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Thermal Conductivity, Viscosity, and Thermal Diffusivity Calculation for Binary and Ternary Mixtures

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A mathematical model is presented for computing viscosity, thermal conductivity, and thermal diffusivity in the liquid and gas domains for pure components and mixtures. To calculate the transport properties of a real fluid, models based on Lennard–Jones intermolecular potential were applied. The new mathematical model is used for the calculation of transport properties for binary and ternary mixtures. The model is based on a new theory for mixtures. The results obtained by statistical thermodynamics are compared with the REFPROP model and show relatively good agreement.

Nomenclature

A = free energy
A_1, A_2 = degree of flammability under American Society of Heating, Refrigeration, and Air Conditioning Engineers standard
c_p = specific heat capacity at constant pressure
F = number of degrees of freedom
G = free enthalpy
g_0 = hard sphere radial distribution function
H_{ii} = part in determinant for calculation of dynamic viscosity of mixtures
k = Boltzmann constant
M = molecular mass
N = number of molecules in system
R_m = universal gas constant
T = temperature
T^* = reduced temperature
T_c = critical temperature
V = volume
V_c = critical volume
Z_{coll} = collision number
α = thermal diffusivity
β = diffusion term
δ = inversed reduced volume
ε, σ = Lennard–Jones parameter
η = dynamic viscosity
κ = correction factor for hydrogen bonding effect
κ_s = shear viscosity
Λ_{ij} = part in determinant for calculation of thermal conductivity of mixtures
λ = thermal conductivity
μ_r = reduced dipole moment
ν = kinematic viscosity
ρ = density
ρ^* = reduced density
τ = inversed reduced temperature
χ = isothermal compressibility
ψ = influence of internal degree of freedom
ψ_i = molar fraction of component i
Ω = collision integral
Ω^* = reduced collision integral
ω = acentric factor

Superscripts and Subscripts

c = critical condition
ig = ideal gas
mix = mixture
r = residual part
p = influence of high densities
0 = dilute gas state

Introduction

IN technical practice, fluid mechanics processes are of vital importance. The mathematical theory of chaos in the future may contribute to our understanding of turbulent flow. At this time in practical engineering, for the prediction of turbulence in almost all cases, classical models such as k–ε or k–ω model are used. Today there are many excellent models (CFX, FIRE, IDEAS, etc.) for available use in fluid engineering. One of the main problems of presented models is the relatively weak database of thermophysical properties. Almost in all cases, thermophysical properties are represented as constants, independent of the temperature and pressure field. Thus, in most cases thermodynamic tables or diagrams or different empirical functions obtained from measurement are used. In this paper, we demonstrate the importance of thermophysical properties for the study of advanced fluid mechanics.

To design devices in this field of activity, it is necessary to be familiar with the equilibrium and nonequilibrium thermodynamic properties of state in a one- and two-phase environment for pure compounds and their mixtures.

In this paper we develop a mathematical model for computing the transport properties of state. The important progress in transport properties theory is not as advanced as the progress in the theory and the application of theory in thermodynamic properties. The difficulties lie in the mathematical treatment for rigorous theories. In theoretical development, it has been over a century since the first gas kinetic theory was established by Boltzmann and Maxwell. From the Maxwell–Boltzmann equation for monoatomic dilute gases, we can calculate transport properties not far from the Maxwellian (see Ref. 1) ones. This means that we treat transport phenomena with small temperature or velocity gradients of the molecules. For the calculation of transport properties for polyatomic molecules, in principle, a quantum mechanical treatment of processes is necessary to account for the changes of internal state. The quantum mechanical kinetic theory of polyatomic gases is based on the Waldman–Snider equation (see Ref. 2) and summarized by McCourt et al.[3]

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Wang–Chang, Uhlenbeck, de Boer (WCUB), and Taxman formulated a semiclassical kinetic theory as described in Ref. 2. The quantum mechanical theory has the advantage that it can treat the degeneracy of rotational energy states and is, therefore, able to describe the effect of magnetic and electric fields on the transport properties. For practical applications, the disadvantage of this theory is that it is only formally established for gases with rotational degrees of freedom. On the other hand, semiclassical theory has the advantages that it treats all forms of internal energy and is the semiclassical limit of the quantum mechanical approach. However, direct application of the complex theories to calculate the transport properties for polyatomic gases is still too complicated for even modern high-speed computers. In this paper, we use simple expressions to take into account rotational contributions. Internal modes have, at relatively low temperatures, almost no influence on viscosity and a relatively high influence on thermal conductivity.

The results of the analysis are compared with REFPROP model obtained based on classical thermodynamics and experimental data and show a relatively good agreement.

Refrigerants

For more than half of century, chlorofluorocarbons (CFCs) have been used as working fluids in refrigeration, heat pump, and air conditioning applications. These compounds are very stable, nontoxic, and nonflammable and, therefore, are regarded as safe refrigerants. For several decades chlorine–fluorine–hydrocarbons were considered harmless refrigerants. In 1968, however, the first serious ozone layer damage was observed. According to meteorologists' findings, the damage resulted from a dramatic increase in the emission of chlorine–fluorine–hydrocarbons. Recently, the greenhouse effect has become substantially more evident. For thousands of years, life on the Earth has been protected by the protective atmosphere layer. This layer consists of ozone, which protects the Earth from harmful ultraviolet radiation of the sun. As far as we know, the Earth is the only planet with such a layer. If the ozone layer disappeared, ultraviolet solar radiation would sterilize the Earth's surface and, consequently, make life for most of Earth's creatures impossible. In areas where there are holes in the ozone layer, an increase of solar radiation has been observed. The data obtained so far have confirmed that even a minimum depletion of the ozone layer can cause a more frequent occurrence of skin cancer, result in a higher number of eye injuries, and reduce the defensive ability of organisms. At the same time, radiation reduces crops and damages forests and sea life.

Most of CFCs have been replaced by hydrofluorocarbons (HFCs), which have a similar molecular structure, but do not contain chlorine atoms. One of the most important CFCs, R12 for example, has been already replaced by 1,1,1,2-tetrafluoroethane (R134a) in several applications.

The main objective of this paper is to provide reliable thermodynamic property information about thermodynamic components of HFC refrigerants R143a, R134a, and R125 and their ternary mixture refrigerant R404A and binary mixture refrigerant R507A. Refrigerantnts 134a, 143a, and R125 are an alternative refrigerants that are suitable as substitutes for R22 and R502.

