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LARGE-SCALE PREPARATION OF THE ANHYDROUS FLUORIDES OF PLUTONIUM

WORK DONE BY:

T/3 S. E. Bakes
T/Sgt. J. Crom
C. S. Garner
I. B. Johns
G. H. Moulton

REPORT WRITTEN BY:

I. B. Johns
G. H. Moulton

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ABSTRACT

The anhydrous fluorides of plutonium have been prepared by the reaction of anhydrous hydrogen fluoride on plutonyl nitrate, trivalent plutoni oxalate and plutonium dioxide. The fluorides of uranium, thorium and cerium have been prepared by some of these reactions also. The reaction of hydrogen fluoride on the oxide has been chosen for the large-scale preparation of plutonium tetrafluoride. The equilibrium constant for this reaction has been determined at 400° and at 600°C. To obtain the most rapid and complete reactio the effects of the following variables have been studied:

Temperature of ignition of the oxide

Temperature for reaction with HF

Rate of rise of temperature

Rate of flow of gas mixture

Depth of oxide layer

Dryness of the gas mixture

Composition of the gas mixture

The best conditions for conversion on the 8-g-to-25-g scale are described. The conversion of fluoride back to oxide is also described.

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LARGE-SCALE PREPARATION OF THE ANHYDROUS FLUORIDES OF PLUTONIUM

Introduction

Research on the large-scale preparation of the anhydrous halides of plutonium has been undertaken as a part of the program for the production of the metal. The initial studies dealt with the production of the fluorides because they were considered to be the most promising compounds for reduction purposes. Failure to obtain efficient reductions, together with the possibility that traces of fluorine in the metal might prove harmful, caused attention at that time to be directed to the production of the trichloride. This work was successful. Good anhydrous plutonium trichloride was prepared in quantities equivalent to 10 g element with which the metallurgists produced satisfactory reduction (LA-112). A little later, the lowering of the purity requirements together with the fact that the yields obtained in reducing the trichloride were never as high as desired lead to a renewed study of the fluorides. The superior yields resulting from the use of the tetrafluoride and the satisfactory purity of the metal indicate that the fluoride is, to date, the best compound for use in reductions. Its non-hygroscopic nature is also a great advantage.

Cerous and ceric fluorides were also prepared in kilogram quantities from cerous oxalate for use as stand-ins by R. D. Baker in scaling up the reduction procedure.

Experimental

A. General Reactions

The following reactions have been employed for the production of the fluorides of plutonium, thorium, uranium and cerium:

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a) $Th(NO_3)_4 \cdot 4H_2O + HF \longrightarrow ThF_4$

b) $PuO_2(NO_3)_2 \cdot xH_2O + HF \longrightarrow PuF_4$

c) $PuO_2(NO_3)_2 \cdot xH_2O + HF + H_2 \longrightarrow PuF_3$

d) $Th(NO_3)_4 \cdot 4H_2O \longrightarrow ThO_2 \longrightarrow ThF_4$, incomplete

e) $PuO_2(NO_3)_2 \cdot xH_2O \longrightarrow PuO_2 \longrightarrow PuF_3$ or PuF_4

f) $UO_2(NO_3)_2 \cdot 6H_2O \longrightarrow UO_3 \longrightarrow U_3O_8 \longrightarrow UO_2 \longrightarrow UF_4$

g) $Th(C_2O_4)_2 \cdot xH_2O + HF \longrightarrow ThF_4$

h) $Ce_2(C_2O_4)_3\ xH_2O + HF \longrightarrow CeF_3$

i) $CeF_3 + F_2 \longrightarrow CeF_4$

j) $U(C_2O_4)_2 \cdot xH_2O + HF \longrightarrow UF_4$

k) $Pu_2(C_2O_4)_3 \cdot xH_2O + HF \longrightarrow PuF_3$

l) $PuF_3 + HF + O_2 \longrightarrow PuF_4$

m) $Pu_2(C_2O_4)_3 \cdot xH_2O \longrightarrow PuO_2 \longrightarrow PuF_3$ or PuF_4

The conversion of the fluorides back to oxide has been studied:

n) PuF_3 or PuF_4 + O_2, H_2O or $NH_3 \longrightarrow PuO_2$

B. Experimental Procedures

1. The formation of fluorides by the reaction of HF with crystalline nitrates gave the earliest successful preparations of the fluorides of thorium and plutonium in this laboratory. The fluorides prepared in this way are rather fine grained and bulky. Because of their bulkiness this method of preparation was not continued. These preparations are tabulated in Table I.

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TABLE I

Reaction of Nitrates with Hydrogen Fluoride

Prep. No.	Sample	Treatment	Product	Analysis
90-18	7.3 g $Th(NO_3)_4 \cdot 4H_2O$	HF 25° to 550°, 6 hrs	ThF_4	Ignition
89-6	3.3 mg Pu as $PuO_2(NO_3)_4 \cdot xH_2O$	HF 21° to 500°, 10 hrs	PuF_3 (a)	X-ray; ignition oxygen 0.24% nitrogen 0.10%
89-9	3.3 mg Pu as $PuO_2(NO_3)_4 \cdot xH_2O$	HF 20° to 250°, 4 hrs	PuF_4	X-ray; oxygen 0.33% nitrogen 0.02%
90-7	3.1 mg Pu as $PuO_2(NO_3)_4 \cdot xH_2O$	HF 20° to 550°, 6 hrs	PuF_3	
89-21	50 mg Pu as $PuO_2(NO_3)_4 \cdot xH_2O$	HF 20° to 320°, 9 hrs	PuF_4	X-ray; ignition
89-23	50 mg Pu as $PuO_2(NO_3)_4 \cdot xH_2O$	HF 20° to 550°, $6\frac{1}{2}$ hrs	PuF_3	X-ray
89-25	1000 mg Pu as $PuO_2(NO_3)_4 \cdot xH_2O$	HF 20° to 550°, 8 hrs	PuF_4	X-ray; oxygen 0.03% nitrogen 0.006%
89-28	1000mg Pu as $Pu(NO_3)_4$	HF 20° to 550°, $5\frac{1}{2}$ hrs	PuF_4 (b)	X-ray; ignition

a) At early stages in the reaction the product was first light brown and then gray in color. X-ray diffraction patterns of this material showed the presence of both tri-and tetrafluoride.

b) Observed after treatment with HF at room temperature. The light-tan-colored tetrafluoride had formed, still wet with the water of crystallization of the nitrate.

