

## *Understanding the Aqueous Phase Oxidation of Hydroxylamine by Nitric and Nitrous Acids Using Computational Chemistry*

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The oxidation of hydroxylamine to nitrous oxide and nitrous acid in aqueous solutions of nitric acid is important in the Plutonium-Uranium Reduction Extraction (PUREX) process. A combination of computational chemistry calculations and limited experimental data was used to construct a detailed chemical kinetic model of the system. Previously proposed models fit experimental data over the narrow range where it was collected, but were much simplified. A method for estimating the thermochemistry of aqueous species based on a combination of ab initio calculations and empirical parameters is outlined. A high-level CBS-QB3 gas-phase calculation was corrected for solvation energy at the B3LYP/CBSB7 level. Empirical bond-additivity corrections were included to reduce the error between predicted and experimental values. The solvation entropy, which is very important to non-equal molar reactions, was estimated using Pieriotti's equation for the free energy of solvation and an empirical part to account for solute-solvent interactions. Traditional transition state theory was used to estimate rate constants in solution, along with many diffusion-limited reaction rates. A kinetic model of the system was constructed using these estimates, with several layers of modifications. The first layer was altering the thermochemistry slightly to match experimentally-determined  $pK_A$  values. The second layer was including experimental activity coefficients for the major species, which modified the equilibrium constants of a number of reactions, especially at high acid concentrations. The final modification involved modest corrections to several rate parameters, guided by sensitivity analyses, to achieve good agreement with much of the available experimental yield data. The results show that with a small amount of experimental thermochemical data, the methodologies outlined here may yield qualitatively reasonable predictions. The resulting models can be used to understand complicated systems, and may help guide experiments or more precise solution phase rate estimation techniques. The model does not predict the stability of the system accurately, which is the main deficiency in the model. It is hoped that the present study will encourage the development of more accurate, practical methods for estimating energies and entropies of solvation needed for accurate modeling in condensed phases.