Excess properties of liquid mixtures from the perturbation theory of Barker–Henderson

M. Koyuncu*, A. Demirtas, R. Ogul
Department of Physics, Selcuk University, 42031 Kampus, Konya, Turkey
Received 6 July 2001; accepted 25 September 2001

Abstract
Using a truncated Lennard–Jones (6–12) interaction potential for the molecular interactions, we have calculated thermodynamical excess functions of various binary mixtures from Barker–Henderson perturbation theory. In the calculations of thermodynamic quantities, we used the Carnahan–Starling equation of state as a hard sphere reference system. It is seen that our results are quite satisfactory when compared to the existing theoretical and experimental results. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Binary mixtures; Liquid mixtures; Thermodynamic functions; Excess properties

1. Introduction
The topic of this study, excess thermodynamic properties of the binary mixtures, is one of the most interesting phenomena in molecular physics. They provide us information to understand the observed properties of the mixtures from the point of view of microscopic interactions. Properties of the binary mixtures have been extensively discussed in the context of perturbation [1–8] and variational models [9,10]. In these theories, the properties of the liquids can be determined by the repulsive forces which are usually perturbed by the attractive forces between the molecules. The results obtained by these approaches are quite satisfactory.

In this study, we have used Leonard–Henderson–Barker (LHB) theory [11] to determine the thermodynamic quantities, such as Helmholtz energy, enthalpy and entropy of some binary mixtures. For the perturbation term of the molecular potential, we consider a truncated Lennard–Jones (LJ) potential. Molecular parameters for each components of the mixture can usually be determined from the thermodynamical data for pure species. But, the potential parameters between two species of a binary mixture cannot be determined directly. In this respect, we have presented a new approach to determine the potential
parameters for the calculation of various excess thermodynamic functions. In this approach, free volume fraction based on Carnahan–Starling has been used to calculate the properties of binary mixtures. As can be seen in Tables 2 and 3, our results extend the existing theoretical predictions for the thermodynamic quantities at various temperatures.

2. Calculation of the thermodynamic functions of binary mixtures

Using the extended Barker–Henderson (BH) theory for the binary mixtures, one may express the Helmholtz energy $A$ of a liquid mixture as

$$ A_{\text{NLT}} = \frac{A_0}{NkT} + \frac{2\pi \rho}{kT} \sum_{i,j=1}^{2} \int_{\sigma_{ij}}^{\infty} g_{ij}^{0}(r)u_{ij}(r)r^2 \, dr $$

(1)

where $A_0$ is the free energy of hard sphere mixture, $k$ the Boltzmann constant, $\rho$ the molecule number density of the mixture, $N$ the number of molecules, $x_i$ and $x_j$ the mole fraction of the $i$th and $j$th species, respectively, $g_{ij}^{0}(r)$ the pair distribution function and $u_{ij}(r)$ the perturbing potential function for the mixture. For the temperature dependent effective hard sphere diameter of mixture, we assume that

$$ d_{ij} = d_{ii} + d_{jj} \frac{r}{2} $$

(2)

where $d_{ii} = \int_{0}^{\sigma_{ii}} \left[ 1 - \exp \left\{ -\beta u_{ii}(r) \right\} \right] \, dr$ and $\beta = \frac{1}{kT}$

Direct application of Eq. (1) involves extensive numerical calculations, because of the radial distribution function and the form of the potential function. Therefore, calculations can be simplified in the following considerations [12]. First of all, one can use an appropriate analytical expression, for the radial distribution function of reference hard sphere mixture, proposed by de Boer [13] as follows:

$$ g_{ij}^{0}(r) = \begin{cases} 
0 & \text{for } r < \sigma_{ij} \\
1 + \frac{4\pi \rho \sigma_{ij}^3}{3} \left[ 1 - \frac{3}{4} \left( \frac{r}{\sigma_{ij}} \right) + \frac{1}{16} \left( \frac{r}{\sigma_{ij}} \right)^3 \right] & \text{for } \sigma_{ij} \leq r \leq 2\sigma_{ij} \\
1 & \text{for } r > 2\sigma_{ij}
\end{cases} $$

(2)

