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SECTION C-I

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COMPOSITION AND THERMAL DECOMPOSITION OF URANYL PEROXIDE

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Studies have been made on the composition and thermal decomposition of uranyl peroxide. The conditions of precipitation and drying have been found to have no appreciable effect on the composition of the compound, but do affect the physical appearance of the precipitate and the rate of thermal decomposition. The $UO_4 \cdot 2H_2O$ appears to be thermodynamically unstable with respect to UO_3 at 25°C and atmospheric pressure, although the rate of conversion is extremely slow. The $UO_4 \cdot 2H_2O$ is completely converted to UO_3 on standing at 150°C and atmospheric pressure for two weeks. Partially decomposed uranyl peroxide samples contain "extra" oxygen which is released on immersing the sample in water.

I. INTRODUCTION

The composition and thermal behavior of uranyl peroxide are a subject of some debate in the literature. When the compound is precipitated from a solution containing excess hydrogen peroxide, the mol ratio of peroxide oxygen* to uranium is reported to be about two.[1][2][3][4] When, however, the compound is precipitated from a solution containing excess uranium, the ratio is reported to decrease to approximately 1.5.[3] The mol ratio of water to uranium has been reported as 4.5, 3.0, and 2.0.[2][3][4][5][6] Heating the compound causes loss of water and oxygen, but different experimenters do not agree on the compounds obtained in the decomposition. One explanation for the decomposition curves obtained assumes the formation of several compounds and solid solutions with compositions in the range between $UO_4 \cdot 4.5H_2O$ and UO_3.[2][4][6]

*Peroxide oxygen is defined as having an oxidation number of -1; i.e., hydrogen peroxide contains two peroxide oxygens.

To resolve some of these discrepancies, and to extend the understanding of uranyl peroxide, an investigation of its composition and thermal decomposition was initiated. The conditions of preparation and drying of the uranyl peroxide precipitate were varied over wide limits to ascertain their effect on the composition. The effects of reduced pressures and increased temperatures were studied to detect differences between samples prepared in different ways, and to clarify the thermal behavior of the compound.

II. EFFECT OF CONDITIONS OF PREPARATION ON THE CHEMICAL AND PHYSICAL PROPERTIES OF URANYL PEROXIDE

A. Preparation of Samples

All the samples were prepared by adding hydrogen peroxide to the uranyl solution** and separating the resulting precipitate after the designated digestion period by filtration through a Büchner funnel. The samples were then washed 10 times with large volumes of distilled water. In some cases "wet" samples were removed at this point, but in most cases the samples were dried before analysis and further experimentation.

**Pure uranyl nitrate and uranyl sulfate solutions were prepared from Mallinkrodt uranyl nitrate by fractional crystallization in the case of the nitrate, and conversion followed by fractional crystallization in the case of the sulfate. Spectrographic assay indicated insignificant amounts of extraneous materials.

The specific conditions of precipitation and drying for each individual sample are shown in Table 1. The difference in molar concentration

between H_2O_2 and uranium is shown in column 2, a positive sign indicating an excess of hydrogen peroxide over a 1:1 mol ratio and a negative sign indicating a deficiency. The total uranium concentration after all reagents had been added is shown in column 6; it includes all uranium present either in solution or as a precipitate after the addition of the hydrogen peroxide. The uranium was added either as the sulfate or the nitrate, the corresponding acid (H_2SO_4 or HNO_3) being used to adjust the acidity in each case. The hydrogen ion concentration after precipitation, which includes both the initial acid added and the H^+ liberated in the reaction

$$UO_2^{++} + H_2O_2 \longrightarrow UO_4 + 2H^+ \quad , \qquad (1)$$

is shown in column 4. The hydrogen ion concentration was measured in all cases in which the pH was greater than one, and calculated in the remaining cases. (In experiment 16, ammonium hydroxide was added, together with the hydrogen peroxide, to keep the pH at ca. 2.) The digestion time, shown in column 7, was measured from the time of addition of the hydrogen peroxide to the beginning of the filtration.

