

H₂O activity in H₂O-N₂ fluids at high pressure and temperature measured by the displacement of the brucite-periclase equilibrium

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The activity of water in binary H₂O-N₂ fluids has been determined experimentally at pressures of 5-13 kbar and temperatures of 680°-840°C. Temperature displacement of the simple brucite dehydration reaction was used to monitor H₂O activity. The experiments were performed in a conventional 22mm piston-cylinder apparatus with NaCl pressure medium and silver azide, AgN₃, as a source of nitrogen. Reversal runs of the dehydration reaction were used to bracket the equilibrium fluid compositions. Final fluid compositions were obtained by a weight loss method.

Water activities were computed relative to the equilibrium brucite dehydration conditions in pure H₂O as determined by Aranovich and Newton (1996) using thermodynamic data of Holland and Powell (1998). The mixing properties of the binary H₂O-N₂ fluid were modelled with a van Laar-type equation:

$$RT \ln \gamma_1 = (X_2)^2 W \left\{ \frac{V_1^\circ (V_2^\circ)^2}{(V_1^\circ + V_2^\circ)(X_1 V_1^\circ + X_2 V_2^\circ)^2} \right\}$$

where γ_1 is the activity coefficient of H₂O, X_i is the mole fraction of endmember i ($1=H_2O$ and $2=N_2$), V_i° is the molar volume of the pure endmember i 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 with the expression $W = (A - BT)[1 - \exp(-20P)] + CP^{0.3}T$, 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, the activity-composition relations in H₂O-N₂ fluids can be reconstructed over a broad P-T-X range using any equation of state (EOS) for pure H₂O and N₂. The activity-composition relations are similar to those predicted by the semi-empirical EOS of Duan et al. (2000) and the theoretical EOS of Churakov and Gottschalk (2001).

References

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Variations in atmospheric ¹⁴C content and implications for dating

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Production rate of cosmogenic C and global carbon cycle shape the level of atmospheric ¹⁴C content. Variations of the past 12000 years have been best documented in the tree ring-radiocarbon chronology. However radiocarbon time scale beyond 11,000 BP to 40,000 BP remains un-calibrated and is a subject of extensive search for appropriate records, which can be applied to calibrate the ¹⁴C time scale. Studies of various archives such as: sediments, corals and stalagmites reveal substantial fluctuations in atmospheric ¹⁴C content, which occurred during the last 40,000 years. A review of newest results and implications those findings have for application of radiocarbon chronology in archaeology and palaeoclimatology will be presented.