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# STUDIES ON THE PREPARATION, PROPERTIES, AND COMPOSITION OF PLUTONIUM PEROXIDE

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# ABSTRACT

Two distinct crystalline structures of plutonium peroxide have been prepared. Face-centered cubic peroxide (a = 16.46 A) has been precipitated from various mineral acid solutions at low acidities. At higher acidities (~3M) a pure hexagonal structure was obtained. Both structures are plutonium(IV) compounds. Preparation methods, chemical analyses, and the general properties of both structures have been determined.

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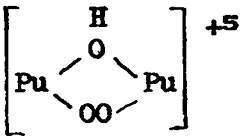
# INTRODUCTION

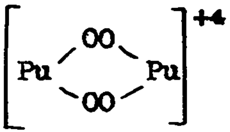
When a small amount of hydrogen peroxide is added to an acid solution of plutonium(IV), a brown complex forms. This complex contains two plutonium atoms, two peroxy-oxygen atoms, and one hydroxyl group. Connick and McVey[1] have proposed the following possible structures for this complex:

$(\mathrm{Pu{-}OO{-}Pu{-}OH})^{+5}$ or



As more $H_2O_2$ is added, this species is converted to a red complex having the formula:

$(\mathrm{HO{-}Pu{-}OO{-}Pu{-}OOH})^{+4}$ or



The brown complex has one peroxy-oxygen atom per plutonium atom, whereas the red complex has two.

On further addition of $H_2O_2$, green plutonium peroxide is precipitated. This compound has been studied by numerous investigators. Koshland, Kroner and Spector[2] have shown that plutonium is present in the tetrapositive state in the precipitate, and that there are three peroxy-oxygen atoms per plutonium atom.* Hopkins[3] also found three peroxy-oxygen

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*Peroxide oxygen may be expressed either on an equivalent basis, as $(O^-)$, or on a molecular basis, as $(O_2^{=})$. The former designation will be used throughout this report; i.e., $H_2O_2$ has two peroxy oxygens.

atoms per plutonium atom in the wet precipitate. Hamaker and Koch[4] have analyzed the dry peroxide precipitate and found variable compositions such as:

$$Pu(O^-)_{2.73}\ (SO_4^{=})_{0.33}\ (O^{=})_{0.30}\cdot 2.06H_2O$$

when precipitated from 0.5M $H_2SO_4$;

$$Pu(O^-)_{3.24}\ (SO_4^{=})_{0.05}\ (NO_3^-)_{0.30}\ (O^{=})_{0.18}\cdot 1.75H_2O$$

when precipitated from 1M $HNO_3$; and

$$Pu(O^-)_{2.54}\ (SO_4^{=})_{0.02}\ (Cl^-)_{0.45}\ (O^{=})_{0.48}\cdot 2.97H_2O$$

when precipitated from 1M HCl.*

X-ray analyses showed that the precipitates of Hamaker and Koch as well as those of Koshland were frequently mixtures of two crystalline phases. One phase was presumably a two-dimensional hexagonal lattice with constant $a_1$ = 4.00 A. The hexagonal sheets containing two plutonium atoms per sheet were held together by various anions such as $NO_3^-$, $SO_4^{=}$, $HSO_4^-$, $Cl^-$, $OOH^-$, $O_2^{=}$, etc. The other phase was described as possibly cubic with a lattice constant a = 16.5 A. It was not possible to correlate structure with the method of preparation.

This study was undertaken to further elucidate the preparation, composition, and structure of plutonium peroxide.

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*The sulfate in the last two preparations was due to the presence of an unspecified amount of sulfate in the hydrogen peroxide reagent.

## 1. Effect of Precipitation Medium on Crystal Structure

Plutonium peroxide was precipitated from various solutions by the following standard procedure:

Pure plutonium(III) stock solution was prepared by dissolving 99.8 per cent Pu metal in the desired acid. An aliquot containing approximately 100 mg plutonium was then diluted with the appropriate sodium salt-acid solution and an equivalent amount of $H_2O_2$ was added to oxidize the plutonium to the tetravalent state. Ten molar $H_2O_2$ (Baker's 30 per cent reagent) solution was added dropwise at room temperature to precipitate the plutonium. All solutions were stirred vigorously during precipitation. The resulting slurry was digested for 16 hours and then separated by centrifugation. The precipitate was washed three times with 50 per cent ethanol and once with absolute ethanol. The sample was dried by passing filtered air at room temperature through the powder for 1 hour prior to x-ray analysis by F. H. Ellinger of LASL Group CMR-5.

Several preparations were digested for periods varying from 1 to 72 hours. X-ray analyses were made on several slurries prior to separating and drying. There was no evidence of changes in structure due either to digestion time or to separation procedure.

The results of the various acid systems studied are shown in Table 1.1. The concentrations listed in this table are uncorrected for concentration changes that occur due to precipitation. They represent the reagent concentrations if no reaction had occurred.