R404A is near azeotropic refrigerant containing 44 wt% R125, 52 wt% R143a, and 4 wt% R134a; R507A is azeotropic refrigerant containing 50 wt% R125 and 50 wt% R143a. Both refrigerants are developed as substitutes for R22 and R13B1. Possible applications of these refrigerants are in cold-storage cells, supermarket display cases, ice machines, air-conditioning units, etc. They are nonflammable (A1). However, their zero ozone depletion potential (ODP) and very low global warming potential (GWP) make them interesting ozone-friendly refrigerants for applications where hazards can be kept under control (Tables 1 and 2).

Nonequilibrium Thermodynamics[1–17]

Accurate knowledge of nonequilibrium or transport properties of pure gases and liquids is essential for the optimum design of various items for chemical process plants, for determination of intermolecular potential energy functions, and for development of accurate theories of transport properties in dense fluids. Transport coefficients describe the process of relaxation to equilibrium from a perturbed state by application of 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.

Table 1 Physical properties of pure refrigerants

Property	R125	R143a	R134a
Chemical formula	CHF_2-CF_3	CF_3CH_3	CF_3CH_2F
Molecular weight, kg/kmol	120.02	84.041	102.032
Critical temperature, K	339.16	345.86	374.18
Critical pressure, bar	36.17	37.64	40.59
Triple point, K	172.5	161.34	169.85
ODP	0.	0.	0.
GWP_{100}	2800	3800	1300
Flammability	A1	A2	A1

Table 2 Physical properties of R404A and R507A

Property	R507A	R404A
Molecular weight, kg/kmol	98.9	97.6
Critical temperature, K	70.8	72.07
Critical pressure, bar	37.2	37.32
Boiling point at 1 bar	−46.5	−46.4/−45.7
ODP	0.	0.
GWP_{100}	3300	3260
Flammability	A1	A1

Kinetic Theory of Dilute Polyatomic Gases[1–18]

From semiclassical kinetic theory for polyatomic fluids, we can express the coefficient of thermal conductivity, shear viscosity, and bulk viscosity,

$$\lambda = (2k^2T/3m)[\boldsymbol{A}_t, \boldsymbol{A}_t], \qquad \eta = (1/10)kT[\boldsymbol{B}, \boldsymbol{B}]$$

$$\kappa_s = kT[\boldsymbol{\Gamma}, \boldsymbol{\Gamma}] \tag{1}$$

where $\boldsymbol{A}_t$, $\boldsymbol{B}$, and $\boldsymbol{\Gamma}$ are complex vector, tensor, and the scalar functions.[1–4] The detailed description of the physical origin of bulk viscosity may be found in the literature.[2] It arises in dense polyatomic gases and liquids.

Available literature[2,19] indicates that in collisions between rotating molecules generally only one or a few quanta of rotational energy are exchanged, and because the rotational quantum for fluids at ordinary temperatures is much smaller than the relative kinetic energy of a colliding pair, the assumption of a very small influence 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. For these reasons, in our model inelastic scattering is completely ignored and the cross section is independent of the internal states of the molecules. In such cases, the original bracket integral equations are reduced to those for a monoatomic gas.

The kinetic theory of dilute gases assumes a macroscopic system at densities low enough so that molecules move freely most of the time and only interact through binary encounters. Neverthless, the densities are high enough to ensure that the effects of molecule–wall collisions can be neglected compared to those from molecule–molecule encounters. Note that in this paper 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 on systems containing polyatomic molecules and on the traditional transport properties such as the viscosity and thermal conductivity. The ease of the practical evaluation of the transport properties of a dilute gas by means of these relationships decreases as the complexity of the molecules increases. Thus, for a pure monoatomic gas, with no internal degrees of freedom, the calculations are now trivial, consuming minutes on a personal computer. For systems involving atoms and rigid rotors, the computations now are almost routine and take hours on work stations. For systems that involve molecules other than rigid rotors, the theory is still approximate and calculations are heuristic.

The background 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. Contribution for the critical enhancement are not included in these background functions.

From the Boltzmann equation, for monoatomic dilute gases we can calculate transport properties not far from the Maxwellian properties (Refs.1–3). This means that we treat transport phenomena with small temperature or velocity gradients of the molecules. On this basis, we can express the dynamic viscosity and thermal conductivity for single-component gas as

$$\eta_0 = \frac{5kT}{8\Omega^{(2,2)}}\left[1 + \frac{3}{49}\left(\frac{\Omega^{(2,3)}}{\Omega^{(2,2)}} - \frac{7}{2}\right)^2\right]$$

$$\lambda_0 = \frac{25kTC_V}{16M\Omega^{(2,2)}}\left[1 + \frac{2}{21}\left(\frac{\Omega^{(2,3)}}{\Omega^{(2,2)}} - \frac{7}{2}\right)^2\right] \tag{2}$$

where M is molecular mass of the molecule and $\Omega^{(l,s)}$ is the transport collision integral. For the Lennard–Jones intermolecular potential, it is almost impossible to obtain 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 the tables, we used the Neufeld[5] et al. empirical formulation, which was obtained based on numerical simulations and interpolation procedure,

$$\begin{aligned}\Omega^{(l,s)^*} &= A/T^{*B} + C/\exp(DT^*) + E/\exp(FT^*)\\ &\quad + G/\exp(HT^*) + RT^{*B}\sin(ST^{*W} - P)\end{aligned} \tag{3}$$

Equation (3) contains 12 adjustable parameters and is developed for 16 collision integrals.

The dilute gasdynamic viscosity is obtained from kinetic theory assuming that a Lennard–Jones (LJ) potential applies and using the expression

$$\eta_0(T) = 26.69579 \times 10^{-1}\frac{\sqrt{MT}}{\Omega^{(2,2)^*}\sigma^2} \tag{4}$$

where η is in Pascal seconds, M is the molecular mass in grams per mole, T is in degrees Kelven, and $\Omega^{(2,2)}$ is a collision integral.

The dilute gas thermal conductivity[2–4] is found from kinetic theory using a sum of rotational and translational contributions:

$$\lambda_0(T) = \left\{f_1(T)\left[C_p^{ig} - (5/2)R_m\right] + (15/4)R_m\right\}[\eta_0(T)/M] \tag{5}$$

whereas the function f_1 is given as

$$f_1 = 1.35558587 - 0.11306676(T_c/T) \tag{6}$$

The dependence of the thermal conductivity on molecular structure is more intensive than in the case of viscosity.

The Chung–Lee–Starling model (CLS) (see Refs. 14–16) is presented. Equations for the viscosity and the thermal conductivity are developed based on kinetic gas theories and correlated with the experimental data. The low-pressure transport properties are extended to fluids at high densities by introducing empirically correlated, density-dependent functions. These correlations use the acentric factor ω, dimesionless dipole moment μ_r, and empirically determined association parameters to characterize the molecular structure effect of polyatomic molecules κ, the polar effect, and the hydrogen bonding effect. New constants for fluids are determined.