It is to be noted that the product was in some cases tri- and in some cases tetrafluoride and in some a mixture of both. Later the Chicago group showed (CK-1372) that either the tri- or tetrafluoride could be prepared by admixing H_2 or O_2, respectively with the HF.

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II. The formation of fluorides by the reaction of HF on oxalates was also successful. The results of studies with thorium, uranium, cerium and plutonium are given in Table II.

TABLE II

Reaction of HF on Oxalates

Prep. No.	Sample	Treatment	Product	Analysis
90-9	345 mg $Th(C_2O_4)_2 \cdot 6H_2O$	HF, 20° to 550°, 6 hrs	100% ThF_4	ign. to ThO_2
90-20	2500 mg $Th(C_2O_4)_2 \cdot 6H_2O$	HF, 20° to 550°, 6 hrs	100% ThF_4	ign. to ThO_2
89-13	2774 mg $U(C_2O_4)_2$	HF, 22° to 580°, 1½ hrs	UF_4	
89-14	2456 mg $U(C_2O_4)_2$	HF, 22° to 550°, 2 hrs	100% UF_4	ign. to U_3O_8
90-84	1200 mg $Ce_2(C_2O_4)_3 \cdot 10H_2O$	HF, 20° to 500°, 4 hrs	100% CeF_3	F analysis
90-84	1187 mg CeF_3	HF + O_2, 20° to 500°, 1 hr	100% CeF_3	no wt. change
90-87	5000 mg $Ce_2(C_2O_4)_3 \cdot H_2O$	HF, 20° to 500°, 1 hr	100% CeF_3	
90-88	3400 mg CeF_3	F_2, 20°, 45 min	no change	
90-88	3400 mg CeF_3	F_2, 210°, 1¼ hr	100% CeF_4	wt. increase
90-89	47.5 g $Ce_2(C_2O_4)_3 \cdot H_2O$	HF, 500°, 3 hrs		
90-77	81.4 mg Pu as $Pu_2(C_2O_4)_3$	HF + O_2, 350°, 1 hr	100% PuF_4	X-ray; F analysis; ign. to PuO_2
90-102	3320 mg Pu as $Pu_2(C_2O_4)_3$	HF + O_2, 25° to 600°, 3 hrs	100% PuF_4	wt. change
90-105	847 mg Pu as $Pu_2(C_2O_4)_3$	HF, 25° to 600° 1 hr	100% PuF_3	wt. change
90-107	847 mg Pu as PuF_3	HF + O_2, 600°, ½ hr	100% PuF_4	wt. change

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This reaction represents the easiest method for the preparation of these fluorides in all cases where the oxalate is available. In the case of uranium, the +4 oxalate is somewhat difficult to prepare in good yields. A critical study of the preparation of UF_4 is given by Walsh and Lasovick in LA-159.

III. The formation of fluorides by the action of HF on oxides has been successful in the preparation of PuF_3, PuF_4 and UF_4 but was unsuccessful for the preparation of ThF_4. The ease of reaction depends upon the nature of the oxide, i.e., compound from which made and temperature of ignition.

When crystalline plutonyl nitrate is dehydrated at elevated temperatures in dry air, it reaches a weight corresponding to that of the anhydrous nitrate at 150° to 175°C. It begins to decompose at about this same temperature. The decomposition is essentially complete at 275°C though the resulting oxide shows continual small decreases in weight when heated to higher temperatures, attaining constant weight only after being heated to 800° to 1000°C. The oxide formed is PuO_2. No evidence of a higher oxide, corresponding to UO_3 has been observed (LA-172).

The conversion of the oxalate to oxide proceeds smoothly. The hydrated oxalate becomes anhydrous at about 225° and begins to decompose at 300°. The decomposition is rapid at 325° and essentially complete at 400° though the weight is not constant until the material has been heated to 800° to 1000°C. No evidence of a stable carbonate or sesquioxide has been observed (LA-172). The oxide prepared from the oxalate does not adhere to the platinum boat as does that prepared from the nitrate. The so-called "high-temperature oxide", i.e., ignited to 1000°C, was chosen for use in preparing the fluoride because the resulting fluoride possesses the most suitable density.

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Four reactions have been studied:

a) $PuO_2 + 3HF + \frac{1}{2}H_2 \longrightarrow PuF_3 + 2H_2O$

b) $PuO_2 + 4HF\ (+O_2) \longrightarrow PuF_4 + 2H_2O$

c) $PuF_4 + \frac{1}{2}H_2\ (+HF) \longrightarrow PuF_3 + HF$

d) $2PuF_3 + 2HF + \frac{1}{2}O_2 \longrightarrow 2\,PuF_4 + H_2O$

Of these reactions (b) was studied most thoroughly because it is to be used in the large-scale preparations. The study consists of the following parts:

1. Determination of the equilibrium constant for reaction (b).
2. Effect of temperature of ignition of the oxide.
3. Effect of temperature on reaction with HF.
4. Effect of rate of rise of temperature during reaction.
5. Effect of rate of flow of gases over the charge.
6. Effect of depth of the layer of oxide.
7. Effect of moisture in the gas mixture.
8. Composition of gas mixture, ratio of HF/O_2, HF/H_2.

In order to study the effect of these factors on the rates of reaction, an apparatus was constructed in which the sample, suspended from the beam of a torsion balance, could be weighed continually during the course of the reaction. The apparatus is shown in Fig. I, which is self-explanatory.

