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SOME OBSERVATIONS ON THE BASIC CHEMISTRY OF PLUTONIUM

by

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ABSTRACT

On prolonged heating in dilute nitric acid (0.5M to 6.8M) a considerable amount of Pu^{+4} is oxidized to Pu^{+6}. Precipitation of the plus three plutonium oxalate is complete in fifteen minutes. Oxidation of Pu^{+4} to Pu^{+6} by bromine is quantitative at 105°C after 1/2 hour; at 50°C the rate of oxidation is slow, but measurable. At room temperature the rate is too slow to measure. A method of converting $PuCl_3$ to $Pu(NO_3)_4$ is given. A solubility of $NaPuO_2Ac_3$ increases with temperature, the value at 25°C being 19.5 g/liter and that at 95°C, 37.5 g/liter. Supersaturation was observed on slow cooling of a saturated solution.

OXIDATION OF Pu^{+4} TO Pu^{+6} BY NITRIC ACID

In order to determine the oxidation state of plutonium in stock solution and in solution which had stood for 22 hours at 90°C in various concentrations of nitric acid, two methods were used. The first consisted of a rough determination of the solubility of the hydroxide; the results obtained through use of this method are presented in the fourth column of Table 1. The second method involved the precipitation of any Pu^{+6} as $NaPuO_2Ac_3$.

In the second method the supernatant was removed and the precipitate was washed twice and dissolved in a known volume of nitric acid. A cut of the dissolved precipitate was taken and assayed. The $NaPuO_2Ac_3$ was then reprecipitated and a cut of the supernatant was taken and assayed. The amount of Pu in the final precipitate, as determined by the difference of these two assays, was taken as the amount of Pu^{+6} in the original solution. The conditions for the $NaPuO_2Ac_3$ precipitations throughout were:

$$HAc = Ac^{-} = \sim 1M$$

$$Na^{+} > 3M$$

The results are shown in Table 1.

Table 1.

Concentration HNO_3	Initial concentration Pu^{+4}	Treatment	Hydroxide solubility (mg/liter)	% total Pu ppt. as $NaPuO_2Ac_3$
1.5M	0.08M	None	1.1	2
0.5M	0.08M	22 hr, 90°C	276	33
1.5M	0.08M	22 hr, 90°C	22.5	38
6.6M	0.17M	22 hr, 90°C	111	29
13.0M	0.08M	22 hr, 90°C	8.8	None*

*Failure to obtain a precipitate may be due to the low concentration of Pu during the attempted precipitation. Dilution was necessary to obtain the conditions of precipitation.

In order to show more conclusively that the Pu in the acetate precipitations was in the Pu^{+6} state, ether extractions were tried on two precipitates obtained after treatment in 1.6M HNO_3 in Table 1. In the first attempt 17.4 per cent of original Pu was extracted by ether; in the second, 8.4 per cent was extracted.

RATE OF Pu^{+3} OXALATE PRECIPITATION

In order to determine roughly the rate of the Pu^{+3} oxalate precipitation, four tubes were prepared, each containing about 1 mg Pu^{+4}. Sufficient KI solution was added to reduce all Pu^{+4} to Pu^{+3} and to give an excess such that $I_3^-/I^- = 1/3$. About one hour was allowed for the reduction. At the end of the reduction period oxalic acid was added, and the oxalate was precipitated. The precipitates were stirred for various times, after which they were centrifuged. A cut of the supernatant was taken and assayed to determine the solubility of the precipitate. Conditions of supernatant were

$$HNO_3 = .75M$$

$$H_2C_2O_4 = .25M$$

The results are shown in Table 2.

The solubility product as determined from an average of 2 and 3, since the concentrations in these two were most accurately known, is 53×10^{-26}.

OXIDATION OF Pu^{+4} TO Pu^{+6} BY BROMINE

An excess of liquid bromine was added to tubes containing about 1 mg Pu^{+4} in 1.5M HNO_3. The tubes were sealed and placed at various temperatures for various times. After the oxidation period the excess Br_2 was removed, and HF-KNO_3 solutions were added in order to precipitate Pu^{+4} as K_2PuF_6. La^{+3} was added to carry traces of Pu^{+4} if almost complete oxidation had occurred.

