LA-63 c.3

CLASSIFICATION CANCELLED For The Atomic Energy Commisson The Atomic Energy Common Officer
by the Declassification
per section of the Declassification

CIC-14 REPORT COLLECTION

PUBLICLY RELEASABLE
Per MAR ON LS FSS-16 Date: 8/22/95
By KROWN CIC-14 Date: 9/19/95

REPRODUCTION COPY

February 22, 1944

This document contains 8 pages

ULTRAMICROCHEMICAL INVESTIGATION OF THE SOLUBILITIES OF SCHE PLUTONIUM COMPOUNDS

Fork done by:

D. F. Mastick

A. C. Wahl

Report written by:

D. F. Mastick

A. C. Wahl

C. T. Transvirance Clements





UNCIASSIFIED

~2.

ABSTRACT

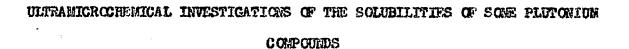
The solubilities of the lodate and peroxide of the +4 state, and the fluorides and oxalates of the +4 and "+3" states have been investigated. A discussion of the preparation of the lower state of plutonium (purple aqueous solution) is given.



UNCLASSIFIED

APPROVED FOR PUBLIC RELEASE

-3-



The following investigations were carried out on an ultramicrochemical scale with volumes from 0.1 to 0.5 of a microliter and 0.5 mg. of plutonium being used. All calculations were made on the basis of 50% geometry for the air chember 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 IN HNO₃ solution of plutonium with SO₂ for 30 minutes. The SO₂ was then boiled out at 90°C, and the hydroxide precipitated by saturation of the solution with NH₃. After mashing with water, this precipitate was dissolved in the desired amount of 1.04N HNO₃. This reduction was carried out since icdete precipitations on Pu solutions not so treated have given erratio high values for the solubility of "Pu(10₃),".

When strempting to reduce 100 A.g. of Pu with a saturated aqueous solution of SO₂ a purple solution was obtained after standing five minutes. After this solution (0.6N HNO₃) 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 HNO₃ solutions when SO₂ 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 exalate of the +4 and lower state were found. We prepared a stock solution of the



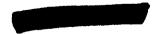
∞ൂം

lower state in the following manner. The hydroxide was precipitated with NH₂, washed twice with H₂O and dissolved in 1N HCl. On treating this solution with a saturated SO₂ 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 SO₂ were added with subsequent removal by heating after each addition. The first probable indication of a different oxidation state was therein obtained: SO₂ did not give a precipitate from the purple solution as it did from the former green solution of the

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 74 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.





حزات

SOLUBILITY OF "Tu(103)4" AT 25°C.

Composition of Supernatant Conditions	_	2n hno ₃ .2m h1o ₃	•	
HNO ₂ solution of Pu ^{t 1} added to dry crystals of preci- pitating agent	.46 mg. Pu/l. 36	40 mg. Pu/1	. 44 mg. Pu/l.	39 mg. Pu/1.
Solution of precipi- tating agent added to HNO3 solution of Pu	18 mg. Pu/1.	7 mg. Pu/1 8 " 19 " 20 " 20 "	The state of the s	

^{*} Solubility of "Pu(IO₃)₄" when washed 10 min. to 2 days with 1-4N HNO₃, 0.2M KIO₃ or HIO₃ is 1-10 mg. Pu/1.

Solubility of "Pu(IO₃)₄" when washed 10 min. with H_2O is ~ 1 mg. Pu/1.

•6°=

SOLUBILITY OF PLUTONIUM OXALATE

Oxidation state	. Pu *4		"Pu ⁺³ "	
Composition of Supernatant Conditions	0.6N HNO. 0.25M H ₂ C ₂ O ₄	H ₂ O	In HCL 0.25% H ₂ C ₂ O _{&}	R ₂ ∩
H ₂ C ₂ O ₂ solution added to HNO ₃ solution of Pu ⁺⁴ , stirred 5 min. at 25°C.	860 mg. Pu/l.			
Crystals washed in ${ m H_2O}$ 10 min. at 25°C.		260 mg. Pu/l.		
H ₂ C ₂ O ₄ solution added to IXI stock solution of "Pu ^{†3} " stirred 10 min. at 25°C.			25 mg. Pu/l. 56 " 90 "	
Precipitate and super- natant heated at 80°C. for 30 min.		,	82 mg. Pu/1.	
Precipitate washed in H ₂ O 10 min. at 25°C.			1	7 mg. Pu/1.

-70

SOLUBILITY OF PLUTONIUM FEROXIDE

Composition of Supernatant Conditions	0.43M HNO ₃ 1.6M H ₂ O ₂ (5%)	H ² O
H ₂ O 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 ₂ O ₂ wash solution added to pre- eipitate, stirred, and stood 10 min. at 25°C.	5 mg. Pu/l. 6 #	
H ₂ O added to precipitate, stirred and stood 10 min. at 25°C.	gar garagahn garran ki jamil bir yarna an kirafili. Karajik 900 apan an akrafili a 1900 a a a araban kirafili	180 mg. Pu/l. 90 *

∞80∞

SOLUBILITY OF PLUTONIUM FLUORIDE AT 25°C.

Cyidation state	Pu ⁺⁴	«բ _ս +3 _ո	
Composition of Supernatant Conditions	0.6N HNO3 0.5N HF	0.33N HNO: ~ 0.5M H2EO4 0.7N HF	in eci in hp
F edded to ENO3 solu- tion of Pu (no pre- lipilate in 10 min.)	>1300 mg. Pu/1.		
Saturated SO ₂ solution added to HWO ₃ solution of Pu ^{+k} . After purple color appeared, HF added.		50 mg. Pu/1.*	
HF odded to "Pu ⁺³ " stock solution after 1 day " " 2 days " " 3 days	- -	And the control of th	50 mg. Pu/1. 90 " 25 "

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

UNCLASSIFIED