1. <u>Determination of the Equilibrium Constant for the Reaction:</u>

$$PuO_2 + 4HF \longrightarrow PuF_4 + 2H_2O$$

The concentration of H_2O vapor in the gas stream was progressively increased until the ratio, H_2O/HF, was found at which reaction ceased or was reversed, as judged by change in weight of the sample on the torsion balance. Fixed rates of flow of HF and O_2 were used. In these experiments the rate of flow of HF was

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accurately determined during the experiment by drawing the exit gases from the reaction tube through standard alkali and back titrating the excess alkali. At these elevated temperatures HF is known to be unassociated. Oxygen was measured by means of the usual glass flow meter. The oxygen was bubbled through water and the concentration of water vapor calculated from the temperature of the flask. The oxygen was considered as an inert gas, serving merely to carry the water vapor into the reaction tube. Its presence is necessary, however, to prevent reduction of the tetrafluoride to trifluoride by the traces of hydrogen present in the hydrogen fluoride.

The equilibrium constant was determined at 400° and at 600°C. At temperatures lower than 400° the reaction was found to be too slow for a reliable determination by this method. The data are presented below:

Temperature °C	Partial Pressures, atm.			$K_t = p^2_{H_2O}/p^4_{HF}$
	HF	H_2O	O_2	
400	0.384	0.175	0.442	1.40
600	0.535	0.141	0.325	0.244

The observed change in K with temperature requires the heat of reaction to be -9000 cal/mole (heat evolved). The thermal data are not known for plutonium. For the conversion of UO_2 to UF_4 the heat of reaction is -46 K cal/mole at 600°C and one may assume that the heats of formation of PuO_2 and PuF_4 are reasonably comparable to those of UO_2 and UF_4.

2. <u>The temperature of ignition of the oxide</u> has little effect on the rate of reaction (b) unless the ignition is carried above 1200°. Oxide ignited at 1400°C reacts with HF only about half as rapidly as oxide ignited to 1000°. Igniting at lower temperatures does not materially increase the reactivity. The comparison of the rates for 1000° and 1400° oxides can be seen in Fig. II.

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3. The temperature used in the reaction with HF has a great effect. At room temperature the oxide will absorb 13 to 14% of its weight of anhydrous HF. This corresponds to the addition of 2 mols of HF per mol of PuO_2. About 70 to 75% of this weight increase is lost again on warming to 150°. If the HF is not admitted to the oxide until the temperature has reached 150° then no appreciable reaction occurs until the temperature reaches 250°. With samples of 7 to 8 grams it has been found that the product formed in the room-temperature reaction is converted only very slowly to tetrafluoride at higher temperatures. The conversion to tetrafluoride is accomplished more rapidly when HF is not admitted until the temperature is well above 150°.

The rates of conversion of 200-mg samples of oxide to the trifluoride (reaction a) at 250°, 350°, 450°, 550° and 650° are given on Fig. III. In each experiment 50 ml/min. H_2 and 175 ml/min HF were used, the HF being admitted only after the desired temperature had been reached.

The rates of conversion of 200-mg samples of oxide to tetrafluoride (reaction b) at the same temperatures and rates of gas flow are given on Fig. IV.

A comparison of Fig. III and IV shows that the reaction to form trifluoride (a) is considerably faster than the formation of tetrafluoride (b). The reactions were not carried to completion, only the weight change during the first half hour being recorded.

The oxidation of trifluoride to tetrafluoride and the reduction of this latter back to trifluoride have been studied with the torsion apparatus. The reduction proceeds from 5 to 8 times as fast as the oxidation, as shown by the curves on Fig. VI. The same sample was used in all these reactions, the trifluoride obtained in the first reaction, A, prepared from the oxide, was then oxidized by means of HF and O_2 to the tetrafluoride, curve B. The tetrafluoride being then reduced to trifluoride again using HF and H_2, curve C, [illegible] the reactions were

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Run at 600° with 175 ml/min of HF and 50 ml/min of O_2 or H_2.

The reactions were run only for a short time. It is to be noted that each oxidation and reduction brings the conversion more nearly to completion. Reduction followed by oxidation is a trick that has been used in this laboratory in cases where the sample has refused to convert completely by direct reaction with HF and O_2. Reaction can be forced by alternate reductions and oxidations at 600°. This treatment results in a progressive swelling of the fluoride and is not desirable when the highest density is required. As an example of the effectiveness of this procedure the data on Lot 201 P are given. This lot of 8.45 g oxide almost ceased to react after being 92% converted to tetrafluoride. After a reduction to trifluoride it was then converted to tetrafluoride 99.4% in 40 minutes.

Lot 201 P	8.45 g oxide
HF + O_2, 2 hrs, 600°	91.4% conversion
HF + O_2, 2 3/4 hrs, 650°	92.0% conversion
HF + H_2, 1 3/4 hrs, 650°	
HF + O_2, 40 min, 600°	99.4% conversion

4. The rate of rise of temperature was found to be very important when using larger samples of oxide (7 to 8 g). As indicated in section 3, the presence of moisture at low temperatures produces a more slowly reacting substance. For this reason the reaction must not be started at temperatures below 200° and the moisture formed in the reaction must not be formed too rapidly but must be removed as rapidly as possible. If the reaction is started at too low a temperature, some of the unreactive material mentioned above (sec. 3) is formed. If the reaction is started at 600° with a rapid flow of HF, the rapid evolution of water will cause caking. These difficulties can both be eliminated by introducing the HF when the

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charge has reached 400°C at which temperature the reaction is still rather slow, and increasing the temperature to 600° in the course of an hour, using a rapid flow of gases during the whole conversion.

The data on lots 200 P, 205 P and 206 P illustrate these points.

Lot 200 P, 8.2 g oxide
Temp. raised to 600° in 38 min.
Temp. held at 600° 2 hrs. 91.2% conversion
Heated at 600°, 3½ hrs. longer 94.1% conversion
Heated at 600°, 1 hr. longer 94.8% conversion

Lot 205 P 7.89 g oxide
Temp. raised to 200° in oxygen only
HF and O_2 on at 200°
Temp. raised 200° to 400° in 40 min.
Temp. raised 400° to 600° in 1 hr.
Temp. held at 600° 1 hr. 99.0% conversion

Lot 206 P 8.21 g oxide
Temp. raised to 200° in oxygen only
HF and O_2 on at 200°
Temp. raised 200° to 600° in 18 min.
Temp. held at 600° 2 hrs. 93.4% conversion
Temp. held at 600° 2 hrs. longer 95.6% conversion

The effect of rapid heating from 200° to 600° is shown by the poor conversion of lot 206 P compared to that of lot 205 P. The still more harmful effect of admitting HF at room temperature, together with rapid rise of temperature is illustrated by the performance of lot 200 P.

