Calculation of thermophysical properties of binary helium-based gas mixtures

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Abstract. A modified methodology for calculating thermophysical properties of binary helium He based mixtures with a heavier gas component is presented. To obtain the properties of the pure components and mixtures in the limit of zero density, the most recent \textit{ab initio} calculation results and modified mixing rules are implemented. To calculate the properties at high pressures, the extended laws of corresponding states are used. A verification procedure was carried out, and the results are presented for deviations of calculated thermal conductivity $\lambda$ and dynamic viscosity $\mu$ values from available experimental data for mixtures He-Ar and He-N$_2$ at temperatures from 183 K up to 603 K, and pressures up to 10 MPa. It is shown that in the considered range of thermodynamic parameters the deviations of the calculation results from the experimental values are less than 3 \% for $\lambda$ and less than 2 \% for $\mu$.

1. Introduction

It is known that helium He based binary gas mixtures with a heavier component are considered as the working fluids of choice for the gas dynamic temperature stratification device in a compressible gas flow (Leontiev tube) [1, 2], thermoacoustic refrigerators [3] and closed Brayton cycle gas turbine powerplants [4–6]. The attractivity of these mixtures can be explained by a possibility of attaining low Prandtl number $Pr$ values for compositions close to equimolar, thus, rendering the Reynolds analogy of thermal and dynamic flow processes invalid. For example, for the Leontiev tube a decrease of the $Pr$ value results in a decrease of the temperature recovery factor $r$ values [7] and growth of the temperature difference between the compressible and incompressible gas flows [8, 9]. At the same time, flow of a gas mixture produces a thermal diffusion boundary layer, i.e., a heavier component displacement from the wall to the flow core, which results in an increase of the $Pr$ and $r$ values in the boundary layer. Such a phenomenon can be counteracted, for example, by partial evaporation of the heavier component from the wall surface at high pressures [10].

Accordingly, in order to be able to design the aforementioned devices and engines, and to conduct research on the peculiarities of thermophysical and gas dynamic processes [11–13], it is mandatory to be in possession of thermophysical properties of the gas mixtures in a wide range of pressures $p$ and temperatures $T$ (from the zero density limit and up to critical point densities). There are many well-known methodologies for calculation of thermophysical properties of gases and their binary mixtures. For example, to calculate the properties at low pressures or in the limit of zero density, empirical correlations derived as regressions of
many experimental data may be used along with mixing rules [4, 5]. Another widely used procedure is the Lennard-Jones potential calculations with mixing rules [14] (or any other form of intermolecular interaction potentials), where the potential parameters are derived by fitting the resulting calculated thermophysical properties values to experimental data. A relatively new technique is the implementation of quantum physics theory mathematical models [15–23] (ab initio calculations) to derive the intermolecular interaction potential instead of experimental fitting procedure described. To calculate thermophysical properties at high pressures (high density), the extended laws of corresponding states may be used [4, 5].

The problem of the known methodologies lies in their inaccuracy when He based gas mixtures are considered at high densities [4]. The accuracy of the widespread mixing rules deteriorate with an increase of difference of the components molecular masses and number of atoms in the molecule of the heavier component. Thus, special care should be taken when obtaining interaction parameters (virial coefficients, thermal conductivities, viscosities, etc.) from regressions of the limited experimental data for mixtures, and when using generalized expressions to calculate their values. The quantum methodology state of the art potentials and calculations are considered to be superior or equal to experimental data only for He [15], Ne [16] and Ar [17] in the limit of zero density. As for other pure gases with higher molecular masses [18, 19] and more complex molecules [20], and for mixtures of gases [21–23], the ab initio calculations superiority to experimental data regression derived values is still a matter of dispute given the complexities and inaccuracies of mathematical quantum models, and increased computational times. An even more challenging problem is the calculation of thermophysical properties at high densities for He based binary mixtures. One of the possible ways is to implement the extended laws of corresponding states, which was successfully attempted and extensively described in [4, 5]. As will be shown in the following sections, the prediction of the dynamic viscosity values by the methodology [4, 5] is perfect up to 10 MPa and at T as low as 183 K for He-Ar and He-N\textsubscript{2} mixtures, however, there are considerable deviations with experimental data present for the thermal conductivity values for the same range of parameters and mixtures.