In experiments 14 and 17, 3% H_2O_2 at 25°C was added to an equal volume of uranyl nitrate solution containing 100 grams of uranium per liter at 70°C. The total uranium concentration during digestion was 50 grams per liter and the temperature about 50°C. In all other cases, a 30% solution of hydrogen peroxide was added.

The drying conditions are summarized in the last four columns of the table. Before placing the sample in the desiccator or oven, the wet precipitate was broken up and spread in a thin layer over a large area. After being dried as indicated, the samples were placed in weighing bottles which were kept at room temperature inside desiccators containing calcium sulfate as drying agent. As discussed in the following sections, no deviation in results was noted as a function of time of standing after drying.

B. Physical Characteristics

The physical appearance of the precipitates appeared to be a function of the anion present at the time of precipitation. Those precipitates formed in sulfate solutions were fluffy and light yellow after drying; those formed in nitrate solutions were coarse and a deep yellow. It was further noted that the precipitates formed in sulfate solution appeared to dissolve in sulfuric acid less readily than those formed in nitrate solution.

Microscopic examinations were made by slurrying the precipitates in glycerine and observing them under a magnification of ca. 210. In most cases the precipitates were too small (1-3 microns in diameter) to allow detailed observations. The surfaces were shiny, however, giving a crystalline appearance. In two samples (experiments 3 and 7), some fairly large needles were observed, the largest in each case having the dimensions of 30 microns x 4 microns x 4 microns.

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Table 1

Conditions of Preparation of Uranyl Peroxide Samples

Expt. No. (1)	Conditions of Precipitation: Conc. H_2O_2 in Excess After Precipitation in Moles/Liter (2)	Anion of Salt and Acid Used (3)	Hydrogen Ion Conc. After Precipitation Moles/Liter (4)	Temp. °C (5)	Total Uranium Conc. Grams/Liter (6)	Digestion Time in Hours (7)	Conditions of Drying: Temp. °C (8)	Pressure Cm. of Hg (9)	Drying Agent (10)	Time in Days (11)
1	+0.46	$SO_4^=$	1.25	25	10	(a)	25	76	$CaSO_4$	20
2	+0.08	"	1.8	"	100	"	"	20	"	"
3	+0.44	"	1.12	"	15	"	"	"	"	"
4	+0.08	"	0.84	"	100	"	"	"	"	"
5	+0.44	"	0.12	"	15	"	"	"	"	"
6	+0.10	NO_3^-	1.8	"	95	"	"	"	"	"
7	+0.44	"	1.1	"	15	"	"	"	"	"
8	+0.10	"	0.8	"	95	"	"	"	"	"
9	+0.44	"	0.13	"	15	"	"	"	"	"
10	+0.48	"	0.04	"	5	"	"	6	"	7
11	+0.44	"	0.13	"	15	"	"	"	"	"
12	+0.14	"	0.13	"	15	"	"	"	"	"
13	-0.35	"	0.13	"	100	"	"	"	"	"
14	+0.23	"	0.8	70(b)	50(b)	0.3	64	76	None	1.5
15	-0.05	"	0.13	"	25	3	"	"	"	2
16	+0.40	"	0.0[illegible]	25	25	4	25	6	H_2SO_4	7
17	+0.23	"	0.8	70(b)	50(b)	0.3	"	"	$CaSO_4$	100
18	-0.10	NO_3^-	0.1	90	50	4(c)	--(d)	--	--	--(e)
19	-0.10	"	"	90	50	4(c)	25-35(e)	76	None	2
20	-0.10	"	"	90	50	4(c)	65	"	"	2
21	-0.10	"	"	90	50	4(c)	25	76	"	6

(a) Stirred ½ hour, then allowed to stand for 12 hours.
(b) To the solution containing 100 grams of uranium per liter at 70°C was added an equal volume of 3% H_2O_2 at 25°C.
(c) Original precipitation at 90°C. Stirred 4 hours while cooling to 35°C.
(d) Analyzed as moist solid.
(e) 22 hours at 25°C and 22 hours at 35°C.

