CLASSIFICATION
For The Atomic Energy Commisson
by the Declassification Officer
per Albert Campbell

UNCLASSIFIED

[redacted]

PUBLICLY RELEASABLE
Per M Jones, FSS-16 Date: 3-22-96
By L Kolar, CIC-14 Date: 4-17-96

CIC-14 REPORT COLLECTION
REPRODUCTION
COPY

LA - 463

[redacted] C.3

December 4, 1945

This document contains 8 pages

OXIDATION OF TRACER AMOUNTS OF PLUTONIUM BY PERCHLORIC ACID

WORK DONE BY:

M. Kahn

REPORT WRITTEN BY:

M. Kahn

[redacted]

[redacted]

UNCLASSIFIED

UNCLASSIFIED

[redacted]

ABSTRACT

The rate of oxidation of plutonium from the 4^+ state to the 6^+ state[1) by a 70 percent perchloric acid solution was studied as a function of temperature. The oxidation reaction was found to be essentially completed in 10 minutes at a temperature of 195° C. The presence of H_2SO_4 did not noticeably affect the rate of oxidation.

---

1) The existance of the 6^+ state was inferred by the plutonium not being carried by LaF_3.

UNCLASSIFIED

[redacted]

[redacted]

OXIDATION OF TRACER AMOUNTS OF PLUTONIUM BY PERCHLORIC ACID

The early work[2] on oxidation studies of plutonium showed $Cr_2O_7^{=}$ to be an effective oxidizing agent in taking plutonium from the 4^+ state to the 6^+ state, and since Cr^{+++} can be oxidized to $Cr_2O_7^{=}$ quantitatively[3] by a 70 percent perchloric acid solution it seemed probable that perchloric acid under similar conditions could be an effective oxidizing agent for plutonium. The experiments described below show that a 70 percent perchloric acid solution under certain conditions is a very effective oxidizing agent for plutonium.

Experimental

The procedure used throughout this investigation was essentially as follows: approximately 0.1 ml of a 4^+ plutonium tracer solution[4] containing about 0.7 μg of Pu was transferred to a 3-ml cone. This solution was centrifuged to the bottom of the cone and then exaporated to dryness. 0.2 ml of a 70 percent perchloric acid solution was added and the cone was then placed in a phosphoric acid bath. The setup is shown in Fig. 1. After a given time the cone was removed from the bath and cooled under the tap. The perchloric acid was then diluted to a volume of approximately 2.5 ml with a 1N HNO_3 solution nearly saturated with bromine. 0.15 mg of lanthanum was then added; and finally enough 27N HF was added to make the solution about 2N in HF.

---

[2] See LA-30

[3] Perchloric Acid as Oxidizing Agent in the Determination of Chromium. James J. Lichtin, Ind. Eng. Chem., Anal. Ed. 2, 126-7 (1930).

[4] The tracer solution was 3 M in HNO_3. The solution had previously been treated with SO_2 and then boiled to get rid of the SO_2; thus obtaining a solution of Pu in the 4 state.

[redacted]

[redacted]

The LaF_3 precipitate was slurried and spread over an area of approximately 1.1 sq. cm. on a platinum disc. The samples were counted in a proportional alpha counter[5].

A calibration experiment was performed in which the above procedure was carried out omitting the heating step. The activity obtained was used as a standard from which the percent of Pu oxidized in subsequent experiments was calculated. The results are shown in Table I.

A series of experiments were performed to determine the effect of sulphuric acid on the rate of oxidation. The procedure outlined above was repeated but in addition to 0.2 ml of 70 percent $HClO_4$, 0.1 ml of conc. H_2SO_4 was added to the cone. The results are shown in Table II.

The precision of the experiments was of the order of 2 percent principally because of the variation in the carrying power of LaF_3 and the uniformity of the samples.

---

[5] See Reports CP-1527 and CP-1817.

[redacted]

[redacted]

TABLE I.

Temperature of bath	Time	Percent Oxidized	Activity of Sample in counts per minute	Remarks
25° C		0	50,500	Standard
195° ± 3° C	5 min.	90	5,050	
195° ± 3° C	10 min.	98	880	
195° ± 3° C	15 min.	99	590	
195° ± 3° C	30 min.	97	1,550	
195° ± 3° C	60 min.	98	920	
174° ± 3° C	10 min.	90	5,210	
174° ± 3° C	40 min.	98	896	
174° ± 3° C	60 min.	99	638	
153° ± 3° C	10 min.	12	44,500	
153° ± 3° C	30 min.	19	41,000	
153° ± 3° C	60 min.	69	15,900	
153° ± 3° C	2 hrs.	79	10,600	
153° ± 3° C	4 hrs.	91	4,375	
153° ± 3° C	18 hrs.	96.5	1,775	
132° ± 3° C	3 hrs.	23	39,000	
132° ± 3° C	6 hrs.	24	38,300	
101° ± 3° C	3 hrs.	0	51,000	
101° ± 3° C	6 hrs.	0	50,500	

[redacted]

[redacted]

TABLE II.

