

# Technical Notes

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## Analytical Calculation of Diffusion Coefficients and Other Transport Properties in Binary Mixtures

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### Nomenclature

$D_{12}$	=	binary diffusion coefficient, m <sup>2</sup> /s
$F_c$	=	second- and third-order correction factor of viscosity
$k$	=	Boltzmann constant, J/K
$k_t$	=	thermal diffusion ratio
$M$	=	molecular mass, kg/kmol
$N$	=	number of molecules in system
$R_m$	=	universal gas constant, J/kmol K
$T$	=	temperature, K
$T^*$	=	reduced temperature
$\alpha_t$	=	thermal diffusion factor
$\varepsilon$	=	Lennard–Jones parameter, J
$\eta$	=	dynamic viscosity, Pas
$\sigma$	=	Lennard–Jones parameter, m
$\psi_i$	=	molar fraction of component $i$
$\Omega$	=	collision integral, m <sup>3</sup> /s
$\Omega^*$	=	reduced collision integral

Superscript and Subscript

0 = dilute gas state

### I. Introduction

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 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.<sup>1</sup> There are approximately 30 thermomechanical properties for each pure substance, essential to engineering practice, with some 12 among them being dependent on pressure and temperature. If every pure substance were to be measured at 10 different temperatures and 10 different pressures, 600 measurements should be made for each pure substance. We would need 100 billion years of work to carry out measurement of properties for every pure substance

and for known mixtures.<sup>1</sup> Of course, in addition to time-consuming measurements a lot of money would be needed to purchase the measuring equipment. This has resulted in the need to compute the properties and forecast certain new or not yet measured substances. A combination of measuring technique and analytical procedures has actually proved to be the right way in the research of thermo-mechanical properties of substances.

### II. Nonequilibrium Mechanics and Kinetic Theory of Dilute Polyatomic Gases

From the Boltzmann equation we can for monoatomic dilute gases calculate transport properties not far from the Maxwellian.<sup>1–4</sup> This means that we treat transport phenomena with small temperature or velocity gradients of the molecules. For Lennard–Jones intermolecular potential,<sup>2</sup> 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 obtainable by linear interpolation of the tables, we used Neufeld et al.<sup>5</sup> empirical formulation, obtained on the basis of numerical simulations and interpolation procedure.

$$\Omega^{(l,s)*} = A/T^{*B} + C/\exp(DT^*) + E/\exp(FT^*) + G/\exp(HT^*) + RT^{*B} \sin(ST^{*W} - P) \quad (1)$$

where the reduced collision integral  $\Omega^{(l,s)*}$  and reduced temperature are defined as

$$\Omega^{(l,s)*} = \Omega^{(l,s)} / \pi \sigma^2, \quad T^* = kT / \varepsilon \quad (2)$$

Equation (1) contains 12 adjustable parameters and is developed for 16 collision integrals.

The presented Note features a purely analytical model for calculation of viscosity.<sup>2,4,6</sup> The kinetic theory expression for the viscosity is defined as

$$\eta_0(T) = \frac{5}{16} \frac{\sqrt{\pi M k T}}{\pi \Omega^{(2,2)*} \sigma^2} F_c \quad (3)$$

The factor  $F_c$  is called the second-order Kihara correction factor<sup>2</sup>:

$$F_c = 1 + \frac{(H_{01})^2}{H^{00} H^{11}} + \left\{ \left[ \frac{(H^{01})^2}{H^{00} H^{11}} \right]^2 + \frac{(H^{01} H^{12} - H^{11} H^{02})^2}{H^{00} (H^{11})^2 H^{22}} \right\} \quad (4)$$

where the constants  $H^{pq}$  satisfy the symmetry relation. With help of Kihara solution<sup>2</sup> and Sonine expansion,<sup>2,4</sup> we can express the coefficients  $H^{pq}$ :

$$H^{00} = \frac{2}{5kT} 4\Omega^{(2,2)}, \quad H^{01} = \frac{2}{5kT} [7\Omega^{(2,2)} - 2\Omega^{(2,3)}]$$

$$H^{11} = \frac{2}{5kT} \left[ \frac{301}{12} \Omega^{(2,2)} - 7\Omega^{(2,3)} + \Omega^{(2,4)} \right]$$

