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ULTRAMICROCHEMICAL INVESTIGATION OF THE SOLUBILITIES OF SOME PLUTONIUM COMPOUNDS

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Chemistry ~ Transuranic Elements

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ABSTRACT

The solubilities of the iodate and peroxide of the +4 state, and the fluorides and oxalates of the +4 and "+3" states have been investigated. A discussion of the preparation of the lower state of plutonium (purple aqueous solution) is given.

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ULTRAMICROCHEMICAL INVESTIGATIONS OF THE SOLUBILITIES OF SOME PLUTONIUM COMPOUNDS

The following investigations were carried out on an ultramicrochemical scale with volumes from 0.1 to 0.5 of a microliter and 0.5 μg. of plutonium being used. All calculations were made on the basis of 50% geometry for the air chamber used for counting the samples and 155,000 disintegrations per minute per microgram of plutonium.

The stock solutions used in the study of the +4 compounds were prepared by first saturating a 1N HNO_3 solution of plutonium with SO_2 for 30 minutes. The SO_2 was then boiled out at 90°C. and the hydroxide precipitated by saturation of the solution with NH_3. After washing with water, this precipitate was dissolved in the desired amount of 1.04N HNO_3. This reduction was carried out since iodate precipitations on Pu solutions not so treated have given erratic high values for the solubility of "$Pu(IO_3)_4$".

When attempting to reduce 100 μg. of Pu with a saturated aqueous solution of SO_2 a purple solution was obtained after standing five minutes. After this solution (0.6N HNO_3) was heated in steam for fifteen minutes, the purple color faded to the light green of the +4 state. Apparently this lower state was unstable in hot HNO_3 solutions when SO_2 was not present.

To determine if this color truly represented a +2 or +3 state of plutonium, a difference in solubility of the fluoride and oxalate of the +4 and lower state were found. We prepared a stock solution of the

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lower state in the following manner. The hydroxide was precipitated with NH_3, washed twice with H_2O and dissolved in 1N HCl. On treating this solution with a saturated SO_2 solution a light green precipitate came down, presumably the bisulfite or sulfite of the +4 state. On addition of 5N HCl and heating, the precipitate dissolved slowly to give a purple solution. Three more portions of SO_2 were added with subsequent removal by heating after each addition. The first probable indication of a different oxidation state was therein obtained: SO_2 did not give a precipitate from the purple solution as it did from the former green solution of the +4 state.

Because of the similarity between the solubilities of the fluoride and oxalate of lanthanum and this lower state, we shall designate it as the +3 state, if only to expedite discussion.

It might be mentioned that under the microscope with reflected light the lower fluoride appeared white, the lower oxalate green and the +4 oxalate white or very pale-green.

Since this work was completed, it has come to our attention that the chemical group in Chicago has independently discovered the lower state mentioned in this report.

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SOLUBILITY OF "$Pu(IO_3)_4$"* AT 25°C.

Composition of Supernatant / Conditions	1N HNO_3 .2M KIO_3	2N HNO_3 .2M KIO_3	2N HNO_3 .2M HIO_3	3N HNO_3 .2M KIO_3	4N HNO_3 .2M KIO_3
HNO_3 solution of Pu^{+4} added to dry crystals of precipitating agent	20 mg. Pu/l.	36 mg. Pu/l. 36 " 39 " 38 "	40 mg. Pu/l.	44 mg. Pu/l.	39 mg. Pu/l.
Solution of precipitating agent added to HNO_3 solution of Pu^{+4}		18 mg. Pu/l.	7 mg. Pu/l. 8 " 19 " 20 " 20 " 20 "		

* Solubility of "$Pu(IO_3)_4$" when washed 10 min. to 2 days with 1-4N HNO_3, 0.2M KIO_3 or HIO_3 is 1-10 mg. Pu/l.

Solubility of "$Pu(IO_3)_4$" when washed 10 min. with H_2O is ~1 mg. Pu/l.

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SOLUBILITY OF PLUTONIUM OXALATE

Oxidation state	Pu^{+4}		"Pu^{+3}"	
Composition of Supernatant / Conditions	0.6N HNO_3 0.25M $H_2C_2O_4$	H_2O	1N HCL 0.25M $H_2C_2O_4$	H_2O
$H_2C_2O_4$ solution added to HNO_3 solution of Pu^{+4}, stirred 5 min. at 25°C.	860 mg. Pu/l.			
Crystals washed in H_2O 10 min. at 25°C.		260 mg. Pu/l.		
$H_2C_2O_4$ solution added to HCl stock solution of "Pu^{+3}" stirred 10 min. at 25°C.			25 mg. Pu/l. 56 " 90 "	
Precipitate and supernatant heated at 80°C. for 30 min.			82 mg. Pu/l.	
Precipitate washed in H_2O 10 min. at 25°C.				7 mg. Pu/l.

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SOLUBILITY OF PLUTONIUM PEROXIDE

Composition of Supernatant / Conditions	0.43M HNO_3 1.6M H_2O_2 (5%)	H_2O
H_2O_2 added to HNO_3 solution of Pu^{+4} stood one hour at ice temp.	30 mg. Pu/l. 31 " 35 " 34 "	
HNO_3, H_2O_2 wash solution added to precipitate, stirred, and stood 10 min. at 25°C.	5 mg. Pu/l. 6 "	
H_2O added to precipitate, stirred and stood 10 min. at 25°C.		180 mg. Pu/l. 90 "

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SOLUBILITY OF PLUTONIUM FLUORIDE AT 25°C.

Oxidation state	Pu^{+4}	"Pu^{+3}"	
Composition of Supernatant Conditions	0.6N HNO_3 0.5N HF	0.33N HNO_3 ~ 0.5M H_2SO_4 0.7N HF	1N HCl 1N HF
HF added to HNO_3 solution of Pu^{+4} (no precipitate in 10 min.)	>1300 mg. Pu/l.		
Saturated SO_2 solution added to HNO_3 solution of Pu^{+4}. After purple color appeared, HF added.		50 mg. Pu/l.*	
HF added to "Pu^{+3}" stock solution after 1 day " " 2 days " " 3 days			50 mg. Pu/l.* 90 " 25 "

* If acidic HF supernatant is allowed to stand in contact with precipitate over one-half hour, precipitate dissolves.

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