H$_2$O activity in H$_2$O-N$_2$ fluids at high pressure and temperature measured by the brucite-periclase equilibrium

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ABSTRACT

We present experimental results constraining water activity in H$_2$O-N$_2$ fluids containing 40–90 mol% water at pressures of 6–13 kbar and temperatures of 680–840 °C. In the experiments, the displacement of the brucite dehydration equilibrium was used as a gauge of water activity. The experiments were performed in a conventional piston-cylinder apparatus, with NaCl pressure medium and silver azide, AgN$_3$, as a source of nitrogen. Reversals of the dehydration reaction were used to bracket the equilibrium fluid compositions within 3 mol% H$_2$O. Water activities were computed from the equilibrium brucite dehydration conditions in pure H$_2$O as determined by Aranovich and Newton (1996) using thermodynamic data of Holland and Powell (1998). The experimentally derived activities were fit to a van Laar-type equation that reproduces our compositional data with a standard error of 1.6 mol% H$_2$O:

$$RT \ln \gamma_i = (X_i)^2 W \{ V_i (V_2)^2 / [(V_1 + V_2)(X_i V_1 + X_2 V_2)] \}$$

where $\gamma_i$ is the activity coefficient of H$_2$O, $X_i$ is the mole fraction of end-member $i$ (1 = H$_2$O and 2 = N$_2$), $V_i$ is the molar volume of the pure end-member at the pressure ($P$) and temperature ($T$) of interest, and $W$ is analogous to a regular solution parameter. The parameter $W$ was fit as a function of pressure and temperature by the expression

$$W = (A - B) [1 - \exp(-20P)] + C P^{0.3} T,$$

with $A = 40005$, $B = 51.735$, $C = 14.848$ J/(K·kbar$^0.3$), $P$ in kbar and $T$ in K. With these expressions, activity-concentration relations in H$_2$O-N$_2$ fluids can be reconstructed in a broad P-T-X range using any equation of state (EOS) for pure H$_2$O and N$_2$. The activity-concentration relations are similar to the semi-empirical EOS of Duan et al. (2000) and the theoretical EOS of Churakov and Gottschalk (2001a), although the former somewhat underestimates activities within the experimental pressure range whereas the latter appears to overestimate activities of the components at pressure above 20 kbar.

INTRODUCTION

Nitrogen is a common constituent of natural fluids. Nitrogen-bearing fluid inclusions have been reported in minerals from a variety of geological settings, including eclogite (e.g., Andersen et al. 1989), high-grade metapelite (Janak et al. 1999), magmatic enderbite (Knudsen and Lidwin 1996), ultrahigh-pressure metamorphic rocks (De Corte et al. 1998), and upper mantle ultramafic rocks (e.g., Turner et al. 1990; Andersen et al. 1995; Mohapatra and Murty 2000). In the form of NH$_3$, N can substitute for alkalis in alkali feldspars and micas (e.g., Voncken et al. 1993; Moine et al. 1994). Nitrogen is also found as a major impurity in natural diamonds of kimberlite affinity (e.g., Shiryaev et al. 2000; Boyd et al. 1994), which indicates its potential role in mantle fluids of deep origin. Problems as diverse as metamorphic phase equilibria, interpretation of fluid inclusions and volcanic gas emanations, modeling of planetary atmospheres and interstellar clouds—all require quantitative knowledge of the thermodynamic mixing properties of nitrogen with water at high pressure ($P$) and temperature ($T$).

The system H$_2$O-N$_2$ has been extensively studied experimentally at temperatures below ca. 400 °C in the pressure range up to 4 kbar (see Anovitz et al. 1998, p. 815–816, for references). Data at higher temperatures and/or pressures are scarce. Chou (1990) measured the water activity ($\alpha_{H_2O}$) in H$_2$O-N$_2$ mixtures over the compositional range $X_{H_2O} = H_2O/(H_2O + N_2) = 0.2$ – 0.7 at 600 °C and 2 kbar using the H sensor technique, and found a significant positive deviation from the ideal mixing. Anovitz et al. (1998) determined $\alpha_{H_2O} - X_{H_2O}$ relations at 500 °C and 0.5 kbar by the H membrane technique. Their data also indicate large positive deviations from ideality in H$_2$O-N$_2$ mixtures. The values for $\alpha_{H_2O}$ derived in the latter study depend strongly upon the thermodynamic data for the Ni-NiO and Co-CoO buffers used to control oxygen fugacity in the experiments (Anovitz et al. 1998).

