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Journal of Nuclear Materials 334 (2004) 225–228

journal of nuclear materials

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Author's reply to "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"

John M. Haschke

Actinide Sciences Consulting, Waco, TX 76712, USA

Received 2 June 2004; accepted 2 June 2004

Abstract

In the accompanying letter, Newton and Hobart comment on a recent paper [J. Nucl. Mater. 305 (2002) 187] and conclude that a proposed alternative explanation for self-reduction of Pu(VI) is based on misinterpretation of data. Result of quantitative kinetic modeling contradicts this conclusion and the accepted explanation by showing that self-induced α-particle reduction of ^{239}Pu(VI) at pH 1.5 does not account for the observed reduction rate of Pu(VI) or for dependence of the rate on [Pu(VI)]. Similar modeling shows that kinetic behavior is consistent with a self-reduction process based on disproportionation of Pu(VI). Validity of the alternative concept is supported by close similarities in the kinetic behavior of Pu(V) and Pu(VI).

1. Response

The accompanying letter by Newton and Hobart [1] focuses needed attention on processes that control speciation and steady-state concentrations of Pu in aqueous solution. Pu(VI) instability and spontaneous reduction to Pu(V) are part of this larger concern that was addressed in the earlier report [2]. α-induced reduction is the generally accepted explanation for Pu(VI) instability suggested by Gevantman and Kraus on the basis of parallels between rates of self-reduction and rates of H_2O_2 reduction [3]. Those authors state that their observations 'do not prove such a mechanism to be correct.' Instability of Pu(VI) in a radiolytic environment does not prove that reduction results from radiolysis. Newton and Hobart [1] apparently equate a first-order kinetic dependence of $-d[Pu(VI)/dt$ on [Pu(VI)] with α-induced reduction, but fail to cite any studies showing that reduction of ^{239}Pu(VI) is actually self-induced by radiolysis.

Reduction of Pu(VI) to Pu(V) by excess hydrogen peroxide in acidic solution is well documented [4,5]. *G* values for species formed by alpha radiolysis of water [6] show that H_2O_2 accounts for 80% of radiolytic reductant capacity. Reaction of peroxide is a reliable and quantifiable basis for evaluating the concept of α-induced reduction at pH 1.5:

$$2PuO_2^{2+}(aq) + H_2O_2(aq) \rightarrow 2PuO_2^{+}(aq) + 2H^{+}(aq) + O_2(g) \qquad (1)$$

E-mail address: johnhaschke@msn.com.

0022-3115/$ - see front matter
doi:10.1016/j.jnucmat.2004.06.002

The letter [1] refutes a suggestion that self-reduction occurs by disproportionation [2]:

$$2PuO_2^{2+}(aq) \rightarrow PuO_2^{+}(aq) + PuO_2^{3+}(?)(aq) \qquad (2)$$

Immediate reaction of the unobserved, but highly reactive, Pu(VII) species with water to reform Pu(VI) is expected. The net reaction results in reduction of Pu(VI) to Pu(V). Eq. (2) is similar to the well known Pu(V) disproportionation reaction that occurs over the pH 0–15 range [7,8] and proceeds at pH 1.5 according to Eq. (3):

$$2PuO_2^{+}(aq) + 2H^{+}(aq) \rightarrow Pu(OH)_2^{2+}(aq) + PuO_2^{2+}(aq) \qquad (3)$$

Reduction of Pu(VI) is linked to Eq. (3) in a process that forms Pu(IV) and ultimately precipitates Pu(IV) hydrous oxide if K_{sp} is satisfied. Proposed reduction schemes are evaluated by examining consistency of Eqs. (1) and (2) with observation and on similarities in thermodynamic and kinetic behavior of Pu(V) and Pu(VI).

Inconsistency of α-induced reduction with observation is shown by comparing the calculated [^{239}Pu(VI)]–time dependence for Eq. (1) with data from Newton et al. [9] in Fig. 1. Comparison during the first 40 days is unambiguous because Pu(VI) was not reformed via Eq. (3). Initial absence of detectable Pu(V) implies that the solution was freshly prepared and that the [H_2O_2] was also small at zero time. The time dependence of [Pu(VI)] (Fig. 1, Curve A) is derived by iterative numerical integration of rate equations for [H_2O_2] formation and [Pu(VI)] reduction. The radiolytic H_2O_2 formation rate (4×10^{-5} mol H_2O_2 L^{-1} d^{-1}) is a constant determined by the initial [^{239}Pu], ^{239}Pu activity, the α-particle energy, and the *G* value for H_2O_2 [6]. The rate law for peroxide is $-d([Pu(VI)/dt) = k[Pu(VI)][H_2O_2]/[H^+]$ with values of *k* bracketing 0.5 min^{-1} [4]. Results show that H_2O_2 accumulates in solution and the reduction rate increases until the rate of peroxide consumption equals its rate of formation after about 35 min. Thereafter, [Pu(VI)] decreases at a radiolysis-controlled constant maximum rate (8×10^{-5} mol L^{-1} d^{-1}) that is independent of [Pu(VI)] at concentrations greater than 6×10^{-5} M. Modeling of [^{242}Pu(VI)]–time data for pH 6 [10] predicts similar behavior and a radiolysis-limited rate (1×10^{-7} mol L^{-1} d^{-1}) that is a factor of 15 less than the observed initial reduction rate.