$$H^{02} = \frac{2}{5kT} \left[ \frac{63}{8} \Omega^{(2,2)} - \frac{9}{2} \Omega^{(2,3)} + \frac{1}{2} \Omega^{(2,4)} \right]$$

$$H^{12} = \frac{2}{5kT} \left[ \frac{1365}{32} \Omega^{(2,2)} - \frac{321}{16} \Omega^{(2,3)} + \frac{25}{8} \Omega^{(2,4)} - \frac{1}{4} \Omega^{(2,5)} \right]$$

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$$H^{22} = \frac{2}{5kT} \left[ \frac{25,137}{256} \Omega^{(2,2)} - \frac{1755}{32} \Omega^{(2,3)} + \frac{381}{32} \Omega^{(2,4)} - \frac{9}{8} \Omega^{(2,5)} + \frac{1}{16} \Omega^{(2,6)} + \frac{1}{2} \Omega^{(2,4)} \right] \quad (5)$$

### III. Prediction of Viscosity for Mixtures

For the determination of viscosity for fluid mixtures, we have used a purely analytical model.<sup>2,7</sup> According to this theory, the viscosity of dense fluid mixtures containing  $N$  components can be written in the form<sup>2,7</sup>

$$\eta = - \frac{\begin{vmatrix} H_{11} & \cdots & H_{1N} & \psi_1 \\ \vdots & & \vdots & \vdots \\ H_{N1} & & H_{NN} & \psi_N \\ \psi_1 & & \psi_N & 0 \end{vmatrix}}{\begin{vmatrix} H_{11} & \cdots & H_{1N} \\ \vdots & & \vdots \\ H_{N1} & \cdots & H_{NN} \end{vmatrix}} \quad (6)$$

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

$$H_{ij} (j \neq i) = - \frac{\psi_i \psi_j}{2\eta_{ij} A_{ij}^*} \frac{M_i M_j}{(M_i + M_j)^2} \left( \frac{20}{3} - 4A_{ij}^* \right) \quad (7)$$

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.<sup>7</sup>

$$A_{ij}^* = \Omega_{ij}^{(2,2)*} / \Omega_{ij}^{(1,1)*} \quad (8)$$

The symbol  $\eta_i$  represents the viscosity of pure component  $i$ , and  $\eta_{ij}$  represents the viscosity of  $i$ - $j$  interaction. We have used the new equation for  $\eta_{ij}$ :

$$\eta_{ij} = \sqrt{\eta_i \eta_j} \quad (9)$$

We applied the presented rule for the computation of viscosity mainly to avoid intermediate links and a repeated calculation of viscosity, molecular masses for a pseudofluid, composed of the combinations of masses  $M_1$  and  $M_2$ , most frequently used in international literature. The presented equation also proved to give very good results if compared with the measured values.

### IV. Diffusion Coefficients for Binary Mixtures

In the case of binary mixtures, there is only one independent diffusion coefficient  $D_{12}$ . From the kinetic theory and Chapman-Cowling approximation, we can express the next expression<sup>2,4</sup>:

$$D_{12} = \frac{3}{16nM_{12}} \frac{(2\pi M_{12}kT)^{\frac{1}{2}}}{\pi \sigma_{12}^2 \Omega_{12}^{(1,1)*}} (1 - \Delta)^{-1} \quad (10)$$

$$\Delta = \frac{1}{10} (6C_{12}^* - 5)^2 \frac{P_1 \psi_1^2 + P_2 \psi_2^2 + P_{12} \psi_1 \psi_2}{Q_1 \psi_1^2 + Q_2 \psi_2^2 + Q_{12} \psi_1 \psi_2} \quad (11)$$