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C. Peroxide Oxygen to Uranium Ratio

Two procedures were used for the titration of peroxide oxygen in the compound. (1) In the case of precipitates which dissolved readily in 5 N sulfuric acid, separate aliquots of the solution were removed for uranium and peroxide analysis. Uranium was determined, using the method of Kolthoff and Lingane.[7] The results obtained on a standard uranyl sulfate solution were reproducible to within one-half per cent. The hydrogen peroxide in another aliquot of the same sulfuric acid solution was determined by direct titration with standard potassium permanganate solution. (2) In the case of precipitates which were not readily soluble in 5 N sulfuric acid, the sample was dissolved in a known excess of standard potassium permanganate solution which was 2 N in sulfuric acid. Sodium oxalate was added to this solution in slight excess, and it was back-titrated with potassium permanganate at 55°C. From these data the peroxide content could be calculated. The solution was then evaporated to a convenient volume and assayed for uranium, using the previously mentioned method of Kolthoff and Lingane. The results for uranium and hydrogen peroxide were reproducible to within approximately one-half per cent.

The results of the analyses of the dried samples are shown in Table 2. The data for the "wet samples", taken after washing and before drying, are not listed but are within experimental error of the results for the dried samples. The maximum deviation from a value of 2.00 is two per cent. Uranyl peroxide, therefore, contains two peroxide oxygens per uranium, and this quantity is not affected by the conditions of drying or precipitation used in these experiments. Only 9 of the samples were specifically titrated for peroxide oxygen, since the consistency of the ratio of total oxygen to uranium obtained by gas analysis made further titrations superfluous.

Table 2

Ratio of Peroxide Oxygens to Uranium in Uranyl Peroxide

Experiment Number	Ratio of Peroxide Oxygens to Uranium	Experiment Number	Ratio of Peroxide Oxygens to Uranium
1	2.01	6	1.99
2	2.02	8	1.96
3	2.01	9	2.04
4	2.02	10	2.04
5	2.02		

D. Sulfate to Uranium Ratio

Sulfate analyses were performed, using a modification of the procedure of Hoffpauir and Guthrie.[8] When used with known comparable amounts

of sulfate and uranium, the ratio obtained was found to be within two per cent of the calculated value.

The compounds prepared in experiments 2-5 inclusive were analyzed and found to contain less than 1 mole of sulfate per four hundred moles of uranium.

E. Nitrate to Uranium Ratio

The absence of nitrate was determined by the lack of nitric oxide color in the gases liberated on ignition of a dried sample. One-half gram of sample was ignited to ca. 700°C and the escaping gases compressed in a Toepler pump. It was found with known mixtures that an amount of nitrate equivalent to 1 mole of nitrate per 100 moles of uranium gave a very noticeable color and oxidized the mercury in the Toepler pump appreciably.

All samples prepared from uranyl nitrate solutions were examined in this manner, and no nitric oxide color or appreciable oxidation of mercury was noted in any case. It is, therefore, concluded that the uranyl peroxide precipitated from nitrate solutions contained less than 1 nitrate per 100 uranium atoms.

F. Total Oxygen to Uranium Ratio

The total oxygen to uranium ratio was determined by ignition of the precipitates to U_3O_8, followed by measurement of the evolved oxygen. This method gave an exceedingly accurate determination of this ratio.

The procedure was as follows: Approximately 0.6 grams of the dried sample to be analyzed was weighed into a platinum boat. The boat was then inserted into a quartz tube which was connected to the gas analysis apparatus, and the entire system was evacuated to approximately 10^{-3} mm of mercury with a mercury diffusion pump. The quartz tube containing the sample was then heated to 700-725°C for 1½ hours, the final oxygen pressure corresponding to approximately 40 mm of mercury. After cooling the sample below 200°, the evolved oxygen was transferred quantitatively by means of a Toepler pump into a calibrated bulb where its pressure was measured with a manometer. The water evolved during the ignition was trapped and measured separately (cf. Section G).

The temperature of ignition in this procedure was chosen on the basis of the decomposition curve shown in Figure 1 and described in Part III. This curve was obtained using the same procedure as outlined above except that the temperature of ignition was varied. The plateau which occurred above 700°C indicated that the temperature 725°C would give quantitative conversion to U_3O_8.