The Lennard–Jones potential provides a fair description of the interaction between pairs of rare-gas atoms and also of quasispherical molecules such as CH₄. Moreover, careful measurements, particularly those of second virial coefficients at low temperatures, have shown that the true pair potential for rare gas atoms is not of the Lennard–Jones form but has a deeper bowl and weaker tail [14]. Therefore, we assume a truncated LJ potential for the perturbing pair potential for a mixture as follows:

$$ u_{ij}(r) = \begin{cases} 
0 & \text{for } r < \sigma_{ij} \\
4\epsilon_{ij} \left( \frac{\sigma_{ij}}{r} \right)^{12} - \left( \frac{\sigma_{ij}}{r} \right)^{6} & \text{for } \sigma_{ij} \leq r \leq \lambda_{ij}\sigma_{ij} \\
0 & \text{for } r > \lambda_{ij}\sigma_{ij}
\end{cases} $$

(3)
Table 1

<table>
<thead>
<tr>
<th>Liquid</th>
<th>T (K)</th>
<th>ε/k</th>
<th>σ (Å)</th>
<th>d (Å)</th>
<th>V (cm³/mol)</th>
<th>λ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>83.82</td>
<td>119.8</td>
<td>3.405</td>
<td>3.34</td>
<td>28.17</td>
<td>1.83685</td>
</tr>
<tr>
<td></td>
<td>91</td>
<td>3.330</td>
<td>29.12</td>
<td>1.78890</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>115.8</td>
<td>3.315</td>
<td>33.82</td>
<td>1.65763</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N₂</td>
<td>83.82</td>
<td>101.3</td>
<td>3.612</td>
<td>3.522</td>
<td>36.07</td>
<td>1.74285</td>
</tr>
<tr>
<td></td>
<td>91</td>
<td>3.522</td>
<td>37.87</td>
<td>1.69848</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O₂</td>
<td>83.82</td>
<td>119.8</td>
<td>3.360</td>
<td>3.290</td>
<td>27.29</td>
<td>1.83588</td>
</tr>
<tr>
<td></td>
<td>91</td>
<td>3.531</td>
<td>37.29</td>
<td>1.71369</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH₄</td>
<td>91</td>
<td>152</td>
<td>3.740</td>
<td>3.671</td>
<td>35.56</td>
<td>1.92892</td>
</tr>
</tbody>
</table>

where \( \varepsilon_{ij} \) represents the potential depths, \( \sigma_{ij} \) are the values of \( r \) at which the potential is effectively zero and \( \lambda_{ij} \) is a parameter whose value depends on the nature of the mixture. The value of \( \lambda_{ii} \) can be estimated by fitting to an experimental data [12] or to second virial coefficient data [15]. We assume that the potential parameters \( \varepsilon_{ij} \) and \( \sigma_{ij} \) obey the following combining rules:

\[
\varepsilon_{ij} = \zeta_{ij} (\varepsilon_i \varepsilon_j)^{1/2} \tag{4}
\]

\[
\sigma_{ij} = \frac{1}{2} (\sigma_i + \sigma_j) \tag{5}
\]

where \( \zeta_{ij} \) are adjustable parameters. In these calculations, we have used the values \( \zeta_{ij} = 1 \) and \( \zeta_{ij} \neq 1 \) determined by fitting the excess Gibbs energy, \( G^E \), to the experimental data at a given temperature. The parameters \( \lambda_{ii} \) and \( \lambda_{ij} \) which are related to a pure component and a mixture, respectively, are estimated by fitting to second virial coefficient data at a given temperature. The values of \( \lambda_{ii} \) are given in Table 1. The values of \( \lambda_{ij} \), however, are given in Tables 2 and 3.

Using Eqs. (2) and (3) and, performing the integration in Eq. (1), one may obtain the following expression for the free energy of the binary mixture,

\[
\frac{A}{NkT} = \frac{A_0}{NkT} - \sum_{i,j=1}^{2} x_ix_jy_{ij} \eta_{ij} (a_{ij} + b_{ij}) \tag{6}
\]

where

\[
y_{ij} = \frac{\varepsilon_{ij}}{kT}, \quad \eta_{ij} = \frac{\pi N \sigma_{ij}^3}{6V}, \quad a_{ij} = \frac{32}{3} \frac{\lambda_{ij}}{\sigma_{ij}} - \frac{16}{3\lambda_{ij}} + \frac{16}{3\sigma_{ij}} \tag{7}
\]

\[
b_{ij} = 24 \ln \lambda_{ij} - \frac{80}{3} + \frac{144}{\lambda_{ij}^4} - \frac{128}{\lambda_{ij}^6} + \frac{4}{\pi} \frac{36}{\sigma_{ij}^6} + \frac{128}{3\sigma_{ij}^2} \tag{8}
\]