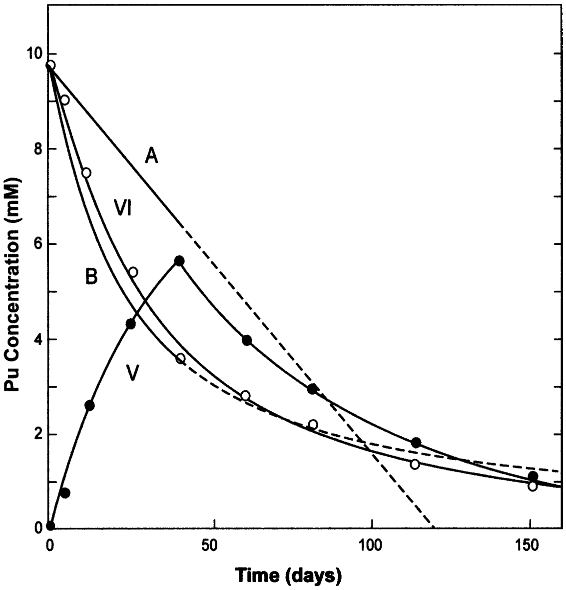

Fig. 1. Comparison of time dependencies of Pu(V) and Pu(VI) concentrations measured during self-reduction of ^{239}Pu(VI) in perchlorate solution at pH 1.5 [9] with those calculated for α-induced reduction according to Eq. (1) (Curve A) and for disproportionation of Pu(VI) according to Eq. (2) (Curve B). Measured Pu(V) and Pu(VI) concentrations are indicated by solid and open symbols, respectively.

Attainment of equilibrium in solution is presumed because [Pu(VI)] and [Pu(V)] are stable (1×10^{-3} and 4×10^{-4} M, respectively) beyond day 250 [9]. The proposed equilibrium reaction, $2PuO_2^{+} = PuO_2^{2+} + PuO_2(s)$, does not involve H_2O_2 even though the radiolytic product continues to accumulate in solution. Either the observed steady state is fixed by equal and opposing rates of oxidation and reduction reactions or Pu(VI) reduction is not α-induced. Respective values of [H_2O_2] from kinetic modeling are 3.8×10^{-7}, 3.5×10^{-6}, and 0.01 M at days 5, 150, and 400. Use of these results, reference data [11,12] and Pu concentrations at the corresponding times [9] gives Gibbs energies of −49, −46, and −66 kJ mol^{-1}, respectively, for Eq. (1) at pH 1.5. Therefore, continuing α-induced Pu(VI) reduction, followed by Pu(V) disproportionation and Pu(IV) precipitation, should force [Pu(VI)] and [Pu(V)] to low values over time as indicated by the dashed portion of Curve A in Fig. 1. Since treatment with peroxide drives [Pu(VI)] below detectable limits at pH 1 [5], existence of the observed steady state implies that reduction is not α-induced.

Value of the thermodynamic argument of Newton and Hobart [1] in assessing kinetics is limited because the PuO_2^{2+}–H_2O reaction does not define parameters that control the rate of Eq. (2). For example, the effect of [H^+] on the rate of Eq. (2) is determined by the pH dependence of the rate law, not by the pH dependence of the equilibrium expression.

