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

ANDREAS HAEFNER,1,* LEONID Y. ARANOVICH,2 JAMES A.D. CONNOLLY,1 AND PETER ULMER1

1Institute for Mineralogy and Petrography, ETH-Zentrum, CH-8092 Zurich, Switzerland
2Institute of Experimental Mineralogy RAS, Chernogolovka 142432, Russia

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:

\[
RT \ln \gamma_i = (X_i)^2 W \left[ (V_i^0)^2 + (V_i^0 + V_2^0)(X_1 V_1^0 + X_2 V_2^0)^2 \right]
\]

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$_2$), \( V_i^0 \) 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 \( W = (A - B T)[1 - \exp(-20P)] + C P^{0.3} T \), with \( A = 40005 \), \( B = 51.735 \), \( C = 14.848 \), \( J/K \), \( P \) 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 (2002a), 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 \( (a_{H_2O}) \) 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 \( a_{H_2O} \) 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 \( a_{H_2O} \) 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