Since Tanford and Larson had indicated that after ignition at 875°C the final product was not always U_3O_8,* an experiment was run to verify the

*On ignition to 875°C in the presence of atmospheric oxygen, Tanford and Larson[9] converted the $UO_{2.667}$, i.e., U_3O_8, to $UO_{2.63}$ which was only partially reoxidized (to $UO_{2.65}$) on cooling slowly from this temperature to 25°C.

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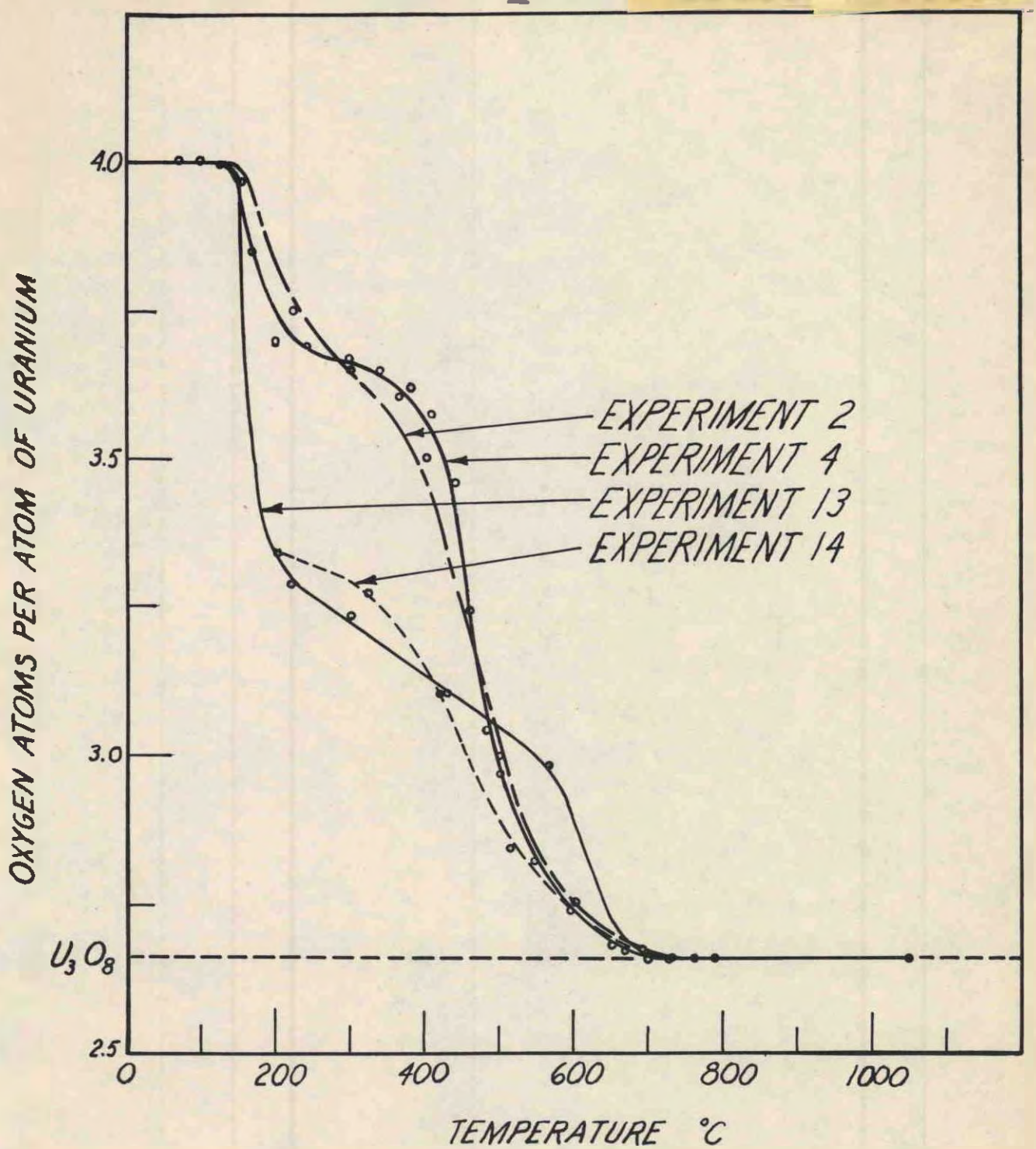

