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Abstract

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On the Preparation of Certain Compounds of Pu(V)

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For carrying out the synthesis of Pu(V) compounds, it became necessary to obtain solutions concentrated with respect to plutonium. In this connection, the methods described in the literature for obtaining Pu(V) solutions were examined ([1]-[8]). It turned out that in most methods pentavalent plutonium (concentrations of 10^{-3}—10^{-4} mol/l) was obtained at acidities of 0.1—0.5 mol/l, and only in work ([6]) were Pu(V) solutions obtained at pH 3—4.

The reduction of Pu(VI) or the oxidation of Pu(IV) for the purpose of obtaining Pu(V) must be carried out under conditions in which the Pu(V) formed is most stable.

To elucidate these conditions, we carried out work on studying the stability of nitric-acid solutions. Pu(V) solutions were prepared: a) with the same plutonium concentration and different pH values; b) with the same pH value but different plutonium concentrations. The solutions were studied in the pH interval 2—6. The lower pH limit was chosen as 2, since beginning with this pH the Pu(IV) formed is removed from solution in the form of hydroxide ([9]).

We established that at pH 6.8 hydrolysis of the Pu(V) solution begins; therefore, the upper pH limit for studying the stability of nitric-acid solutions was chosen as 6. In solutions with a constant pH value, the plutonium concentration was varied from 5 to 0.5 g/l. It was established that in solutions having an initial pH of 4—6, the pH decreases to 3.5—4, whereas in solutions with pH below 3.5, after 50 days the pH value was the initial one or somewhat higher.

The disproportionation process at solution pH values above 2 is accompanied by the hydrolysis reaction of the Pu(IV) formed. The simultaneous occurrence of these reactions should not lead to a change in the acidity of the solution. Apparently, changes in the pH of solutions of pentavalent plutonium are caused by the interaction of Pu(V) with products of water radiolysis. Indeed, most probable reactions of reduction of Pu(V) by products of water radiolysis proceed with acidification of the solution. The oxidation of Pu(V) by products of radiolysis, however, proceeds with an increase in the pH of the solution. The increase in the stability of Pu(V) solutions with decreasing plutonium concentration in the solution is also associated with a slowing of the process of water radiolysis and, consequently, of the oxidation-reduction reactions of Pu(V) with products of water radiolysis.

As a result of studying the stability of nitric-acid solutions, it was established that the region of greatest stability of Pu(V) solutions is pH 3.5—4.5. In addition, it was shown that solutions containing 2.5 g/l plutonium or less are the most stable.

Consequently, in order, as a result of the reduction or oxidation of Pu(IV), to enter the region of greatest stability of Pu(V), these processes should be carried out at pH above 3.

To obtain pentavalent plutonium we used the known method of reducing Pu(VI) with hydrogen peroxide. It was shown that the reduction reaction proceeds with acidification of the solution, which is undesirable, since a decrease in pH sharply lowers the stability of the resulting Pu(V) solutions due to the disproportionation process,

which proceeds proportionally to the fourth power of the concentration of hydrogen ions.

Carrying out the reduction with constant monitoring and maintenance of pH in the selected range made it possible to obtain solutions containing Pu(V) up to 8 g/liter. However, a study of the stability of nitric acid solutions showed that, at Pu(V) concentrations above 2.5 g/liter, even in the region of greatest stability with respect to pH, processes involving interaction of Pu(V) with products of water radiolysis become noticeable. Consequently, solutions concentrated with respect to Pu(V) can be used for synthesis only immediately after their preparation.

It is known from the literature that a carbonate compound of pentavalent plutonium with the cations K^+, Na^+, and NH_4^+ has been synthesized (³). From the results of a study of the crystal structure of these compounds, an assumption was made concerning their composition. We synthesized complex compounds of Pu(V) with the following ions: CO_3^{2-}; F^-; HPO_4^{2-}; $C_2O_4^{2-}$; JO_3^-, as well as Pu(V) hydroxide of composition $PuO_2(OH)$.

1. From Pu(V) solutions containing more than 2 g/liter Pu, a carbonate compound with the cations K^+ and NH_4^+ was synthesized.

