H₂O activity in H₂O-N₂ 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_2O-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_2O. Water activities were computed from the equilibrium brucite dehydration conditions in pure H_2O 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_2O:

$$RT \ln\gamma_1 = (X_2)^2 W\{V_1^0 (V_2^0)^2/[(V_1^0 + V_2^0)(X_1 V_1^0 + X_2 V_2^0)^2]\}$$

where γ_1 is the activity coefficient of H_2O, X_i is the mole fraction of end-member i (1 = H_2O 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 $W = (A - BT)[1 - \exp(-20P)] + C \cdot P^{0.3}T$, with A = 40005 J, B = 51.735 J/K, C = 14.848 J/(K·kbar$^{0.3}$), P in kbar and T in K. With these expressions, activity-concentration relations in H_2O-N_2 fluids can be reconstructed in a broad P-T-X range using any equation of state (EOS) for pure H_2O 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.