Table 1.1

EFFECT OF PRECIPITATION MEDIUM ON THE STRUCTURE OF PLUTONIUM PEROXIDE

| Preparation No. | (Pu) M | ($H_2O_2$) M | ($H^+$) M | ($ClO_4^-$) M | ($SO_4^=$) M | ($NO_3^-$) M | ($Cl^-$) M | Structure[(a)] |
|---|---|---|---|---|---|---|---|---|
| 1 | 0.052 | 0.020 | 0.03 | 1.00 | - | - | - | No ppt. (b) |
| 2 | 0.235 | 1.00 | 0.39 | 0.41 | - | - | - | No ppt. (b) |
| 3 | 0.052 | 0.20 | 0.03 | 3.68 | - | - | - | F.C.C. |
| 4 | 0.176 | 3.30 | 1.10 | 1.60 | - | - | - | F.C.C. |
| 5 | 0.229 | 1.35 | 1.44 | 2.12 | - | - | - | F.C.C. |
| 6 | 0.264 | 0.25 | 4.10 | 4.63 | - | - | - | Hex'l (d) |
| 7 | 0.176 | 3.30 | 4.10 | 4.63 | - | - | - | Hex'l (d) |
| 8 | 0.330 | 3.00 | 1.08 | 1.64 | 0.16 | - | - | F.C.C. |
| 9 | 0.033 | 1.00 | 0.48 | 0.25 | 0.16 | - | - | F.C.C. |
| 10 | 0.033 | 1.00 | 0.48 | 4.0 | 0.16 | - | - | Hex'l |
| 11 | 0.033 | 1.00 | 0.48 | 4.0 (c) | 0.16 | - | - | Hex'l |
| 12 | 0.033 | 1.00 | 0.48 | 2.0 | 0.16 | - | - | Mixture |
| 13 | 0.033 | 1.00 | 3.90 | 4.0 | 0.16 | - | - | Hex'l |
| 14 | 0.052 | 0.25 | 0.40 | 0.25 | 0.50 | - | - | F.C.C. |
| 15 | 0.053 | 1.0 | 0.51 | - | - | - | 3.0 | F.C.C. |
| 16 | 0.053 | 1.0 | 2.8 | - | - | - | 3.0 | F.C.C. |
| 17 | 0.053 | 1.0 | 3.6 | - | - | - | 3.8 | Hex'l |
| 18 | 0.033 | 1.0 | 0.45 | 0.25 | - | 3.0 | - | F.C.C. |
| 19 | 0.033 | 3.0 | 0.45 | 0.25 | - | 3.0 | - | F.C.C. |
| 20 | 0.033 | 3.0 | 1.0 | 0.25 | - | 3.0 | - | Mixture |
| 21 | 0.033 | 3.0 | 2.0 | 0.25 | - | 3.0 | - | Hex'l |
| 22 | 0.033 | 3.0 | 3.2 | 0.25 | - | 3.0 | - | Hex'l |
| 23 | 0.033 | 3.0 | 2.0 | - | 0.10 | 3.0 | - | Hex'l |
| 24 | 0.033 | 3.0 | 2.0 | - | 0.90 | 3.0 | - | Hex'l |
| 25 | 0.033 | 1.0 | 0.55 | - | 0.37 | - | - | F.C.C. |
| 26 | 0.053 | 3.0 | 4.0 | - | 2.0 | - | - | Hex'l |
| 27 | 0.176 | 3.0 | 4.2 | 0.53 | 2.0 | - | - | Hex'l |

(a) F.C.C. = face-centered cubic; Hex'l = hexagonal
(b) Green colloidal solution
(c) $Mg(ClO_4)_2$ used in place of $NaClO_4$
(d) X-ray analysis made on slurry

## 1.1 Perchloric Acid System

In the absence of sulfate no precipitate settled from solutions that were less than 0.5M in $HClO_4$. However, Preparation 2 gave a Tyndall cone effect, indicating a colloidal precipitate. By increasing the perchlorate-ion concentration to 3.68M with $NaClO_4$, a precipitate was obtained and separated (Preparation 3). The structure of this precipitate was face-centered cubic, with the cell constant a = 16.46 ± 0.01 A.

Precipitation from a solution of acidity from 1.1 to 1.5M and a perchlorate concentration from 1.6 to 2.1M resulted in the same cubic structure. When the acidity was increased to 4M, the structure changed from the cubic to the hexagonal form (Preparations 6 and 7). Thus, there appears to be a change due to acidity.

In the presence of sulfate (Preparations 9 and 10), the structure can be changed by increasing the perchlorate ion concentration to 4M. This same effect was also observed when $Mg(ClO_4)_2$ was used in place of $NaClO_4$ (Preparation 11) to adjust the perchlorate concentration. This apparently anomalous effect has been reproduced many times.

## 1.2 Hydrochloric Acid Systems

As in the perchloric acid system, precipitation from a solution of low acidity (Preparations 15 and 16) resulted in a cubic structure, whereas precipitation from one of high acidity (Preparation 17) gave the hexagonal structure. Apparently the change occurs between 2.8 and 3.6M hydrogen-ion concentration in hydrochloric acid solutions.

## 1.3 Nitric Acid System

As shown in Preparations 18 through 22, the cubic structure was formed at a hydrogen-ion concentration of 0.45M while the hexagonal structure was obtained from solutions that were at least 2M in total acidity. A mixture of the two structures was obtained at an acidity of 1M.

The presence of sulfate had no effect on the structure in 2M acid (Preparations 23 and 24).

## 1.4 Sulfuric Acid System

As in the case of the other acid systems, precipitation from solutions of low acidity (Preparation 25) resulted in the cubic structure, and the hexagonal structure (Preparation 26) was obtained at high acidity. During these tests the total sulfate concentration could not be held constant owing to solubility limitations. However, the sulfate-ion concentrations were approximately the same.

## 1.5 Effect of Hydrogen Peroxide and Plutonium Concentrations

There does not appear to be any effect due to variations in either the $H_2O_2$ or the plutonium concentrations. In Preparations 3, 4 and 5, the cubic structure was not affected by increasing the plutonium concentration from 0.052 to 0.229M, while the peroxide concentration was increased from 0.20 to 3.30M. At a constant plutonium concentration of 0.033M, the cubic structure was not affected by increasing the $H_2O_2$ concentration from 1.0 to 3.0M (Preparations 18 and 19). The hexagonal structure was not affected by increasing the $H_2O_2$ concentration from 0.25 to 3.30M (Preparations 6 and 7).

## 2. The Composition of Plutonium Peroxides

Several of the preparations listed in Table 1.1 were reproduced on a larger scale (1 to 5 grams plutonium). The precipitates were analyzed for plutonium oxidation state, peroxy-oxygen, sulfate, perchlorate, and chloride.

### 2.1 Determination of the Oxidation State of Plutonium in Peroxides

When a sample of plutonium peroxide is dissolved in an excess of acid-iodide solution, peroxide-oxygen liberates an equivalent amount of iodine according to the reaction:

$$O^- + I^- + 2H^+ = 1/2\ I_2 + H_2O \qquad (2.1.1)$$

If the plutonium is present in an oxidation state greater than tripositive, it will also be reduced and liberate an equivalent amount of iodine according to the equation:

$$Pu^{+n} + (n-3)\ I^- = Pu^{+3} + \frac{(n-3)}{2}\ I_2 \qquad (2.1.2)$$

where n is the oxidation state of plutonium in the precipitate.