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

$$P_{12} = 15 \left( \frac{M_1 - M_2}{M_1 + M_2} \right)^2 + \frac{8M_1 M_2}{(M_1 + M_2)^2} \left( \frac{\sigma_{11}}{\sigma_{12}} \right)^2 \quad (12)$$

$$Q_1 = \frac{2}{M_2(M_1 + M_2)} \left( \frac{2M_2}{M_1 + M_2} \right)^{\frac{1}{2}} \frac{\sigma_{11}^2 \Omega_{11}^{(2,2)*}}{\sigma_{12}^2 \Omega_{12}^{(1,1)*}} \left[ \left( \frac{5}{2} - \frac{6}{5} B_{12}^* \right) M_1^2 + 3M_2^2 + \frac{8}{5} M_1 M_2 A_{12}^* \right] \quad (13)$$

$$Q_{12} = 15 \left( \frac{M_1 - M_2}{M_1 + M_2} \right)^2 \left( \frac{5}{2} - \frac{6}{5} B_{12}^* \right) + 4 \frac{M_1 M_2 A_{12}^*}{(M_1 + M_2)^2} \left( 11 - \frac{12}{5} B_{12}^* \right) + \frac{8}{5} \left[ \frac{M_1 + M_2}{(M_1 M_2)^{\frac{1}{2}}} \right] \frac{\sigma_{11}^2 \Omega_{11}^{(2,2)*}}{\sigma_{12}^2 \Omega_{12}^{(1,1)*}} \frac{\sigma_{22}^2 \Omega_{22}^{(2,2)*}}{\sigma_{12}^2 \Omega_{12}^{(1,1)*}} \quad (14)$$

The expressions  $P_2$  and  $Q_2$  are obtained from  $P_1$  and  $Q_1$  by interchange of subscripts,<sup>2</sup> where the coefficients  $B_{12}$  and  $C_{12}$  are expressed as<sup>4,7</sup>

$$B_{12}^* = \frac{5[\Omega_{12}^{(1,2)*}] - 4[\Omega_{12}^{(1,3)*}]}{[\Omega_{12}^{(1,1)*}]}, \quad C_{12}^* = \frac{[\Omega_{12}^{(1,2)*}]}{[\Omega_{12}^{(1,1)*}]} \quad (15)$$

### V. Thermal Diffusion Factor

In the binary mixture there is only one independent thermal diffusion ratio. With help of the first-order Chapman-Cowling approximation,<sup>2</sup> we can express the thermal diffusion ratio  $k_t$  as<sup>2</sup>

$$[k_t]_1 = [\alpha_t]_1 \psi_1 \psi_2 \quad (16)$$

In Eq. (16)  $\alpha_t$  represents the thermal diffusion factor. An expression for the thermal diffusion factor of a binary mixture is<sup>3,4</sup>

$$\alpha_t = (6C_{12}^* - 5) \left[ \frac{\psi_1 S_1 - \psi_2 S_2}{\psi_1^2 Q_1 + \psi_2 Q_2 + \psi_1 \psi_2 Q_{12}} \right] \quad (17)$$

$$S_1 = \frac{M_1}{M_2} \left( \frac{2M_2}{M_1 + M_2} \right)^{\frac{1}{2}} \frac{\sigma_{11}^2 \Omega_{11}^{(2,2)*}}{\sigma_{12}^2 \Omega_{12}^{(1,1)*}} - 4 \frac{M_1 M_2 A_{12}^*}{(M_1 + M_2)^2} + 15 \frac{M_2 (M_1 - M_2)}{2(M_1 + M_2)^2} \quad (18)$$

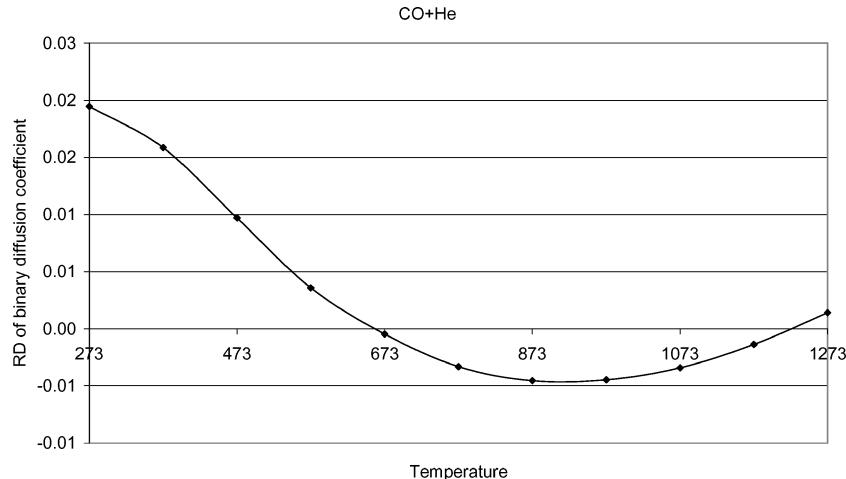


Fig. 1 Relative deviation of binary diffusion coefficient for CO+He mixture at equimolar composition.