The dilutegas dynamic viscosity for the CLS model is

$$\eta_0(T) = 26.69579 \times 10^{-1}\frac{\sqrt{MT}}{\Omega^{(2,2)^*}\sigma^2}F_c \tag{7}$$

Factor F_c has been empirically found to be[14]

$$F_c = 1 - 0.2756\omega + 0.059035\mu_r^4 + \kappa \tag{8}$$

where ω is the acentric factor, μ_r the reduced dipole moment, and κ a correction factor for the hydrogen-bonding effect of the associating substances such as alcohols, ethers, acids, and water.

For dense fluids, Eq. (7) is extended to account for the effects of temperature and pressure by developing an empirically correlated function of density and temperature as[14,15]

$$\eta = \eta_k + \eta_p \tag{9}$$

$$\eta_k = \eta_0\left(\frac{1}{G_2} + A_6Y\right) \tag{10}$$

$$\eta_p = \left\lfloor 36.344 \times 10^{-6} - \frac{(MT_c)^{.5}}{V_C^{\frac{2}{3}}}\right\rfloor A_7Y^2G_2\exp\left(A_8 + \frac{A_9}{T^*} + \frac{A_{10}}{T^{*2}}\right) \tag{11}$$

$$Y = \frac{\rho V_c}{6}, \qquad G_1 = \frac{1.0 - 0.5Y}{(1.0 - Y)^3} \tag{12}$$

$$T_c = \frac{1.2593\varepsilon}{k}, \qquad V_c = [0.809\sigma(\dot{A})]^3 \tag{13}$$

$$G_2 = \frac{\{A_1[1 - \exp(-A_4Y)] + A_2G_1\exp(A_5Y) + A_3G_1\}}{(A_1A_4 + A_2 + A_3)} \tag{14}$$

The constants A_1–A_{10} are linear functions of the acentric factor, reduced dipole moment, and association factor,

$$A_i = a_0(i) + a_1(i)\omega + a_2(i)\mu_r^4 + a_3(i)\kappa, \qquad i = 1, 10 \tag{15}$$

where the coefficients a_0, a_1, a_2, and a_3 are presented in the Table 3.

The same approach was employed to develop the expression for thermal conductivity,

$$\lambda = \lambda_k + \lambda_p \tag{16}$$

where

$$\lambda_k = \lambda_0(1/H_2 + B_6Y) \tag{17}$$

The thermal conductivity in the region of dilute gases for the CLS model is

$$\lambda_0 = 3119.41(\eta_0/M)\psi \tag{18}$$

where ψ represents the influence of polyatomic energy contributions to the thermal conductivity. We used the Taxman theory (see Ref. 2). Taxman solved the problem of influence of internal degrees of freedom on the basis of the WCUB theory[3] and the approximations given by Mason and Monschick (see Refs. 3 and 4). The presented expression is more accurate than the Eucken correction (see Refs. 3 and 4), and the equation is supported by theory. The final expression for the influence of the internal degrees of freedom is

$$\begin{aligned}\psi &= 1 + C_{\text{int}}^*\\ &\quad \times\left\{\frac{0.2665 + (0.215 - 1.061\beta)/Z_{\text{coll}} + 0.28288\left(C_{\text{int}}^*/Z_{\text{coll}}\right)}{\beta + (0.6366/Z_{\text{coll}}) + \left(1.061\beta C_{\text{int}}^*/Z_{\text{coll}}\right)}\right\}\end{aligned} \tag{19}$$

where C_{int}^* is the reduced internal heat capacity at constant volume, β is diffusion term, and Z_{coll} is the collision number, which is defined as the number of collisions required to interchange a quantum of internal energy with translational energy. The correlation of Z_{coll} developed by Chung et al.[15] is used here,

$$Z_{\text{coll}} = 2.0 + 10.5(T/T_c) \tag{20}$$

The heat capacities of ideal gases are calculated by use of statistical thermodynamics. The paper features all of the important contributions (translation, rotation, internal rotation, vibration, intermolecular potential energy, and influence of electron and nuclei excitation).

Table 3 Coefficients needed for calculation of Eq. (15)

i	$a_0(i)$	$a_1(i)$	$a_2(i)$	$a_3(i)$
1	6.32402	50.41190	−51.68010	1189.02
2	0.12102×10^{-2}	-0.11536×10^{-2}	-0.62571×10^{-2}	0.37283×10^{-1}
3	5.28346	254.209	−168.481	3898.27
4	6.62263	38.0957	−8.46414	31.4178
5	19.74540	7.63034	−14.35440	31.5267
6	−1.89992	−12.53670	+4.98529	−18.1507
7	24.27450	3.44945	−11.29130	69.34660
8	0.79716	0.111764	$+0.12348 \times 10^{-1}$	−4.11661
9	−0.23816	0.67695×10^{-1}	−0.81630	4.02528
10	0.68629×10^{-1}	0.34793	0.59256	−0.72663

Table 4 Coefficients needed for calculation of Eq. (24)

i	$\mathrm{b}_0(i)$	$\mathrm{b}_1(i)$	$\mathrm{b}_2(i)$	$\mathrm{b}_3(i)$
1	2.41657	0.7824	−0.91858	121.721
2	−0.50924	−1.50936	−49.9912	69.9834
3	6,61069	5.62073	64.75990	27.0389
4	14.54250	−8.91387	−5.63794	74.3435
5	0.79274	0.82019	−0.69369	6.31734
6	−5.86340	12.8005	9.58926	−65.5292
7	81.171	114.158	−60.841	466.775

It is possible to obtain analytically the transport term β as the ratio between the viscosity and the product between self-diffusivity at dilute gas conditions and density and shear viscosity. Here we have used the correlation function obtained based on the Pitzer acentric factor ω (see Ref. 14),

$$\beta = 0.786231 - 0.710907\omega + 1.31583\omega^2 \tag{21}$$

The residual part of the thermal conductivity λ_p can be represented by the following equation[14]:

$$\lambda_p = \left[0.1272(T_c/M)^{\frac{1}{2}}\left(1\middle/V_c^{\frac{2}{3}}\right)\right]B_7Y^2H_2(T/T_c)^{\frac{1}{2}} \tag{22}$$

where λ_p is in watts per milliKelvin,

$$H_2 = \big\{B_1[1 - \exp(-B_4Y)](1/Y) + B_2G_1\exp(B_5Y) + B_3G_1\big\}[1/(B_1B_4 + B_2 + B_3)] \tag{23}$$

The constants B_1–B_7 are linear functions of acentric factor, reduced dipole moment, and association factor,

$$B_i = b_0(i) + b_1(i)\omega + b_2(i)\mu_r^4 + b_3(i)\kappa, \qquad i = 1, 10 \tag{24}$$

where the coefficients b_0, b_1, b_2, and b_3 are presented in Table 4.