On the other hand, when a peroxide precipitate is dissolved in an excess of $Ce(SO_4)_2$ solution, the peroxy-oxygen is oxidized to free oxygen and the plutonium is oxidized to the hexavalent state according to the reaction:

$$Pu^{+n} + (6-n)\ Ce^{+4} + 2H_2O = PuO_2^{+2} + (6-n)\ Ce^{+3} + 4H^+ \qquad (2.1.3)$$

These reactions were used to determine the oxidation state of plutonium in several precipitates. The iodine liberated by a known amount of plutonium in the form of peroxide was determined by titration with standard 0.1N $Na_2S_2O_3$ solution. From these data the $(O^-)$ to Pu mole ratio was calculated for all possible values of n in Equation 2.1.2. Samples of the same precipitate were also dissolved in a known amount of $Ce(SO_4)_2$ solution, and the excess $Ce(SO_4)_2$ was determined by back-titrating with acid $H_2O_2$ solution. The $(O^-)$ to Pu ratio was then calculated for the possible values of n in Equation 2.1.3. Details of these analytical procedures are given in Appendix A.

As shown in Table 2.1, the $(O^-)$ to Pu ratio will depend on the value of n assumed for each method. However, a given precipitate must have a definite value for this ratio. Consequently, the same ratio will be obtained for both the oxidation and the reduction methods only when the correct plutonium oxidation state is assumed. The results in Table 2.1 show that in both the cubic and the hexagonal structures the plutonium is present in the tetrapositive state.

This method gives only the average oxidation state. If the possibility of plutonium(III) can be eliminated, then it can be said definitely that the oxidation state is tetrapositive. Since precipitation from plutonium(IV) solution (0.3M in Pu) does not liberate any significant amount of free oxygen, it can be assumed that no plutonium(III) is present in the precipitate.

## 2.2 Peroxy-Oxygen to Plutonium Ratio in the Precipitates

By means of the iodometric method, the $(O^-)$ to Pu ratios were determined for both the cubic and the hexagonal structure precipitates.

## Table 2.1

## OXIDATION STATE OF PLUTONIUM IN PEROXIDE PRECIPITATES

| Preparation No. (See Table 1.1) | Method of Analysis | CALCULATED ($O^{=}$) TO PU MOLE RATIO FOR ASSUMED OXIDATION STATE III | IV | V | VI |
|---|---|---|---|---|---|
| 9 (F.C.C.) | $I^-$ reduction | 4.24 | 3.24 | 2.24 | 1.24 |
| | $Ce^{+4}$ oxidation | 2.07 | 3.07 | 4.07 | 5.07 |
| 14 (F.C.C.) | $I^-$ reduction | 4.12 | 3.12 | 2.12 | 1.12 |
| | $Ce^{+4}$ oxidation | 2.13 | 3.13 | 4.13 | 5.13 |
| 26 (Hex'l) | $I^-$ reduction | 4.40 | 3.40 | 2.40 | 1.40 |
| | $Ce^{+4}$ oxidation | 2.40 | 3.40 | 4.40 | 5.40 |

### 2.2.1 The Cubic Structure

As shown in Table 2.2, the cubic structure contains three atoms of peroxy-oxygen per plutonium atom. The average ratio was 3.04 regardless of whether the sample was analyzed wet or immediately after drying for 1 hour at room temperature. Since the plutonium is in the tetrapositive state, there must be additional anions present.

### 2.2.2 The Hexagonal Structure

With the exception of Preparation 10, analyses of the wet precipitates indicated that the hexagonal structure contains more peroxy-oxygen to Pu than does the face-centered cubic. Preparations 6 and 7 of Table 2.2 were washed by reslurrying with 6M $HClO_4$. The maximum $(O^-)$ to Pu ratio that can be attributed to incomplete washing is 0.01 in Preparation 7. Moreover, Preparation 6 was made by adding so little $H_2O_2$ that the $(O^-)$ to Pu ratio was 1.90 in the precipitation medium. However, the peroxy-oxygen to Pu ratio in the precipitate was increased to 3.34. Neither Preparations 6 or 7 could be separated and dried without destruction, so the analysis on the dry preparation could not be made.

Preparation 26 also contained a mole ratio that was greater than 3 after copious washing. The ratio for the dried sample was approximately 3.

### 2.3 Sulfate to Plutonium Ratio

By means of the gravimetric $BaSO_4$ procedure described in Appendix B, the sulfate to Pu ratio was determined for Preparations 8 (cubic) and 26 (hexagonal). Duplicate precipitations were analyzed in duplicate for both preparations.

Table 2.2

## PEROXY-OXYGEN TO PLUTONIUM RATIO IN PRECIPITATES

| Preparation No. | Treatment | $(O^-)$ to Pu Mole Ratio |
|---|---|---|
| 3 (F.C.C.) | Digested for 3 days at 25°C | |
| | Washed 4 times with ethanol | |
| | Analyzed wet | 3.10 |
| | Dried for 1 hr at 25°C | |
| | Analyzed dry | 3.02 |
| 4 (F.C.C.) | Digested for 5 days at 25°C | |
| | Washed 4 times with ethanol | |
| | Analyzed wet | 3.10 |
| 9 (F.C.C.) | Digested for 16 hrs at 25°C | |
| | Washed 6 times with 0.1M HCl,<br>4 times with ethanol | |
| | Dried for 1 hr at 25°C | |
| | Analyzed dry | 3.10 |
| 9 (F.C.C.) | Duplicate | 2.99 |
| 5 (F.C.C.) | Digested for 1 hr at 25°C | |
| | Washed 2 times with 3% $H_2O_2$,<br>1 time with 0.1M $H_2SO_4$,<br>2 times with ethanol | |
| | Analyzed wet | 3.03 |
| 16 (F.C.C.) | Digested for 1 hr at 25°C | |
| | Washed 2 times with 0.01M HCl,<br>2 times with ethanol | |
| | Analyzed wet | 2.99 |
| | Dried 1 hr at 25°C | |
| | Analyzed dry | 2.98 |
| 6 (Hex'l) | Digested for 30 min at 25°C | |
| | Washed 4 times with 6M $HClO_4$ | |
| | Analyzed wet | 3.34 |
| 7 (Hex'l) | Digested for 30 min at 5°C | |
| | Washed 3 times with 6M $HClO_4$ | |
| | Analyzed wet | 3.53 |
| 7 (Hex'l) | Duplicate | |
| | Washed 3 times with 6M $HClO_4$,<br>3 times with ethanol | |
| | Analyzed wet | 3.50 |
| 26 (Hex'l) | Digested for 30 min at 25°C | |
| | Washed 3 times with 1% $H_2O_2$,<br>3 times with ethanol | |
| | Analyzed wet | 3.34 |
| | Dried for 1 hr at 25°C | |
| | Analyzed dry | 3.11 |
| 10 (Hex'l) | Digested 16 hrs at 25°C | |
| | Washed 2 times with 0.1M HCl,<br>3 times with ethanol | |
| | Analyzed wet | 3.15 |
| | Dried at 25°C for 16 hrs | |
| | Analyzed dry | 2.96 |

