

**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 selected
microporous silicates**

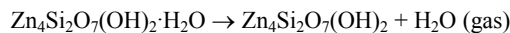
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Hemimorphite ($Zn_4Si_2O_7(OH)_2 \cdot H_2O$) and its dehydrated analog $Zn_4Si_2O_7(OH)_2$ were studied by low-temperature heat-pulse calorimetry and their C_p determined between 5 and 300 K in order to analyze the behavior of the confined molecular H_2O . 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 most similar to the C_p of ice than to liquid water or steam. The H_2O molecule, with its four ordered, planar hydrogen bonds in hemimorphite, as well as its tetrahedral coordination in ice, is more rigidly hydrogen bonded in both than in liquid water. The heat capacity and entropy for the dehydration reaction (rxn), ΔC_p^{rxn} and ΔS^{rxn} , at 298 K of



were calculated using the measured heat capacity and entropy values for hemimorphite and $Zn_4Si_2O_7(OH)_2$ and gives $\Delta C_p^{rxn} = -3.7 \text{ J/(mol}\cdot\text{K)}$ and $\Delta S^{rxn} = 133.7 \text{ J/(mol}\cdot\text{K)}$.

Low-temperature C_p behavior and entropy values at 298 K for confined H_2O in hemimorphite, the three zeolites parnatrolite, analcime and mordenite, as well as hydrous cordierite, are compared and analyzed. The entropy for confined H_2O in hemimorphite at 298 K, and that in analcime and mordenite, have values around 55 J/(mol·K). This is greater than the entropy of ice at 298 K but less than that of liquid H_2O . Hydrous cordierite is considerably different in nature, because its S value of 80.5 J/(mol·K) for H_2O is greater. The strength of the interactions between a H_2O molecule and its surroundings increases approximately from steam > cordierite > analcime > hemimorphite \geq mordenite > natrolite (paranatroilite) \approx scolecite > liquid H_2O > ice and is roughly inversely proportional to the S of H_2O in the phase.

**The interaction of borosilicate glass
with aqueous solutions**

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Understanding the corrosion of nuclear waste borosilicate glasses in aqueous solutions is essential to reliably predict their long-term stability in a geologic repository. Here we report the results of corrosion experiments with borosilicate glass cuboids with edge lengths of about 2.5mm in a HCl solution of pH = 0 at 150°C for 6 to 336 hours, including experiments with ¹⁸O and ²⁶Mg as isotope tracers. Several observations were made in this study such as (i) the occurrence of chemical oscillations in the corrosion rim that is composed of silica, (ii) an enrichment of ¹⁸O and ²⁶Mg in the corrosion rim formed in the isotopically enriched solutions without observable diffusion profiles, (iii) a sharp phase boundary of the corrosion rim towards the pristine glass, (iv) a high porosity in the corrosion rim, and (v) the occurrence of silica spherules at the surface. These features are not compatible with classical theories about the formation of the corrosion or “gel” layer that are based on diffusion-controlled hydration and ion exchange reactions and subsequent solid-state re-condensation of the hydrolyzed glass network [1]. We propose a new mechanistic model for aqueous glass corrosion that is based on the congruent dissolution of the borosilicate glass and the subsequent reprecipitation of silica at an inward moving reaction interface. Both glass dissolution and silica reprecipitation are spatially and temporally coupled, such that the reaction retains the initial shape of the glass fragment, and is thermodynamically driven by the solubility difference between the glass and the silica corrosion product. As a result of this solubility difference and the volume preservation of the initial glass fragment, porosity, which is a common characteristic of corrosion layers around silicate glasses regardless of the physico-chemical alteration conditions, is directly created during the silica precipitation process. Such a corrosion model is based on thermodynamic principles, but contradicts the widely accepted notion that the pores in the corrosion product open up while the hydrolyzed glass network is reconstructed in the solid state. Our new model is able to explain our experimental observations as well as many observations made in other experimental studies and on archaeological glasses and provides a novel framework to evaluate the long-term performance of nuclear waste glasses.

[1] Grambow (2006) *Elements* 2, 357-364.