Conditions in supernatant were:

$$H^+ = \sim .8M$$

$$K^+ = 1M$$

$$HF = 2.7M$$

A cut of the supernatant was taken and assayed giving the amount of Pu oxidized by Br_2. In some cases the supernatant was removed and the precipitate washed, dissolved, and assayed, giving a somewhat more accurate determination of the Pu remaining unoxidized. A control was run on the stock solution untreated with bromine. The results are given in Table 3.

Table 2.

	Time allowed after oxalic acid addition	Solubility Pu^{+3} oxalate
1.	5 min	40.6 mg/liter
2.	15 min	18.4 mg/liter
3.	60 min	23.5 mg/liter
4.	7 hours	38.8 mg/liter

Table 3.

	Control, no oxidation treatment	Temperature and time of oxidation period											
		25°C				50°C				105°C			
		½ hr	1 hr	2 hr	4 hr	½ hr	1 hr	2 hr	4 hr	½ hr	1 hr	2 hr	4 hr
% Pu in supernatant (Pu^{+6})	1%	< 1%	<1%	< 1%	< 1%	10%	15%	20%	45%	82% 93% 120%*	92% 92%	90% 120%*	97% 80%
% Pu in ppt. (Pu^{+4})	------------------Not determined------------------									2.2%	2.2%	2.6%	2.3%

*The presence of percentages above one hundred is indicative of the inaccuracy of the assay.

Some difficulty was encountered in the subsequent use of bromine as an oxidant after one hydroxide precipitation away from 1N H_2SO_4 solution. A test was made to determine the effect of sulfate ion on the oxidation after one and after two hydroxide precipitations. After a period of oxidation of four hours at 50°C, the percentage oxidized was determined as before.

ATTEMPT TO CONVERT $PuCl_3$ TO $Pu(NO_3)_4$

The $Pu(OH)_3$ was precipitated, washed, and dissolved in a mixture of HNO_3 and H_2SO_4 so that the final solution was 2N in each acid. The solution was heated on a steam bath for about 30 minutes in order to oxidize Pu^{+3} to Pu^{+4}. After oxidation the hydroxide was precipitated, washed, dissolved in 5N HNO_3, and reprecipitated. The insoluble residue left after the second precipitation was dissolved in hot concentrated HNO_3, assayed, and found to contain 4.8 per cent of the original material. 95 per cent of the material which went into solution precipitated as K_2PuF_6 showing that it was in the Pu^{+4} state. Less than 1 per cent was found in the supernatant after this precipitation. In a subsequent use of this method 2.3 per cent of material was lost in an insoluble residue.

SOLUBILITY OF $NaPuO_2Ac_3$ AT VARIOUS TEMPERATURES

Three washed and dried $NaPuO_2Ac_3$ precipitates, each containing 5.2 mg of Pu, were prepared from stock solution which had been oxidized with $NaBrO_3$. Fifty microliters of water was added to the first tube, after which it was placed on a steam bath. Water was added at 15-minute intervals, at first in 25-microliter portions and later in 10-microliter portions. When the precipitate just went into solution

Table 4.

	After one hydroxide ppt.	After two hydroxide ppt.
% Pu in supernatant (oxidized)	1.7%	21%
% Pu in ppt. (not oxidized)	85%	71%

the tube was removed, cooled, and the volume marked. Later the tube was calibrated to this mark, and the volume of solution was found to be 200 microliters. After removal from the steam bath the tube was placed in dry ice and cooled to 5°C, where it was left for 2 hours while the $NaPuO_2Ac_3$ settled out. The supernatant was removed as completely as possible without washing. The precipitate was dissolved in nitric acid and both precipitate and supernatant were assayed.

A known volume of water was added to each of the other two tubes, after which they were left standing overnight—one at 25°C, the other at 55°C. The undissolved precipitate settled out, and the solubility was determined by assaying a cut from the supernatant. Results were as follows.

Temperature (°C)	Solubility as $NaPuO_2Ac_3$
5	12.3 g/liter sol.
25	19.5 g/liter H_2O
55	22.0 g/liter H_2O
95	37.5 g/liter sol.

In an attempted fractional crystallization just sufficient water was added to a 7.5-mg $NaPuO_2Ac_3$ precipitate to dissolve it at 95°C. When the precipitate was dissolved, it was immediately placed in a Dewar flask containing water at 90°C and was allowed to cool to room temperature over a period of two days. When the tube was removed, the solution was supersaturated, no precipitate having settled out. After shaking, crystals began to form on the sides of the tubes. The crystals grew over a period of about five hours.