Supercritical phase separation in the H$_2$O-N$_2$ mixtures has been documented recently for the near-critical water isopleths $X_{H_2O} = 0.75$ (Costantino and Rice 1991) and $X_{H_2O} = 0.67$ (van Hinsberg et al. 1993) by direct observations in diamond anvil cells in the temperature range 400–560 °C at pressure up to 22
kbar. These data are important for understanding the pressure dependence of the H$_2$O-N$_2$ solvus, but are difficult to use to quantify $a_{H_2O}$ due to the large uncertainties in pressure calibration (up to ±2 kbar at temperature above ca. 430 °C; Costantino and Rice 1991, p. 9036) and lack of information on the composition of the N-rich fluid.

This paper presents results of the $a_{H_2O}$ measurements in H$_2$O-N$_2$ fluids obtained over a broad pressure, temperature, and compositional range using the brucite (Br) + periclase (Per) + water activity gauge (Franz 1982; Shmulovich et al. 1982; Aranovich and Newton 1996, 1997). An empirical equation describing the mixing properties on the binary join has been calibrated against recent equations of state (Duan et al. 1996, 2000; Churakov and Rice 1991, p. 9036) and lack of information on the composition of the N-rich fluid.

Experimental methods

Application of the brucite (Br) – periclase (Per) reaction:

\[ \text{Mg(OH)}_2 = \text{MgO} + \text{H}_2\text{O} \]

(1)

to monitor the H$_2$O activity in experiments is based on the large buffering capacity of this assemblage due to the high water content of brucite. At any experimental $P$ and $T$ the equilibrium water activity, $a_{H_2O}$, is calculated from the expression for the total Gibbs free energy of Reaction 1:

\[ \Delta G^0_{\text{H}_2\text{O}}(1) + \int \left( \frac{\Delta V}{T} \right) dP + RT \ln f^0_{\text{H}_2\text{O}} + RT \ln a_{\text{H}_2\text{O}} = 0, \]

(2)

where $\Delta G^0_{\text{H}_2\text{O}}(1)$ is the standard Gibbs free energy of Reaction 1 at 1 bar and $T$, $(\Delta V)_T$, is the volume change of the solids at $T$, and $f^0_{\text{H}_2\text{O}}(P,T)$ is the fugacity of pure water at $P$ and $T$. Activity-composition relations for H$_2$O in the H$_2$O-N$_2$ fluid are retrieved in conjunction with Equation 2 by using the final fluid composition determined for experiments in which brucite, periclase, and an H$_2$O-N$_2$ fluid are presumed to have equilibrated.

Starting materials

The experimental procedure of this study is similar to that of Aranovich and Newton (1996, 1997). A mechanical mixture of synthetic periclase and brucite was used as the starting material. The periclase was originally large limpid crystals of ultrahigh-purity MgO prepared by an arc-fusion method, commercially available from Alfa Aesar (article no. 41648). The brucite was prepared from this periclase by reaction with commercially available from Alfa Aesar (article no. 41648).

These compounds have been suggested as a convenient source of N$_2$ for phase-equilibrium experiments at high pressure and temperature: silver azide, AgN$_3$ (Kepper 1989), and copper nitride, Cu$_3$N (Anovitz et al. 1998). Our reconnaissance piston-cylinder runs with Cu$_3$N + H$_2$O at 800 °C and 10 kbar showed, however, that the Cu produced on thermal decomposition of Cu$_3$N was to a large extent converted to Cu$_2$O due to reaction with H$_2$O, apparently at the early stages of the experimental run up (because the intrinsic oxygen fugacity of piston-cylinder apparatus is lower than that of the Cu-Cu$_2$O equilibrium; e.g., Rosenbaum and Slagel 1995). Employing a double-capsule technique with the Ni-NiO-H$_2$O external oxygen buffer prevented the formation of Cu$_2$O, but the experiments still failed to produce a consistent N$_2$ yield. Due to these difficulties with Cu$_3$N, we resorted to AgN$_3$ as the N$_2$ sources in the experiments. This material was prepared and handled as described by Kepper (1989). To test the applicability of AgN$_3$ for the piston-cylinder experiments, we made “dummy” runs, containing only pre-weighed amounts of AgN$_3$ and H$_2$O (Table 1). Analysis of these runs revealed no oxidation of Ag, and showed excellent agreement between the starting amounts of N$_2$ (in the form of AgN$_3$) and H$_2$O weighed in the capsules and those recovered after the runs by a weight-loss method (see below). Another advantage of using AgN$_3$ is that its N$_2$ yield is much higher than that of Cu$_3$N.

