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Mineral solubility in aqueous fluids: constraints on functionality and accuracy of equations of state for aqueous species

David Dolejš (1) and Barbora Hanková (2)

(1) Institute of Earth and Environmental Sciences, University of Freiburg, Germany (david.dolejs@minpet.uni-freiburg.de),
(2) Institute of Petrology and Structural Geology, Charles University, Prague, Czech Republic

Aqueous fluids and their solutes play fundamental role in geochemical mass transport over multiple scales, ranging from magmatic and metamorphic devolatilization through focused flow in hydrothermal systems to grain-scale crystallization or reaction mechanisms at atomic level. Understanding these phenomena using equilibrium or kinetic approaches requires equations of state and thermodynamic data for aqueous species applicable over wide range of temperature and pressure. Recent advances in calibration of electrostatic permittivity of water [1] have allowed extrapolation of thermodynamic models and data from hydrothermal conditions to extreme temperatures and pressures [2,3]. Here we evaluate the extrapolation behavior and accuracy of the Helgeson-Kirkham-Flowers (HKF) model by comparing predictive calculations with experimental solubilities of representative rock-forming minerals.

Quartz dissolves as predominantly neutral species (e.g., H_4SiO_4, $H_6Si_2O_7$), hence the solute thermodynamics is essentially insensitive to the dielectric constant of aqueous solvent. Conventional calibrations of the thermodynamic properties of aqueous silica [4,5] yield unrealistically high quartz solubilities at pressures exceeding 0.6 GPa, as a result of universal correlations between the HKF parameters. By contrast, their recalibration [1] reproduces experimental solubilities within the calibrated range, but underestimates the quartz solubility above 900 ^{o}C. Corundum solubility, owing to more complex homogeneous speciation involving charged species such as $Al(OH)_4^-$ and H^+, is very weakly dependent on the dielectric constant of water. The thermodynamic properties of aluminous species have been recently recalibrated under hydrothermal conditions [5], leading to differences in the predicted corundum solubility by one to three orders of magnitude above 500 ^{o}C and 1 GPa. The experimental solubilities are reproduced within the calibrated range [1], at the expense of overestimation at lower temperatures and pressures. Calcite solubility, including complex speciation involving highly charged species, underlies the need for accurate calibration of the dielectric constant of water above 550 ^{o}C. The predicted solubilities remain one order of magnitude lower above 650 ^{o}C and 6 kbar than experimental determination.

Our comparison indicates that the Helgeson-Kirkham-Flowers model is sufficiently flexible to allow for recalibration of thermodynamic data and reproducibility of experimental solubilities over wide range of pressures and temperatures (PT). However, it rather poorly extrapolates between hydrothermal and high-PT conditions and vice versa. This is due to (i) universal self-correlations among its parameters, and (ii) its functional form that is numerically most significant near the critical points of water. We propose revision of the equation of state, mainly by including the compression contribution of hydration, which results in superior accuracy and interpolability between ambient conditions and 1100 ^{o}C and 2.0 GPa.

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