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Abstract

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STUDY OF THE OXIDATION-REDUCTION POTENTIALS OF PLUTONIUM IN NITRIC ACID

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The literature contains data on the values of formal potentials of various plutonium couples in perchloric and hydrochloric acid solutions (1–6). Data on the values of formal potentials in nitric acid solutions, however, are extremely scarce and are of rather low reliability (2,7–9). The processes of self-oxidation and self-reduction of plutonium in nitric acid solutions have likewise not been investigated.

Table 1

Formal potentials of the Pu(IV)—Pu(III) couple in nitric acid solutions

Concentration of HNO_3, N	Potential, mV
0.20	942
0.40	930
1.00	914

We determined the formal oxidation-reduction potentials of various plutonium couples in nitric acid solutions of different concentrations, and also investigated the disproportionation of Pu(IV) in nitric acid solutions.

Measurement of the potentials of the Pu(IV)—Pu(III) couple was carried out on an apparatus analogous to that described earlier (10), at 25° in an atmosphere of nitrogen carefully freed of oxygen. Pu(III) was obtained by reduction of Pu(IV) on a platinized platinum cathode. The concentrations of Pu(IV) and Pu(III) were measured spectrophotometrically.

The oxidation-reduction potentials were measured over the entire range of concentration ratios of Pu(IV) and Pu(III). From the data obtained, the values of the formal potentials given in Table 1 were determined graphically.

Attempts at direct determination of the potentials of the Pu(VI)—Pu(IV) couple were unsuccessful. The values obtained lie in the interval 1010–1040 mV and depend little on changes in the concentration ratio of Pu(VI) and Pu(IV). To determine the values of the formal potentials of the Pu(VI)–Pu(IV) couple, we used the disproportionation of Pu(IV) at low nitric acid concentrations: 0.40; 0.30; 0.20; and 0.10 *N*.

The disproportionation of Pu(IV) was carried out at 25°; the concentrations of Pu(IV), Pu(III), and Pu(VI), as in the first case, were determined spectrophotometrically. After equilibrium had been reached, the oxidation-reduction potential was measured.

From the measured values of the oxidation-reduction potentials in equilibrium states and the values of the equilibrium concentrations, we calculated the formal potentials for the couples: Pu(IV)–Pu(III), Pu(VI)–Pu(IV), and Pu(VI)–Pu(III), which are given in Table 2.

It is seen from Table 2 that the values of the formal potentials of the Pu(VI)–Pu(IV) and Pu(VI)–Pu(III) couples increase strongly with increasing concentration of hydrogen ions. Calculation shows that the potentials of these couples depend on the concentration of H^+ to the fourth power. Consequently, the following reactions occur at the electrode:

$$PuO_2^{2+} + 4H^+ + 2e \rightarrow Pu^{4+} + 2H_2O, \tag{1}$$

$$PuO_2^{2+} + 4H^+ + 3e \rightarrow Pu^{3+} + 2H_2O. \tag{2}$$

Using these equations, we calculated the formal potentials

pairs: Pu(VI)–Pu(IV) and Pu(VI)–Pu(III) in 1 N HNO_3, taking account of complex formation ([14,15]), which proved to be, respectively, 1054 and 1006 mV.

Table 2

Formal potentials of plutonium in nitric acid solutions

Conc. HNO_3, N	Pu(IV)–Pu(III), mV	Pu(VI)–Pu(IV), mV	Pu(VI)–Pu(III), mV
0.40	927	993	972
0.30	935	973	961
0.20	939	949	946
0.10	952	925	934

The value of the formal potential of the Pu(VI)–Pu(IV) couple in 1 N HNO_3 obtained earlier by Hindman (1110 mV), in our opinion, is too high, since it is not consistent with the data for perchloric (1043 mV) and hydrochloric (1053 mV) acids ([4]), nor with the data on complex formation of Pu(IV) in nitric acid.

The value of the formal potential of the Pu(IV)–Pu(III) couple obtained by us in 1 N HNO_3 (914 mV) agrees well with the value obtained by Hindman (916 mV).

During disproportionation of Pu(IV) in 0.10 N HNO_3, at equilibrium a lowered value is observed for the sum of the concentrations of Pu(IV), Pu(III), and Pu(VI) in comparison with the initial concentration of Pu(IV). We took the difference between the initial concentration of plutonium and the sum of the concentrations of Pu(IV), Pu(III), and Pu(VI) as the concentration of pentavalent Pu and calculated the formal potential of the Pu(VI)–Pu(V) couple in 0.10 N HNO_3. The value obtained, equal to 917 mV, coincides with the value of 920 mV measured directly by us later. There are no other data in the literature on direct measurement of the potential of the Pu(VI)–Pu(V) couple in nitric acid. The agreement of the potentials confirms our assumption that pentavalent plutonium is present in the solution.