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5. <u>The effect of rate of flow of gases over the charge</u> could not be studied with small samples. In all preparations to date the rate of flow has been considerably in excess of actual requirements. This factor will be determined when larger samples are available.

6. <u>The effect of depth of layer of oxide</u> has been investigated in a preliminary way by using approximately the same conditions for the conversion of several sizes of samples and noting the time required to secure 98 to 99% conversion. The data are given below:

Lot No.	g Oxide	Area, cm^2	mg/cm^2	Time, hrs.	% conversion
120 P	0.623	11	56.7	0.78	99.5
203 P	8.174	30	272.5	2.50	98.6
205 P	7.894	30	263.1	2.67	99.0
207 P	9.036	30	301.2	4.00	98.0
213, 214, 215 P	26.384	30	897.5	10.00	97.0

These data indicate that, as a first approximation, a nearly linear relation exists between the thickness of the charge and the time required to secure 98 to 99% conversion of the oxide to the tetrafluoride.

7. <u>The effect of moisture in the gases</u> is illustrated by the three curves in Fig. IV. Curve A shows the rate of reaction using dry oxygen and anhydrous (.02% H_2O) HF. Curve B shows the rate using anhydrous HF and oxygen bubbled through water at 48°C (v.p. 85 mm). With large samples the effect of small concentrations of water vapor seems to be more pronounced as shown by the following data:

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Lot 208 P   6.7 g oxide

Temp. raised to 250° in lab. air only (~30% relative humidity)

HF + lab. air on at 250°

Temp. raised 250° to 600° in 2 hrs.

Temp. held at 600° 2 hrs.	72.8% conversion
Temp. held at 600° 2 hrs. longer	79.7% conversion
Temp. held at 600° 2 hrs. longer	83.6% conversion

Lot 209 P   8.8 g oxide

Temp. raised to 250° in dry air

HF + dry air on at 250°

Temp. raised 250° to 600° in 2 hrs.

Temp. held at 600° 2 hrs.	98.1% conversion
Temp. held at 600° 2 hrs. longer	98.9% conversion

Thus for most rapid conversion the gases should be as dry as possible. it does not seem feasible to attempt to dry the HF. The water content (0.02%) of the best obtainable anhydrous HF is probably low enough.

8. <u>The effect of the composition of the gas mixture</u>, i.e., ratio HF/O_2 has been studied. The reaction will proceed over a wide range of HF concentrations. The ratio $\frac{\text{HF ml/min}}{\text{O}_2\text{ ml/min}}$ has been varied from 15.8 to 0.18. At the lower ratios the reaction is somewhat slower as shown by the following data:

a) Sample 90-113   3.91 g oxide $HF/O_2 = 0.178$

2 hrs. at 600°   80.5% conversion

2 hrs. longer at 600°   96.2% conversion

b) Sample 90-114   3.91 g oxide $HF/O_2 = 0.428$

2 hrs. at 600°   98.3% conversion

2 hrs. longer at 600°   99.3% conversion

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Since the concentration of oxygen required in the reaction is very low -- only enough to remove the traces of hydrogen present in the hydrogen fluoride, the usual practice is to employ a ratio $HF/O_2 = 4.2$. The concentration of oxygen in such a mixture should not noticeably affect the rate of reaction.

3. The best conditions for conversion of plutonium oxide to plutonium tetrafluoride on the 8-g-to-25-g scale can be described in the following steps.

a. Ignite the oxalate in air to 900° to 1000°C.

b. Heat the sample, contained in a platinum boat, in a nickel reactor to 300° to 400° in O_2 allowing time enough for the interior of the mass of powder to reach this temperature.

c. Turn on the HF at 300° to 400° at a rate of approximately 500 ml/min. Regulate O_2 to 100 to 125 ml/min.

d. Raise the temperature to 600°C in one hour.

e. Hold at 600° until reaction is complete, which requires 2 to 4 hrs on the 8-g scale and approximately 10 hrs on the 25-g scale.

f. Cool in HF and O_2 to 100 to 150°C.

g. Shut off HF and allow O_2 to sweep out the reactor until cold.

IV. Conversion of fluorides to oxide can be accomplished by heating to 400° to 600°C in air or oxygen. The reaction of dry oxygen on the fluoride is rather slow. The reaction can be made very rapid by adding H_2O or NH_3 to the air or oxygen. Ammonium carbonate is most convenient when using a muffle furnace for the ignition.

If the temperature is raised rapidly, in the absence of such reagents as H_2O or NH_3, an oxyfluoride will be formed which melts between 900° and 950°C to a very hard black solid. This can be converted to oxide readily in the way described above, yielding, however, a very hard black oxide which does not react readily with

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UF$_6$. The comparison of the reaction rate of this oxide with that of ordinary 1000° oxide is shown in Fig. VII. The solid chunk of oxide was carefully powdered in a steel mortar before being used so that the grain size was reasonably comparable with that of ordinary oxide.

The X-ray diffraction pattern of this oxide, determined by Group CM-8, showed the structure to be identical with that of ordinary dioxide. The low reactivity of the material may be due to lack of porosity.