The second term in Eq. (6) represents the first order perturbation correction to the free energy.
Table 2
Comparison of calculated and experimental (ζ12 = 1) excess properties for binary mixtures at selected temperatures, zero pressure and a mole fraction of 0.5

<table>
<thead>
<tr>
<th>System</th>
<th>T (K)</th>
<th>Property (J mol⁻¹)</th>
<th>Experimental</th>
<th>LHB°</th>
<th>LL°</th>
<th>Bohn°</th>
<th>B°</th>
<th>This work</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar + N₂ (λ₁₂ = 1.78719)</td>
<td>83.82</td>
<td>G°</td>
<td>34</td>
<td>36</td>
<td>40</td>
<td>26</td>
<td>31</td>
<td>23.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H°</td>
<td>51</td>
<td>39</td>
<td>56</td>
<td>19</td>
<td>26</td>
<td>32.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TS°</td>
<td>17</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>8.5</td>
</tr>
<tr>
<td>Ar + O₂ (λ₁₂ = 1.82731)</td>
<td>83.82</td>
<td>G°</td>
<td>37</td>
<td>0.5</td>
<td>–</td>
<td>–10</td>
<td>–3</td>
<td>33.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H°</td>
<td>60</td>
<td>0.5</td>
<td>–</td>
<td>–14</td>
<td>–2</td>
<td>59.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TS°</td>
<td>23</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>26.3</td>
</tr>
<tr>
<td>Ar + CO (λ₁₂ = 1.78719)</td>
<td>83.82</td>
<td>G°</td>
<td>57</td>
<td>23</td>
<td>34</td>
<td>10</td>
<td>20</td>
<td>29.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H°</td>
<td>96</td>
<td>30</td>
<td>54</td>
<td>1</td>
<td>15</td>
<td>74.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TS°</td>
<td>39</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>44.8</td>
</tr>
<tr>
<td>Ar + CH₄ (λ₁₂ = 1.83716)</td>
<td>91</td>
<td>G°</td>
<td>74</td>
<td>–12</td>
<td>4</td>
<td>–</td>
<td>–</td>
<td>115.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H°</td>
<td>103</td>
<td>–31</td>
<td>41</td>
<td>–</td>
<td>–</td>
<td>195.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TS°</td>
<td>31</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>39.5</td>
</tr>
<tr>
<td>N₂ + O₂ (λ₁₂ = 1.78933)</td>
<td>83.82</td>
<td>G°</td>
<td>40</td>
<td>45</td>
<td>47</td>
<td>52</td>
<td>50</td>
<td>37.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H°</td>
<td>60</td>
<td>49</td>
<td>84</td>
<td>54</td>
<td>55</td>
<td>28.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TS°</td>
<td>20</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>–8.6</td>
</tr>
<tr>
<td>N₂ + CO (λ₁₂ = 1.74485)</td>
<td>83.82</td>
<td>G°</td>
<td>23</td>
<td>0.9</td>
<td>–</td>
<td>1</td>
<td>1</td>
<td>15.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H°</td>
<td>43</td>
<td>–0.2</td>
<td>–</td>
<td>0</td>
<td>1</td>
<td>31.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TS°</td>
<td>20</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>16.3</td>
</tr>
<tr>
<td>N₂ + CH₄ (λ₁₂ = 1.79535)</td>
<td>91</td>
<td>G°</td>
<td>170</td>
<td>–</td>
<td>–</td>
<td>33</td>
<td>49</td>
<td>180.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H°</td>
<td>138</td>
<td>–</td>
<td>–</td>
<td>–55</td>
<td>–5</td>
<td>153.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TS°</td>
<td>–32</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>–27.6</td>
</tr>
<tr>
<td>CH₄ + CO (λ₁₂ = 1.79702)</td>
<td>91</td>
<td>G°</td>
<td>115</td>
<td>67</td>
<td>76</td>
<td>2</td>
<td>32</td>
<td>176.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H°</td>
<td>105</td>
<td>27</td>
<td>88</td>
<td>–84</td>
<td>–11</td>
<td>168.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TS°</td>
<td>–10</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>–8</td>
</tr>
</tbody>
</table>

* See [11].
\* See [20].
\* See [21].
\* See [22].