Temperature of bath	Time	Percent Oxidized	Activity of Sample in counts per minute	Remarks
195° ± 3° C	10 min.	96	2,575	
195° ± 3° C	15 min.	98	990	
195° ± 3° C	20 min.	97.5	1,280	
25° C	-	0	50,500	Standard

[redacted]

[redacted]

The use of perchloric acid as an oxidizing agent for tracer amounts of plutonium has several interesting features. One can oxidize the plutonium and then dilute the perchloric acid solution. Thus the final solution is one in which plutonium is present in the oxidized form with no other oxidizing agent present.

The use of perchloric acid in LaF_3 cycles instead of sulphuric acid has several advantages. The perchloric acid may be very easily fumed off and the plutonium oxidized at the same time. However, one must take care to insure the proper temperature for the oxidation step. An experiment was carried out to determine the temperature at which the 70 percent perchloric acid solution begins to fume. Fumes actually were noticeable at 80° C and copious quantities of dense white fumes were coming off at 135° C. Referring to Table I, one can see that the amount of oxidation under these conditions would be nil. After the LaF_3 cycle is carried out one can obtain the plutonium carrier free by precipitating the LaF_3 away from the plutonium in the oxidized state. The supernatant, aside from the usual dirt present in reagents and distilled water, will contain plutonium as the only non-volatile constituent.

The probability that the above information and ideas could be applied to element 93, neptunium, is very high.

[redacted]

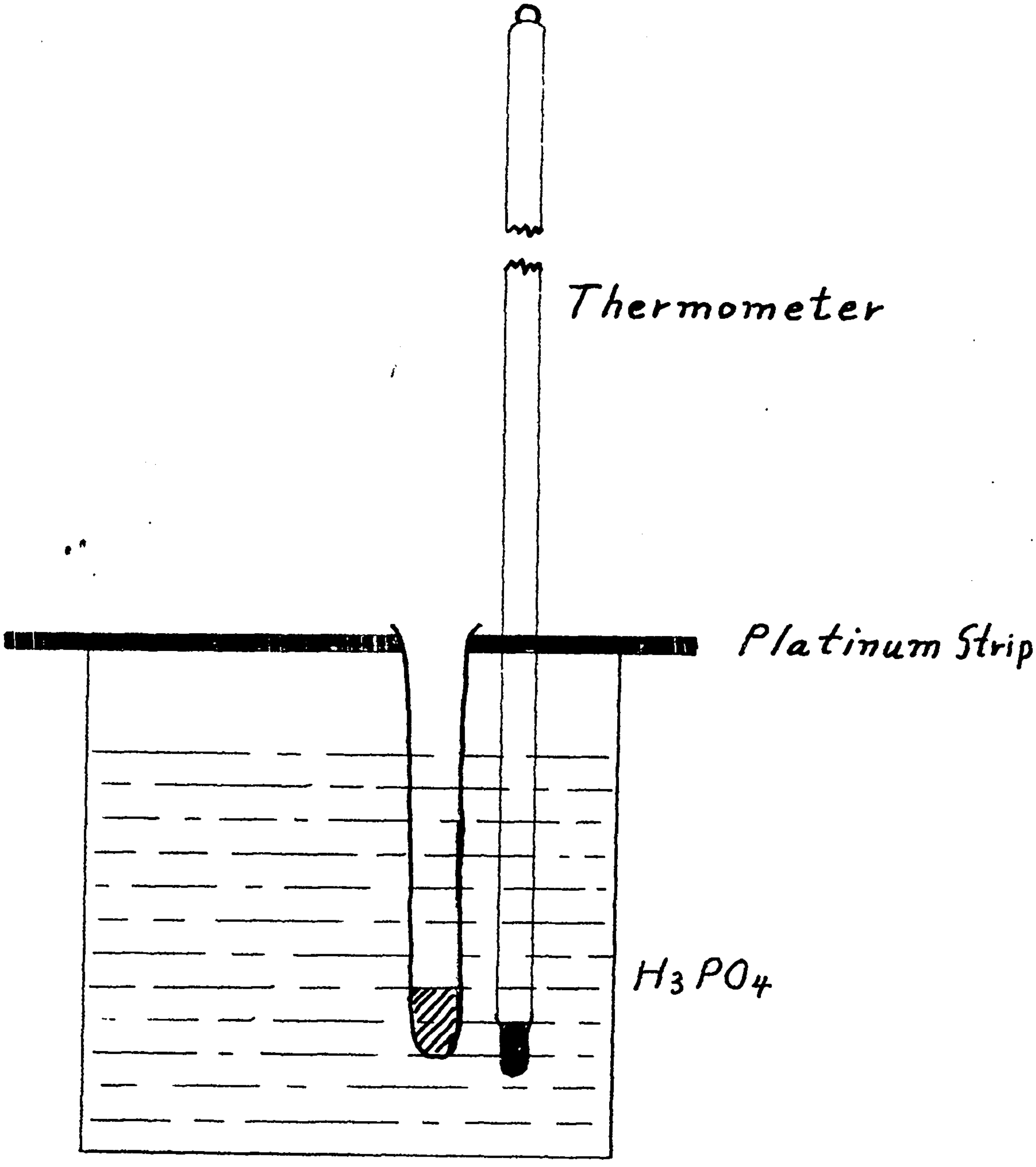

Fig. I

[redacted]