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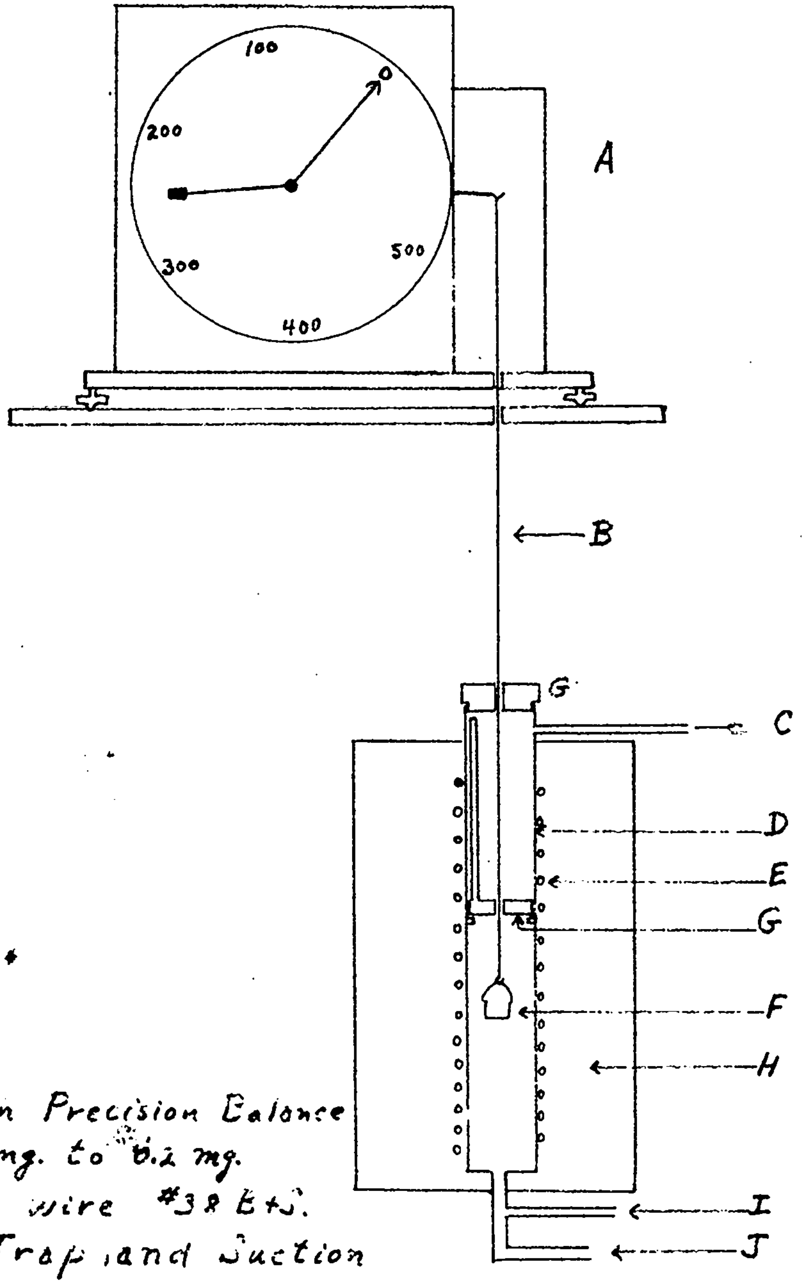
Fig. I. Torsion Apparatus



A. Roller-Smith Precision Balance
0-500 mg. to 0.2 mg.
B. Pt-10%-Rh wire #38 B+S.
C. To NaOH Trap and Suction
D. Nickel Tube, 11/16" I.D.
E. Heating Element, ~ 20 ohm
F. Pt bucket, wt. ~ 130 mg.
G. Nickel Discs, removable.
H. Thermal Insulation
I. Inlet for O_2 (and H_2O vapor)
J. Inlet for HF.