The starting materials were loaded into 1 cm long, 0.23 cm OD Pt capsules in the following sequence. First, an aliquot of AgN$_3$ water suspension was loaded and the capsule was placed in a 1 atm oven at 105 °C for about 10 minutes to dry. After the capsule had reached a constant weight, providing the exact amount of AgN$_3$ and H$_2$O weighed in the capsules and those recovered after the runs by a weight-loss method (see below). Another advantage of using AgN$_3$ is that its N$_2$ yield is much higher than that of Cu$_3$N.

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The experiments were brought to a pressure about 3–4 kbar lower than the final run pressure at room temperature, then...
heated to 320 °C to decompose AgN₃ (Keppler 1989), and, after about 30 min., heated to the final run temperature. Thermal expansion of the NaCl assemblies raised the pressure to its final run value. Pressure was measured by a strain gauge positioned at the apparatus dead end, and monitored and adjusted automatically by computer in the course of the runs. Although the NaCl assemblies are essentially frictionless (Johannes et al. 1971), and pressure fluctuations during the runs did not exceed a few bars, our determination of the brucite dehydration (Equilibrium 1) in pure H₂O, when compared with the results by Aranovich and Newton (1996, 1997), showed that this type of apparatus requires a pressure correction of about −10% (Table 4). At 320 °C resulted in additional weight loss, attributed to removal of H₂O. In most cases, the weight change of the quenched capsules was detected for the successful runs. The capsules were then immersed in liquid N₂ to freeze the water inside, and punctured with a needle while still frozen. An immediate weight loss occurred on warming, indicative of water inside, and punctured with a needle while still frozen. Reaction progress was additionally monitored by comparison of the XRD patterns of the recovered charges with those of the standard starting mix. Significant changes in the relative peak heights were observed in all runs, and were always consistent with the results of the other two methods.

### RESULTS OF EXPERIMENTS AND DISCUSSION

The experimental brackets of brucite–periclase equilibrium in the presence of H₂O-N₂ fluid are shown in Figure 1. The complete data set is given in Table 3. Most of the complementary half-reversal runs showed reasonably tight convergence on the final fluid composition. The subtle change in curvature

### TABLE 1. Experimental results on decomposition of silver azide at 13.3 kbar

<table>
<thead>
<tr>
<th>Run no.</th>
<th>T (°C)</th>
<th>Starting materials, mg:</th>
<th>Run products, mg:</th>
<th>Xₜ₉,O</th>
</tr>
</thead>
<tbody>
<tr>
<td>AGN1</td>
<td>780</td>
<td>AgN₃ 2.33 N₂ nom 0.65 H₂O 0.00</td>
<td>N₂ 0.67 H₂O 0.00</td>
<td>Xₜ₉,O nom measured</td>
</tr>
<tr>
<td>AGN2</td>
<td>875</td>
<td>AgN₃ 2.88 N₂ nom 0.81 H₂O 2.00</td>
<td>N₂ 0.79 H₂O 2.01</td>
<td>Xₜ₉,O nom measured</td>
</tr>
<tr>
<td>AGN3</td>
<td>875</td>
<td>AgN₃ 2.17 N₂ nom 0.61 H₂O 0.00</td>
<td>N₂ 0.61 H₂O 0.00</td>
<td>Xₜ₉,O nom measured</td>
</tr>
<tr>
<td>AGN4</td>
<td>840</td>
<td>AgN₃ 1.99 N₂ nom 0.56 H₂O 0.27</td>
<td>N₂ 0.56 H₂O 0.28</td>
<td>Xₜ₉,O nom measured</td>
</tr>
</tbody>
</table>

Notes: N₂ nom = the amount of N₂ in stoichiometric AgN₃; Xₜ₉,O nom = mole fraction of H₂O according to the amounts of H₂O and N₂ in the starting material.