Prediction of Viscosity and Thermal Conductivity of Mixtures

To determine of viscosity for fluid mixtures, we used a purely analytical model.[2,13,18] According to this theory, the dynamic viscosity of dense fluid mixtures containing N components can be written in the form[2]

$$\eta = -\begin{vmatrix} H_{11} & \cdots & H_{1N} & \psi_1 \\ \vdots & & \vdots & \vdots \\ H_{N1} & & H_{NN} & \psi_N \\ \psi_1 & & \psi_N & 0 \end{vmatrix} \Bigg/ \begin{vmatrix} H_{11} & \cdots & H_{1N} \\ \vdots & & \vdots \\ H_{N1} & \cdots & H_{NN} \end{vmatrix} \tag{25}$$

$$H_{ii} = \frac{\psi_i^2}{\eta_i} + \sum_{\substack{j=1 \\ j \neq i}}^{N} \frac{\psi_i\psi_j}{2\eta_{ij}A_{ij}^*}\frac{M_iM_j}{(M_i + M_j)^2}\left(\frac{20}{3} + \frac{4M_j}{M_i}A_{ij}^*\right) \tag{26}$$

$$H_{ij}(j \neq i) = -\frac{\psi_i\psi_j}{2\eta_{ij}A_{ij}^*}\frac{M_iM_j}{(M_i + M_j)^2}\left(\frac{20}{3} - 4A_{ij}^*\right) \tag{27}$$

where ρ is the molar density, ψ_i and ψ_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. Here η_i is the viscosity of pure component i, and η_{ij} is the viscosity of i–j interaction. On the basis of one fluid theory, we have developed a new equation for η_{ij}:

$$\eta_{ij} = \sqrt{\eta_i\eta_j} \tag{28}$$

To determine thermal conductivity for fluid mixtures, we used a purely analytical model.[2,13,18] According to this theory, the thermal conductivity of dense gas mixtures containing N components can be written in the form[2]

$$\lambda = -\begin{vmatrix} \Lambda_{11} & \cdots & \Lambda_{1N} & \psi_1 \\ \vdots & & \vdots & \vdots \\ \Lambda_{N1} & & \Lambda_{NN} & \psi_N \\ \psi_1 & & \psi_N & 0 \end{vmatrix} \Bigg/ \begin{vmatrix} \Lambda_{11} & \cdots & \Lambda_{1N} \\ \vdots & & \vdots \\ \Lambda_{N1} & \cdots & \Lambda_{NN} \end{vmatrix} \tag{29}$$

For $N = 1$, expression (29) reduces to the one-component gas equation,

$$\Lambda_{ii} = \frac{\psi_i^2}{\lambda_i} + \sum_{\substack{j=1 \\ j \neq i}}^{N} \frac{\psi_i\psi_j}{2\lambda_{ij}A_{ij}^*}\frac{M_iM_j}{(M_i + M_j)^2} \times \left[\frac{(15/2)M_i^2 + (25/4)M_j^2 - 3M_j^2B_{ij}^* + 4M_iM_jA_{ij}^*}{(M_i + M_j)^2}\right] \tag{30}$$

$$\Lambda_{ij}(j \neq i) = -\frac{\psi_i\psi_j}{2\lambda_{ij}A_{ij}^*}\frac{M_iM_j}{(M_i + M_j)^2}\left[\frac{55}{4} - 3B_{ij}^* - 4A_{ij}^*\right] \tag{31}$$

where ρ is the molar density, ψ_i and ψ_j are mole fractions of species i and j, and M_i and M_j are their molecular masses. A_{ij}^* and B_{ij}^* are weak functions of intermolecular potential for i–j interactions. We have calculated both coefficients with the help of the Neufeld et al. expression for reduced collision integrals,[5]

$$A_{ij}^* = \frac{\Omega_{ij}^{(2,2)*}}{\Omega_{ij}^{(1,1)*}}, \qquad B_{ij}^* = \frac{5\Omega_{ij}^{(1,2)*} - 4\Omega_{ij}^{(1,3)*}\big)}{\Omega_{ij}^{(1,1)*}} \tag{32}$$

Here λ_i is the thermal conductivity of pure component i. For the thermal conductivity between i–j interaction λ_{ij}, based on fluid theory, we have developed a new equation:

$$\lambda_{ij} = \sqrt{\lambda_i\lambda_j} \tag{33}$$

The model for computing the transport properties [Eqs. (25–33)] is a novelty in the literature. It is much simpler and theoretically more complete then the famous Vesovic–Wakeham model.[18]

Thermal Diffusivity

The accuracy of engineering calculations depends on the accuracy of the known thermophysical properties.

Thermal conduction may be viewed as the heat transfer from more energetic particles to less energetic particles of a substance due to interaction between the particles.[20] From Fourier law (see Ref. 20), we can state that the heat flux by conduction is proportional to the temperature gradient and the proportial factor is called the thermal conductivity. For isotropic fluids, thermal conductivity has the same value in all three directions. This assumption applies to liquids and simple solids.

The effects of temperature, pressure, and chemical species on the thermal conductivity of a fluid may be explained in terms of the kinetic theory of ideal gases. Based on this theory, it is known that the thermal conductivity is directly proportional to the number of particles per unit volume, the mean molecular speed, and the mean free path. Molecular theory in dense gases and in liquids is more complicated due to complex physical mechanisms.

In heat transfer analysis, the ratio of the thermal conductivity to the heat capacity is an important property, which is termed the thermal diffusivity α. Materials with large thermal diffusivity will respond quickly to changes in their thermal environment,

$$\alpha = \lambda / \rho c_p \tag{34}$$

The thermal diffusivity represents the ability of a material to conduct thermal energy relative to its ability to store thermal energy. In this case, we have used the Tillner-Roth–Wagner–Watanabe (TRWW) model for calculation of isobaric specific heats (see Refs. 21 and 22).

