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Thermodynamics of aqueous solutes at high temperatures and pressures: Application of the hydration theory and implications for fluid-mediated mass transfer

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Magmatic activity and prograde devolatilization of subducting or underplating lithologies release large quantities of aqueous fluids that act as mass and heat transfer agents in the planetary interiors. Understanding of mineral-melt-fluid interactions is essential for evaluating the effects of fluid-mediated mass transport in subduction zones, collisional orogens as well as in igneous provinces. The thermodynamic properties of aqueous species were frequently described by the Helgeson-Kirkham-Flowers equation of state [1] but its utility is limited by inavailability of the solvent dielectric properties at high pressures and temperatures, and by decoupling of species-solvent mechanical and electrostatic interactions that cannot be separated within the Born theory. Systematic description of the hydration process in a Born-Haber cycle leads to the following thermochemical contributions: (i) thermodynamic properties of an unhydrated species, (ii) the pressure-volume work required to create a cavity within the solvent to accommodate the species, described by the scaled particle theory, (iii) entropic contribution related to changes in the solute's and the solvent's kinetic degrees of freedom, and (iv) contribution from the solute-solvent molecular interactions and corresponding rearrangement of the solvent molecules to form the hydration shell. Application of the spatial correlation functions [2, 3] results in apparent Gibbs energy of aqueous species, $\Delta_a G_i = a + bT + cT\ln T + dP + eT\ln\rho + fT\rho\ln\rho$, where $a$through f represent constants related to standard thermodynamic properties of aqueous species ($\Delta_f H$, S, V, c_P) and to solvent volumetric properties at 298.15 K and 1 bar (ρ, α, β etc.). In phase equilibrium calculations, the number of required parameters often reduces to four ($c = f = 0$) while noting that H_2O density as the only solvent-related property is accurately known to extreme temperatures and pressures. The equation of state parameters were calibrated for 30 aqueous species in the system Na-K-Ca-Mg-Fe-Al-Ti-Si-C-Cl-O-H, and the model proves successful for reproducing and predicting mineral solubilities, mineral-fluid activity relationships, and homogeneous association-dissociation equilibria. With $f = 0$, logarithmic values of solubilities, equilibrium and Henry's law constants become linearly dependent on the logarithm of solvent density, as confirmed in a number of experimental studies. Our new thermodynamic model is applicable to fluid-melt-mineral equilibria in a wide range of diverse settings from fluid release from subducting slab at high pressures through mantle wedge metasomatism, fluid-mediated element cycling in continental orogens, and hydrothermal alteration and ore deposit formation in magmatic and metamorphic environments.

[1] Tanger, J.C. & Helgeson, H.C. (1988) *Am. J. Sci.*, 288, 19-98. [2] Kirkwood, J.G. & Buff, F.P. (1951), *J. Chem. Phys.* 19, 774-777. [3] O'Connell, J.P. (1995), *Fluid Phase Eq.*, 104, 21-39.