The cubic structure from Preparation 9 contained 0.24 ± 0.02 mole of sulfate per mole of plutonium, whereas the hexagonal structure from Preparation 26 had a ratio of 0.38 ± 0.01. Although it is true that Preparation 26 was precipitated from a higher sulfate concentration, this difference in amounts of sulfate in the precipitates is not due to incomplete washing. Both preparations were washed four times with 0.1M HCl, four times with 50 per cent ethanol, and twice with absolute ethanol. Hexagonal Preparation 10, which was precipitated from the same low sulfate concentration, contained 0.37 mole of sulfate per mole of plutonium. Furthermore, the cubic structure contains 0.25 mole of sulfate per mole of plutonium when precipitated from 1.6M $HNO_3$ and 0.10M total sulfate; the hexagonal structure, precipitated at the same sulfate concentration (and an acidity of 4M), contains a sulfate to Pu ratio of 0.36.* Therefore, the hexagonal structure definitely takes up more sulfate than does the cubic.

## 2.4 Perchlorate to Plutonium Ratio

Perchlorate was not detectable by the nitron gravimetric procedure (Appendix C) in either the cubic (Preparation 9) or the hexagonal (Preparation 10) structures. Based on the lower limit of detectability, the perchlorate to Pu mole ratio was therefore less than 0.02.

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* Private communication from A. V. Henrickson of this laboratory.

## 2.5 Chloride to Plutonium Ratio

Chloride was determined gravimetrically as AgCl (Appendix D). The cubic structure of Preparation 16 contained 0.029 mole of chloride per mole of plutonium, whereas the hexagonal structure of Preparation 17 had a ratio of 0.160.

## 3. Rates of Decomposition of Plutonium Peroxides

Dried preparations were stored at various temperatures and analyzed periodically for $(O^-)$ to Pu ratio by the iodide reduction method. As shown in Fig. 3.1, decomposition of the cubic structure at room temperature differs from that of the hexagonal form.

The cubic structure (Preparation 9) decomposed uniformly to completion within a period of 50 days, whereas the hexagonal structure (Preparation 26) decomposed to a relatively stable form having a $(O^-)$ to Pu ratio of 1. After 150 days this ratio dropped to 0.40.

X-ray analysis of the decomposed samples showed that the cubic form was almost completely converted to $PuO_2$, but that the hexagonal form was indeterminant except for traces of $PuO_2$.

The effect of temperature on the decomposition rate of the cubic structure is shown in Fig. 3.2. Since the plot of ln $(O^-/Pu)$ against time is linear, this decomposition can be represented by:

$$-\frac{d}{dt}\ln\frac{(O^-)}{Pu} = k \qquad (3.1)$$

where k is a constant. This may be rearranged to the familiar first-order kinetic form:

$$-\frac{d}{dt}\frac{(O^-)}{(Pu)} = k\,\frac{(O^-)}{(Pu)} \qquad (3.2)$$

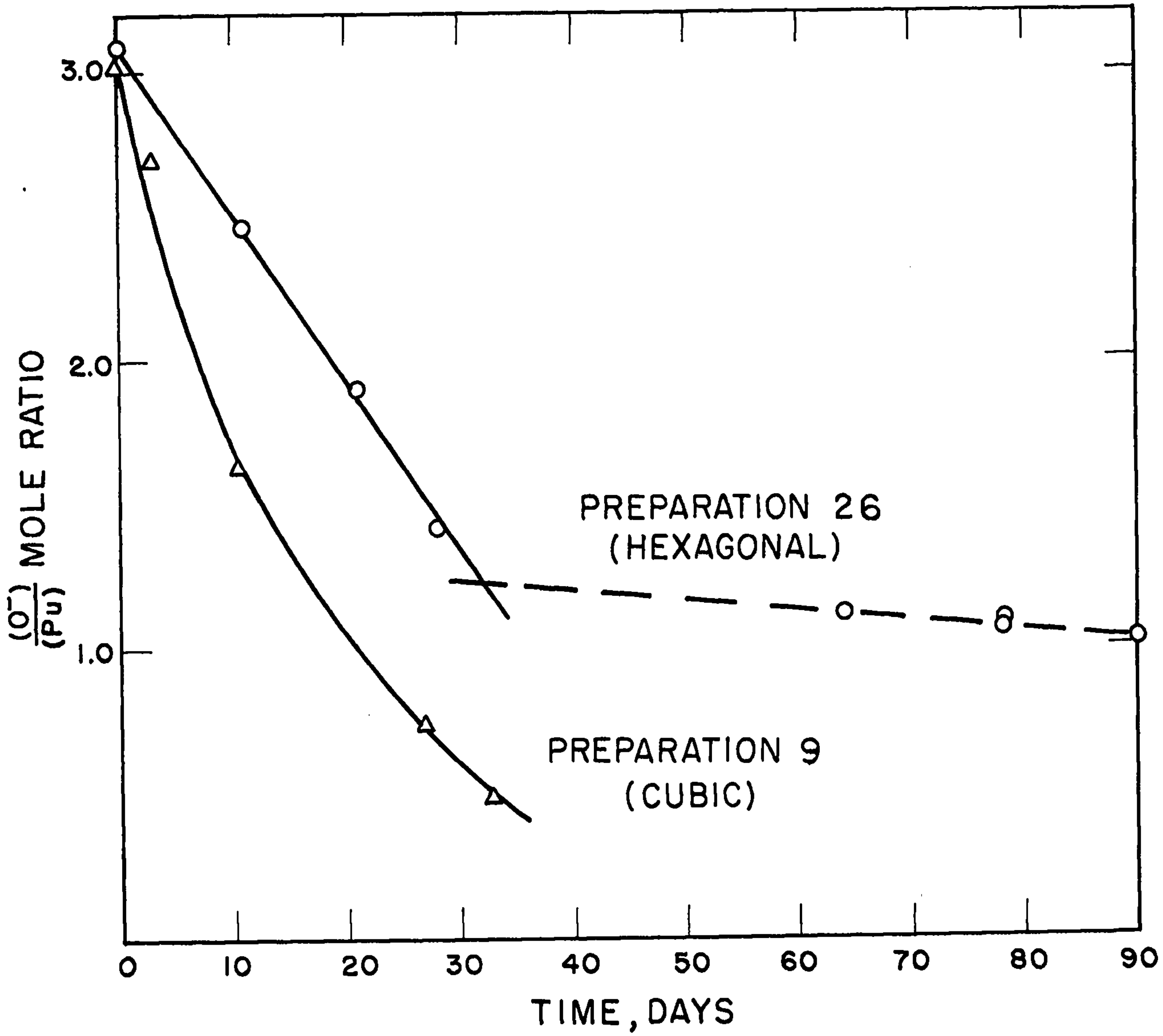

Fig. 3.1 Rates of decomposition of plutonium peroxide at room temperature

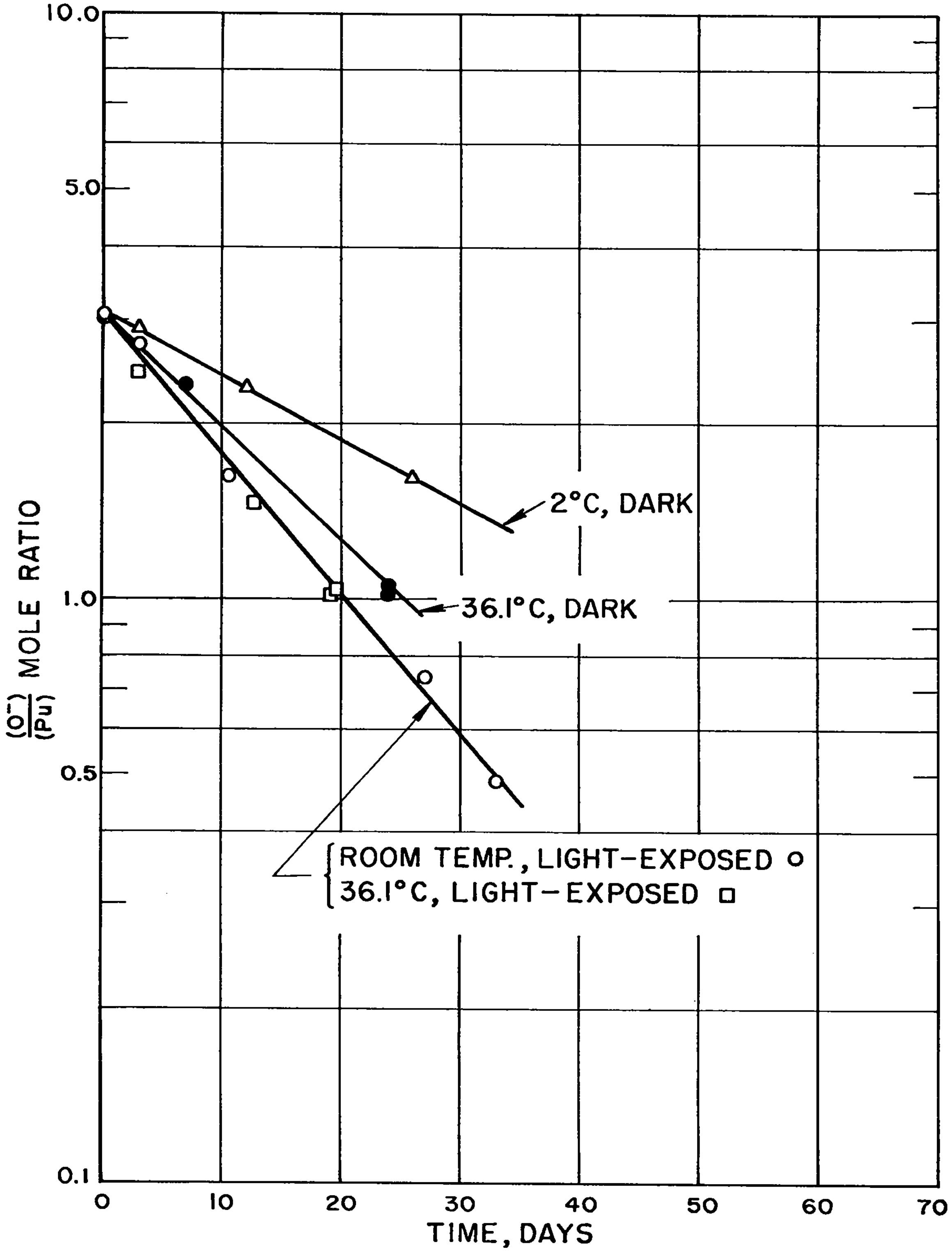

Fig. 3.2 Rates of decomposition of cubic plutonium peroxide

The value of k may be computed for each temperature from the half-time for the decomposition:

$$k = \frac{0.693}{t_{1/2}} \qquad (3.3)$$

If this decomposition is first order over the temperature range indicated, then the activation energy $E_a$ and the frequency factor A can be computed from the Arrhenius equation:

$$k = Ae^{-E_a/RT} \qquad (3.4)$$

Using the "dark" decomposition rate data of Fig. 3.2, $E_a$ was calculated to be 3000 cal/mole and A = 7500 per minute.

The higher values for the $(O^-)$ to Pu ratio reported in Sect. 2.2.2 for the wet hexagonal structure suggest that perhaps this form initially has a ratio of 4, and that the first equivalent decomposes rapidly. A portion of wet Preparation 26 was washed thoroughly and allowed to stand in moist condition for 2 hours. Samples of this precipitate were analyzed every 20 minutes for $(O^-)$ to Pu ratio. There was no indication of any decomposition. The average ratio for the six samples analyzed was 3.47 ± 0.04.

