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February 22, 1944

This document contains 8 pages

# ULTRAMICROCHEMICAL INVESTIGATION OF THE SOLUBILITIES OF SOME PLUTONIUM COMPOUNDS

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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.


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 $\mu$g. 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 $\mu$g. 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.<br>36 "<br>39 "<br>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.<br>8 "<br>19 "<br>20 "<br>20 "<br>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.<br>56 "<br>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.<br>31 "<br>35 "<br>34 " | |
| $HNO_3$, $H_2O_2$ wash solution added to precipitate, stirred, and stood 10 min. at 25°C. | 5 mg. Pu/l.<br>6 " | |
| $H_2O$ added to precipitate, stirred and stood 10 min. at 25°C. | | 180 mg. Pu/l.<br>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 NCl 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<br>" " 2 days<br>" " 3 days | | | 50 mg. Pu/l.*<br>90 "<br>25 " |

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

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