coefficient are illustrated in Fig. 12. The relative deviation in these figures is determined based on comparisons with the HFP model\textsuperscript{36}. In the HFP model, the collision integral correlations are obtained from an extended law of corresponding states, unlike other past methods using a potential function with several parameters adjusted based on experimental data. The NSM model incorporates statistical methods based on models of both Kihara\textsuperscript{24} (K model) and Chapman-Cowling\textsuperscript{25} (CC model). By including all relevant intermolecular interactions (ranging from internal rotations to intermolecular potential energy and nuclei excitation), the current NSM formulation is viewed to provide additional robustness over the HFP model, while providing comparable or better accuracy.

VIII. CONCLUSIONS

The paper presents a mathematical model for computation of transport properties in the gaseous state. In particular, monatomic gases (He, Ar, Kr), binary mixtures (CO + Ar, CO + Kr and CO + He) and a ternary mixture (CO + Kr + Ar) are considered over a range of temperature. The newly developed model based on NSM (non-equilibrium statistical mechanics) is applied to computations of viscosity, thermal conductivity, thermal diffusion factor and the binary diffusion coefficient. The NSM model incorporates past models based on Kihara and Chapman-Cowling (up to the third order). The analytical results are successfully compared against experimental data. Also, the results are compared successfully against the HFP model. The NSM results
indicate comparable or better accuracy, while providing additional robustness over the detailed statistical mechanisms of intermolecular interactions.

Table 1. Important constants for analytical calculations

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<th>CO</th>
<th>He</th>
<th>Ar</th>
<th>Kr</th>
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<td>1.421·10^{-22}</td>
<td>1.9527·10^{-21}</td>
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<td>2.76·10^{-10}</td>
<td>3.35·10^{-10}</td>
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</tr>
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</table>

Figure 1: Viscosity of pure fluids
Figure 2: Thermal conductivity of pure fluids

Fig.3: Viscosity of equimolar mixture CO+Ar
Thermal conductivity of equimolar mixture CO+Ar

Fig. 4: Thermal conductivity of equimolar mixture CO+Ar

Viscosity of equimolar mixture CO+Kr

Figure 5: Viscosity of equimolar mixture CO+Kr
Figure 6: Thermal conductivity of equimolar mixture CO+Kr

Figure 7: Viscosity of equimolar mixture CO+Kr+Ar
Thermal conductivity of equimolar mixture CO+Ar+Kr

Figure 8: Thermal conductivity of equimolar mixture CO+Ar+Kr

Fig. 9: Thermal diffusion factor between CO+He at equimolar composition
Fig. 10: Diffusion coefficient at equimolar composition

Fig. 11: Thermal diffusion factor for CO+He at 300 K
Fig. 12: Binary diffusion coefficient between CO+He and CO+Ar at equimolar composition
References


24 Kihara, T., 1976, “Intermolecular Forces”, University of Tokyo, John Wiley & Sons, Cichester, New York, Brisbane, Toronto


