Equations of state for aqueous solutes over wide range of pressure, temperature, and concentration

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Aqueous fluids are important agents of mass and heat transfer in geodynamic settings as diverse as slab subduction, mantle metasomatism, metamorphic devolatilization, magma degassing, and ore formation. Thermodynamic properties of aqueous solutes applicable over wide range of sub- and supercritical conditions, and concentrations are essential to interpret and predict the fluid-mediated mass transport. Here we review advances in the development of new equations of state, with emphasis on their functional forms, which arise from rigorous applications of critical theory and internal consistency between standard states and mixing properties.

Conventional choice of the asymmetric infinite-dilution standard state for aqueous solutes requires by virtue of the Gibbs-Duhem theorem that the infinite-dilution properties scale proportionally with the derivatives of the respective properties of aqueous solvent. For instance, the dependence of the partial molar volumes of aqueous species on solvent compressibility forms the basis of density models for homogeneous equilibria and mineral solubilities. When this approach is applied rigorously, the empirical polynomials for partial volumetric and caloric properties in the Helgeson-Kirkham-Flowers model may be replaced by physically based functional forms. This leads to a new equation of state for infinite-dilution properties of solutes, which are essentially mapped onto relevant solvent properties using a small number of parameters.

Extensions of infinite-dilution properties to finite concentrations or to supercritical water-silicate systems should benefit from consistency between infinite-dilution, pure solute and excess mixing properties. Expansion of the Helmholtz energy in terms of temperature, volume and composition around the solvent critical point defines the composition dependence of partial molar properties, which, however, scales in a remarkable contrast to the Debye-Hückel theory, but may explain replace the empirical Setchénow correction. For geological applications, the concentrated fluids may be treated by a simple excess mixing models, realizing that functional form and limiting properties of the Margules or Redlich-Kister polynomials are dictated by difference between pure and dilute standard states. These approaches illustrate universal constraints, which dictate functional forms of equations of state for aqueous solutes.