

LETTER

Quasi-ice-like C_p behavior of molecular H_2O in hemimorphite $Zn_4Si_2O_7(OH)_2 \cdot H_2O$: C_p and entropy of confined H_2O in microporous silicates

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ABSTRACT

Hemimorphite, $Zn_4Si_2O_7(OH)_2 \cdot H_2O$, and its dehydrated analog $Zn_4Si_2O_7(OH)_2$ were studied by low-temperature relaxation microcalorimetry and their heat capacity determined to analyze the behavior of the confined H_2O between 5 and 300 K. An analysis of the data, which are corrected for the presence of a phase transition, shows that the C_p of H_2O in hemimorphite behaves more similar to the C_p of ice than to liquid water or steam. The H_2O molecule, with its four planar hydrogen bonds in hemimorphite, as well as its tetrahedral coordination in ice, is more rigidly hydrogen bonded in both than in liquid water. This is reflected in their respective C_p behavior. The heat capacity and entropy for the dehydration reaction at 298 K are $\Delta C_p^{rxn} = -2.1 \pm 3.6$ J/(mol·K) and $\Delta S^{rxn} = 134.7 \pm 4.0$ J/(mol·K). C_p behavior at $0 < T < 300$ K and entropy values at 298 K for confined H_2O in hemimorphite and hydrous Mg cordierite are compared to those in several zeolites. The entropy for confined H_2O in hemimorphite, analcime, and mordenite is around 54 J/(mol·K) at 298 K. The strength of the interactions (e.g., H bonding) between an H_2O molecule and its surroundings increases approximately from steam > cordierite > analcime > hemimorphite \geq mordenite > heulandite > natrolite \approx scolecite > liquid H_2O > ice and, in the case of microporous silicates, is inversely proportional to the S of the confined H_2O .

Keywords: Hemimorphite, heat capacity, entropy, microporous minerals, confined H_2O