Newton and Hobart imply that the linear ln(rate)–ln[Pu(VI)] analysis is inadequate for determining the reaction order (*n*) of Pu(VI) [1]. Unlike error-minimization techniques that give the best fit of several parameters [1], the method directly defines *n* by the slope, but is limited to cases in which Pu is the only reactant or the concentrations of other reactants are constant. The method is adopted because ln(rate)–ln[Pu] data show that behavior of Pu(VI) is indistinguishable from that of Pu(V) [2]. Regression analysis of rate data for Pu(VI) at pH 1.5 [8], pH 6.0 [10], and pH 7.1 [14] gives respective orders of 1.5, 2.6, and 1.9 that center on 2 and lead to $-\mathrm{d}([\mathrm{Pu(VI)}]/\mathrm{d}t) = k_{\mathrm{VI}}[\mathrm{Pu(VI)}]^2$. The k_{VI} of 4×10^{-5} $\mathrm{mol}^{-1}\,\mathrm{s}^{-1}$ derived by Newton and Hobart [1] for $n = 2$ accurately describes the data at pH 1.5. Accuracy of the rate law is shown by agreement of calculated [Pu(VI)]–t behavior (Fig. 1, Curve B) with observation. Neither a second-order dependence on [Pu(VI)] nor that ($n = 1.26$) derived by Newton and Hobart [1] is consistent with α-induced reduction of ^{239}Pu because that process is independent of [Pu(VI)] at pH 1.5.

A second-order dependence of $-\mathrm{d}[\mathrm{Pu(VI)}]/\mathrm{d}t$ on [Pu(VI)] suggests that the rate-determining step of self-reduction is identical to that of Pu(V) [4]. The pH-dependent second-order rate constants (k_{V} and k_{VI}) derived from the available data for Pu(V) and Pu(VI) [7–10,13,14] in non-complexing solutions (Fig. 2) are in close agreement and validate Eq. (2). PuO_2^+ and PuO_2^{2+} are the predominant Pu(V) and Pu(VI) species at the minimum near pH 3–4 [11]. Linear $\ln k_{\mathrm{V}}$–$\ln[\mathrm{H}^+]$ segments in Fig. 2 correlate precisely with a progressive increase in [$\mathrm{PuO_2OH}$] from hydrolysis of PuO_2^+ at pH 4–10 (slope 2) [11], with fixed [$\mathrm{PuO_2OH}$] (complete hydrolysis) at pH 10–13 (slope 0) [11], and with progressive decrease in [$\mathrm{PuO_2OH}$] due to $\mathrm{PuO_2(OH)}_3^{2-}$ formation at high pH (slope −4) [8]. Data are consistent with protonation of PuO_2^+ to PuOOH^{2+} below pH 4 (slope −1) [7]. Hydrolysis reactions of PuO_2^{2+} parallel those of PuO_2^+ below pH 7 [11]. Chemistry of Pu(V) and Pu(VI) and mechanisms that account for observed slopes are entirely consistent with formation and disproportionation of hydroxo-bridged dimers in the rate-determining steps. Self-reduction rates of ^{242}Pu(VI) at pH 6 [10] exceed those of ^{239}Pu(VI) at pH 1.5 [9] because hydrolysis of PuO_2^{2+} increases the concentrations of $\mathrm{PuO_2OH}^+$ (or of $\mathrm{PuO_2\,(OH)_2}$) and the hydroxo dimer at the higher pH.

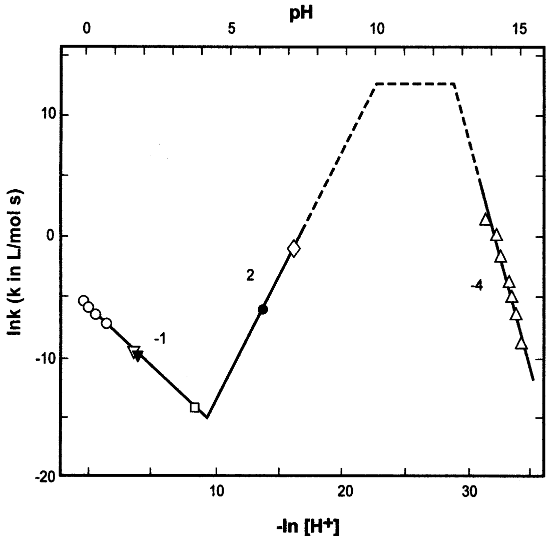

Fig. 2. Dependence of rate constants k_{V} for Pu(V) (open symbols) and k_{VI} for Pu(VI) (solid symbols) on pH. Rate constants are published in the following literature sources or derived from data therein: open circles [7], open and solid inverted triangles [9], open square [14], solid circle [10], open diamond [13], and open upright triangles [8]. Rate constants were determined by substitution of measured rates and corresponding [Pu(V)] or [Pu(VI)] values into the second-order rate law $-\mathrm{d}[\mathrm{Pu}]/\mathrm{d}t = k[\mathrm{Pu}]^2$.

