Thermodynamics of aqueous species at high pressures: constraints from mineral solubilities on applicability of equations of state

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Aqueous fluids and their solutes play fundamental role in geochemical mass transport over multiple spatial and temporal scales in settings ranging from diffuse devolatilization to focused fluid flow. Understanding macroscopic mineral-fluid interaction or reaction mechanisms at atomic level requires thermodynamic equations of state and data for aqueous species applicable over wide range of pressure-temperature conditions and solute concentrations. 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, corundum and calcite. The thermodynamic properties of neutral species (e.g., H_4SiO_4, $H_6Si_2O_7$) are implicitly nearly insensitive to dielectric constant of the aqueous solvent. Calibrations of the thermodynamic properties at hydrothermal conditions [4,5] yield discrepant quartz and corundum solubilities at temperatures above 500 ^oC or pressures exceeding 0.6 GPa, as a result of universal correlations between the HKF parameters. By contrast, thermodynamic calibrations at high-pressure conditions [1] reproduce experimental solubilities but at the expense of extrapolation stability. Fluids involving highly charged species such as carbonate ions require accurate calibration of the dielectric constant of water above 550 ^oC, but predicted solubilities remain one order of magnitude lower above 650 ^oC and 0.6 GPa than experimental determination. Overall, the HKF model offers moderate versatility when the universal correlations among its parameters are removed, but it does not achieve continuous accuracy from low- to very high-PT conditions. These drawbacks are implicit in the model's functional form that was designed to reproduce strong departures in infinite dilution properties near the conventional and sub-ambient critical point of water while ignoring the compressibility of the solute's hydration sphere. We will introduce several universal constraints, which dictate functional forms of new equations of state for aqueous solutes and their applicability to a wide range of crustal and mantle conditions: (*i*) Gibbs-Duhem consistency, which propagates pure solvent properties to those of infinitely dilute species, and (*ii*) internal continuity between infinite-dilution and pure-liquid standard state to cover supercritical water-silicate systems. Exploratory calibration of a five-parameter equation of state results in superior accuracy and interpolability between ambient conditions and 1100 ^oC and 2.0 GPa.

[1] Sverjensky et al., 2014. Geochim. Cosmochim. Acta 129, 125-145. [2] Mikhail & Sverjensky, 2014. Nat. Geosci. 7, 816-819. [3] Facq et al., 2016. Chem. Geol. 431, 44-53. [4] Shock et al., 1989. Geochim. Cosmochim. Acta 53, 2157-2183. [5] Miron et al., 2016. Geochim. Cosmochim. Acta 187, 41-78.