3. Partition function of liquid mixtures

The free volume theories of the liquid state have provided a useful approximate description of the thermodynamic properties of liquids in terms of intermolecular forces. In this theories, the partition function is expressed as a function of the free volume [16]. A partition function \( Q_0 \) at a given volume \( V \) and temperature \( T \) for an assembly of \( r \) components hard sphere mixture is expressed as [17]

\[
Q_0(N, V, T) = \frac{N!}{\prod_{i=1}^{N} n_i!} \prod_{i=1}^{N} \left( \frac{e^{V_i N}}{A_i N} \right)^{n_i}
\]  

(9)
<table>
<thead>
<tr>
<th>System</th>
<th>$T$ (K)</th>
<th>Property (J mol⁻¹)</th>
<th>Experimental</th>
<th>LHB</th>
<th>Bohn</th>
<th>$B$</th>
<th>This work</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar + $N_2$ ($\lambda_{12} = 1.78719$)</td>
<td>83.82</td>
<td>$\zeta_{12}$</td>
<td>–</td>
<td>1.001</td>
<td>0.9970</td>
<td>0.9990</td>
<td>0.9932</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$G^E$</td>
<td>34</td>
<td>34</td>
<td>34</td>
<td>34</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$H^E$</td>
<td>51</td>
<td>35</td>
<td>31</td>
<td>30</td>
<td>42.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$T_{SE}$</td>
<td>17</td>
<td></td>
<td></td>
<td></td>
<td>8.5</td>
</tr>
<tr>
<td>Ar + O₂ ($\lambda_{12} = 1.82731$)</td>
<td>83.82</td>
<td>$\zeta_{12}$</td>
<td>–</td>
<td>0.987</td>
<td>0.9847</td>
<td>0.9867</td>
<td>0.9847</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$G^E$</td>
<td>37</td>
<td>37</td>
<td>37</td>
<td>37</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$H^E$</td>
<td>60</td>
<td>52</td>
<td>54</td>
<td>53</td>
<td>63.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$T_{SE}$</td>
<td>23</td>
<td></td>
<td></td>
<td></td>
<td>26.3</td>
</tr>
<tr>
<td>Ar + CO ($\lambda_{12} = 1.78895$)</td>
<td>83.82</td>
<td>$\zeta_{12}$</td>
<td>–</td>
<td>0.986</td>
<td>0.9831</td>
<td>0.9865</td>
<td>0.9764</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$G^E$</td>
<td>57</td>
<td>57</td>
<td>57</td>
<td>57</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$H^E$</td>
<td>96</td>
<td>79</td>
<td>73</td>
<td>67</td>
<td>101.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$T_{SE}$</td>
<td>39</td>
<td></td>
<td></td>
<td></td>
<td>44.8</td>
</tr>
<tr>
<td>Ar + CH₄ ($\lambda_{12} = 1.85716$)</td>
<td>91</td>
<td>$\zeta_{12}$</td>
<td>–</td>
<td>0.972</td>
<td>–</td>
<td>–</td>
<td>0.9955</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$G^E$</td>
<td>74</td>
<td>74</td>
<td>–</td>
<td>–</td>
<td>74</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$H^E$</td>
<td>103</td>
<td>89</td>
<td>–</td>
<td>–</td>
<td>113.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$T_{SE}$</td>
<td>31</td>
<td></td>
<td></td>
<td></td>
<td>39.5</td>
</tr>
<tr>
<td>$N_2 + O_2$ ($\lambda_{12} = 1.78933$)</td>
<td>83.82</td>
<td>$\zeta_{12}$</td>
<td>–</td>
<td>1.002</td>
<td>1.0042</td>
<td>1.0035</td>
<td>0.9927</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$G^E$</td>
<td>40</td>
<td>42</td>
<td>40</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$H^E$</td>
<td>60</td>
<td>43</td>
<td>37</td>
<td>41</td>
<td>31.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$T_{SE}$</td>
<td>20</td>
<td></td>
<td></td>
<td></td>
<td>–8.6</td>
</tr>
<tr>
<td>$N_2 + CO$ ($\lambda_{12} = 1.74485$)</td>
<td>83.82</td>
<td>$\zeta_{12}$</td>
<td>–</td>
<td>0.990</td>
<td>0.9911</td>
<td>0.9913</td>
<td>0.9870</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$G^E$</td>
<td>23</td>
<td>23</td>
<td>23</td>
<td>23</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$H^E$</td>
<td>43</td>
<td>34</td>
<td>36</td>
<td>33</td>
<td>39.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$T_{SE}$</td>
<td>20</td>
<td></td>
<td></td>
<td></td>
<td>16.3</td>
</tr>
<tr>
<td>$N_2 + CH_4$ ($\lambda_{12} = 1.79535$)</td>
<td>91</td>
<td>$\zeta_{12}$</td>
<td>–</td>
<td>0.9564</td>
<td>0.9598</td>
<td>0.9914</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$G^E$</td>
<td>170</td>
<td>170</td>
<td>170</td>
<td>170</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$H^E$</td>
<td>138</td>
<td>148</td>
<td>164</td>
<td>142.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$T_{SE}$</td>
<td>–32</td>
<td></td>
<td></td>
<td></td>
<td>–27.6</td>
</tr>
<tr>
<td>CH₄ + CO ($\lambda_{12} = 1.79702$)</td>
<td>91</td>
<td>$\zeta_{12}$</td>
<td>–</td>
<td>0.983</td>
<td>0.9670</td>
<td>0.9745</td>
<td>1.0061</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$G^E$</td>
<td>115</td>
<td>115</td>
<td>110</td>
<td>110</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$H^E$</td>
<td>105</td>
<td>96</td>
<td>76</td>
<td>98</td>
<td>107</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$T_{SE}$</td>
<td>–10</td>
<td></td>
<td></td>
<td></td>
<td>–8</td>
</tr>
</tbody>
</table>

