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Potential–pH Behavior of Plutonium Solutions Containing Hydrous Oxides

G. L. SILVER

Monsanto Research Corp./Mound, Miamisburg, Ohio 45 342, U.S.A.*

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Abstract

The oxidation–reduction potential decreases linearly with increasing pH in solutions that contain both tetravalent and hexavalent plutonium hydrous oxides. An equation predicting the potential is compared to an equation describing some potentials found experimentally by Rai. The corresponding slopes and intercepts of the two equations differ by only a few per cent.

Comments have recently been made on the merits of some experimental data obtained by Rai [1, 2]. Rai's data showed three potential-pH regions in dilute plutonium solutions. These were denoted A, B, and C in Fig. 4 of Rai's paper.

At pH values less than about 1 (region A of Rai's Fig. 4), the potential-pH behavior agrees with the behavior predicted for dissolved plutonium with average oxidation number $N = 4.00$. The predicted potentials are obtained by substituting the ratio $[PuO_2^{2+}]/[PuO_2^{+}] = Q$ appropriate for $N = 4$ and the experimental acidity into the Nernst equation [3]. At $[H^+] = 0.3$ M and 0.15 M the Q values are 9.877 and 3.825, respectively.

Between pH values of about 1 and 3 (region B of Rai's paper), the potential appears to be independent of pH. In this region, the acidity is low enough to allow precipitation of the hydrous oxide of the tetravalent state, but high enough to prevent the precipitation of the hydrous oxide of the hexavalent state:

$$2PuO_2^{+} + 2HOH = PuO_2^{2+} + Pu(OH)_4 \qquad (1)$$

At pH values higher than about 3 (region C), the potential diminishes with increasing pH. In this region, the hexavalent state is being removed by precipitation as the hydrous oxide, while pentavalent plutonium is being removed as a mixture of hydrous oxides as in eqn. (4). The rate of removal of the hexavalent plutonium with increasing pH is faster than the rate of removal of the pentavalent state, so Q diminishes with rise in pH.

The concentration of soluble hexavalent plutonium is determined, to a first approximation, by its solubility product [4]:

$$PuO_2(OH)_2 = PuO_2^{2+} + 2OH^- \quad K_{sp} = 10^{-22} \qquad (2)$$

The concentration of tetravalent plutonium is similarly determined [5]:

$$Pu(OH)_4 = Pu^{4+} + 4OH^- \quad K_{sp} = (2.5)(10^{-56}) \qquad (3)$$

Solubility products allow estimation of the standard free energies of formation of the hydrous oxides of hexavalent and tetravalent plutonium as about −1196.17 kJ and −1428.57 kJ, respectively. The equilibrium constant for eqn. (4) can therefore be estimated:

$$2PuO_2^{+} + 2OH^- + 2HOH = Pu(OH)_4 + PuO_2(OH)_2 \quad K = (6.08)(10^{23}) \qquad (4)$$

It follows from eqn. (2) that

$$[PuO_2^{2+}] = 10^{-22}/[OH^-]^2 \qquad (5)$$

and from eqn. (4) that

$$[PuO_2^{+}] = 1/[OH^-][(7.8)(10^{11})] \qquad (6)$$

In the pH region where both reactions (2) and (4) occur, the ratio $[PuO_2^{2+}]/[PuO_2^{+}] = Q$ is therefore

$$Q = (10^{-22})(7.8)(10^{11})/[OH^-] \qquad (7)$$

or

$$\log(Q) = -10.108 + \text{pOH} \qquad (8)$$

The Nernst equation for the hexavalent/pentavalent couple is

$$E = E^\circ + 0.05916[\log(Q)] \qquad (9)$$

where E is the measured potential and E° is taken as 0.9164 V. In eqn. (8), pOH = 14 − pH, and log(Q) can be obtained from eqn. (9). When the substitutions are made, the potential is predicted to be related to the pH by eqn. (10)

$$E = 1.147 - 0.05916\text{pH} \qquad (10)$$

Table III in Rai's paper contains potential–pH data that span the pH region where the hydrous oxides of both tetravalent and hexavalent plutonium are present. As Rai points out, potential data ob-

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tained in solutions barely containing dissolved plutonium are not trustworthy because the electrode is not poised in these solutions. According to Rai, such data occur at pH 4 and higher pH values. On the other hand, data obtained at pH values low enough to dissolve the hydrous oxide of hexavalent plutonium are not useful because they lie outside the pH region in which both hydrous oxides occur.

Although there may be objection to the choice of data, six of Rai's samples in his Table III, Nos. 207–212 inclusive, appear to fall within region C, the region of simultaneous presence of two hydrous oxides. The six (pH, E) points are (2.30, 0.9586), (2.80, 0.9408), (3.10, 0.9183), (3.40, 0.9006), (3.70, 0.8734), (3.80, 0.8657). The pH of sample 213 is too high to be reliable, while sample 206 seems to fall in Region B, where the potential is independent of the pH.

Both the potential and pH data contain errors. The errors in the pH and potential data are about (plus-or-minus) 0.03 and 0.005, respectively. The least squared perpendicular distances line [6] through Rai's six (pH, E) points is

$$E = 1.113 - 0.06388\text{pH} \qquad (11)$$

The intercept of the predicted line, eqn. (10), exceeds the intercept of the observed line, eqn. (11), by a mere 3%! The slopes differ by only 8%.

The suggested solubility product for hexavalent plutonium hydrous oxide allows the concentration of the Pu(VI) cation to be one molar at pH 3, a circumstance that is at variance with Rai's observations. Cleveland quotes the value (3) (10^{-25}) as the solubility product [7]. Using this number yields

$$E = 1.072 - 0.05916\text{pH} \qquad (12)$$

The predicted intercept is now about 4% less than the observed intercept. Considering the difficulty of the experimental work, and the uncertainties in the solubility products and potentials, this agreement between theory and experiment may be fortuitous. It should be pointed out, however, that Rai's data do not contradict expectations.

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