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Potential–pH Behaviour of Weakly Acidic Plutonium Solutions

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Rai [1] has recently published a paper, the complete significance of which may not at first be perceived. Figure 4 of that paper contains a diagram of pE *vs.* pH, the experimental points being divided into three regions: A, B and C. Line A represents the pE–pH behavior of plutonium derived from dissolving pure $Pu(OH)_4$. Hence the oxidation number of this plutonium should be N = 4.00 if accidental impurities did not effect some change in it. The behavior of the ratio $[PuO_2^{2+}]/[[PuO_2^{+}]$ = M for N = 4.00 as a function of acidity may be obtained from eqn. (1) of ref. [2], limiting the hydrolysis products to $PuOH^{3+}$ for the sake of illustration. The acidities at which Rai worked in region A were about 0.3 M and 0.15 M, for which the alpha coefficients for tetravalent plutonium, $AX = ([Pu^{4+}] + [PuOH^{3+}])/[Pu^{4+}]$, are about 1.1 and 1.2, respectively [3]. At these acidities, therefore, M = 9.877 and 3.825, respectively. These M values lead to calculated potentials of about 0.9752 V and 0.9509 V, respectively, so that $\Delta E = -0.0243$ V, $\Delta pE = -0.4107$ and $\Delta pH = 0.2067$. Hence $\Delta pE/\Delta pH = -1.99$, close to the value −2.0 experimentally observed. To be sure, the ratio $\Delta pE/\Delta pH$ is not constant with pH, but the point is that the disproportionation of the dissolved tetravalent plutonium [4]:

$$(2 + 3M)Pu(IV) = (I + 2M)Pu(III) + Pu(V) + MPu(VI) \qquad (1)$$

appears sufficient to account for the observed pE–pH behavior without complicating matters by trying to choose 'dominant' half reactions.

As the pH is gradually increased, tetravalent plutonium hydroxide remains as a second phase while trivalent plutonium, one of the disproportionation products, disappears. The system $Pu(OH)_4/Pu^{3+}$ is reducing, its potential at pH 3 being only about 0.3 V. Compare this to the system iodine–iodide–water (formal potential about 0.5 V) which is easily oxidized by air [5]. So trivalent plutonium can be oxidized to $Pu(OH)_4$ by atmospheric oxygen, leaving some approximately constant remainder of dissolved Pu(V) and Pu(VI) – presumably obtained by disproportionation – as well as undissolved $Pu(OH)_4$. But a system of constant total concentration of plutonyl cations (whatever their origin) and also containing undissolved $Pu(OH)_4$ was examined many years ago [6]. This system is characterized by two eqns.:

$$[PuO_2^{+}] + [PuO_2^{2+}] = \text{a constant} \qquad (2)$$

$$2PuO_2^{+} + 2HOH = PuO_2^{2+} + Pu(OH)_4 \qquad (3)$$

It was pointed out that for such a system there exists a short range of pH values where the solution composition is practically constant, so the potential is fixed and independent of the pH. (The reader may observe that eqn. (3) has no pH dependence). Thus, line B of Rai's Fig. 4 and line B of Silver's diagram represent the same system. The significance of Rai's work which is apt to be overlooked is that he has provided what is probably the first experimental demonstration of this limited pH region where pE does not depend upon pH [6, 7].

As the pH of the system continues to rise, the point is finally reached where the solubility product of $PuO_2(OH)_2$ is exceeded and Pu(VI) begins to be removed from the solution by precipitation. Again the system can be described by two eqns.:

$$PuO_2^{2+} + 2OH^- = PuO_2(OH)_2 \qquad (4)$$

$$2PuO_2^{+} + 2OH^- + 2HOH = Pu(OH)_4 + PuO_2(OH)_2 \qquad (5)$$

Using the data in Silver's paper [6], at pH 4 the concentrations of Pu(V) and Pu(VI) are about $(8.5)(10^{-4})$ M and 10^{-3} M, respectively. But at pH 5 this near equality no longer prevails, the concentrations of Pu(V) and Pu(VI) being about $(8.5)(10^{-5})$ M and 10^{-5} M, respectively. In other words, hexavalent plutonium is now being removed from the solution by eqn. (4) faster than the pentavalent plutonium is being removed by eqn. (5). Hence the ratio Pu(VI)/Pu(V) diminishes with rise in pH. But the solution potential is directly related to this ratio [8], so the potential of the solution also diminishes with increasing pH, just as Rai has observed. Thus, line C of Rai's diagram and line C of Silver's diagram also represent the same system, and there is still no need to complicate matters by trying to select 'dominant' half reactions. The explanation of the pE–pH behavior lies in the unequal rates of removal of Pu(VI) and Pu(V) from the solution.

The reader may make his own selections of equilibrium constants when studying these matters: although the exact pH values of the transitions from the regions A to B to C will certainly be affected, the

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essence of the foregoing arguments is sufficient to explain the observed behavior [3].

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