During the auto-decomposition of hydrogen peroxide one atom of oxygen is released for each O-O bond broken. The following experiment was done to see if plutonium peroxide followed the same stoichiometry:

A weighed amount (~ 600 mg) of dry plutonium peroxide was placed in a sealed flask in a constant temperature bath. The volume of the flask had been determined by filling with water and weighing. The gas pressure over the sample was measured by means of a capillary manometer. A drop of water had been added to the flask to keep the water vapor pressure constant during peroxide decomposition.* (The water did not come in contact with the peroxide powder.) From the gas temperature, pressure increase, and volume, the amount of $O_2$ liberated was calculated using the equation of state for an ideal gas.

Portions of the peroxide were also analyzed for $(O^{=})$ to Pu ratio before and after decomposition. By comparing this decomposition with the amount of $O_2$ liberated, the number of oxygen atoms liberated per peroxy-oxygen bond broken was computed.

The values obtained (0.96 for the cubic form at 67 per cent decomposition and 0.98 for the hexagonal form at 90 per cent decomposition) indicate that the plutonium peroxide decomposition stoichiometry is the same as that for $H_2O_2$.

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* Plutonium peroxide is known to be hydrated, but the decomposition product ($PuO_2$) is not.

## 4. Infrared Absorption Spectra of Solid Plutonium Peroxides

The differences in decomposition rates between the two structures suggested that there may be differences in peroxy-oxygen to Pu bonding. Therefore, several samples were submitted to L. H. Jones of LASL Group CMR-4 for analysis by absorption spectrum in the infrared region. Samples were mounted in KBr as thin windows and examined with a Perkins-Elmer recording spectrophotometer. The following differences were observed between the cubic and the hexagonal forms.

The cubic structure has an absorption band at $\tilde{\nu} = 834 \pm 1\ \text{cm}^{-1}$. The hexagonal structure absorbs sharply at $\tilde{\nu} = 861\ \text{cm}^{-1}$. There is an additional absorption band at $\tilde{\nu} = 2953\ \text{cm}^{-1}$ in the hexagonal form. (Solid $H_2O_2$ absorbs at $\tilde{\nu} = 881\ \text{cm}^{-1}$ due to the O-O vibration, and at $\tilde{\nu} = 2843\ \text{cm}^{-1}$ due to the O-H vibration.)

From the above results there is no evidence of the (O-O-H) form of peroxide in the cubic structure.

If the hydrogen in $H_2O_2$ is replaced by deuterium, the O-O band is shifted to $\tilde{\nu} = 879\ \text{cm}^{-1}$ and the O-D band is shifted to $2120\ \text{cm}^{-1}$. A special cubic preparation was made in a deuterium medium, using $D_2O_2$ as the precipitant. The isotopic abundance of the deuterium in the precipitation medium was 84 per cent. Presumably a small but measurable shift in the characteristic frequency should have been observed if (-OOH) had been present. Since none was observed, it was assumed that all of the peroxide is present in the -Pu-O-O-Pu form.

### 5. Densities of the Dry Precipitates

The bulk density of the settled hexagonal structure appears to be much less than that of the cubic structure. Bulk densities of the dry powders were determined by tamping a weighed amount of the ground powder to constant volume. For the hexagonal form, the bulk density was 0.79 g/cc; for the cubic form this density was 1.53 g/cc.

Apparent densities were also determined by measuring the weight of 0.01M $H_2SO_4$ solution displaced by a weighed sample of powder in a pycnometer. From the density of the $H_2SO_4$ solution, the volume of powder was calculated and used to compute the apparent particle density. This value was 3.43 g/cc for the hexagonal form and 3.71 g/cc for the cubic form.

## 6. Solubilities

It is not possible to determine equilibrium solubilities in water due to the formation of plutonium polymer at low acidity. The supernatant liquids from various preparations were sampled for plutonium content. These values, shown in Table 6.1, are not strictly comparable because of differences in the $H_2O_2$ complexing, etc. They represent only the "apparent" solubilities. In general, the solubility increases very rapidly with increasing acidity due to the mass action effect.

Table 6.1

APPARENT SOLUBILITIES OF VARIOUS PLUTONIUM PEROXIDES

| Preparation No. (See Table 1.1) | "Solubility" at Room Temperature mg Pu/liter |
|---|---|
| 9 | 6.0 |
| 21 | 40.0 |
| 25 | 32.0 |
| 26 | 266.0 |

## 7. Colloidal Nature of the Cubic Structure

In the absence of sulfate, the cubic structure peptizes very readily when washed with 0.01M HCl or alcohol. However, if the samples are washed with either 0.01M $H_2SO_4$ or sodium malonate solution, the precipitate remains in a coagulated state. This indicates that the cubic structure is a positive-charged colloid.

In order to study this colloidal behavior, a simple manometric electrophoresis cell was used in the standard manner.[5] The compositions of the colloidal peroxide solutions and their relative mobilities are shown in Table 7.1. All measurements were made at a potential gradient of 2.5 volts/cm, and the interface migration was checked by a Tyndall cone. Considering the apparatus and the slight temperature variations during these tests, the mobilities reported are only relative and approximate. In all tests the colloid migrated towards the cathode.

The qualitative appearance of these colloidal solutions is also indicated in Table 7.1.

As a coagulant, sulfate appears to be several hundred times as effective as perchlorate, based on the amount required to reduce the mobility from $6.6 \times 10^{-4}$ to $3.6 \times 10^{-4}$ cm/sec. The relative effectiveness

Table 7.1

COLLOIDAL SOLUTIONS USED FOR ELECTROPHORESIS TESTS

| Test | (Pu) M | (H+) M | ($H_2O_2$) M | ($ClO_4^-$) M | ($SO_4^=$) M x $10^{-4}$ | Relative Mobility, cm/sec x $10^4$ | Qualitative Appearance of Colloidal Test Solutions |
|---|---|---|---|---|---|---|---|
| 1 | 0.235 | 0.39 | 1.00 | 0.41 | 0 | 6.6 | Clear green solution; Tyndall cone slight |
| 2 | 0.235 | 0.39 | 1.00 | 0.84 | 0 | 4.5 | Translucent colloidal solution; Tyndall cone very pronounced |
| 3 | 0.235 | 0.39 | 1.00 | 1.50 | 0 | 1.2 | Opaque |
| 4 | 0.235 | 0.39 | 1.00 | 0.41 | 1.5 | 3.6 | Clear green solution; Tyndall cone slight |

No settling of colloids 1, 2, or 3 within 24 hours.