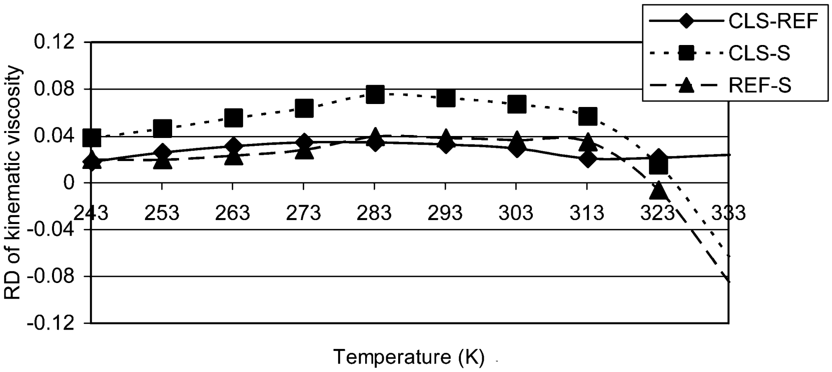
The TRWW equation of state for pure hydrocarbons is given in terms of the dimensionless Helmholtz free energy function (see Refs. 22–24),

$$A/R_mT = A^{ig}/R_mT + A^r/R_mT \tag{35}$$

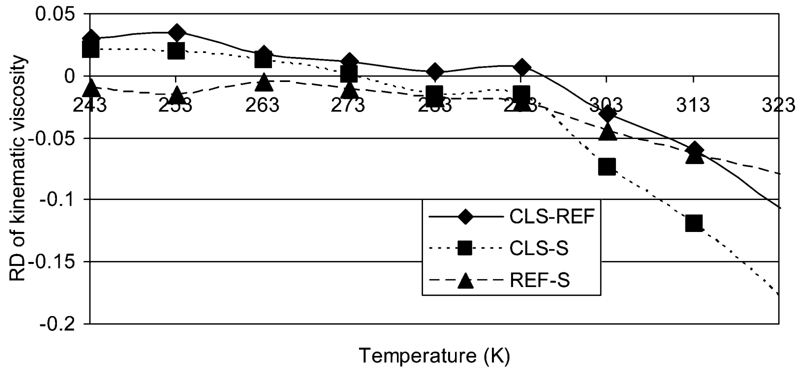
In Eq. (35), A^{ig} is related to the free energy ideal gas function, and A^r is the residual part, which corrects the ideal–gas part to real fluid behavior. The general structure of the ideal gas part and residual part is written as

$$\frac{A^{ig}}{R_mT} = \ln\delta + a_1^0 + a_2^0\tau + a_3^0 \ln\tau + \sum_{i=4}^{10} a_i\tau^{n_i} + \sum_{i=11}^{16} a_i \ln[1-\exp(-n_i\tau)], \qquad \left(\delta = \frac{V_c}{V}, \qquad \tau = \frac{T_c}{T}\right) \tag{36}$$

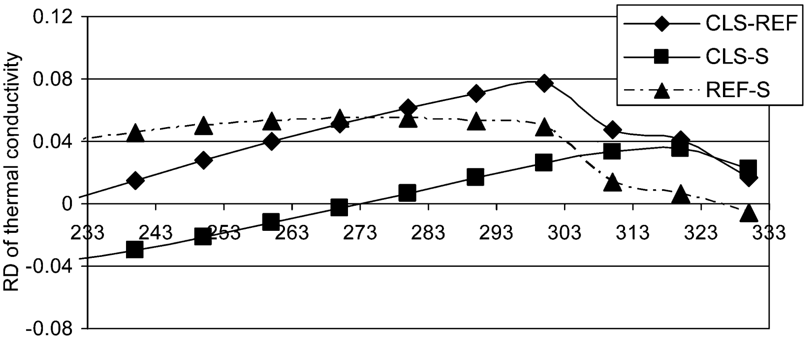
$$\frac{A^r}{R_mT} = \sum_{i=1}^{15} a_i\tau^{t_i}\delta^{d_i} + \sum_{i=16}^{45} a_i\tau^{t_i}\delta^{d_i}\exp(-\delta c_i) + \sum_{i=46}^{60} a_i\tau^{t_i}\delta^{d_i}\exp\left[-\alpha_i(\delta-\nu_i)^2 - \beta_i(\tau-\gamma_i)^2\right] \tag{37}$$



a) Saturated liquid



b) Saturated vapor



c) Saturated liquid

Fig. 1 Viscosity and thermal conductivity of R507A.

The equations of state for the different refrigerants result from the use of coefficients a_i and different exponents t_i, d_i, e_i, α_i, and β_i. In Eqs. (36) and (37) δ and τ are inverse reduced volume and inverse reduced temperature.

The TRWW model for mixtures contains more than 100 constants.[21] Currently, this model is one of the most accurate models for calculation of equilibrium thermodynamic properties for hydrocarbons in the gaseous and liquid states. The absolute deviations of experimental thermodynamic property data from the analytical model are usually within ±1% (Ref. 21).

The Helmholtz free energy, A_{mix}, models for binary and ternary hydrocarbon mixtures are given by

$$A_{\text{mix}} = A^{ig}_{\text{mix}}\left(\tau_i^{\text{pure}}, \delta_i^{\text{pure}}, \psi_i\right) + A^{r}_{\text{mix}}(\tau, \delta, \psi_i) \tag{38}$$

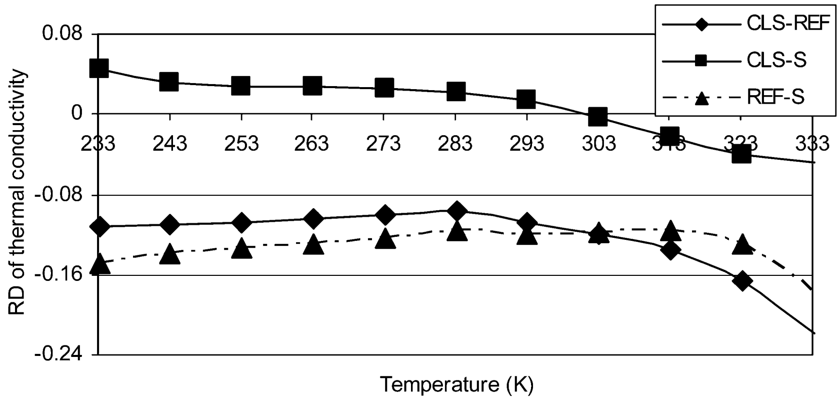
The ideal gas part of the present mixture model is given by a combination of the ideal gas parts of the equations of state for pure components as follows:

$$A^{ig}_{\text{mix}}\left(\tau_i^{\text{pure}}, \delta_i^{\text{pure}}, \psi_i\right) = \sum_{i=1}^{l} \psi_i A_i^{ig}\left(\tau_i^{\text{pure}}, \delta_i^{\text{pure}}\right) + \sum_{i=1}^{l} \psi_i \ln \psi_i \tag{39}$$

