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Thermodynamic models for aqueous solutes to very high temperatures and pressures

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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. Interpretation and prediction of these phenomena using equilibrium or irreversible approaches requires equations of state and thermodynamic data for aqueous species applicable over wide range of temperature and pressure. Here we review advances in the development of new equations of state, with emphasis on their functional forms, which arise from rigorous applications of hydration theory, solvent critical theory, and internal Gibbs-Duhem consistency between solvent and solutes. The hydration behavior of aqueous species is primarily a function of solvent density, which dictates individual short or long range interaction mechanisms. At very low fluid densities, solute species are successively hydrated whereas long-range or electrostatic interactions are negligible. With increasing fluid density, the inner hydration of species is complete and the bulk hydration properties are defined by volumetric and structural reorganization and electrostatic long-range interaction of the solvent. 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) rigorous conversion between pure and infinitely dilute standard state, (ii) consistency with the Gibbs-Duhem theorem, which propagates pure solvent properties to those of solute species, and (iii) separation of mechanical and electrostatic contributions, which improve the extrapolation behavior in the temperature-pressure space. With increasing solute concentration, when upper critical points in silicate or salt systems are approached, the solute components associate but their thermodynamic properties are heuristically described by simple mixing models when realizing that functional form and limiting properties of the mixing functions are directly dictated by difference between pure and dilute standard states. These approaches illustrate diverse fundamental and universal constraints, which guide selection of functional forms of equations of state for aqueous solutes. Furthermore, this leads to partial mapping onto relevant solvent properties and it reduces the number of species-specific parameters.