Gibbs Energy Local Basis Function Representations for Aqueous NaCl and Ammonia-Water Solutions to 10 GPa and 2000 K

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Local Basis Function Gibbs Energy representations extending to high pressure are constructed based on sound speed measurements obtained in both hydraulic pressure vessels and in diamond anvil cells. The current analysis reverses conventional electrolytic solution precepts where assumptions for the standard state and excess quantities underly calculation of Gibbs energy. Here, densities and specific heats at high pressures, determined by integration of the sound speeds, are linearly inverted to obtain a starting Gibbs energy representation that is non-linearly optimized using regularization and *a priori* limiting behavior constraints. Standard state and excess properties are then predicted by the representation. Aqueous solutions of NaCl exhibit a transition from electrolytic solution behavior below about 500 MPa to being a simpler dense fluid mixture at higher pressures and temperatures. The apparent volume of NaCl in water at high pressure is nearly equal to the crystalline volume while the apparent specific heat approaches a Dulong-Petit value. Similarly, the apparent volume of ammonia in water is essentially equal to that of pure ammonia for pressures beyond 500 MPa. For both aqueous systems the greatest challenges in constructing accurate representations are associated with the regime near freezing for pressures less than about 500 MPa.

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