No settling of colloid 4 within 5 hours.

## 8. Discussion

In the case of cubic plutonium peroxide, only three-fourths of the plutonium(IV) valence is taken up by peroxide oxygen. Consequently, the remaining one-fourth must be satisfied by one equivalent of either oxide, hydroxide, or the anion of the acid system from which the peroxide was precipitated. However, the analyses indicate that much less than an equivalent of either sulfate, chloride, or perchlorate is associated with 1 mole of plutonium in the precipitate. In view of the colloidal nature of the cubic structure, these anions probably are present in an absorbed state. From the infrared absorption spectra it would appear that this structure has the empirical formula $Pu_2(O^-)_6(O^=)\cdot xH_2O$. Such a compound could be formed by linking plutonium(IV) dimers such as $PuOPu^{+6}$ with peroxide groups to give the structure as shown in Fig. 8.1. This would be consistent with the observed peroxy-oxygen to Pu ratio of 3.

Although the existence of such plutonium dimers has not been investigated, evidence for dimeric forms of cerium(IV) is abundant.[7,8] Heidt and Smith[8] have calculated that approximately 40 per cent of the ceric-ions in 1M $HClO_4$ are dimerized by the following mechanisms:

$$Ce^{+4} + H_2O = Ce(OH)^{+3} + H^+ \qquad (8.1)$$

$$Ce(OH)^{+3} + H_2O = Ce(OH)_2^{+2} + H^+ \qquad (8.2)$$

$$2Ce(OH)^{+3} = CeOCe^{+6} + H_2O \qquad (8.3)$$

$$2Ce(OH)_2^{+2} = (HO)CeOCe(OH)^{+4} + H_2O \qquad (8.4)$$

$$Ce(OH)^{+3} + Ce(OH)_2^{+2} = (HO)CeOCe^{+5} + H_2O \qquad (8.5)$$

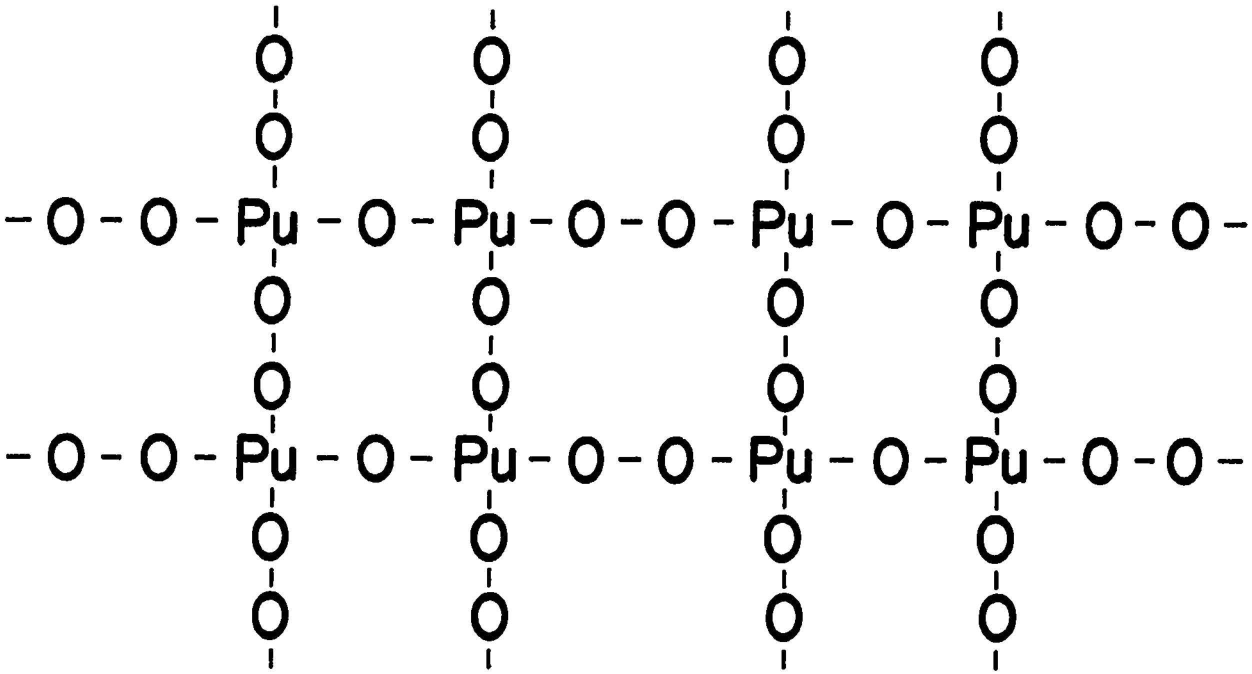

Fig. 8.1 Possible $(Pu)_2(O^-)_6(O^=)$ Structure

Similar species are probably present in acid solutions of tetravalent plutonium. Plutonium (IV) is known to form a stable colloidal polymer in solutions that are less than 0.3M in total acidity.[9] The initial stages of polymerization probably involve the formation of dimers by reactions similar to those given above.

At low acidity the cubic structure is formed in preference to the hexagonal structure, as would be expected from the above considerations.

The composition and structure of the hexagonal peroxide is consistent with the results of Hamaker and Koch.[4] Their results were obtained on dried samples after partial decomposition of the peroxide-oxygen. Moreover, the samples were frequently mixtures of the two structures.

Although the hexagonal form contains a minimum peroxy-oxygen to Pu ratio of 3.0, normally there is a greater amount of peroxide-oxygen associated with this form than with the cubic form. In addition the hexagonal structure contains considerably more sulfate when precipitated from sulfate solution, and more chloride when precipitated from HCl. This is reasonable if the hexagonal sheets are held together by various anions such as $SO_4^=$, $HSO_4^-$, $Cl^-$, $O_2^=$, $OOH^-$, etc., as proposed. The differences in decomposition rates and in absorption spectra further indicate a difference in the type of peroxide bonding on these two structures.

# APPENDIX A

## PEROXIDE-OXYGEN TO PLUTONIUM RATIO DETERMINATION

Peroxide-oxygen to Pu ratio in precipitates was determined by two methods.