### TABLE 2. Results of calibration runs on reaction Br = Per + H₂O in pure H₂O

<table>
<thead>
<tr>
<th>Run no.</th>
<th>Duration (h)</th>
<th>Pnom (kbar)</th>
<th>T (°C)</th>
<th>Stable phase</th>
<th>Pcor (kbar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BPN66</td>
<td>41</td>
<td>15</td>
<td>870</td>
<td>Br</td>
<td>13.3</td>
</tr>
<tr>
<td>BPN70</td>
<td>47</td>
<td>15</td>
<td>875</td>
<td>Br</td>
<td>13.3</td>
</tr>
<tr>
<td>BPN67</td>
<td>30</td>
<td>15</td>
<td>880</td>
<td>Per</td>
<td>13.3</td>
</tr>
<tr>
<td>BPN20</td>
<td>50</td>
<td>10</td>
<td>820</td>
<td>Br</td>
<td>9</td>
</tr>
<tr>
<td>BPN25</td>
<td>58</td>
<td>10</td>
<td>825</td>
<td>Per</td>
<td>9</td>
</tr>
<tr>
<td>BPN17</td>
<td>40</td>
<td>10</td>
<td>830</td>
<td>Per</td>
<td>9</td>
</tr>
<tr>
<td>BPN7-8</td>
<td>24</td>
<td>7</td>
<td>745</td>
<td>Br</td>
<td>5.4</td>
</tr>
<tr>
<td>BPN7-9</td>
<td>65</td>
<td>7</td>
<td>750</td>
<td>Br</td>
<td>5.4</td>
</tr>
<tr>
<td>BPN7-5</td>
<td>43</td>
<td>7</td>
<td>750</td>
<td>Per</td>
<td>5.4</td>
</tr>
<tr>
<td>BPN7-12</td>
<td>24</td>
<td>7</td>
<td>755</td>
<td>Per</td>
<td>5.4</td>
</tr>
</tbody>
</table>

Note: Pnom = nominal pressure; Pcor = pressure corrected according to the data by Aranovich and Newton (1996) on reaction 1 in pure H₂O (text).

### Figure 1. Experimental reversals on the reaction Br = Per + H₂O in the presence of the H₂O-N₂ fluids at 5.4, 9, and 13.3 kbar (Table 3). Opposing arrows show fluid composition equilibrated with Br and Per (arrowheads) starting from initial fluids indicated by the arrow tails. Isobaric curves are plotted according to the calculated compositions (Table 4). At Xₜ₉,O = 1.0, solid squares show periclase stable, open squares show brucite stable for calibration runs in pure H₂O (Table 2).
the equilibrium fractions of the remaining species, $x_i$, where $i$ indexes H$_2$O (1), H$_2$ (2), N$_2$ (3), and NH$_3$ (4), can be found by solving the following equations derived from thermodynamic (the equilibrium constant) and mass-balance constraints:

$$K_4 = \frac{x_2y_3f_4^{\phi}}{x_3y_1f_1^{\phi}}$$

$$K_4 = \frac{x_1y_1f_1^{\phi}}{x_2y_2f_2^{\phi}}$$

where $K_4$ and $K_4$ are the equilibrium constants for Equations 3 and 4, $f_i^\phi$ is the fugacity of pure species, and $\gamma$ is its activity coefficient. These equations were solved for a range of $f_{O_2}$ values at 13.5 kbar, 700 °C and $x_{H_2O} = 0.7$ and 0.3 using values for the equilibrium constants from Robie and Hemingway (1995), and the fugacities of the pure fluid species and their activity coefficients from Churakov and Gottschalk (2001a, 2001b). The results (Fig. 2) confirm that even at high pressure H$_2$ and NH$_3$ are only important species in this system at very low $f_{O_2}$ (compare with Holloway and Reese 1974 at low pressure) and can be neglected for present purposes.

Solubility of MgO is very low in pure H$_2$O and H$_2$O-NaCl solutions (e.g., Aranovich and Newton 1997; Newton and Manning 2000a), and in all likelihood should be lower still in the H$_2$O-N$_2$ fluids (compare with the effect of CO$_2$ on the silica solubility: Newton and Manning 2000b; Shmulovich et al. 2001).

