POTENTIAL ENERGY OF INTERACTION BETWEEN UNLIKE NONPOLAR MOLECULES

R. M. Sevast'yanov and N. A. Zykov

It is shown that calculations for the (12-7, δ) model of pair interaction potential consistently agree with experimental data on the interdiffusion coefficients and the mixed second virial coefficient for nonpolar mono- and polyatomic gases.

For calculating the thermophysical properties of gas mixtures, one must know the potential pair interaction energy (pair interaction potential) of all like and unlike molecules. The models of interaction potentials must, moreover, consistently (i.e., with unique values of the force constants) agree with various experimental data over the entire range of measurement [1]. For nonpolar molecules of arbitrary symmetry this requirement is met by the quasispherical model potential (12-7, δ) [2]:

\[
\psi(r) = \begin{cases} 
\infty, & r^2 \leq \delta, \\
5.1042 \left[ \left( \frac{1 - \delta}{r^2 - \delta} \right)^6 - \left( \frac{1 - \delta}{r^2 - \delta} \right)^{7/2} \right], & r^2 \gg \delta,
\end{cases}
\]

where \( \varepsilon \) is the depth of the potential well; \( \sigma \), molecule "diameter," \( r_0 \), characteristic linear dimension ("core" of a molecule); \( \overline{r} = r/\sigma \); and \( \delta = (r_0/\sigma)^2 \), asphericity of a molecule.

For calculating the thermophysical properties of gas mixtures one uses, as a rule, the same model potential as for the pure components. The main difficulty thus is in determining the force constants in the interaction potential of unlike molecules. For this one generally uses the combining rules

\[
\sigma_{12} = \frac{1}{2} (\sigma_{11} + \sigma_{22}),
\]

<table>
<thead>
<tr>
<th>System</th>
<th>( \overline{r}/K )</th>
<th>( \sigma/10^{-4} \text{ cm} )</th>
<th>( \delta )</th>
<th>( \Lambda^* )</th>
<th>( T_D/K )</th>
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</thead>
<tbody>
<tr>
<td>He--Ar</td>
<td>24.9</td>
<td>3.092</td>
<td>0</td>
<td>1.053</td>
<td>62</td>
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<td>He--Kr</td>
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<td>3.271</td>
<td>0</td>
<td>0.976</td>
<td>62</td>
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<tr>
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<td>0</td>
<td>0.944</td>
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<td>Ar--Xe</td>
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</tr>
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<td>4.036</td>
<td>0.3595</td>
<td>0.107</td>
<td>576</td>
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</table>

TABLE 2. Comparison of Experimental and Theoretical Values of the Mixed Second Virial Coefficient for Nonpolar Gases

<table>
<thead>
<tr>
<th>System</th>
<th>T, K</th>
<th>$\Delta B_{12,\text{mix}}$ cm$^3$/mole</th>
<th>$\Delta B_{12,\text{max}}$ cm$^3$/mole</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>He–Ne</td>
<td>148–323</td>
<td>1.3</td>
<td>1.7</td>
<td>[6]</td>
</tr>
<tr>
<td>He–Ar</td>
<td>148–323</td>
<td>3.4</td>
<td>4.3</td>
<td>[6]</td>
</tr>
<tr>
<td>He–N$_2$</td>
<td>148–323</td>
<td>3.4</td>
<td>4.5</td>
<td>[6]</td>
</tr>
<tr>
<td>He–CO$_2$</td>
<td>303–373</td>
<td>0.3</td>
<td>0.8</td>
<td>[7]</td>
</tr>
<tr>
<td>Ne–Ar</td>
<td>148–323</td>
<td>1.5</td>
<td>1.9</td>
<td>[6]</td>
</tr>
<tr>
<td>Ar–Kr</td>
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<td>6.4</td>
<td>[8]</td>
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<tr>
<td>Ar–Xe</td>
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<td>0.8</td>
<td>3.9</td>
<td>[9]</td>
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<tr>
<td>Ar–N$_2$</td>
<td>148–323</td>
<td>0.8</td>
<td>1.4</td>
<td>[6]</td>
</tr>
<tr>
<td>Ar–CH$_4$</td>
<td>107–274</td>
<td>1.6</td>
<td>3.7</td>
<td>[8]</td>
</tr>
<tr>
<td>Ar–CO$_2$</td>
<td>303–373</td>
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<td>2.5</td>
<td>[10]</td>
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<tr>
<td>Ar–SF$_6$</td>
<td>300–550</td>
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<td>5.0</td>
<td>[11]</td>
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<tr>
<td>Kr–Xe</td>
<td>213–500</td>
<td>1.3</td>
<td>2.8</td>
<td>[11]</td>
</tr>
<tr>
<td>Kr–CH$_4$</td>
<td>119–271</td>
<td>1.4</td>
<td>3.0</td>
<td>[8]</td>
</tr>
<tr>
<td>CH$_4$–SF$_6$</td>
<td>300–550</td>
<td>4.5</td>
<td>9.7</td>
<td>[10]</td>
</tr>
</tbody>
</table>