In this paper a modified methodology based on the sequence [4, 5] is described. Results of calculations of thermal conductivity \( \lambda \) and dynamic viscosity \( \mu \) are presented for the mixtures of He with nitrogen N\textsubscript{2} and argon Ar, carried out with the modified methodology, along with verification against experimental data available in open sources. To obtain the properties for the pure gases and mixtures at the limit of zero density, the latest ab initio calculation results [15,17,20,22] are used along with improved mixing rules. The high pressure (high density) properties values are calculated with implementation of the extended laws of corresponding states.

2. Proposed calculation methodology

The proposed calculation methodology for thermophysical properties of binary He based gas mixtures with a heavier component is based on the sequence outlined in [4, 5]. The calculation process is conceived by obtaining the properties values \( \lambda_0 \) and \( \mu_0 \) in the limit of zero density as functions of \( T \) and molar fraction of a heavier component \( x_2 \). For He-Ar mixture the results of ab initio mixture calculations [22] are used, and for He-N\textsubscript{2} — the results of ab initio calculations for pure gases [15,20] along with mixing rules as presented in [5].

To calculate the values of \( \lambda_0 \) and \( \mu_0 \) at high pressures, the extended laws of corresponding states are implemented as follows:

\[
\Delta \lambda^* = f_\lambda\left(\frac{\rho(x_2, T, p)}{\rho_{cr}(x_2)}\right) = \frac{\lambda(x_2, T, p) - \lambda_0(x_2, T)}{\lambda_{cr}(x_2) - \lambda_0(x_2, T_{cr}(x_2))},
\]

\[
\Delta \mu^* = f_\mu\left(\frac{\rho(x_2, T, p)}{\rho_{cr}(x_2)}\right) = \frac{\mu(x_2, T, p) - \mu_0(x_2, T)}{\mu_{cr}(x_2) - \mu_0(x_2, T_{cr}(x_2))},
\]
where \( \lambda \) and \( \mu \) are the values of interest as functions of \( x_2, T \) and \( p \); \( \Delta \lambda^* \) and \( \Delta \mu^* \) --- excess reduced thermal conductivity and dynamic viscosity. Henceforth, all the parentheses without a multiplication sign denote a functional dependence; indices \( 1 \) and \( 2 \) --- values for pure gases (1 for a lighter component and 2 for a heavier component); \( 0 \) --- values at the limit of zero density; \( \text{cr} \) --- values at critical points. It should be noted that for He based gas mixtures due to a substantial difference in molecular masses of the pure components, assumptions about constant relations of thermal conductivities \( \lambda_{\text{cr}}/\lambda_0 = \text{const} = 2.94 \) and dynamic viscosities \( \mu_{\text{cr}}/\mu_0 = \text{const} = 2.3 \), adopted in [4, 5], are inaccurate, thus, in the proposed methodology the initial expression forms (1) and (2) are used.

Direct implementation of expressions (1) and (2) is impeded by absence of the \( \rho/\rho_{\text{cr}} \) values as functions of \( x_2, T \) and \( p \) for the mixtures is carried out by means of virial equation of state with second virial density coefficients. For these mixing rules \( B_1, B_2 \) and \( C_1, C_2 \) for the pure components were taken from the \( \text{ab initio} \) calculation results [15, 17, 20], and the second interaction virial coefficients \( B_{12} \) for He-Ar and He-N\(_2\) are calculated using the law of corresponding states as proposed in [4, 5].

The mixtures \( \rho_{\text{cr}} \) values in the proposed methodology are found using a modified expression in terms of molar volumes \( V_{\text{cr}} \) at critical points:

\[
\rho_{\text{cr}}(x_2) = \frac{M(x_2)}{V_{\text{cr}}(x_2)} = \frac{M(x_2)}{(\frac{V_{\text{cr}1}}{V_{*1}} \cdot (1 + x_2) + \frac{V_{\text{cr}2}}{V_{*2}} \cdot x_2) \cdot V^*(x_2)}. \tag{3}
\]

In this expression: \( M \) --- mixture molecular mass; \( V_{\text{cr}} \) --- molar volume of a mixture/gas at the critical point; \( V^* \) --- molar volume of a mixture/gas calculated by equation of state of the ideal gas with \( p_{\text{cr}} \) and \( T_{\text{cr}} \) as parameters. For the mixtures the \( V^* \) values are computed using standard mixing rules [4]. It should be noted that for He based mixtures due to a substantial difference in molecular masses of the pure components, assumptions about constant relations of molar volumes \( V_{\text{cr}}(x_2)/V^*(x_2) = 0.291 \), adopted in [4, 5], are inaccurate, thus, the modified expression (3) is used.

