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Thermodynamics of dehydration in analcime: Absorption calorimetry and equilibrium observations

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ABSTRACT

Analcime forms in a wide range of geologic environments from alkaline lakes to primary igneous occurrences in Si-undersaturated lavas and pegmatites and is present in many radioactive waste repository settings. To evaluate its hydration state in these environments, calorimetric-hydration heat measurements, equilibrium observations, and thermodynamic modeling were performed. The enthalpy of hydration of analcime determined by isothermal adsorption calorimetry was found to be independent of degree of hydration and relatively insensitive to temperature. Equilibrium hydration states of analcime as a function of temperature and vapor pressure were assessed by isothermal thermogravimetry. In light of the lack of excess enthalpy of mixing in this solution, an ideal solution model was applied to the equilibrium observations along with previously determined heat capacities hydration to retrieve the standard Gibbs energy of hydration from water vapor (–47.29 ± 0.56 kJ/mol H_2O), standard enthalpy of hydration (–85.10 ± 1.03 kJ/mol H_2O), and entropy of hydration (–126.81 ± 1.60 J/mol $H_2O·K$) at 298.15 K, 1 bar. The standard enthalpy of hydration at 298.15 K, 1 bar regressed from the calorimetric data are consistent with these results (–86.4 ± 1.9 kJ/mol H_2O). Calculations of the hydration state of analcime as a function of temperature and pressure indicate that analcime is essentially fully hydrated at temperature and pressure conditions attending its formation in geologic and experimental systems. Dehydration of analcime under water-undersaturated conditions (as during heating in a radioactive waste repository) may contribute significantly to thermal budgets in systems where this phase is important.

Keywords: Analcime, thermodynamics, hydration heat, dehydration, differential scanning calorimetry, thermogravimetry, equilibrium