\[ \varepsilon_{12} = \sqrt{\varepsilon_{11}\varepsilon_{22}} \] (3)

on various more intricate ones [3]. Certain empirical combining rules are, however, unsatisfactory [3].

Theoretically sound combining rules have been derived by Kong [4]. The expressions relating the force constants $\sigma_{12}$ and $\varepsilon_{12}$ in the interaction potential of unlike molecules to the corresponding force constants for like molecules depend on the form of the model of pair interaction potential which is used for the calculations. Calculations for the (12-7) potential by Kong's combining rules [4] consistently agree with experimental data on the interdiffusion coefficients and the mixed second virial coefficient for monoatomic gases. This has made it possible to calculate the transport coefficients for binary mixtures of monoatomic gases with low densities at temperatures from 100 to 6000°K [5].

In this study Kong's combining rules have been extended to the quasispherical (12-7, $\delta$) model of pair interaction potential (1) and an evaluation made of the accuracy of describing, on this basis, experimental data on the interdiffusion coefficient and the mixed second virial coefficient.

TABLE 3. Comparison of Experimental and Theoretical Values of the Interdiffusion Coefficients for Nonpolar Gases under a Pressure of 0.1013 MPa

<table>
<thead>
<tr>
<th>System</th>
<th>T, K</th>
<th>$\delta D_{12}$ %</th>
<th>$\delta D_{12,\text{max}}$ %</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>He–Ar</td>
<td>300–1400</td>
<td>1.5</td>
<td>2.0</td>
<td>[12]</td>
</tr>
<tr>
<td>He–Kr</td>
<td>300–1100</td>
<td>0.7</td>
<td>1.5</td>
<td>[12]</td>
</tr>
<tr>
<td>He–Xe</td>
<td>300–1000</td>
<td>1.0</td>
<td>1.5</td>
<td>[12]</td>
</tr>
<tr>
<td>He–N$_2$</td>
<td>298–973</td>
<td>6.6</td>
<td>8.0</td>
<td>[13]</td>
</tr>
<tr>
<td>He–CH$_4$</td>
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<td>3.0</td>
<td>4.7</td>
<td>[14]</td>
</tr>
<tr>
<td>He–SF$_6$</td>
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<td>6.7</td>
<td>8.5</td>
<td>[14]</td>
</tr>
<tr>
<td>Ne–Ar</td>
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<td>1.3</td>
<td>2.2</td>
<td>[12]</td>
</tr>
<tr>
<td>Ne–Kr</td>
<td>300–1400</td>
<td>1.4</td>
<td>2.3</td>
<td>[12]</td>
</tr>
<tr>
<td>Ne–Xe</td>
<td>300–1400</td>
<td>1.2</td>
<td>2.1</td>
<td>[12]</td>
</tr>
<tr>
<td>Ne–N$_2$</td>
<td>298–973</td>
<td>5.0</td>
<td>6.5</td>
<td>[12]</td>
</tr>
<tr>
<td>Ne–CO$_2$</td>
<td>298–973</td>
<td>9.1</td>
<td>10.6</td>
<td>[14]</td>
</tr>
<tr>
<td>Ne–CH$_4$</td>
<td>298–473</td>
<td>6.4</td>
<td>1.1</td>
<td>[14]</td>
</tr>
<tr>
<td>Ne–SF$_6$</td>
<td>298–483</td>
<td>2.6</td>
<td>5.2</td>
<td>[14]</td>
</tr>
<tr>
<td>Ar–Kr</td>
<td>300–1400</td>
<td>2.0</td>
<td>2.6</td>
<td>[12]</td>
</tr>
<tr>
<td>Ar–Xe</td>
<td>300–1400</td>
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<td>0.9</td>
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