FIG. 1 THERMAL DECOMPOSITION OF URANYL PEROXIDE AS A RESULT OF IGNITION FOR 1¼ HOURS

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plateau obtained in Figure 1. A 0.6 gram sample of $UO_4 \cdot 2H_2O$ was treated according to the standard procedure outlined above except that the temperature of ignition was varied. The sample was first heated to 680°C, then cooled below 200°, and the evolved oxygen measured as described above. The procedure was then repeated at 725°C and 1050°C. The volume of oxygen was the same in all three cases, proving that the final cooled product after ignition at 1050°C was the same as the final product after ignition at 680°C and 725°C. The compound at 1050°C undoubtedly contains a lower oxygen to uranium ratio than U_3O_8, but it regains oxygen on cooling.

To check this, the sample was again ignited to 1050°C, at which temperature the oxygen was transferred to the calibrated bulb with the Toepler pump. The volume of oxygen measured showed that the oxygen to uranium ratio in the solid was less than 2.621. The oxygen was then allowed to diffuse back over the sample, and the system cooled to less than 200°C. Measurement of the oxygen at this temperature showed that the compound had regained oxygen and was again U_3O_8, i.e., $UO_{2.667}$.

It is clear, therefore, that the same final cooled product is obtained after ignition for 1¼ hours in the presence of oxygen at any temperature above 700°C. It was then necessary to prove that this ignition product was $U_3O_{8.00}$. This was done by S. W. Rasmussen on the sample described above which had been ignited to 1050°C and cooled in the presence of oxygen. The U(IV) to total uranium ratio in this sample was determined by dissolving the solid in ceric sulfate solution and back-titrating with ferrous ammonium nitrate, using ortho-phenanthroline indicator. In quadruplicate runs he obtained values of $U_3O_{8.00}$, $U_3O_{8.02}$, $U_3O_{8.03}$, and $U_3O_{8.00}$.[10] This gives a mean oxygen to uranium ratio of 8.01 with a standard deviation of ± 0.02. This measurement gives independent evidence that the final ignition product is $U_3O_{8.00}$ within experimental error.

Having established the formula of the ignition product, the reproducibility of the method of analysis was checked by making identical runs on four different portions of the same dried uranyl peroxide precipitate.* The

*Experiment 4, Table 1.

formulas for the peroxide, assuming the final ignition product was $U_3O_{8.000}$, were $UO_{3.994}$, $UO_{3.994}$, $UO_{3.995}$, $UO_{3.996}$.

The results obtained by analyzing the uranyl peroxide samples, prepared as described in Table 1, are summarized in Table 3. None of the twenty compounds prepared under widely varied conditions show a mol ratio of oxygen to uranium which deviates from the value of 4.000 by more than 0.017. The experimentally observed precision as shown by the standard deviation is ± 0.006. In contradiction to the work of Sieverts and Muller,[3] the oxygen to uranium ratio does not decrease when uranium is in excess at the time of precipitation. This was true even though the hydrogen peroxide solution was added to the uranium solution, giving conditions which would favor the formation of a compound with a low peroxide oxygen content. Precipitates dried for two days at 65°C also had the same atomic ratio of oxygen to uranium as those which

were analyzed while still moist. Thus, the atomic ratio of oxygen to uranium in uranyl peroxide is not affected by wide variations in the method of preparation of the compound.

The accuracy of the atomic oxygen to uranium ratio can be estimated from the estimated accuracies of the individual measurements, i.e., temperature, pressure, etc. This gives a value for the ratio of 4.00 ± 0.02.

Table 3

Oxygen to Uranium Ratio in Uranyl Peroxide Samples

Experiment Number	Oxygen to Uranium Ratio	Experiment Number	Oxygen to Uranium Ratio
2	4.00_2	12	4.00_3
3	3.99_8	13	3.99_4
4	3.99_5	14	3.98_3
5	3.99_7	15	3.99_6
6	4.00_3	16	4.00_2
7	3.99_4	17	3.99_9 (a)
8	4.00_9	18	3.99 (a)
9	3.98_9	19	3.99_9 (a)
10	3.99_7	20	3.99_8
11	3.99_9	21	3.99

(a) Samples analyzed moist (cf. Table 5).