On the basis of the foregoing, the following schemes of the formal potentials of plutonium in nitric acid solutions may be proposed:

$$1N\ \mathrm{HNO_3},\ t = 25^\circ$$

$$\mathrm{Pu(III)} \xrightarrow{914} \mathrm{Pu(IV)} \xrightarrow{1054} \mathrm{Pu(VI)}$$

$$\mathrm{Pu(III)} \xrightarrow{\qquad\qquad\qquad\qquad 1006 \qquad\qquad\qquad\qquad} \mathrm{Pu(VI)},$$

$$0.1N\ \mathrm{HNO_3},\ t = 25^\circ$$

$$\mathrm{Pu(IV)} \xrightarrow{\qquad\qquad\qquad 925 \qquad\qquad\qquad} \mathrm{Pu(VI)}$$

$$\mathrm{Pu(III)} \xrightarrow{952} \mathrm{Pu(IV)} \longrightarrow \mathrm{Pu(V)} \xrightarrow{917} \mathrm{Pu(VI)}$$

$$\mathrm{Pu(III)} \xrightarrow{\qquad\qquad\qquad\qquad\qquad 934 \qquad\qquad\qquad\qquad\qquad} \mathrm{Pu(VI)}.$$

As indicated, in order to determine the potentials, the disproportionation of Pu(IV) in nitric acid was studied. The change in the concentrations of Pu(III), Pu(IV), and Pu(VI) with time in 0.40 N HNO_3 is shown in Fig. 1.

The data obtained confirm that the disproportionation of Pu(IV) proceeds according to the overall equation proposed by Katz and Sheline ([12,13]) for hydrochloric and perchloric acids

$$3\mathrm{Pu(IV)} leftarrows 2\mathrm{Pu(III)} + \mathrm{Pu(VI)}, \qquad (3)$$

which in ionic form may be written as follows:

$$3\mathrm{Pu}^{4+} + 2\mathrm{H_2O} leftarrows 2\mathrm{Pu}^{3+} + \mathrm{PuO_2}^{2+} + 4\mathrm{H}^+. \qquad (4)$$

Figure 1. Disproportionation of Pu(IV) in 0.40 N HNO3. Total plutonium concentration $7.7 \cdot 10^{-3}$ M. 1—Pu(IV), 2—Pu(III), 3—Pu(VI).

Figure 1: Figure 1. Disproportionation of Pu(IV) in 0.40 N HNO3. Total plutonium concentration $7.7 \cdot 10^{-3}$ M. 1—Pu(IV), 2—Pu(III), 3—Pu(VI).

However, it should be noted that in nitric acid the equilibrium constant for reaction (3) is inversely proportional to the concentration of hydrogen ions to the power 5.3, instead of the expected dependence $K \sim [\mathrm{H}^+]^{-4}$. It is easy to show that this deviation is entirely due to the formation of nitrate complexes of Pu(IV).

Fig. 1. Disproportionation of Pu(IV) in 0.40 N $\mathrm{HNO_3}$. Total plutonium concentration $7.7 \cdot 10^{-3}$ M. 1—Pu(IV), 2—Pu(III), 3—Pu(VI).

In previously published works (^{12,13}) it was shown that the disproportionation of Pu(IV) in hydrochloric and perchloric acids proceeds in two stages according to the equations:

$$\mathrm{Pu(IV)} + \mathrm{Pu(IV)}\ \overset{k_1}{\underset{k_2}{leftarrows}}\ \mathrm{Pu(V)} + \mathrm{Pu(III)} \tag{5}$$

$$\mathrm{Pu(V)} + \mathrm{Pu(IV)} leftarrows \mathrm{Pu(III)} + \mathrm{Pu(VI)} \tag{6}$$

The question of the mechanism of disproportionation of Pu(IV) in nitric acid has not been considered in the literature. We calculated the rate constant of the forward disproportionation reaction according to the equation

$$-\frac{d[\mathrm{Pu(IV)}]}{dt} = k_1[\mathrm{Pu(IV)}]^2 - \frac{k_1}{K}\frac{[\mathrm{Pu(III)}]^2[\mathrm{Pu(VI)}]}{[\mathrm{Pu(IV)}]}, \tag{7}$$

derived from equations (5) and (6), assuming that reaction (5) is the rate-limiting step, while reaction (6), accompanied by a one-electron transition, rapidly reaches equilibrium. The calculated rate constant proved to be constant for different stages of the process; therefore it may be asserted that in nitric acid also the disproportionation of Pu(IV) proceeds according to equations (5) and (6).

Table 3

Equilibrium constants for the disproportionation of Pu(IV) in nitric acid solutions

HNO_3 concentration, N	Total plutonium concentration, $M \cdot 10^3$	Equilibrium constant, K
0.40	7.7	$5.66 \cdot 10^{-3}$
0.30	7.6	$5.01 \cdot 10^{-2}$
0.20	3.04	$4.55 \cdot 10^{-1}$
0.10	2.25	7.91

However, despite the presence of complex formation by Pu(IV), the values of the rate constant of the disproportionation of Pu(IV) in nitric acid that we obtained are the same as in perchloric acid. This permits the supposition that not only Pu^{4+} ions take part in the reaction, but also complex Pu(IV) ions; moreover, the latter possess a higher reactivity.

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Note: Figure translations are in progress. See original paper for figures.