Emphasis is placed on the need for an additional source of energy to drive the PuO_2^{2+}–$\mathrm{H_2O}$ reaction [1]. Gibbs energies derived for Eq. (3) using reference data [11] and concentrations of Pu(V) and Pu(VI) measured at pH 1.6 [9] vary from $-13\ \mathrm{kJ\,mol^{-1}}$ at 1% reaction to $+15\ \mathrm{kJ\,mol^{-1}}$ at steady state (98% reaction). Continuation of reaction after ΔG reaches 0 near 50% completion [9] shows that disproportionation of Pu(V) is not controlled by thermodynamics and implies that disproportionation of Pu(VI) (Eq. (2)) is also possible despite a positive ΔG. An additional energy source is unnecessary for a plausible kinetic process involving hydroxo dimers. Asymmetric electron distributions due to quantum tunneling [15] create a finite probability of instantaneously forming Pu(IV) and Pu(VI) in Pu(V) dimers or Pu(V) and Pu(VII) in Pu(VI) dimers. Random dissociation of these asymmetric dimers accounts for occurrence of Eqs. (2) and (3) at similar rates. Reverse reactions are negligible because Pu(IV) is removed from solution by precipitation and Pu(VII) is eliminated by immediate reaction with water.

Pu(VI) self-reduction occurs via the most rapid pathway as determined by rate laws, the concentration and isotopic distribution of Pu, and pH. Calculations based on the experimental rate law show that α-induced reduction of ^{239}Pu(VI) by $\mathrm{H_2O_2}$ at pH 1.5 [9] is independent of [Pu(VI)] and proceeds at a slower-than-observed maximum rate. A first-order dependence of rate on [Pu(VI)] is implied by $n = 1.26$ [1], but is expected only if the initial reductant concentration significantly exceeds the initial [Pu(VI)]. Modeling of ^{238}Pu(VI) self-reduction at pH 0 shows that the results [16] agree with a sigmoidal [Pu(VI)]–t curve predicted for α-induced reduction. Self-reduction rates of ^{239}Pu(VI) at pH 1.5 and ^{242}Pu(VI) at pH 6 coincide with disproportionation rates of Pu(V) at the corresponding pH values and do not support a proposed change in the reduction pathway of Pu(VI) near pH 3 [1]. The time dependence of [^{239}Pu(VI)] at pH 1.5 [9] is accurately predicted using a second-order rate law identical to that for Pu(V) and is most consistent with kinetically controlled disproportionation of Pu(VI) to Pu(V) and Pu(VII).

References

[1] T.W. Newton, D.E. Hobart, Accompanying Letter to the Editors.

[2] J.M. Haschke, V.M. Oversby, J. Nucl. Mater. 305 (2002) 187.

[3] L.H. Gevantman, K.A. Kraus, in: G.T. Seaborg, J.J. Katz, W.M. Manning (Eds.), The Transuranium Elements, National Nuclear Energy Series IV, 14B, McGraw-Hill, New York, 1949, p. 500, Paper 4.16.

[4] J.M. Cleveland, The Chemistry of Plutonium, American Nuclear Society, La Grange Park, IL, 1979 (Chapter 3); S.W. Rabideau, J. Am. Chem. Soc. 79 (1957) 6350.

[5] R. Knopp, V. Neck, J.I. Kim, Radiochim. Acta 86 (1999) 101.

[6] H. Christensen, Nucl. Technol. 124 (1998) 165.

[7] S.W. Rabideau, J. Am. Chem. Soc. 79 (1957) 6350.

[8] V.P. Shilov, Radiochemistry 39 (1997) 328 (transl. Radiokhim. 39 (1997) 330).

[9] T.W. Newton, D.E. Hobart, P.D. Palmer, Radiochim. Acta 39 (1986) 139.

[10] D.T. Reed, D.G. Wygmans, S.B. Aase, J.E. Banazak, Radiochim. Acta 82 (1998) 109.

[11] R.J. Lemire, J. Fuger, H. Nitsche, P. Potter, M.H. Rand, J. Rydberg, K. Spahiu, J.C. Sullivan, W.J. Ullman, P. Vitorge, H. Wanner, Chemical Thermodynamics of Neptunium and Plutonium, Elsevier, Amsterdam, 2001, p. 55 and 301.

[12] R.C. Weast, CRC Handbook of Chemistry and Physics, CRC Press, Boca Raton, FL, 1988, p. D69.

[13] H. Nitsche, K. Roberts, R. Xi, T. Prussin, K. Beacraft, I.A. Mahamid, H.B. Silbers, S.A. Carpenter, R.C. Gatti, C.F. Novak, Radiochim. Acta 66/67 (1994) 3.

[14] C. Madic, G.M. Begun, D.E. Hobart, R.L. Hahn, Inorg. Chem. 23 (1984) 1914.

[15] R.J. McMahon, Science 299 (2003) 833.

[16] K. Büpplemann, J.I. Kim, C. Lierse, Radiochim. Acta 44&45 (1988) 65.