G. Analysis for Water

The amount of water present was determined simultaneously with the total oxygen (cf. Section F) by trapping and weighing the water evolved on ignition of the sample. To do this, the gas analysis apparatus was fitted with a small U-tube of approximately 4 millimeters bore, which was immersed in liquid nitrogen. After the ignition was complete, one end of this U-tube was disconnected from the line and connected to a small weighed pyrex tube. The water in the U-tube was then distilled into the weighed tube and weighed with a precision of 1 per cent. To check the reproducibility of the method, four aliquots from one of the precipitates* were analyzed in this manner,

*Experiment 4, Table 1.

giving the following ratios for water to uranium: 2.14, 2.18, 2.10, and 2.13. Both the precision and estimated accuracy of the method appear to be ± 0.04.

A summary of the mol ratios of water to uranium is shown in Table 4. Except for the two samples which were deliberately analyzed while moist, the mol ratio of water to uranium was approximately two in spite of the widely varied drying conditions, itemized in Table 1. The values of 3.0 and 4.5

obtained by other investigators[2][4][6] were probably the result of insufficient drying. It was noticed that unless the samples were pulverized or spread in thin layers, only the surface would dry, leaving a moist center. For example, a large lump in one experiment had a moist center after 16 hours at 65°C. These experiments agree with the values of Biltz who obtained mol ratios of 2.0 by drying his precipitates with acetone or liquid ammonia.[5] The ratios are in general slightly greater than two, a result which might be ascribed to experimental error. The difference, however, appears to be larger than the expected experimental error, and no systematic error in such a direction has been discovered.

Table 4

Water to Uranium Ratio in Uranyl Peroxide Samples

Experiment Number	Water to Uranium Ratio	Experiment Number	Water to Uranium Ratio
2	2.0_7	12	2.3_7
3	2.0_8	13	2.0_8
4	2.1_4	14	2.0_4
5	2.0_7	15	2.0_3
6	2.1_6	16	2.0_8
7	2.1_0	17	2.0_5
8	2.1_7	18	16.0 (a)
9	2.2_1	19	11.2_5 (a)
10	2.1_8	20	2.0_0
11	2.3_6	21	2.0_5

(a) Samples still moist.

H. Crystal Structure Data

A number of the uranyl peroxide samples were sent to Dr. W. H. Zachariasen who prepared and interpreted X-ray patterns of the compound. The results are shown in Table 5. The phase designated as alpha corresponds to an orthorhombic structure containing two molecules per unit cell, with $a_1 = 8.74 \pm 0.04$ Å, $a_2 = 6.50 \pm 0.03$ Å, and $a_3 = 4.21 \pm 0.02$ Å. The two uranium atoms are at (0, 0, 0) and ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$).[11] The X-ray patterns corresponding to the beta phase have not yet been interpreted. It was found, however, by Dr. Zachariasen that the beta phase changes over to the alpha phase on standing a few days.[12] Since the samples were not sent to Dr. Zachariasen immediately after preparation, it is impossible to conclude whether any correlation exists between conditions of preparation and crystal structure.

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Table 5

Crystal Structure of the Uranyl Peroxide Samples

Experiment Number	Crystal Structure
2	alpha
3	alpha
4	alpha
5	alpha
6	alpha
7	alpha
8	alpha
9	alpha
10	30% alpha, 70% beta
11	alpha
12	beta
13	beta

I. Effect of Reduced Pressure

Since it had been established that the variation in precipitation and drying conditions had no appreciable effect on the composition of the precipitate, it was of interest to compare the behaviors of the various precipitates upon standing under reduced pressures. Accordingly, portions of nine of the dried samples were allowed to stand at 25°C for 48 hours at a pressure of less than 10^{-5} mm of mercury. They were then analyzed for water and oxygen contents and samples again submitted to Dr. Zachariasen for X-ray examination. The observations are shown in Table 6.

The reduced pressures caused a change in color, a slight decrease in the oxygen to uranium ratio, a slight decrease in the water to uranium ratio, and a change to the alpha crystal structure in all cases in which the initial compound was wholly or partially beta.