For \( \mu_{\text{cr}}(x_2) \) the same expressions are used as in [4, 5]. However, some modifications were made for \( \lambda_{\text{cr}}(x_2) \) calculation procedure:

\[
\lambda_{\text{cr}12}(x_2) = \frac{0.304 \times 10^{-4} \cdot T_{\text{cr}}(x_2)^{0.277}}{M(x_2)^{0.465} \cdot V_{\text{cr}}(x_2)^{0.115}}, \tag{4}
\]

\[
\lambda_{\text{cr}}(x_2) = (1 - x_2)^2 \cdot \lambda_{\text{cr}1} + (1 - x_2) \cdot x_2 \cdot \lambda_{\text{cr}12}(x_2) + x_2^2 \cdot \lambda_{\text{cr}2}. \tag{5}
\]

3. Calculation results and verification

In this section deviations \( \Delta \lambda \) and \( \Delta \mu \) of the calculated values (\textit{calc}) from experimental (\textit{exp}) are presented in graphical form for the mixtures He-N\(_2\) and He-Ar as follows:
\[ \Delta \lambda = \frac{\lambda_{\text{exp}} - \lambda_{\text{calc}}(x_2, T, p)}{\lambda_{\text{exp}}} \]  
(6)

\[ \Delta \mu = \frac{\mu_{\text{exp}} - \mu_{\text{calc}}(x_2, T, p)}{\mu_{\text{exp}}} \]  
(7)

The deviations were calculated with the proposed methodology, and also, for comparison purposes, with the methodology [4, 5] for the complete range of mixtures compositions \( x_2 \) at pressures \( p \) up to 10 MPa, and temperatures \( T \) from 273 K up to 603 K for He-Ar and from 183 K up to 323 K for He-N\(_2\).

From the calculation results for \( \Delta \lambda \) presented in figures 1 and 2 it can be concluded that the proposed methodology accounts better for the dependence of \( \lambda \) on \( p \) than the methodology [4,5]. Significant deviations \( \Delta \lambda \) on figure 1(a), which are independent of \( p \), for mixture He-N\(_2\) with high \( x_2 \) values are caused by experimental error, for these deviations were not confirmed by other experimental data at low pressures [29]. That being said, it can be concluded that the deviations \( \Delta \lambda \) calculated with the proposed methodology do not exceed 3 % for the considered mixtures at high densities (high pressures and low temperatures).

The calculation results for \( \Delta \mu \) delineated in figure 3 show that the proposed methodology grants no significant improvements for He-N\(_2\) mixture, although, it does provide for slightly lower deviations at \( T = 183 \) K and high pressures \( p \). The calculation results for \( \Delta \mu \) for He-Ar are not presented, since for the both methodologies considered the deviations \( \Delta \mu \) from experimental data [30] are mostly identical and less than ±2 % for \( p \) up to 5 MPa (the maximum available in the experiments) and \( T = 293 \ldots 303 \) K.

*Figure 1. \( \Delta \lambda \) as functions of \( p \) at different \( T \) and \( x_2 \) for mixtures He-N\(_2\) and He-Ar: (a) the proposed methodology, (b) methodology [4,5].*
5.

4. Conclusion

A modified methodology for calculating thermophysical properties of binary helium He based mixtures with a heavier gas component is presented with implementation of the most recent \textit{ab initio} calculation results, modified expressions for the properties at the critical points and the extended laws of corresponding states. The deviations of calculated thermal conductivity and dynamic viscosity values from available experimental data are less than 3\% and 2\%, accordingly, at pressures up to 10 MPa and temperatures from 273 K up to 603 K for He-Ar mixture and from 183 K up to 323 K for He-N$_2$ mixture.
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