Thermophysical properties of binary mixtures containing oxygen and noble gases

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Abstract. This work deals with the determination of reliable transport and equilibrium thermophysical properties of binary mixtures of O₂ and the noble gases Ar, Kr, and Xe. The second virial coefficients B(T), the viscosities η(T), and the binary diffusion coefficients D_{12}(T) were calculated for each mixture in the temperature range between 200 K and 1000 K using a temperature dependent (n-6) Lennard-Jones intermolecular interaction potential model. The properties of the mixtures were obtained by using the Lorentz-Berthelot and Hohm-Zarkova-Damyanova mixing rules. Our results were compared to other theoretical and experimental data and acceptable agreement was found in all cases. Fitting formulae for the calculation of the intermolecular potential parameters and equilibrium and transport properties of the examined mixtures are recommended proposed.

1. Introduction

Binary mixtures containing molecular oxygen and the noble gases Ar, Kr, and Xe are used in many industrial processes, e.g. Ar/O₂ is applied as a shielding gas in weldings [1]; Ar/O₂, Kr/O₂, and Xe/O₂ are used in magnetron sputtering [2]; Ar/O₂ or Kr/O₂ are applied in etching processes [3]. Recently, medical applications became popular; e.g., a Xe/O₂ mixture is used as a respiratory and anesthetic gas mixture [4-5] and Ar/O₂ [6] is used in tissue regeneration. In all applications, reliable information is needed on the equilibrium and transport properties at different concentrations and in a wide range of temperatures. The variety of possible constituents of mixtures, as well as various experimental difficulties, stimulate the calculation of thermophysical data by different models.

Our calculations were based on the (n-6) Lennard-Jones temperature dependent potential (LJTDP). By using the Lorentz-Berthelot [7] and Hohm-Zarkova-Damyanova [8] mixing rules, the intermolecular interaction potentials of the binary mixtures were obtained from the pure component data. Subsequently, these potentials were used to calculate the second virial coefficients (B_{12}, B_{mix}), the viscosities η_{12}, η_{mix} and the binary diffusion coefficients (D_{12}) for all three mixtures in the temperature range between 200 K and 1000 K. Our findings were compared to available theoretical and experimental data.

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2. Theoretical background
All thermophysical properties of gas mixtures in the low pressure (under 1 atm) range depend on the binary intermolecular interaction energies between like and unlike constituents of the corresponding mixture. In our model, the intermolecular interactions between molecule 1 and 2 are described by the \(n\)-6 Lennard-Jones potential with the characteristic potential parameters \(R_{m12}\) (equilibrium distance), \(\varepsilon_{12}\) (potential well depth), and \(n_{12}\) (repulsive parameter). In the case of molecules, we consider to be \(R_{m12}\) and \(\varepsilon_{12}\) as being functions of the temperature \(T\), which leads us to using the Lennard-Jones temperature-dependent potential (LJTDP)\[9]\.

The intermolecular interaction potential parameters \(R_{m11}\), \(\varepsilon_{11}\), and \(n_{11}\) for the pure gases have already been determined by Damyanova et al. and are given in Ref. \[10\] for pure \(O_2\) and Ref. \[11\] for the noble gases.

The potential parameters \(R_{m12}\) and \(\varepsilon_{12}\) for unlike pairs are obtained via the Lorenz-Berthelot (LB) and Hohm-Zarkova-Damyanova (HZD) mixing rules; the latter is given in full detail in Ref. \[8\]. In both cases, the repulsive parameter \(n_{12}=\left(n_1+n_2\right)/2\) does not depend on the temperature. The molecular properties used in this work are given in table 1.

| Substance | Molar mass/ \((\text{g/mol})\) | \((\varepsilon_{11}(0)/k_B)\)/K | \(10^{10}R_{m11}(0)/\text{m}\) | \(n_1\) | \(\alpha/\text{a.u.}^a\) | \(C_d/\text{a.u.}^a\) |
|-----------|-------------------------------|-------------------------------|---------------------------------|-------|----------------|----------------|
| Ar        | 39.95                         | 155.00 [11]                  | 3.600 [11]                     | 17.10 | 11.08 [12]    | 64.30 [14]    |
| Kr        | 83.80                         | 221.00 [11]                  | 3.860 [11]                     | 17.8  | 16.79 [12]    | 129.6 [14]    |
| Xe        | 131.30                        | 310.90 [11]                  | 4.204 [11]                     | 18.76 | 27.16 [12]    | 285.90 [14]   |
| \(O_2\)   | 32.00                         | 185.53 [10]                  | 3.460 [10]                     | 23.20 | 10.585 [12]   | 61.57 [13]    |

\(^a\) Conversion factors are for \(\alpha\): 1 a.u. = 1.64878 \times 10^{-46} \text{C}^2\text{m}^7\text{J}^{-1} and \(C_d\): 1 a.u. = 9.57345 \times 10^{-69} \text{Jm}^6.

