

Heat capacity of hydration in zeolites

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ABSTRACT

Dehydration of zeolites is a critical factor in their stability, effectiveness as storage media for thermal energy, and influence on the thermal evolution of radioactive waste repositories. Prediction of the hydration states of zeolites as a function of temperature, pressure, and water activity is often hampered by limited data on the heat capacity changes associated with (de)hydration reactions. This property is often assumed to be temperature invariant based on statistical-mechanical reasoning. To test this assumption, heat capacities of homologous hydrated and dehydrated zeolites (analcime, natrolite, wairakite) were measured by differential scanning calorimetry from 130 to 600 K that were subsequently used to calculate the heat capacity of hydration. Simultaneous monitoring of sample mass was used to discard data for hydrated phases affected by thermal effects associated with dehydration at elevated temperature. All three phases exhibited marked variations in the heat capacity of hydration with temperature. This behavior appears to be related to second-order phase transitions involving the water molecules. In wairakite, a second-order phase transition associated with a change in framework symmetry from monoclinic to tetragonal only occurs in the hydrated form, and leads to a prominent peak in the temperature dependence of the heat capacity of hydration. Above the transition temperature, the heat capacity of hydration becomes negligible. Neglecting the temperature dependence of the heat capacity of hydration in zeolites can have a significant effect on thermodynamic properties of dehydration reactions regressed from equilibrium observations at elevated temperatures.

Keywords: Zeolite, analcime, wairakite, natrolite, heat capacity, differential scanning calorimetry, hydration, phase transitions