where $\Lambda_i = h/\sqrt{2\pi m_i kT}$ and $f_0$ is the equivalent free-volume fraction of a hard sphere binary mixtures which can be calculated from

$$f_0 = \frac{V_i}{V} = \exp \left[ - \int_{0}^{\rho_{\text{ref}}} \left( Z_0 - 1 \right) \frac{d\rho}{\rho} \right]$$

for a given equation of state [18], where $Z_0$ is compressibility factor of reference hard sphere mixture.
In this paper we use the Carnahan–Starling equation of state [19] as
\[ Z_0 = \frac{1 + \eta_m + \frac{\eta_m^2}{2} - \frac{\eta_m^3}{3} (1 - \eta_m^2)^{3/2}}{1} \quad (11) \]
and one obtains
\[ f_0 = \exp \left[ \frac{\eta_m (4 - 3 \eta_m)}{(1 - \eta_m)^2} \right] \quad (12) \]
where \( \eta_m = \pi d_m^3 \rho / 6 \) is packing fraction and \( d_m \) is assumed to have the following composition dependence
\[ d_m = \left( \sum_{i,j} x_i x_j d_{ij} \right)^{1/3} \]
In an analogous way, the partition function of a real liquid mixture may be written as
\[ Q(N, V, T) = \frac{N!}{\prod_{i=1}^{N} N_i!} \prod_{i=1}^{N} \left( \frac{eV_f}{A_i N} \right)^{N_i} \quad (13) \]
where \( f = f_0 \exp (B) \) and \( B \) is given by
\[ B = \sum_{i,j=1}^2 x_i x_j y_{ij} (a_{ij} + \eta_{ij} b_{ij}) \quad (14) \]
Using the standard relation
\[ A = -kT \ln Q \]
one obtains for the free energy of hard sphere liquid mixtures from Eq. (9) that
\[ \frac{A_{\text{HS}}}{NkT} = \sum_{i} (x_i \ln x_i + x_i \ln A_i) - \ln \frac{eV_f}{N} \quad (15) \]
In a similar way, the free energy of the real liquid mixtures follows from Eq. (13) that
\[ \frac{A}{NkT} = \sum_{i} (x_i \ln x_i + x_i \ln A_i) - \ln \frac{eV_f}{N} \quad (16) \]

4. Excess functions

4.1. Excess Gibbs function

The excess Gibbs function \( G^E \) is given by
\[ G^E = G - \sum_{i} x_i G_i - NkT \sum_{i} x_i \ln x_i \]
where \( G \) is the Gibbs energy of the liquid mixture having mole fraction \( x_i \) and \( G_i \) the Gibbs energy of the \( i \)th species. Using the standard relation \( G = A + pV \), one may express \( G^E \) as

\[
G^E = A - \sum_{i} x_i A_i - NkT \sum_{i} x_i \ln x_i + pV - \sum_{i} x_i pV_i
\]

(17)

Substituting the expressions for \( A \) and \( A_i \) from Eq. (16) into Eq. (17) one obtains

\[
G^E = -NkT \left[ \sum_{i} x_i \ln \frac{f_{0}^{0} V_{i}}{f_{0}^{0} V_{i}} + B - \sum_{i} x_i B_i \right] + pV^E
\]

(18)

where \( B_i \) is defined by Eq. (14).