The expressions for  $S_2$  are obtained from those of  $S_1$  by interchanging subscripts 1 and 2. The thermal diffusion ratio is a very complex function of the temperature, the concentration, and the molecular masses, and depends parametrically on the force law of the molecules. The primary concentration dependence is given by  $\psi_1\psi_2$  and to the function  $S_1\psi_1 - S_2\psi_2$ . The main dependence is on the masses of the molecules given by  $S_1$  and  $S_2$ . The thermal diffusion ratio could be positive or negative. If  $k_t$  is positive, then compo-

nent 1 tends to move into the cooler region and component 2 into the warmer region. The temperature at which  $k_t$  is equal to zero is called the inversion temperature.

## VI. Results and Comparison with Experimental Data

Figures 1–7 show the deviation of the results (binary diffusion coefficient, thermal diffusion factor, and viscosity) for binary mixture CO + He between the analytical computation on the basis

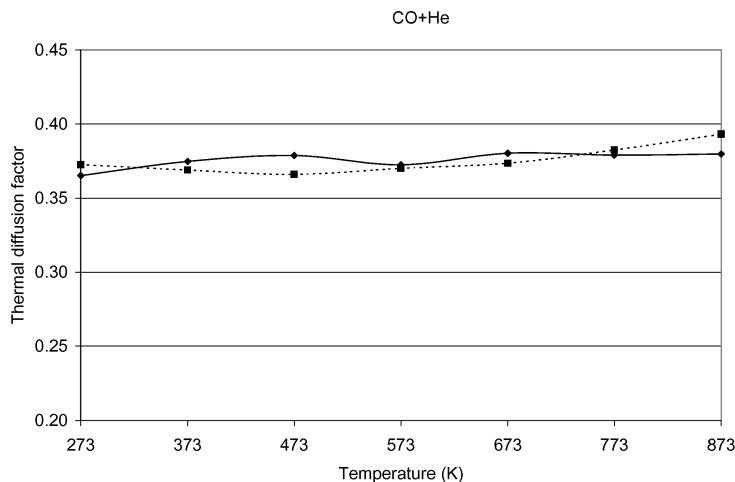


Fig. 2 Thermal diffusion factor for CO+He mixture at equimolar composition.

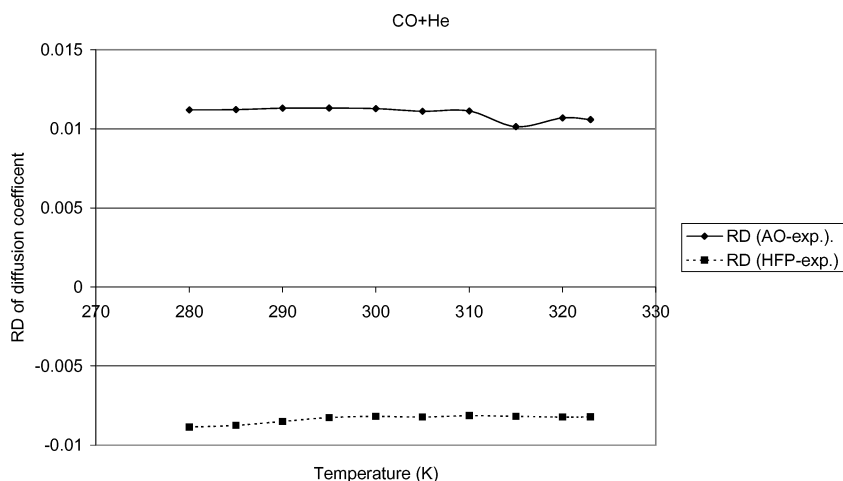


Fig. 3 Relative deviation of binary diffusion coefficient for CO+He mixture at equimolar composition.