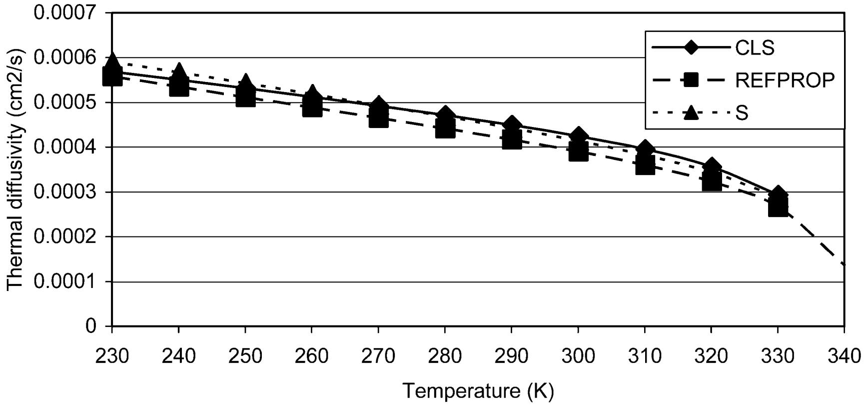
where l denotes the number of components and x_i is the mole fraction of a component i. The second sum in Eq. (39) describes the entropy increase of the ideal gas mixture, and the dimensionless variables, $\tau_i^{\text{pure}} = T_{C,i}^{\text{pure}}/T$ and $\delta_i^{\text{pure}} = \rho/\rho_{C,i}^{\text{pure}}$, used to evaluate the ideal gas function for pure component are different due to respective reducing parameters, $T_{C,i}^{\text{pure}}$ and $\rho_{C,i}^{\text{pure}}$, used in the equations of state for pure fluids.

The residual real fluid contribution of the dimensionless Helmholtz free energy of a mixture is expressed by

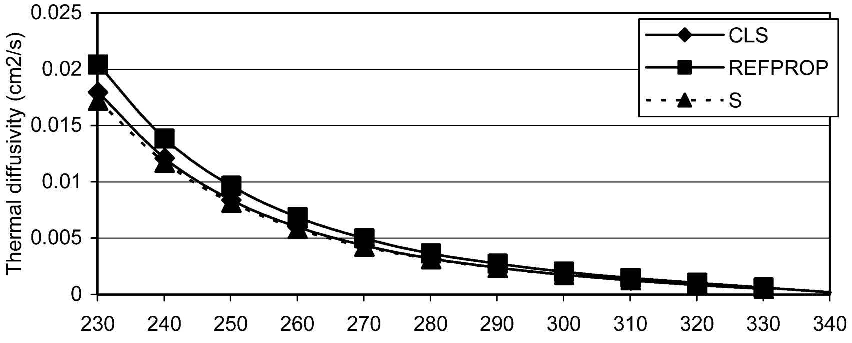
$$A^{r}_{\text{mix}}(\tau, \delta, x_i) = \sum_{i=1}^{l} \psi_i A_i^{r}(\tau, \delta) + \sum_{i=1}^{l} \sum_{j=i+1}^{l} \psi_i \psi_j \Delta A_{ij}^{r}(\tau, \delta) \tag{40}$$



a) Saturated vapor



b) Saturated liquid



c) Saturated vapor

Fig. 2 Thermal diffusivity and thermal conductivity for R507A.

The dimensionless variables are $\tau = T_{C,\mathrm{mix}}/T$ and $\delta = \rho/\rho_{C,\mathrm{mix}}$, and the pseudocritical temperature $T_{C,\mathrm{mix}}$ and density $\rho_{C,\mathrm{mix}}$ are defined as follows:

$$T_{C,\mathrm{mix}} = \sum_{i=1}^{l}\sum_{j=1}^{l} x_i x_j T_{C,ij}$$

$$T_{C,ij,i\neq j} = \frac{T_{C,i} + T_{C,j}}{2} k_{T,ij} \tag{41}$$

$$\frac{1}{\rho_{C,\mathrm{mix}}} = v_{C,\mathrm{mix}} = \sum_{i=1}^{l}\sum_{j=1}^{l} x_i x_j v_{C,ij}$$

$$v_{C,ij,i\neq j} = \frac{v_{C,i} + v_{C,j}}{2} k_{V,ij} \tag{42}$$

where $k_{T,ij}$ and $k_{V,ij}$ are the interaction parameters in the cross terms for temperature and molar volume, respectively.

The second sum of Eq. (40) consists of an excess term for binary mixtures, as well as the ideal mixing of the residual part for the components. The generalized excess term for the three binary mixtures was then determined as follows:

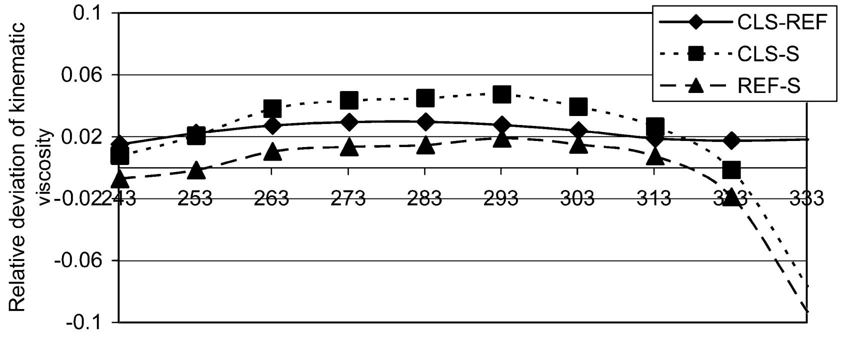
$$\Delta A^r_{ij}(\tau, \delta) = a_1\delta^2 + a_2\tau\delta^4 + a_3\delta^{12}\exp(-\delta) + a_4\tau\delta^5\exp(-\delta) \tag{43}$$

For each binary mixture, the values of the coefficients a_i of Eq. (43) and the interaction parameters, $k_{T,ij}$ and $k_{V,ij}$, of Eqs. (41) and (42) were adjusted to the experimental data by using the nonlinear fitting process. The coefficients needed for Eq. (41) are found in Ref. 21.

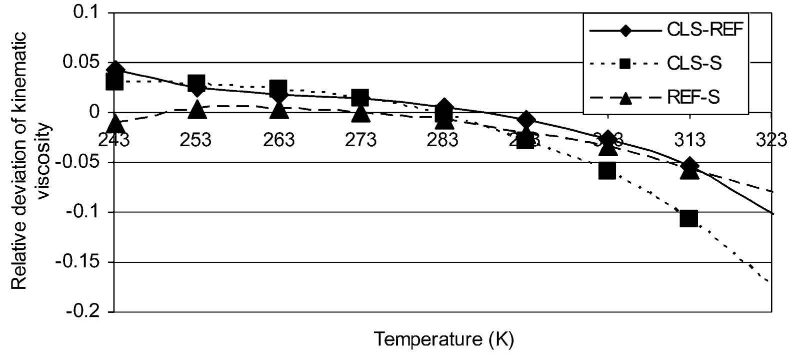
Using Eqs. (36–43), we can calculate and express along with the free energy some derived thermodynamic properties of state, which are very important in planning and monitoring the engineering processes[24]:

Table 5 Important constants for analytical calculation for R125

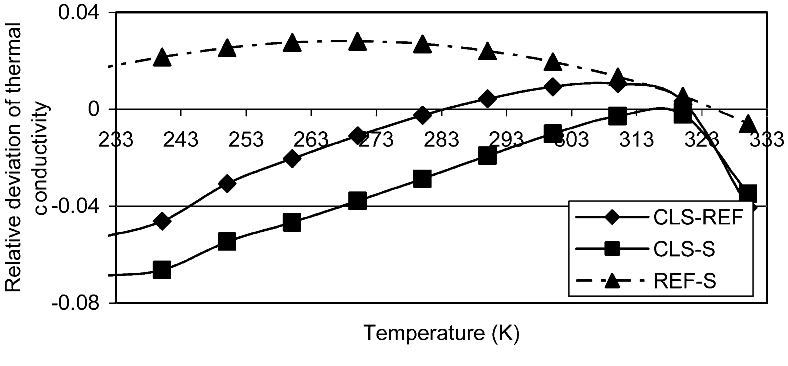
R125	CLS–thermal conductivity	CLS–viscosity
ε, J	$367.67E{-}23$	$337.678E{-}23$
σ, m	$4.80005E{-}10$	$5.005E{-}10$
ω	0.3061	0.3061
μ_r	0.6	0.6
κ	0	0



a) Saturated liquid

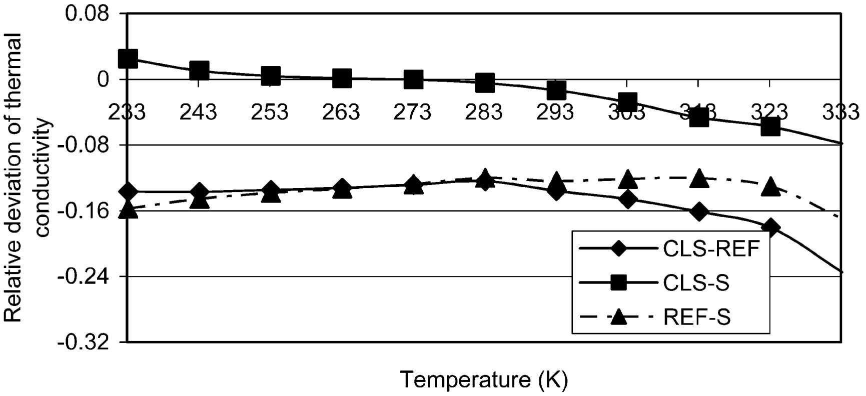


b) Saturated vapor

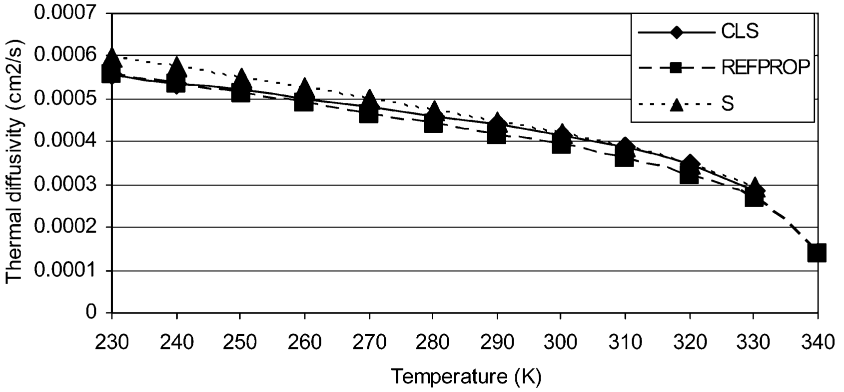


c) Saturated liquid

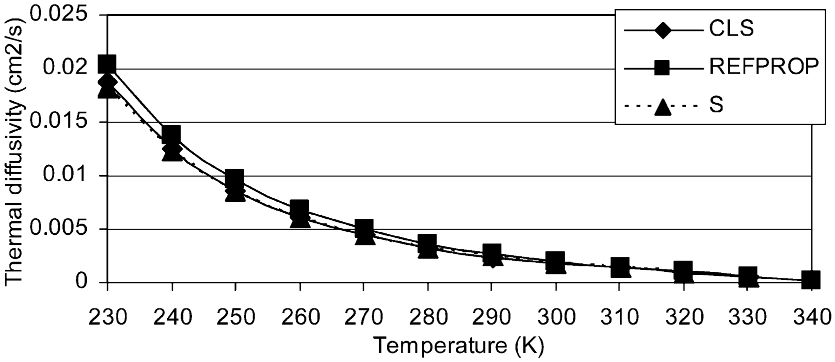
Fig. 3 Viscosity and thermal conductivity of R404A.



a) Saturated vapor



b) Saturated liquid



c) Saturated vapor

Fig. 4 Thermal diffusivity and thermal conductivity for R404A.

$$c_P = \left(\frac{\partial H}{\partial T}\right)_{p,\psi} = -\frac{1}{M}\left(\frac{\partial A}{\partial T}\right)_{V,\psi} - T\frac{1}{M}\left(\frac{\partial^2 A}{\partial T^2}\right)_{V,\psi} - V\frac{1}{M}\left(\frac{\partial}{\partial T}\left(\frac{\partial A}{\partial V}\right)_{T,\psi}\right) \tag{44}$$

Results and Discussion

Figures 1–4 show the deviation of the results for thermal conductivity and kinematic viscosity for the ternary mixture R404A and the binary mixture in the real gas region and real liquid region between the analytical computation (CLS model), Solvay 3.1.3 package (S 3.1.3), and REFPROP 7.0 (REF) empirical model obtained by classical thermodynamics.

Kinematic viscosity ν is presented as the ratio between dynamic viscosity η and density of fluid,[20]

$$\nu = \eta/\rho \tag{45}$$

Tables 5–7 show the most important data for the calculation. The results for all transport properties obtained by the CLS model show relatively good agreement. The results for the CLS model show good agreement with the REF model through the entire temperature and pressure regions. Somewhat larger deviations, however, can be found in the region of the real liquid due to the large influence of the attraction forces because the LJ potential is only an approximation of the actual real intermolecular potential (see Ref. 6). The best results in the real liquid domain are obtained with the CLS model. The relative deviation (RD) is defined by

$$\mathrm{RD(CLS-REF)} = \frac{(\mathrm{data_{CLS}} - \mathrm{data_{REF}})}{\mathrm{data_{REF}}} \tag{46}$$

In Eq. (46), RD(CLS-REF) indicates the relative deviation between CLS and the REF model. Similarly, RD(CLS-S) is the relative deviation between CLS and the S model, and RD(REF-S) is the relative deviation between the REF and the S model.