Figure II. Rates of Reaction of 1000° and 1400° Oxides

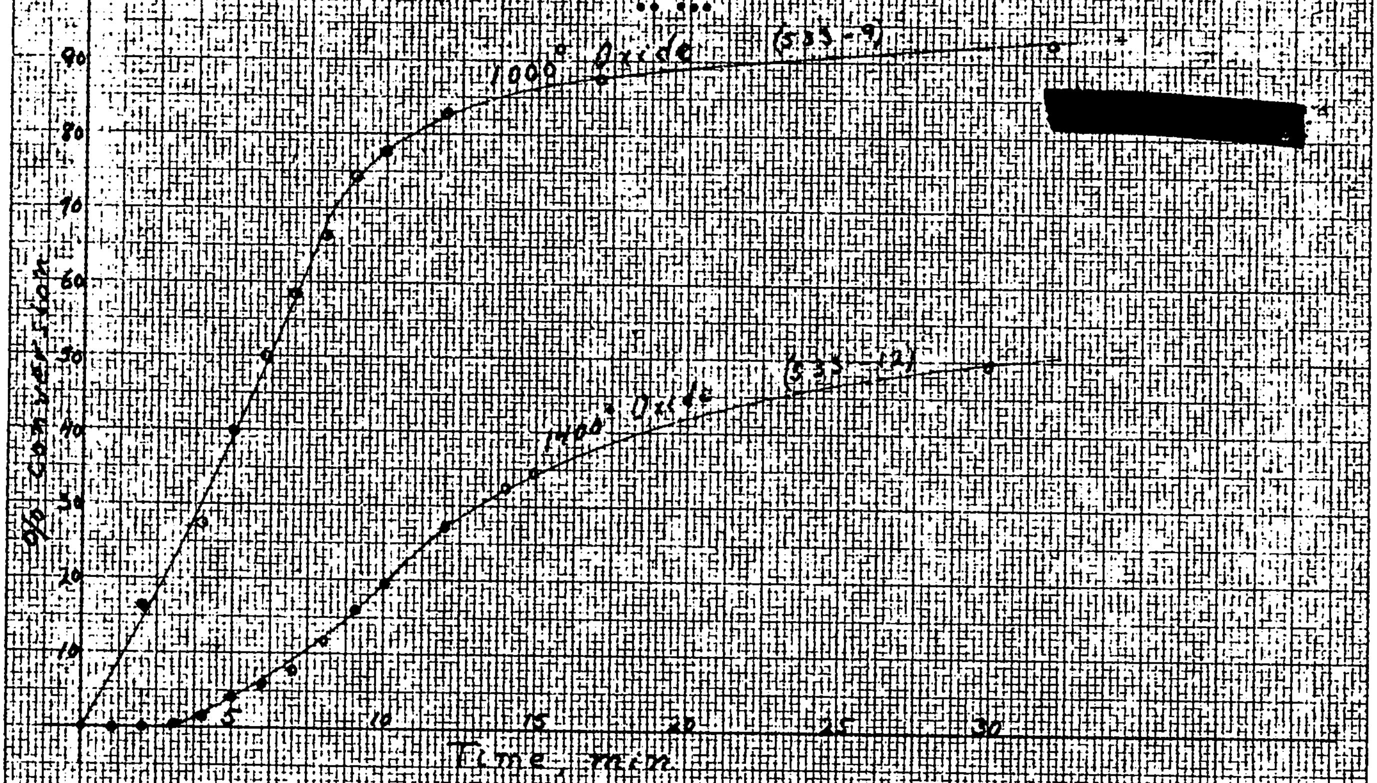


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Figure III. Effect of Temperature on Rate of Formation of PuF_3 from PuO_2

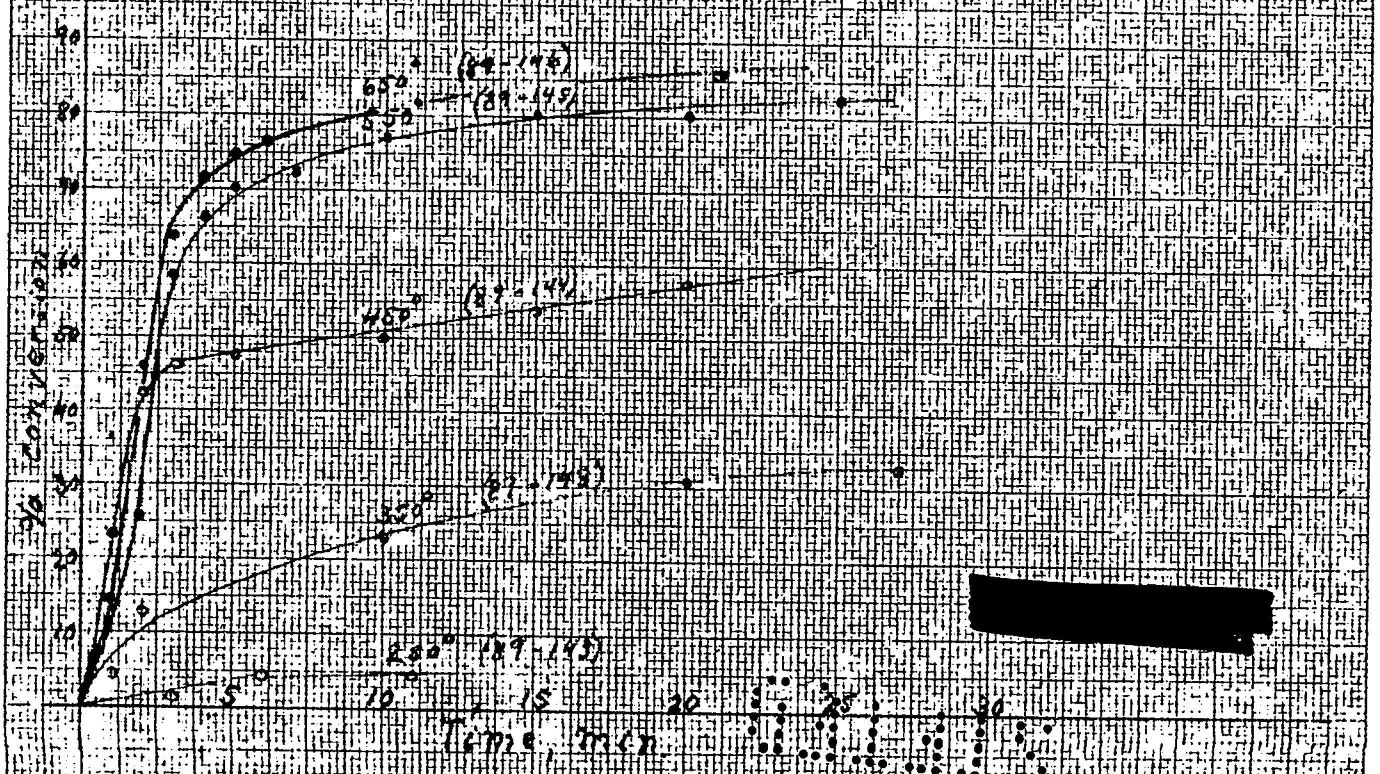

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Figure IV. Effect of Temperature on Rate of Formation of PuF_4 from PuO_2