### A.1 By Reduction with Iodide

Approximately 100-mg samples of the precipitate were dissolved in duplicate in 25 ml of solution that was 3M in $HClO_4$ and contained ~ 2 grams of NaI. After a period of 2 hours at room temperature the $I_2$ that had been liberated was determined by titrating with 0.1N $Na_2S_2O_3$ solution to the starch endpoint. (The $Na_2S_2O_3$ solution had been standardized against $KIO_3$, Merck A. R.) Spectrophotometric examination of this solution indicated that all of the plutonium was in the tripositive oxidation state at this endpoint.

The titrated solution was then diluted to the mark in a 50-ml volumetric flask and the plutonium concentration was determined by radio-assay. Radio-assays were done by the dilution-evaporation method by LASL Group CMR-1.

From the total plutonium in the sample, it was then possible to calculate the $I_2$ liberated by the reduction of plutonium(IV) to (III). This amount of $I_2$ was subtracted from the total amount determined to give the $I_2$ liberated by peroxy-oxygen.

In order to keep the $I_2$ blank to 1 drop of $Na_2S_2O_3$ solution, the $HClO_4$ solution was flushed with argon for 30 minutes prior to dissolution of the NaI and peroxide sample. The sample was then stored in the dark and titrated under an argon atmosphere.

This procedure was checked by adding known amounts of $PuO_2^{++}$ and $H_2O_2$ solutions to acid iodide. The plutonium had been determined by electrometric titration to within ±0.3 per cent. As shown in Table A.1, the $(O^-)$ to Pu mole ratio, and the main source of error in the $(O^-)$ to Pu ratio, was the radio-assay.

Table A.1

PEROXIDE-OXYGEN TO PLUTONIUM RATIO DETERMINATION

| | Added | Found | Per Cent Error |
|---|---|---|---|
| Plutonium(VI), millimole | 0.368 | 0.362 | -2.2 |
| $I_2$ liberated, millequivalent | 2.015 | 2.014 | <0.1 |
| $I_2$ from Pu, millequivalent | 1.104 | 1.086 | - |
| $I_2$ from $(O^-)$, millequivalent | 0.911 | 0.928 | +1.9 |
| Calculated $(O^-)$ to Pu mole ratio | 2.48 | 2.56 | +3.2 |

## A.2 By Oxidation with $Ce(SO_4)_2$

Duplicate samples of precipitate (~100 mg each) were dissolved in 30.00 ml of 0.1N $Ce(SO_4)_2$ solution that had been standardized against $As_2O_3$ (Mallinckrodt, A. R.). After a period of 2 hours the excess $Ce(SO_4)_2$ was determined by back-titrating to the o-phenanthroline, ferrous sulfate endpoint with freshly standardized 0.1N $H_2O_2$ solution. This titrated solution was examined spectrophotometrically; all of the plutonium was in the hexapositive oxidation state at this endpoint. After titration the sample was diluted to 50.00 ml and the plutonium was determined by radio-assay. The $(O^-)$ to Pu ratio was then calculated from the amount of $Ce(SO_4)_2$ consumed by the precipitate and the total amount of plutonium in the sample.

# APPENDIX B

## SULFATE TO PLUTONIUM RATIO DETERMINATION

Approximately 800 mg of sample was dissolved in duplicate in 10 ml of 2.8N HI. The solution was then filtered on Whatman No. 42 paper and the excess $I_2$ was removed from the filtrate by extraction with benzene. After diluting to 150 ml, $BaSO_4$ was precipitated at 80°C by adding 0.2M $BaCl_2$ solution dropwise with vigorous stirring. This slurry was then digested for 1 hour at 80°C and then overnight at room temperature prior to filtering on Whatman No. 42 paper. After washing ten times with water, the sample was ignited to constant weight at 800°C. From the gravimetric factor the total sulfate present in the sample was then calculated.

The plutonium was determined by diluting the $BaSO_4$ filtrate to 200.0 ml and removing an aliquot for radio-assay.

This procedure was checked by adding known amounts of plutonium and $H_2SO_4$ to an HI solution. As shown in Table B.1 the analysis was satisfactory.

## Table B.1

## SULFATE TO PLUTONIUM RATIO DETERMINATION

| Sample No. | Determination | Added | Found |
|---|---|---|---|
| 1 | Sulfate, mg | 23.51 | 23.4 |
|  | Pu, mg | 578 | 577 |
|  | $SO_4^=$ to Pu mole ratio | 0.101 | 0.101 |
| 2 | Sulfate, mg | 47.02 | 46.9 |
|  | Pu, mg | 289 | 290 |
|  | $SO_4^=$ to Pu mole ratio | 0.405 | 0.403 |

## APPENDIX C

## PERCHLORATE TO PLUTONIUM RATIO DETERMINATION

The determination of perchlorate in the precipitates was done by the LASL Analytical Group, CMR-1.

In general the method consisted of dissolving ~800 mg of the precipitate in $H_2SO_4$ and adjusting the acidity to 3M. Plutonium was determined from an aliquot of this solution by radio-assay. A second aliquot was reduced with Devard's metal (Al, Cu, and Zn) and the acidity was adjusted. The perchlorate was precipitated with nitron reagent and digested for 24 hours. The precipitate was filtered, washed, dried at 105°C, and weighed as nitron perchlorate.

This procedure was checked with known amounts of $HClO_4$ and $Pu(SO_4)_2$ in $H_2SO_4$. As shown in Table C.1 the results were probably sufficiently accurate.

Table C.1

## PERCHLORATE TO PLUTONIUM RATIO DETERMINATION

| Sample No. | Determination | Added | Found |
|---|---|---|---|
| 1 | Perchlorate, mg | 1.19 | 1.05 |
| | Pu, mg | 9.60 | 9.53 |
| | $ClO_4$ to Pu mole ratio | 0.298 | 0.264 |
| 2 | Perchlorate, mg | 2.40 | 2.37 |
| | Pu, mg | 4.80 | 4.81 |
| | $ClO_4$ to Pu mole ratio | 1.20 | 1.18 |

# APPENDIX D

## CHLORIDE TO PLUTONIUM RATIO DETERMINATION

The determination of chloride in the precipitate was done by the LASL Analytical Group, CMR-1.

Chloride was determined by dissolving ~800 mg of precipitate in 8M $HNO_3$, diluting to a known volume, and removing aliquots for chloride determination by the gravimetric AgCl method. The plutonium concentration was determined by radio-assay.

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