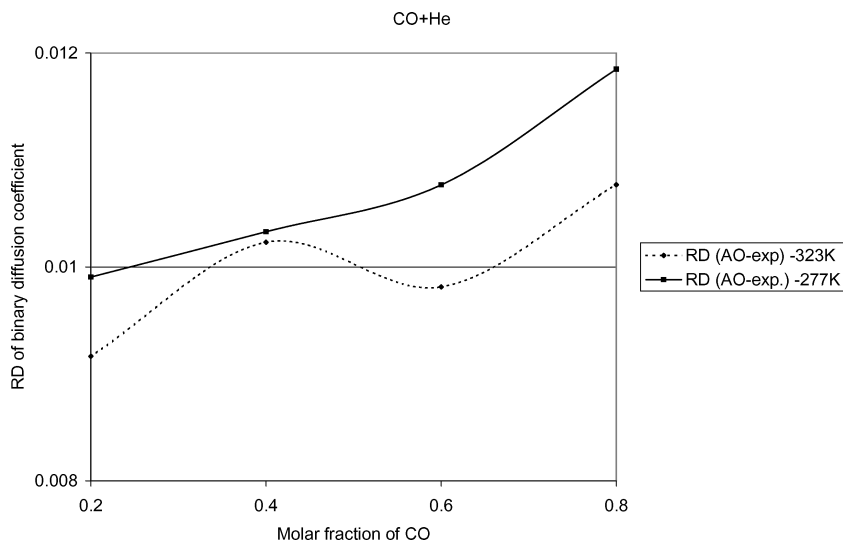


Fig. 4 Binary diffusion coefficient for CO+He mixture at various compositions.

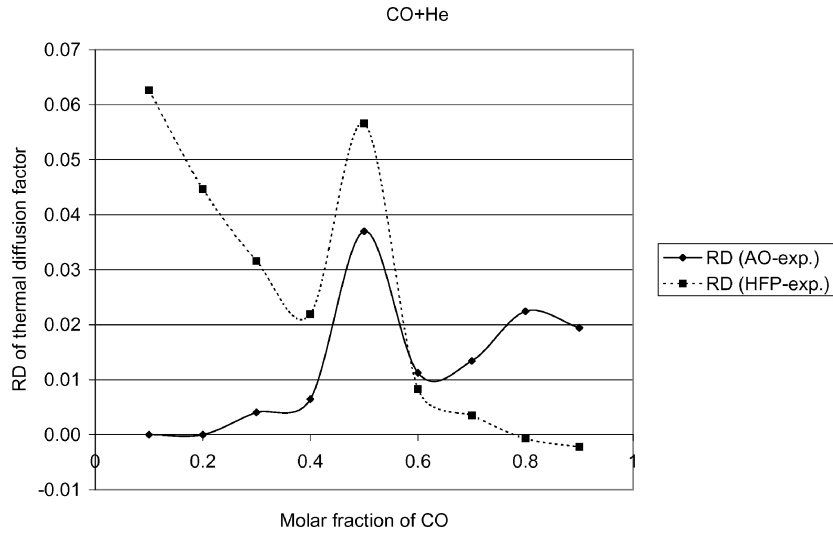


Fig. 5 Thermal diffusion factor for CO+He equimolar mixture at 300 K.