The water activity, calculated for each of the experimental brackets $P-T$ according to Equation 2, is given in Table 4. For these calculations, we adopted $\Delta G^{\phi}_R(1)$ and $f_{H_2O}^{\phi}(P,T)$ from the thermodynamic data of Holland and Powell (1998) ($\sigma_{H_2O}$ in Table 4), which exactly reproduces the experimental brackets on Reaction 1 in pure H$_2$O as obtained by Aranovich and Newton (1996). Essentially the same activity values for the two lower pressures of our experiments are calculated with the thermodynamic data for Reaction 1 from Berman and Aranovich (1996) ($\sigma_{H_2O}$ in Table 4). For the 13.3 kbar experiments, $\sigma_{H_2O}$ and $\sigma_{H_2O}$ values are somewhat farther apart. The discrepancy is caused by the differences in $f_{H_2O}^{\phi}(P,T)$ employed in the two data sets. As discussed by Brodholt and Wood (1994) and Aranovich and Newton (1999), the Haar et al. (1984) EOS for H$_2$O, used by Berman and Aranovich (1996), predicts too low fugacities at pressure above 10 kbar. We therefore based our analysis of the experimental activity–composition relations on the $a_{H_2O}$ values.

Activity–composition data retrieved from the experiments are shown in Figure 3. There are several sources of uncertainty in these water activities. The uncertainties due to the values for the Gibbs free energy of Reaction 1 are relatively small: ±174 J for the $\Delta G^{\phi}_R(1)$ (Aranovich and Newton 1996; Holland and Powell 1998) and ±100 J for the $f_{H_2O}^{\phi}(P,T)$, which translates into a 1–2 relative percentage uncertainty in each of the calculated activities. Experimental $P-T$ uncertainties contribute another 8–10 relative percent. By far the largest uncertainty in the activity–composition relations is that related to the width
of the compositional brackets on Reaction 1 at each experimental T and P. Both the uncertainties of the weight-loss method and lack of complete equilibration of the run products cause this uncertainty. The weighing uncertainties, taken as two times precision of the balance, are relatively minor for the water-rich runs (±0.003–0.005 in terms of the water mole fraction), but can amount to \( \sigma(X_{H_2O}) = \pm 0.01 \) for the runs at the lowest temperature/lowest \( X_{H_2O} \) at each given \( P \). The half-width of the compositional brackets on reaction 1 does not exceed 0.015 for most runs listed in Table 3. The overall compositional uncertainty of the experiments at each given \( P \) and \( T \) is a sum of the width of the half-bracket and weighing uncertainty, and is given in Table 4.

Our results show that \( H_2O-N_2 \) fluids are characterized by large positive departure from ideal mixing (Fig. 3). This conclusion agrees qualitatively with the previous experimental phase-equilibrium studies at lower pressure and temperature (Chou 1990; Anovitz et al. 1998), as well as with the large positive volume (Basaev et al. 1974) and enthalpy (e.g., Lancaster and Wormald 1990) of mixing. No quantitative comparison can be made because of the lack of direct experimental data in the \( P-T \) range of our experiments.

Recently, Duan et al. (1996, 2000) published an EOS that predicts thermodynamic properties of fluids in the system \( H_2O-CO_2-CH_4-N_2 \) up to 2000 K and 100 kbar. The EOS of Duan et al. (1996) is based on a combination of the theoretical virial-type equation describing pure fluids with a semi-empirical mixing rule for the fluid mixtures. The mixing model involves two empirical parameters for each binary system to be fit from experimental data on the binaries. Water activities calculated with their equation for the \( T-P-X_{H_2O} \) conditions of our experiments agrees well with the experimental values (Fig. 3) but appears to underestimate the degree of non-ideality in this system. Also shown for comparison in Figure 3 are the \( a_{H_2O} \) values calculated with the EOS of Churakov and Gottschalk (2001b). These authors derived a model for fluid mixtures based entirely on the equations for the end-member species, which, therefore, makes it less empirical than that of Duan et al. The model of Churakov and Gottschalk (2001b) agrees very well with the experimental values within their uncertainties.