Table 6 Important constants for analytical calculation for R143a

R143a	CLS–thermal conductivity	CLS–viscosity
ε, J	$379.0E-23$	$379.0E-23$
σ, m	$4.48E-10$	$4.68E-10$
ω	0.2615	0.2615
μ_r	0	0
κ	0	0

Table 7 Important constants for analytical calculation for R134a

R134a	CLS–thermal conductivity	CLS–viscosity
ε, J	$450.04E-23$	$410.04E-23$
σ, m	$4.5463E-10$	$4.76E-10$
ω	0.32684	0.32684
μ_r	0.15	0.15
κ	0	0

Summary

A new mathematical model is presented for computation of transport properties in the liquid and gaseous states for pure fluids and multicomponent mixtures. The presented paper shows how to take into account the influence of polarity. The heat capacities are calculated by the use of the TRWW model.

We have developed the new model for calculation of transport properties of mixtures. The analytical results are compared with the REF and S models and show relatively good agreement. In the region of real gases, the results are equally good.

References

[1] Millat, J., Dymond, J. H., and Nieto de Castro, C. A., *Transport Properties of Fluids*, Cambridge Univ. Press, Cambridge, England, U.K., 1996, pp. 1–112.

[2] Ferziger, J. H., and Kaper, H. G., *Mathematical Theory of Transport Processes in Gasses*, North–Holland, London, 1972, pp. 107–263.

[3] McCourt, F. R. W., Beenakker, J. J., Köhler, W. E., and Kuscer, I., *Nonequilibrium Phenomena in Polyatomic Gases*, Clarendon, London, 1990, pp. 1–204.

[4] Chapman, S., and Cowling, T. G., *The Mathematical Theory of Non-Uniform Gases*, 3rd ed., Cambridge Univ. Press, Cambridge, England, U.K., 1970, pp. 110–195.

[5] Neufeld, P. D., Janzen, A. R., and Aziz, R. A., “Empirical Equations to Calculate 16 of the Transport Collision Integrals for the Lennard–Jones (12-6) Potential,” *Journal of Chemical Physics*, Vol. 57, No. 2, 1972, pp. 1100–1102.

[6] Kiselev, S. B., Perkins, R. A., and Huber, M. L., “Transport Properties of Refrigerants R32, R125, R134a, and R125 + R32 Mixtures in and Beyond the Critical Region,” *International Journal of Refrigeration*, Vol. 22, No. 6, 1999, pp. 509–520.

[7] Kiselev, S. B., and Huber, M. L., “Transport Properties of Carbon Dioxide + Ethane and Methane + Ethane Mixtures in the Extended Critical Region,” *Fluid Phase Equilibria*, Vol. 142, Nos. 1–2, 1998, pp. 253–280.

[8] Assael, M. J., Dalaouti, N. K., and Gialou, K. E., “Viscosity and Thermal Conductivity of Methane, Ethane and Propane Halogenated Refrigerants,” *Fluid Phase Equilibria*, Vol. 124, No. 1, 2000, pp. 203–211.

[9] Assael, M. J., Dalaouti, N. K., Dymond, J. H., and Feleki, E. P., “Correlation for Viscosity and Thermal Conductivity of Liquid Halogenated Ethane Refrigerants,” *International Journal of Thermophysics*, Vol. 21, No. 2, 2000, pp. 367–376.

[10] Dymond, J. H., “Second Virial Coefficients and Liquid Transport Properties at Saturated Vapour Pressure of Haloalkanes,” *Fluid Phase Equilibria*, Vol. 174, Nos. 1–2, 2000, pp. 13–32.

[11] Assael, M. J., Dymond, J. H., Papadaki, M., and Patterson, P. M., “Correlation and Prediction of Dense Fluid Transport Coefficients,” *Fluid Phase Equilibria*, Vol. 75, No. 1, 1992, pp. 245–255.

[12] Kihara, T., *Intermolecular Forces*, Wiley, Chichester, England, U.K., 1976, pp. 59–161.

[13] Rigby, M., Smith, E. B., Wakeham, W. A., and Maithland, G. C., *The Forces Between Molecules*, Clarendon Press, Oxford, 1986, pp. 107–125.

[14] Chung, T.-H., Lee, L. L., and Starling, K. E., “Applications of Kinetic Gas Theories and Multiparameter Correlation for Prediction of Dillute Gas Viscosity and Thermal Conductivity,” *Industrial and Engineering Chemical Research*, Vol. 27, No. 4, 1988, pp. 671–659.

[15] Chung, T.-H., Ajlan, M., Lee, L. L., and Starling, K. E., “Generalized Multiparameter Correlation for Nonpolar and Polar Fluid Transport Properties,” *Industrial and Engineering Chemical Research*, Vol. 23, No. 1, 1984, pp. 8–13.

[16] Xiang, W. H., “The New Simple Extended Corresponding-States Principle: Complex Molecular Transport Properties in Dilute Gas State,” *Fluid Phase Equilibria*, Vol. 187–188, No. 2, pp. 221–231.

[17] Holland, P. M., and Hanley, H. J. M., *Journal of Physical and Chemical Reference Data*, No. 8, 1979, pp. 859–873.

[18] Vesovic, V., and Wakeham, W., “The Prediction of Viscosity for Dense Gas Mixtures,” *International Journal of Thermophysics*, Vol. 10, No. 1, 1989, pp. 125–131.

[19] Mason, E. A., and Monchick, L., “Heat Conductivity of Polyatomic and Polar Gases,” *Journal of Chemical Physics*, Vol. 8, No. 6, 1962, pp. 1622–1639.

[20] Incropera, F. P., and Dewitt, D. P., *Heat and Mass Transfer*, 5th ed., Wiley, New York, 2001, pp. 60–70.

[21] Tillner-Roth, R., Yokezeki, A., Sato, H., and Watanabe, K., *Thermodynamic Properties of Pure and Blended Hydrofluorocarbon (HFC) Refrigerants*, Japan Society of Refrigerating and Air Conditioning Engineers, Tokyo, 1997.

[22] Avsec, J., Marcic, M., and Watanabe, K., “Study for Lennard–Jones Chains for Hydrocarbons,” *Journal of Thermophysics and Heat Transfer* (to be published).

[23] Avsec, J., “Calculation of Transport Coefficients of R-32 and R-125 with the Methods of Statistical Thermodynamics and Kinetic Theories of Gas,” *Archives of Thermodynamics*, Vol. 24, No. 3, 2003, pp. 69–82.

[24] Avsec, J., and Marčič, M., “Influence of Multipolar and Induction Interactions on the Speed of Sound,” *Journal of Thermophysics and Heat Transfer*, Vol. 14, No. 4, 2000, pp. 496–503.