A chemical analysis was carried out of the carbonate compound obtained by interaction of a nitric acid solution of Pu(V) with ammonium carbonate. This substance is gray-white in color, finely dispersed, with a solubility in water equal to $\sim 1.5 \cdot 10^{-4}$ mole/liter.

The precipitate, washed with alcohol and dried in a desiccator over calcium chloride, was analyzed for NH_3, CO_2, and Pu. Water in all compounds was determined by difference. The results of the chemical analysis of the carbonate compound and the proposed formula are given in Table 1.

Table 1

	For $NH_4PuO_2CO_3(\ )3H_2O$					For $NH_4PuO_2F_2$		
	NH_4^+	PuO_2^+	CO_3^{2-}	H_2O		NH_4^+	PuO_2^+	F^-
Calculated, %	4.5	67.2	14.9	13.4	Calculated, %	5.5	82.8	11.7
Found, %	4.8; 4.9	67.6; 67.5	13.2; 12.3	14.4; 15.3	Found, %	6.16; 5.82	81.5; 85.0	14.8; 12.85

	For $NH_4PuO_2C_2O_4(\ )6H_2O$					For $NH_4PuO_2HPO_4(\ )4H_2O$		
	NH_4^+	PuO_2^+	$C_2O_4^{2-}$	H_2O		NH_4^+	PuO_2^+	$\Sigma\ HPO_4^{2-} + 4H_2O$
Calculated, %	3.7	55.9	18.1	22.3	Calculated, %	3.90	59.3	36.80
Found, %	3.5; 3.6	52.9; 53.9	16.3; 17.5	27.3; 25.0	Found, %	4.03; 4.1	57.9; 58.0	38.07; 37.9

Note. The composition of the compounds was determined from samples weighing 30–60 mg.

When the carbonate compound is isolated from solutions containing less than 2 g/liter, a complex is formed with the following ratio of groups:

$NH_4^+ : PuO_2^+ : CO_3^{2-} \simeq 1.7 : 1 : 1$. The proposed formula is:

$$NH_4PuO_2CO_3 \cdot OH \cdot nH_2O.$$

Decomposition of the carbonate precipitates by acid leads to the production of Pu(V) solutions with its characteristic spectrum.

2. When ammonium fluoride or potassium fluoride is added to a nitric acid solution of Pu(V), a sparingly soluble gray-white precipitate is formed. A chemical analysis was carried out of the substance obtained by the action of NH_4F on a nitric acid solution of Pu(V). The analysis results and the proposed formula are given in Table 1. Probably, when KF acts on Pu(V) solutions, a compound analogous in composition is formed.
3. As a result of the interaction of a nitric acid solution of Pu (V) with disubstituted ammonium phosphate, a white precipitate is formed (in a thin layer), with a greenish tint in bulk. The air-dry precipitate was analyzed for NH_3 and Pu. The ratio $NH_3 : Pu = 1 : 1$. The results of the chemical analysis and the proposed formula of the compound are given in Table 1.

4. When ammonium oxalate acts on a Pu (V) solution, a soluble complex is formed. Upon salting out with alcohol, a pink precipitate is separated, readily soluble in water. The spectrum of the aqueous solution has no peaks characteristic of other valence forms of plutonium. The results of the chemical analysis of the compound obtained and the proposed formula are given in Table 1. Upon repeated treatment of the oxalate precipitate with alcohol and ether, complexes with a smaller amount of water were obtained.

5. From a nitric acid solution of Pu (V), Pu (V) iodate was isolated. The white precipitate, poorly soluble in water, is readily separated from the mother liquor. The composition of the precipitate is being established.

6. From the titration curve of a nitric acid solution of Pu (V) with 0.1 N NaOH solution, it was established that formation of the Pu (V) hydroxide begins at pH equal to ~ 6.8. In this process, one OH^- group is added to the PuO_2^+ ion. Plutonium hydroxide is an amorphous precipitate of gray-white or pink color. When the precipitate is dissolved in HNO_3, a Pu (V) solution is formed. The solubility product of Pu (V) hydroxide, calculated from the pH at the onset of precipitation, is equal to $\sim 0.5 \cdot 10^{-9}$.

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