Since it was known that the beta crystal structure changed to alpha on standing, portions of each of the original dried samples which had been standing at atmospheric pressure were analyzed simultaneously with the samples which had been kept at reduced pressures. The change recorded in Table 6 is the difference between these two samples. Thus, the conversion from the beta form to the alpha form appears to have been accelerated by the reduced pressures.

The decrease in the oxygen to uranium ratio was very small but observable. The sample prepared in the presence of excess uranium (experiment 13) gave a slightly larger decrease than the other samples, although the differences are very small. The decrease in the water to uranium ratio appeared

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to be correlated roughly with the amount of water originally in the sample. Thus the final water to uranium ratios in all the samples subjected to reduced pressures were approximately the same, the greater decreases occurring in the samples which contained more water initially. The final value for the ratio is again slightly greater than two, as mentioned in Section G.

The behavior of all samples on standing at reduced pressures was similar. Any effect of the conditions of preparation of the sample on this behavior is small if it exists.

Table 6

Effect of Standing at Reduced Pressures on the Uranyl Peroxide Samples

Expt. No.	Change in Color	Decrease in O/U Ratio	Decrease in H_2O to U Ratio	Final H_2O to U Ratio	Change in Crystal Structure
2	Darkened slightly	0.004	0.00	2.07	None (alpha)
5	" "	--	--	--	--
6	" "	--	--	--	--
10	Yellow to tan	0.005	0.14	2.04	30% alpha, 70% beta to 100% alpha
11	" " "	0.00	0.25	2.11	None (alpha)
12	" " "	0.005	0.26	2.11	beta to alpha
13	" " "	0.010	0.02	2.06	beta to alpha

J. Effect of Increased Temperature

A further test for differences between the samples was obtained by ignition at 300°C for 1½ hours. The procedure was essentially the same as that used in the analysis for total oxygen described in Section F above. The sample was placed in a quartz tube and the system evacuated to approximately 10^{-3} mm of mercury. The temperature was then raised to 300°C. After 1½ hours at this temperature, the system was cooled and the volume of the evolved oxygen measured with a Toepler pump. The water was caught in a U-tube cooled with liquid air and was measured as described in Section G above. The oxygen pressure over the sample before measurement was approximately 10 mm of mercury.

Since, as discussed in Part III, the values obtained in the thermal decomposition of uranyl peroxide are a function of the time of heating, a simple experiment was run to determine the reproducibility of the procedure and the effect of the particle size of the initial sample on the values obtained. Three portions of the dried precipitate prepared in experiment 14 were ignited at 300°C as described above. One portion was an average sample containing all particle sizes present. Another portion contained only those particles of smaller than 100 mesh size, and the third portion contained only

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those particles larger than 20 mesh. The results of the three ignitions are shown in Table 7. The method evidently gives very reproducible results which are not dependent (within limits) on the particle size of the sample ignited. These conclusions were confirmed in other experiments of a similar nature.

Table 7

Effect of Particle Size of the Initial Sample on the Composition of the Product Formed by Ignition of Uranyl Peroxide at 300°C

Particle Size	Oxygen to Uranium Ratio	Water to Uranium Ratio
Less than 100 mesh	3.319	0.12
Average sample	3.334	0.15
Greater than 20 mesh	3.309	0.12

The results of the ignitions of eleven of the samples are shown in Table 8. The water to uranium ratios are remarkably constant except for the value in experiment 17, which appears to be high. The oxygen to uranium ratios, however, vary appreciably in spite of the fact that the values for a particular preparation are reproducible. It is to be noted that all the samples prepared by addition of 30% hydrogen peroxide in excess have O/U ratios after ignition greater than 3.4 (experiments 2, 5, 7, 8, 9). Samples prepared from solutions containing excess uranium or by addition of 3% hydrogen peroxide have values less than 3.4 (experiments 13, 14, 17, 18, 19, 20). Thus, it appears as though there were some correlation between the rate of thermal decomposition and the method of preparation of the sample. This is discussed further in Part III.