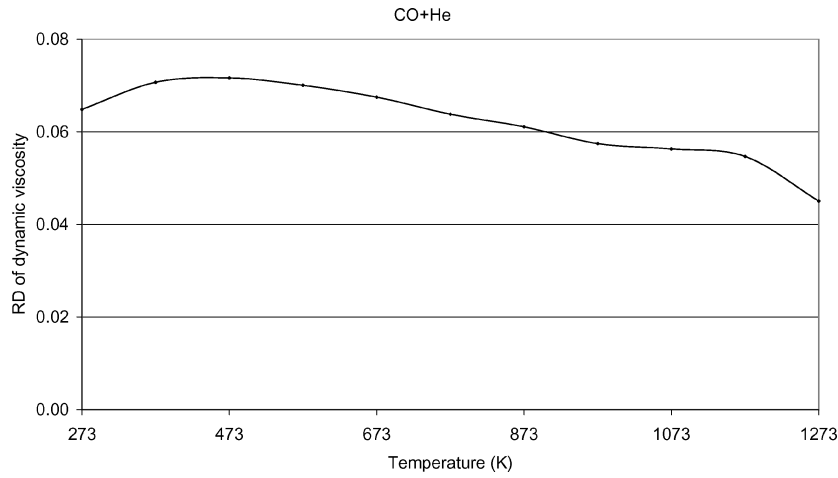


Fig. 6 Relative deviation of dynamic viscosity for CO+He equimolar mixture.

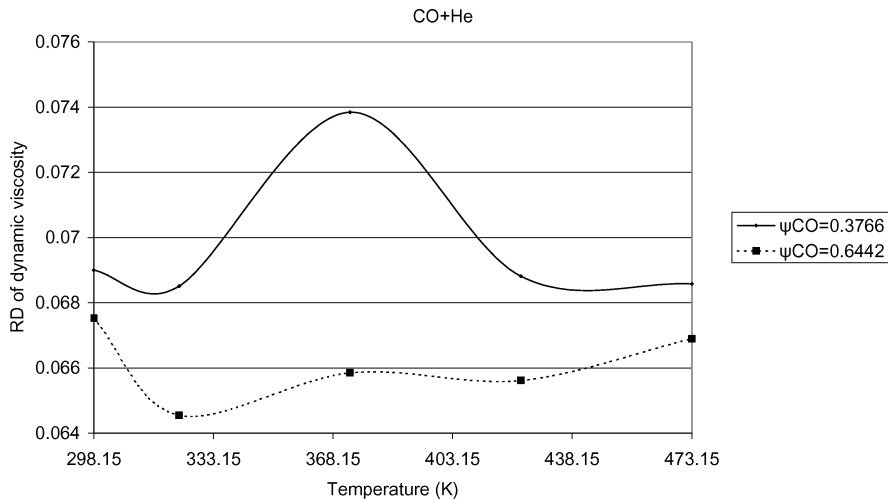


Fig. 7 Dynamic viscosity for mixture CO+He at various composition.

of nonequilibrium statistical mechanics (AO), analytical calculation from the model published by Haghighi et al. (HFP),<sup>8</sup> and experimental data (Exp.).<sup>8–10</sup> Table 1 shows the most important data for analytical calculation for AO model. The presented constants are obtained on the basis of comparison with experimental data. The results for all transport properties obtained by analytical model show relatively good agreement. All of the figures demonstrate a relatively good agreement between the measured results and

the presented model (approximately 1.5%). The binary diffusion coefficient gives very accurate results within a very wide temperature range and at different molar compositions (Figs. 1, 3, and 4). Similarly, the comparison between the measured values, HFP model, and our model for the thermal diffusion coefficient (Figs. 2 and 5) also gives very good results. Somewhat larger discrepancies between the measured results and our model occur for the viscosity, namely, maximum about 6%.

**Table 1 Important constants  
for analytical calculation for CO and He**

Lennard-Jones parameters	CO	He
$\epsilon$ , J	$138 \times 10^{-23}$	$1.421 \times 10^{-22}$
$\sigma$ , m	$3.6 \times 10^{-10}$	$2.76 \times 10^{-10}$

The relative deviation (RD) is defined by the next expression:

$$RD(AO - \exp) = \frac{(\text{data}_{AO} - \text{data}_{\exp})}{\text{data}_{\exp}} \quad (19)$$

## VII. Summary

The Note features the mathematical model of computing binary diffusion coefficient, thermal diffusion factor, and viscosity in the real-gas region on the basis of nonequilibrium statistical mechanics. For the analytical calculation of transport properties, we have used the Kihara and Chapman–Cowling model up to the third order. In the presented Note we calculated transport properties for mixtures between carbon monoxide and helium. We have developed the new mixing rules for the calculation of transport properties for mixtures. The analytical results obtained by statistical mechanics are compared with the experimental data, and they show relatively good agreement.

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