3. Results and discussion
The LJTDP model was used to calculate the thermophysical properties \(B_{12}\), \(B_{\text{mix}}\), \(\eta_{12}\), \(\eta_{\text{mix}}\), and \(D_{12}\) for all three \(O_2/X\)-mixtures (X=Ar, Kr, Xe) in the temperature range between 200 K and 1000 K. Both mixing rules, LB and HZD, were used. Our calculated results (“calc”) were compared to other experimental and theoretical data in the literature (“other”) (see the deviation plots given in figures 1–8). The absolute deviations \(\Delta B = B_{\text{other}} - B_{\text{calc}}\) are displayed in the case of the second virial coefficient, whereas for \(\eta\) and \(D\) we show the relative deviations. The empty symbols are used for the results obtained by the LB mixing rule; the full symbols denote results obtained by the HZD mixing rule. We should first we note that most of the thermophysical properties of the three mixtures have not been well investigated. One can find measured \(B_{12}\) data \[15,16\] for the \(O_2/Ar\) mixture only. Calculated values for \(B_{\text{mix}}\), \(\eta_{\text{mix}}\) and \(D_{12}\) of equimolar \(O_2/Ar\), \(O_2/Kr\), and \(O_2/Xe\) gas mixtures were published by Bzowski et al. \[17\]. Except for their calculations of \(\eta_{\text{mix}}\), mixture viscosity measurements for different \(O_2\) concentrations were reported by Hellemans et al. \[18\] for \(O_2/Ar\) and \(O_2/Kr\) mixtures; calculations were published by Katz et al. \[19\] for \(O_2/Xe\). Measurements of the diffusion coefficients \(D_{12}\) were performed by Boardman et al. \[20\], Arrora et al. \[21\] and Trengove et al. \[22\] for \(O_2/Ar\); Dunlop et al. \[23\] and Ivakin et al. \[24\] for \(O_2/Kr\); and Dunlop et al. \[23\] for \(O_2/Xe\). Calculated \(D_{12}\) data are given in Refs. \[21, 25\] for \(O_2/Ar\), \[24\] for \(O_2/Kr\), and \[19\] for \(O_2/Xe\).

Figures 1-8 show that in the case of \(B_{\text{mix}}\) and \(D_{12}\), the HZD mixing rule yields a slightly better agreement between the literature data and our findings, whereas the more popular LB mixing rule seems to work a little bit better in the case of \(B_{12}\) and \(\eta_{\text{mix}}\).
Figure 1. Absolute deviations $\Delta B_{12}$ of the interaction second virial coefficient, $B_{12}$, between Refs. [15,16] and our findings for O$_2$/Ar gas mixture.

Figure 2. Absolute deviations $\Delta B_{\text{mix}}$ of the mixture second virial coefficient, $B_{\text{mix}}$, between Refs [17] and our findings for O$_2$/Ar, O$_2$/Kr, and O$_2$/Xe gas mixtures.

Figure 3. Relative deviations of the mixture viscosity, $\eta_{\text{mix}}$, between Refs. [17,18] and our findings for O$_2$/Ar gas mixture.

Figure 4. Relative deviations of the diffusion coefficient, $D_{12}$, between Refs. [17,20,21,22,25] and our findings for O$_2$/Ar gas mixture.

Figure 5. Relative deviations of the mixture viscosity, $\eta_{\text{mix}}$, between Refs. [17,18] and our findings for O$_2$/Kr gas mixture.

Figure 6. Relative deviations of the diffusion coefficient, $D_{12}$, between Refs. [17,23,24] and our findings for O$_2$/Kr gas mixture.
Our recommended values of \(R_{m12}(T), \xi_{12}(T), B_{12}(T), \eta_{12}(T)\) and \(D_{12}(T)\) in the temperature range between 200 K and 1000 K are presented in the form of fitting formulæ. For the sake of consistency, all of them are based on the HZD mixing rule. The equilibrium distance \(R_{m12}(T)\) is fitted to the dimensionless expression:

\[
R_{m12}(T)/(10^{10} \text{m}) = R_{m12}(0)/(10^{10} \text{m}) + A_1 \exp[-A_2/(T/K)] + A_3 \exp[-A_4/(T/K)].
\] (1)

Subsequently, the well depth \(\xi_{12}(T)\) can be calculated via \(\xi_{12}(T) = \xi_{12}(0)[R_{m12}(0)/R_{m12}(T)]^{6}\).

