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Experimental determination of the standard partial molal enthalpies of Nd hydroxyl complexes in hydrothermal aqueous solutions

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The thermodynamic properties used to determine the stability of rare earth elements (REE) hydroxyl complexes are still largely based on the data derived by Haas et al. [1] and the semi-empirical Helgeson-Kirkham-Flowers (HKF) equation of state at high temperature [2,3]. However, recent work on the REE chloride, fluoride and sulfate complexes [4] has shown significant discrepancies between experiments and theoretically derived high temperature thermodynamic data for such species. The hydrolysis of Nd^{3+} was measured by Wood et al. [5] several decades ago, but more experimental data are needed to accurately predict the stability of REE hydroxyl complexes at high temperature. In this study, we present new standard partial molal enthalpy data for Nd hydroxyl species from the heat of solution of synthetic $Nd(OH)_3$ solids in perchloric acid and $NaClO_4$-based aqueous solutions with variable initial ionic strength (0.01, 0.05 and 0.1). The enthalpy measurement were conducted at a pH of 2 using a Setaram C80 heat flow calorimeter with two mini hastelloy reversal cells workable to up to 150 ºC at saturated water vapor pressure. This setup was first tested for the enthalpy of solution of NaCl which yielded an accurate standard enthalpy of reaction extrapolated to infinite dilution of -5.25 ± 0.25 kJ/mol at 148.5 °C. Preliminary experiments for the enthalpy of solution of $Nd(OH)_3$ solids at pH of 2 indicates similar (within uncertainty) exothermic enthalpy values at ionic strengths of 0.01 and 0.05, with a mean value of -151±5 kJ/mol, whereas enthalpies were increasingly negative enthalpy at high ionic strength of the experimental solutions. Using these data permits deriving the standard molal enthalpies of the major Nd species participating in this dissolution reactionat pH of 2 at pH of 2, including Nd^{3+} and $NdOH^{2+}$, and assess the accuracy of high temperature predictions from the HKF model [1-3].

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