Improvements in thermodynamic models of hydrothermal fluids through better configurational entropy terms.

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Quantitative thermodynamic calculations on aqueous fluids in Earth systems have proved difficult because of the complexity of the interactions that occur in the aqueous solutions. This has led to thermodynamic approaches that combine a simple configurational entropy, or ideal activity, term, with a complicated excess energy, or non-ideal, activity term.

The new DH-ASF model activity-composition model allows the Gibbs energy associated with ideal mixing to be formulated so that the physical distribution of molecules in solution is taken into account. Non-ideal mixing is represented by an activity coefficient term that combines Debye-Hückel with asymmetric formalism (Van Laar) terms.

This activity-composition model is applied to description of the solubility of quartz in salt solutions. Quartz solubility in such solutions exhibits complex behaviour. A variety of configurational entropy terms are tested; results show that traditional formulations for the ideal activity may not always be the most appropriate, and that substantial reductions in the apparent excess free energy of mixing can be obtained.

Ultimately, correct specification of the ideal mixing term plays an important role in identification of the physical arrangement in molecules in solution. Once models are based on physical reality, the degree of empiricism of the activity model is decreased, and it becomes possible to extrapolate calibrated parameters across a greater range of pressure, temperature, and fluid composition than was previously possible.