In the sequence \(\text{O}_2/\text{Ar}, \text{O}_2/\text{Kr},\) and \(\text{O}_2/\text{Xe}\), the zero temperature potential parameters \(R_{m12}(0)/(10^{10} \text{m})\) and \((\xi_{12}(0)/k_b)/K\) of the unlike interactions are given as 3.52987 and 169.368, 3.6630 and 198.875, 3.84464 and 225.440, respectively. For the thermophysical properties we have used the following fitting formulæ.

The fitting constants are given in table 2. Here \(\Delta P\) is the standard error of the fit.

\[
B_{12}(T)/(\text{cm}^3/\text{mol}) = \sum_{k=1}^{5} A_k \left( \frac{T}{K} \right)^{1-k} 
\] (2)

\[
\eta_{12}(T)/(\mu\text{Pa} \cdot \text{s}) = \sum_{k=1}^{5} A_k \left( \frac{T}{K} \right)^{1-k} 
\] (3)

\[
D_{12}(T)/(10^{-6}\text{ m}^2/\text{s}) = \sum_{k=1}^{5} A_k \left( \frac{T}{K} \right)^{1-k} 
\] (4)

| Property      | \(A_1\)  | \(A_2\)  | \(A_3\)  | \(A_4\)  | \(\Delta P\) |
|---------------|----------|----------|----------|----------|-------------|
| \(R_{m12}(T)\) | 0.076001 | 2275.20  | 0.075426 | 4920.25  | -           | 5.9 \cdot 10^{-7} |
| \(B_{12}(T)\)  | 33.439   | -1.00095 \cdot 10^{6} | -1.82492 \cdot 10^{6} | 1.88479 \cdot 10^{6} | -1.47868 \cdot 10^{10} | 0.0034 |
| \(\eta_{12}(T)\) | -1.07170 | 9.65437 \cdot 10^{-6} | -8.53242 \cdot 10^{-6} | 5.73430 \cdot 10^{-6} | -1.68199 \cdot 10^{-11} | 0.0055 |
| \(D_{12}(T)\)  | -1.88266 | 1.98262 \cdot 10^{-2} | 1.91183 \cdot 10^{-4} | -7.6572 \cdot 10^{-4} | 1.80548 \cdot 10^{-11} | 0.0083 |
| \(R_{m12}(T)\) | 0.075498 | 2274.87  | 0.074673 | 4911.94  | -           | 6.1 \cdot 10^{-7} |
| \(B_{12}(T)\)  | 38.310   | -1.41118 \cdot 10^{6} | -2.20146 \cdot 10^{6} | 1.88790 \cdot 10^{6} | -1.72271 \cdot 10^{11} | 0.0040 |
| \(\eta_{12}(T)\) | -1.41488 | 9.60991 \cdot 10^{-6} | -7.64399 \cdot 10^{-6} | 4.70388 \cdot 10^{-6} | -1.28366 \cdot 10^{-11} | 0.0027 |
| \(D_{12}(T)\)  | -1.30221 | 1.23991 \cdot 10^{-2} | 1.57433 \cdot 10^{-4} | -6.59022 \cdot 10^{-4} | 1.67906 \cdot 10^{-11} | 0.0084 |
| \(R_{m12}(T)\) | 0.077214 | 2289.01  | 0.091152 | 5312.12  | -           | 3.8 \cdot 10^{-7} |
| \(B_{12}(T)\)  | 45.241   | -1.92441 \cdot 10^{6} | -2.75729 \cdot 10^{6} | 1.95156 \cdot 10^{6} | -2.16278 \cdot 10^{10} | 0.0057 |
| \(\eta_{12}(T)\) | -1.28771 | 8.54281 \cdot 10^{-2} | -5.89447 \cdot 10^{-3} | 3.12228 \cdot 10^{-8} | -7.32284 \cdot 10^{-12} | 0.0050 |
| \(D_{12}(T)\)  | -0.86444 | 7.62039 \cdot 10^{-3} | 1.37370 \cdot 10^{-4} | -5.92489 \cdot 10^{8} | 1.55300 \cdot 10^{-11} | 0.0077 |
4. Conclusions
Our recommended fitting formulae can be used for easy and reliable calculation of the HZD potential parameters and the thermophysical properties $B_{12}$, $\eta_{12}$ and $D_{12}$ of the binary mixtures O$_2$/Ar, O$_2$/Kr, and O$_2$/Xe in the temperature range between 200 K and 1000 K, covering the whole concentration range. The formulae for the potential parameters $R_{m12}(T)$ and $\delta_{ij}(T)$ might be useful for the calculation of other properties of oxygen/noble gas mixtures as well.

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