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Comment on 'Plutonium chemistry: a synthesis of experimental data and a quantitative model for plutonium oxide solubility' by J.M. Haschke and V.M. Oversby

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Abstract

In part of a recent paper [J. Nucl. Mater. 305 (2002) 187] the authors examined the published data on the disproportionation of Pu(V) and the self-reduction of Pu(VI) in aqueous solution. They conclude that alpha particle-induced reduction of Pu(VI) is contrary to the experimental observations. It is shown here that, with the exception of results at pH 6, the authors have misinterpreted the published data. It is also demonstrated that the published data are in agreement with the generally accepted alpha-reduction mechanism.

1. Introduction

The recent paper by Haschke and Oversby [1] is primarily a discussion of reactions that are important in the dissolution of plutonium oxide solids. In addition, there is a section on the disproportionation kinetics of aqueous Pu(V) and Pu(VI). Haschke and Oversby propose that the generally accepted explanation for the instability of Pu(VI) in acidic solutions is inconsistent with experimental evidence. Instead, the authors propose that in these solutions Pu(VI) disproportionates into Pu(V) and very unstable Pu(VII). This is followed by the rapid oxidation of water by the Pu(VII) to give Pu(VI) and oxygen. The net reaction would be:

$$PuO_2^{2+} + 1/2\,H_2O = PuO_2^{+} + H^{+} + 1/4\,O_2. \qquad (1)$$

Although the equilibrium for this reaction is well to the right in near neutral solutions, it is well to the left in acidic solutions. Thus the reactions that influence the stability of Pu(VI) could be quite pH dependent.

2. Discussion

A recent critical review [2] gives standard free energies of formation and reduction potentials from which ΔG° for the reaction is calculated to be 28.4 kJ/mol at zero ionic strength and about 30.6 kJ/mol at unit ionic strength. The equilibrium quotients from these values show that for oxygen partial pressures of 0.21 atm, the concentration ratio, $[PuO_2^+]/[PuO_2^{2+}]$, is less than or equal to 0.01 for $p[H^+] < 2.9$ for zero ionic strength or $p[H^+] < 3.2$ for unit ionic strength.

At pH 6 the $[PuO_2^+]/[PuO_2^{2+}]$ ratio would be about 12. Thus at this pH Pu(VI) is thermodynamically unstable with respect to Pu(V) and O_2. But in acid

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solutions with pH less than about 3, no matter what the mechanism might be, reaction (1) cannot proceed to a significant extent without an additional source of energy. On the contrary, the authors in Ref. [1] state 'Alpha-induced reduction has been proposed as the driver for Pu(IV) formation in solutions containing Pu(VI); however, this explanation is inconsistent with experimental evidence.' Instead, they propose the disproportionation of Pu(VI) mentioned above, followed by the well-known disproportionation of Pu(V).

In Ref. [1] the authors have examined the results of experiments, described in several papers [3–6] on the instability of both Pu(V) and Pu(VI) and found the data to be fit by:

$$\text{rate} = k[\text{Pu}]^2, \tag{2}$$

where [Pu] is the concentration of either Pu(V) or Pu(VI). Values for the apparent 2nd order rate constants are listed in their Table 1 [1]. However, our data in Ref. [4] do not support this rate law.

We carefully measured the plot for pH 1.5 (Fig. 4(a)) to obtain the same concentration versus time data as used in [1]. Eq. (2) was generalized to rate = $k[\text{Pu(VI)}]^N$ which in integrated form is:

$$[\text{Pu(VI)}] = \{[\text{Pu(VI)}]_0^{(1-N)} + k(N-1)t\}^{(1/(1-N))}, \quad N \neq 1. \tag{3}$$

A simple non-linear least squares procedure was used to find the values for k and N that minimize the sum of the squares of the differences between the observed and calculated concentrations. These values for k and N were found to be 0.0792 $\text{M}^{-0.263}$ da^{-1}, and 1.263, respectively. The root-mean-square deviation using these values is 3.68×10^{-4} M (3.9% of the initial [Pu(VI)]). If N is fixed at 2, the fit is very much poorer; the root-mean-square deviation is 6.02×10^{-4} M. This shows that, contrary to the values listed in Table 1 in [1], the disproportionation of Pu(V) and the disappearance of Pu(VI) do not have the same rate laws and rate constants. It should be noted, however, that if N is set equal to 2 the best value for the rate constant is 3.301 M^{-1} da^{-1} or 3.8×10^{-5} M^{-1} s^{-1}, reasonably close to 5.2×10^{-5} M^{-1} s^{-1}, the value listed in Table 1 in Ref. [1].

We also determined values for concentration versus time from Fig. 2(a) in Ref. [4] for a solution initially 4.4×10^{-5} M in Pu(VI) with a pH of 2.2. The best values for k and N from these data were then found to be 7.75×10^{-4} $\text{M}^{-0.328}$ da^{-1} and 0.672, respectively. These two data sets have different concentrations and pH values and show quite different [Pu(VI)] dependences. However, they do have nearly the same initial apparent first-order rate constants: 0.023 and 0.021 da^{-1}. The data for 1 M HClO_4 in Ref. [3] lead to 0.014 da^{-1}.

If the reduction of Pu(VI) is alpha-induced over the pH range from 0 to 7, the $[\text{H}^+]$ dependence should be essentially zero and the rate of change of average oxidation number of plutonium should depend on the radiation dose rate. Büppelmann et al. [7] studied the reduction of ^{238}Pu(VI) in 1 M HClO_4 and found that a 1.1×10^{-3} M solution was self-reduced by a factor of 2 in 65.5 h. This amounts to about 18% per day, very much larger than about 1.5% per day reported by Rabideau et al. [8] for ^{239}Pu. Thus the alpha-induced reduction should be much less with ^{242}Pu(VI) than with ^{239}Pu(VI). The apparent second-order rate constants listed in [1] are 5.2×10^{-5} M^{-1} s^{-1} for ^{239}Pu at pH 1.5 and 2.1×10^{-3} M^{-1} s^{-1} for ^{242}Pu at pH 6. This shows that at pH 6 the reduction is about 40 times faster using ^{242}Pu than with the same concentration of ^{239}Pu. Thus an alpha-reduction mechanism cannot contribute significantly to the reaction at pH 6. However for pH values less than about 3, the thermodynamic data quoted above show that the energy supplied by the alpha decay of plutonium is required for the reaction.

The data on the instability of Pu(VI) in brine, Ref. [5], at pH 7.1 are difficult to relate to the other data considered here because of the high chloride concentration. This will complex the Pu(VI) and will probably affect possible alpha-induced reduction.

3. Conclusions

Our conclusions are: (a) alpha-induced reduction of Pu(VI) is consistent with the experimental results for solutions with pH values less than about 2.2 and (b) the statement quoted in the third paragraph of this letter should be extended to read 'Alpha-induced reduction has been proposed as the driver for Pu(IV) formation in solutions containing Pu(VI); however, this explanation is inconsistent with the experimental evidence at pH 6.'

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