4.2. Excess entropy \( S^E \)

Differentiation of Eq. (18) with respect to the temperature at a constant pressure yields

\[
S^E = -\left( \frac{\partial G^E}{\partial T} \right)_p = Nk \sum_{i} x_i \ln \frac{f_{0}^{0} V_{i}}{f_{0}^{0} V_{i}}
\]

(19)

4.3. Excess enthalpy \( H^E \)

Using the standard relation \( H^E = G^E - T S^E \) from Eqs. (18) and (19) one obtains

\[
H^E = -NkT \left[ B - \sum_{i} x_i B_i \right] + pV^E
\]

(20)

We should remark that, the values of excess molar volume are not included in the tables, since we have used the data to calculate the molar volume of mixture by

\[
V^E = V_m - \sum_{i} x_i V_i
\]

where \( V_m \) and \( V_i \) are molar volumes of mixture and pure components, respectively.

5. Results and conclusion

In this study, we have based the calculation of the free volume fraction on Carnahan–Starling for the calculation of the excess properties of eight various mixtures at zero pressure. The excess functions such as excess Gibbs energy, entropy and enthalpy are calculated from Eqs. (18)–(20), where we have used Eq. (12) for the calculation of the values of \( B_{0} \) appearing in excess functions. As can be seen from the tables, our calculations were performed at zero pressure and at selected temperatures to be able to make a comparison with experimental values in the literature. After all, the good agreement between our results
at the literature asserts that Carnahan–Starling equation of state may be used conveniently for hard sphere mixtures. Of course, further analysis to determine vapor pressure curves and caloric data for the present mixtures would be very interesting for future studies to examine Carnahan–Starling equation.

The predicted values of thermodynamic quantities for \( \zeta_{12} = 1 \) are given in Table 2 and we have shown the results for \( \zeta_{12} \neq 1 \) in Table 3. The parameters for pure components used in the calculations are given in Table 1. As can be seen from these tables, the theoretical results are very sensitive to changes in \( \zeta_{12} \) which is taken as an adjustable parameter. The agreement is poor for \( \zeta_{12} = 1 \), however, one may note a very good agreement with experimental and theoretical results when we assume that \( \zeta_{12} \neq 1 \). This is, simply, due to the fact that errors in theories can be obscured by the uncertainties in the value of \( \zeta_{12} \) and by the well-known inadequacies of the intermolecular LJ potential. On the other hand, the used expression for the radial distribution function makes it possible to solve the first order perturbation integral analytically; however, this term corresponds to the inclusion only of the (second and) third virial coefficient(s) for attractive forces. Thus, thermodynamic functions of mixtures and of the corresponding components are determined at densities, which differ considerably from those typical for liquids. In this respect, higher order corrections may give rise a reasonable contribution to the results. Therefore, further analysis to improve the accuracy of the theory would be worthwhile.

List of symbols

- \( A \): Helmholtz energy
- \( d \): hard sphere diameter
- \( f \): equivalent free volume fraction
- \( g \): distribution function
- \( G \): Gibbs energy
- \( H \): enthalpy function
- \( k \): Boltzmann constant
- \( N \): number of molecules
- \( p \): pressure
- \( Q \): partition function
- \( r \): distance of interacting particles
- \( S \): entropy function
- \( T \): absolute temperature
- \( u \): pair potential
- \( V \): volume
- \( x \): mol fraction
- \( Z \): compressibility factor

Greek letters

- \( \beta \): Boltzmann factor
- \( \varepsilon \): parameter of pair potential
- \( \eta \): reduced density
- \( \lambda \): parameter of pair potential
- \( \rho \): number density
- \( \sigma \): parameter of pair potential
ξ adjustable parameter
Λ thermal wavelength

Subscripts
i,j component
0 reference system

Superscript
E excess function

References