

# **Kinetics of discrete aqueous redox reaction sub-steps using computational methods: application to reactions of plutonyl ( $\text{PuO}_2^{+2+}$ ) with $\text{Fe}^{2+}$ , $\text{Fe}^{3+}$ , and ( $\bullet\text{OH}$ )**

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The solubility and mobility of actinides, such as plutonium, are highly-dependent on their oxidation state, with the penta- and hexavalent species forming soluble actinyl ions (for example,  $\text{PuO}_2^{+2+}$ ). To understand the kinetics of these reactions, this study assesses the degree to which different sub-steps affect the overall rate of an aqueous reaction. In this approach, reactions are broken into three steps: (1) the diffusion of reactants toward each other in solution to form an outer-sphere complex, (2) the transition from outer- to inner-sphere complex, and (3) the transfer of an electron. We address encounter frequency using collision theory and the last two steps using quantum-mechanical modeling to analyze the energy, as well as atomic charges and spins, as a function of distance between the two reactants.

This approach is applied to the reactions of  $\text{PuO}_2^{2+}$  and  $\text{PuO}_2^+$  with  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ , and hydroxyl radical ( $\bullet\text{OH}$ ). Regardless of spin configuration (ferromagnetic vs. antiferromagnetic), once species are within distances of 7-11 Å, the formation of an outer-sphere complex is found to be energetically favorable. This process proceeds rapidly even at low, environmentally-relevant plutonyl concentrations. The half-life of plutonyl in the bulk solution (that is, that which has not yet formed an outer-sphere complex) is found to be <2 min even with initial concentrations as low as the pM range, increasing rapidly if concentrations are more elevated. Results indicate that the outer-sphere configuration(s) are consumed over similar time scales as those of outer-sphere complex formation due to collision and then convert quickly to thermodynamically-favorable inner-sphere complexes.

This methodology can provide insight into rate-limiting sub-processes and allow us to explore the redox behavior of Pu and other metals in greater detail. The computational scheme can now be reasonably extended to determine the kinetics of complex formation at mineral-solution interfaces and also combined with Marcus theory calculations to determine explicit electron transfer rates for complex-dependent redox processes.