Aranovich and Newton (1999) used an alternative, entirely empirical approach to describing activity-composition relations in binary fluid mixtures for analytical representation of their experimental measurements in the \( H_2O-CO_2 \) system. This approach is based on the van Laar equation for the integral excess Gibbs free energy of binary mixtures (e.g., Saxena and Fei 1988):

\[
G^{ex} = X_1X_2W[V_1V_2/(V_1V_2 + V_1V_2)(X_1V_1 + X_2V_2)]
\]

where \( V_1 \) and \( V_2 \) are the pure end-member volumes, \( X_1 \) and \( X_2 \) the mole fractions of the components, and \( W \) is a regular solu-
tion energy parameter as defined by Guggenheim (1952). From Equation 5, the activity coefficients of the solution end-members can be shown to be:

\[
RT \ln g_1 = (X_2)^2 W \left\{ V_1^2 / (V_1 + V_2)(X_1 V_1 + X_2 V_2)^2 \right\} \quad (6a)
\]

\[
RT \ln g_2 = (X_1)^2 W \left\{ V_2^2 / (V_1 + V_2)(X_1 V_1 + X_2 V_2)^2 \right\} \quad (6b)
\]

In principle, the \( W \) term for various binary fluids can be calculated from intermolecular potentials describing the pair interactions between various types of molecules present in a mixture (Saxena and Fei 1988; Shi and Saxena 1992). Alternatively, \( W \) can be treated as an empirical parameter to be calculated by fitting the experimental data into Equations 6a and 6b (Aranovich and Newton 1999). The advantage of Equations 6a and 6b is that they have very simple analytical form and are not linked to any particular EOS for the end-member gases. We used Equation 6a with the \( W \) term expanded in \( T \) (K) and \( P \) (kbar) as

\[
W = (A - BT)[1 - \exp(-20P)] + CP^{0.3} \quad (7)
\]

to process the experimental \( a_{H_2O} - X_{H_2O} \) data of Table 4. The best-fit parameters, obtained with the standard volumes of \( H_2O \) and \( N_2 \) from Churakov and Gottschalk (2001a) and the optimization procedure described in Aranovich and Newton (1996), are:

\[
A = 40005 \text{ J}, \quad B = 51.735 \text{ J/K}, \quad C = 14.848 \text{ J/(K·kbar)}^{0.3}. \quad (8)
\]

The standard deviation of the midpoints of the experimental compositional brackets from the best-fit equation is only 0.016 (1σ); that is, the calculated equilibrium compositions lie well within the uncertainties of our experiments (see Table 4). The three parameters (see Eq. 8 [auth: is this correct?]) of the empirical binary model are insensitive, within reasonable limits, to the input volumes of the pure fluids, and therefore may be used along with any reasonably accurate EOS of \( H_2O \) and \( N_2 \).

The \( a_{H_2O} \) values calculated with the present model at 500 °C and 0.5 kbar satisfy all the experimental constraints by Anovitz et al. (1998), although they are somewhat higher than their preferred values for the low water compositions (Fig. 4a). Extrapolation with Equation 6a also agrees reasonably well with the Chou (1990) experiments at 600 °C and 2 kbar (Fig. 4b).

A noteworthy feature of the \( H_2O-N_2 \) system is the existence of a broad miscibility gap at supercritical \( P-T \) conditions, experimentally documented by direct observations in diamond anvil cells by Costantino and Rice (1991) and van Hinsburg et al. (1993). We calculated the solvus in this system with Equations 6 and 7 and the parameters given it in Equation 8 [auth: ??] by solving numerically the equations that define equilibrium between the coexisting phases at each given pressure and temperature, where \( \gamma \) is the activity coefficient:

\[
(\gamma X)'_{H_2O} = (\gamma X)''_{H_2O}
\]

\[
(\gamma X)'_{N_2} = (\gamma X)''_{N_2}
\]

The results (Fig. 5) are in good agreement with the experimental data by Costantino and Rice (1991) (triangles) and van Hinsburg et al. (1993) (squares).
mental observations (Costantino and Rice 1991; van Hinsburg et al. 1993) as well as with the predictions of the semi-empirical EOS (Duan et al. 2000, as shown in Fig. 3). Churakov and Gottschalk (2001b) predicted critical pressure (at each given temperature) at the lower limit of the uncertainties of the Costantino and Rice (1991) and van Hinsburg et al. (1993) experiments, which appears to indicate that their model slightly overestimates the activities of the components in this system at very high pressure. The advantage of this model is, however, that it provides accurate activity values without requiring experimental information for fluid mixtures.

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