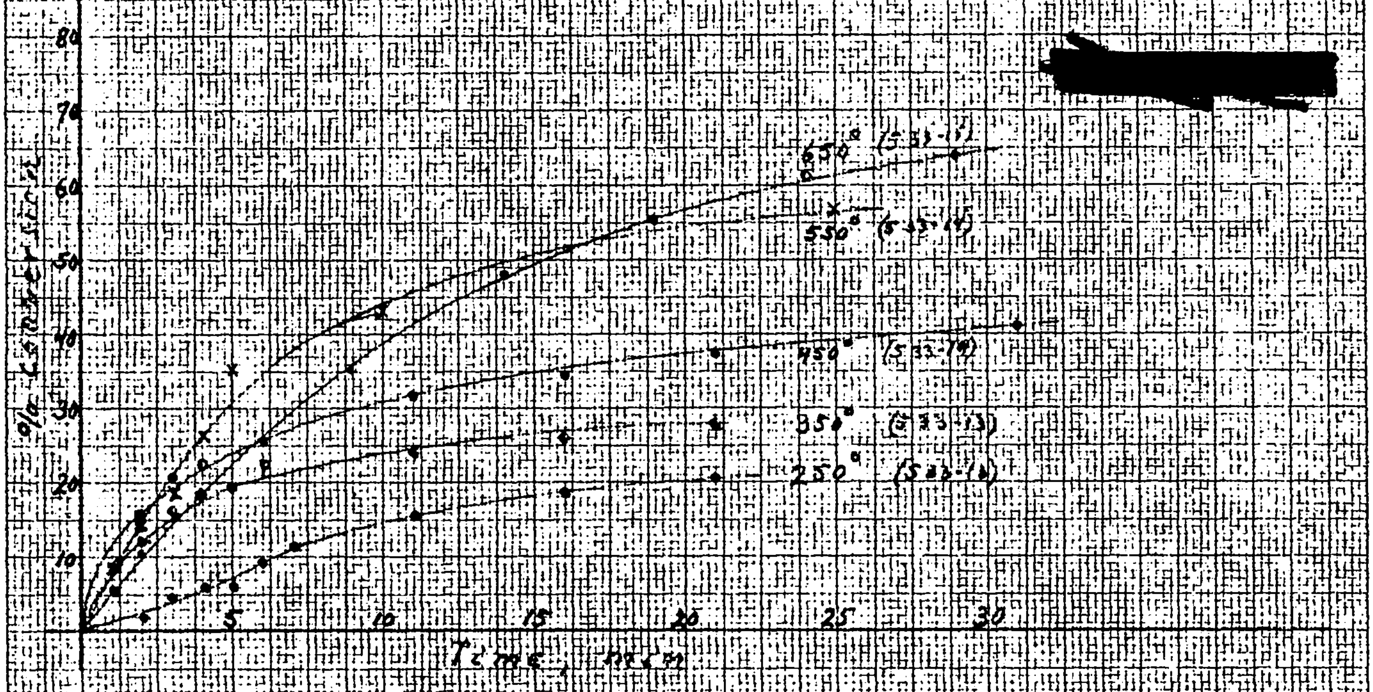

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Figure V. Effect of Water Vapor on Rate of Reaction at 550° C

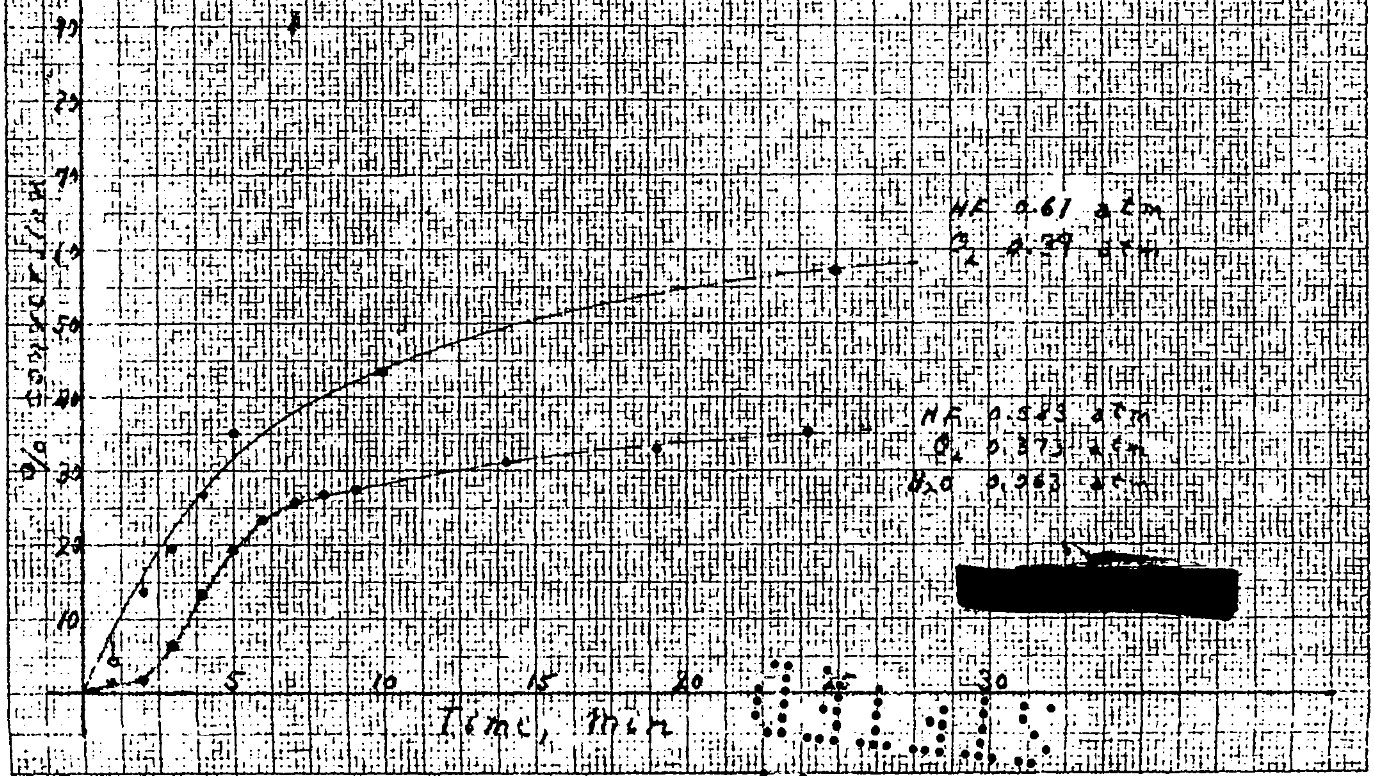

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Figure VI Relative Rates of Conversion to PuF_3 and PuF_4, 600° (533-4)

