Examining the Equilibrium Thermodynamics of High-pressure Ice Polymorphs and Aqueous NaCl

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Equilibrium properties of NaCl(aq) solutions for concentrations to 7 mol/kg and coexisting ice phases are examined between 230 K and 500 K and from 0 MPa to 2300 MPa. Key properties include the volume, entropy, and latent heat differences across liquid-solid and solid-solid phase boundaries for fluids and ice Ih, ice III, ice II, ice V, and ice VI. Phase boundaries closely matching experimental data are delineated, and key properties of individual phases are determined self-consistently for the first time on the equilibrium surfaces. Local basis function representations for the Gibbs energy of solutions were developed through a novel hybrid approach integrating theoretical constraints, data from the literature, and new experimental data.[1] Here they are compared with high pressure ice polymorph equations of state from the SeaFreeze framework.[2] We find ΔS largely increases with increasing concentrations and temperatures, except for ice II, for which it is relatively constant. ΔH is relatively constant, though for ice Ih it increases with increasing concentration and decreasing pressure. ΔV decreases with increasing concentration, and density inversions are observed (in which the aqueous solutions become denser than the ice polymorphs) in agreement with previous experimental data.

References

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