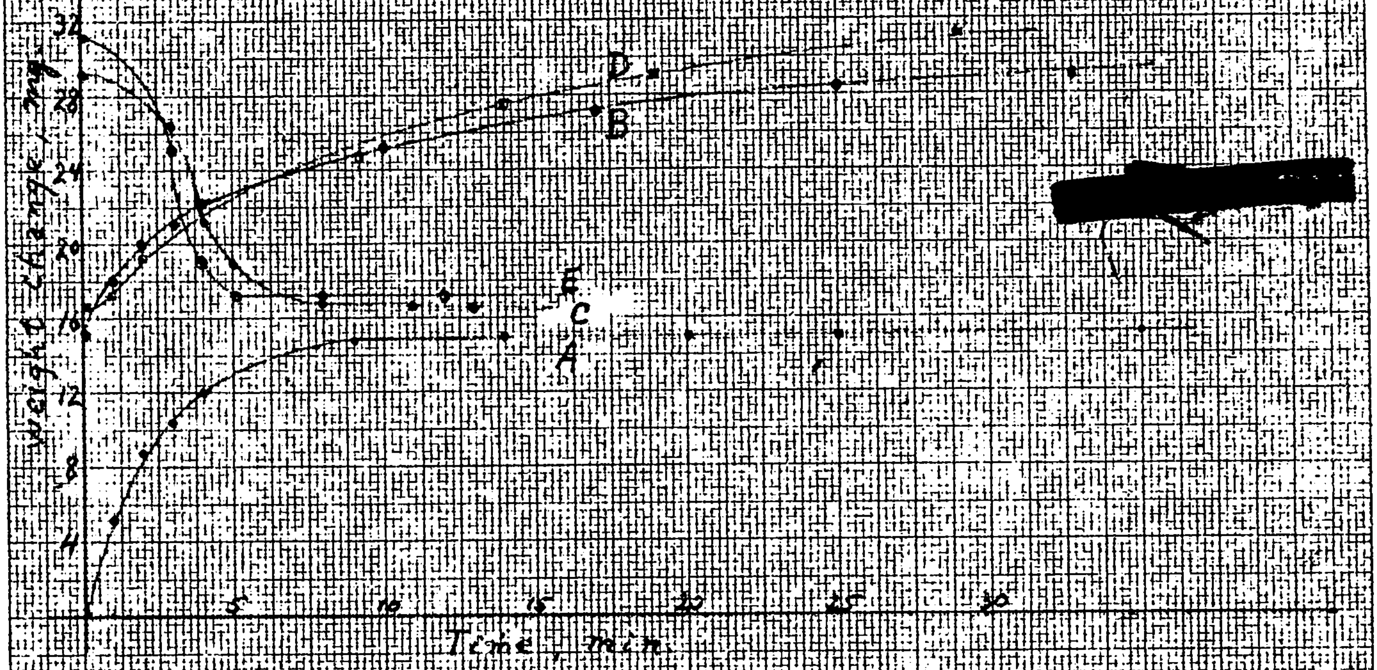

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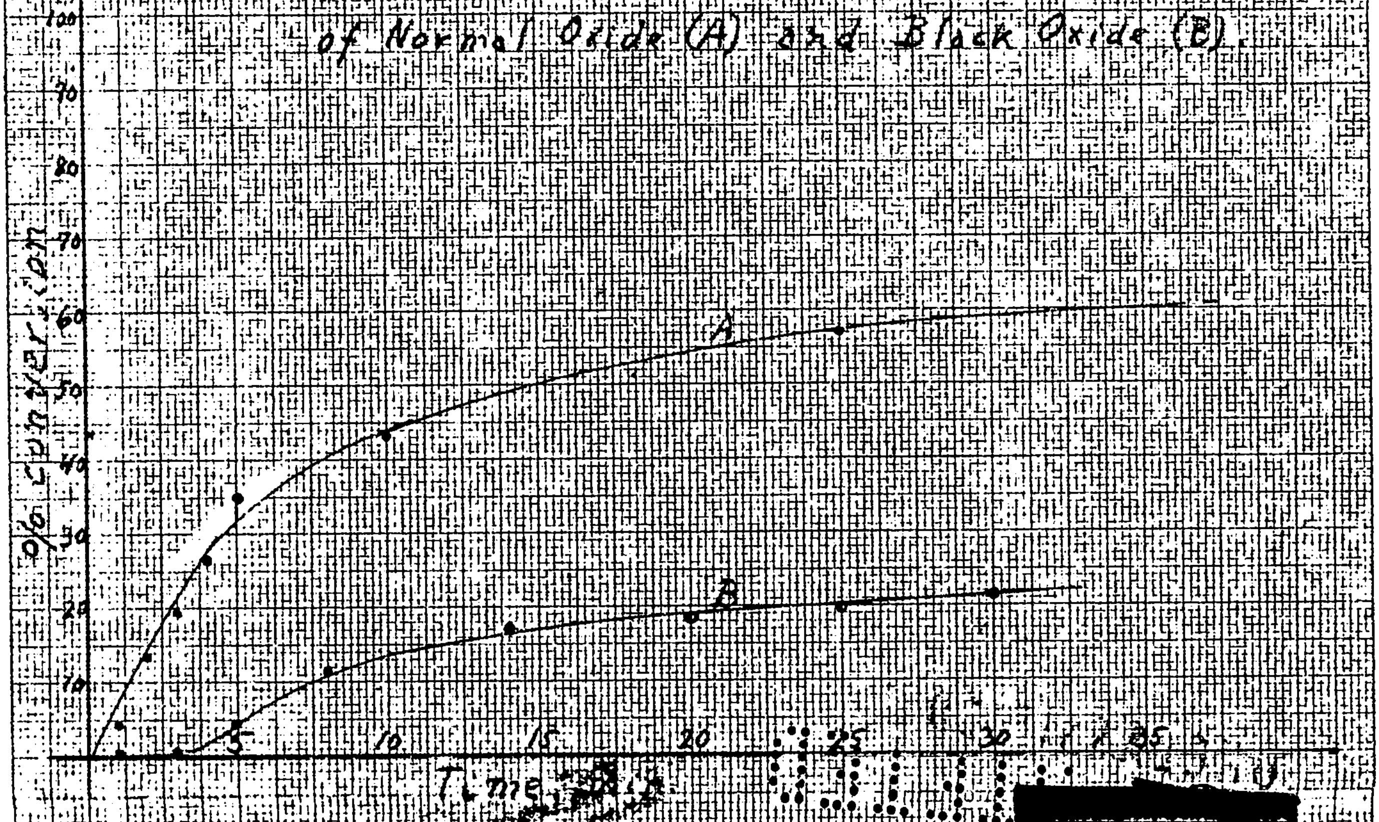
Figure VII Comparison of Conversion Rates of Normal Oxide (A) and Black Oxide (B).



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