Table 8

Effect of Ignition at 300°C

Experiment Number	Total Oxygen to Uranium Ratio	Water to Uranium Ratio
2	3.653	0.09
5	3.532	0.10
7	3.535	0.1
8	3.359	0.11
9	3.445	0.14
13	3.230	0.09
14	3.334	0.1
17	3.259	0.25
18	3.291	0.11
19	3.272	0.12
20	3.348	0.13

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III. THERMAL DECOMPOSITION OF URANYL PEROXIDE

It has been shown that uranyl peroxide can be quantitatively converted to U_3O_8 by ignition at temperatures above 700°C (cf. Section F, Part II). It has further been shown that a particular sample of uranyl peroxide can be decomposed reproducibly to a structure whose formula is intermediate between $UO_4 \cdot 2H_2O$ and UO_3, by ignition at 300°C for 1½ hours (cf. Section J, Part II). Hüttig and von Schroeder assumed a number of compounds of the type $UO_{3.5} \cdot 2H_2O$ to explain their curve on the thermal decomposition of uranyl peroxide. The anomalies in the values obtained by igniting differently prepared samples as well as a very rough thermodynamic calculation, however, indicated that a slow rate of reaction rather than an equilibrium was responsible for the intermediate compositions obtained.

The thermodynamic calculation was made to determine the ΔF for the reaction:

$$UO_4 \cdot 2H_2O = UO_3(s) + 2H_2O(g) + \tfrac{1}{2}O_2(g) \quad . \qquad (2)$$

The heats of formation and entropy values which are known for the substances in equation (2) are given in Table 9.

Table 9

Entropies and Heats of Formation at 25°C

Substance	heat of Formation kcal/mole	Entropy cal/°C/mole
$UO_4 \cdot 2H_2O$ (s)	-426 (13)	--
UO_3 (s)	-291 (14)	23.5 (14)
H_2O (g)	- 57.8 (15)	45 (16)
O_2 (g)	0	50 (16)

It is seen that the ΔF^o of the reaction could be calculated if the entropy of $UO_4 \cdot 2H_2O$ was known. An approximation for this quantity was obtained in the following manner: The molar entropy of hydrates at 25°C can be approximated by adding 10 cal/°C to the entropy of the less hydrated form for each molecule of water added.(16) The entropy of UO_4 was calculated using Latimer's empirical approximation:(17)

$$S = \frac{3}{2} R \ln A_1 A_2 \ldots A_N - 0.94N \qquad (3)$$

where N is the number of atoms and A_N the atomic weight of atom N in the molecule. To this was added 20 cal/°C to give a value of 65 for $UO_4 \cdot 2H_2O$. The approximation may be quite inaccurate in this case but should, if anything, give a high value. Thus, the actual value of ΔF^o would probably be more negative than that calculated with these assumptions.

The ΔH^o_{298} of the reaction shown in equation (2) is 19 kcalories. The ΔS^o_{298}, using the assumptions stated above, is 74 cal/°C. Since $\Delta F = \Delta H - T\Delta S$, the ΔF^o for the reaction at 25°C is calculated to be -3 kcals. Furthermore, since $\Delta F^o = -RT \ln K_p$, the K_p for equation (2) can be shown to be approximately 150 (atmospheres$^{5/2}$).

The accuracy of the ΔF^o and K_p values is open to question in view of the assumptions for the entropy and possible errors in the ΔH of formation of $UO_4 \cdot 2H_2O$. It is probable, however, that $UO_4 \cdot 2H_2O$ is thermodynamically unstable with respect to UO_3 at 25°C and pressures of O_2 of the order of one atmosphere. The $UO_4 \cdot 2H_2O$ should, therefore, decompose completely to UO_3 unless intermediate compounds or solid solutions of greater stability exist. If the calculations are correct, the failure of the $UO_4 \cdot 2H_2O$ to decompose to UO_3 or to a well-defined intermediate state is a rate phenomenon.

To settle this question and to obtain a greater understanding of the thermal decomposition, the following experiment was performed: Portions of the uranyl peroxide prepared in experiment 14 (cf. Table 1) were placed in a pyrex tube open to the atmosphere. The temperature was maintained at the value shown in Table 10 by surrounding the tube with a reflux system in which an organic compound with the proper boiling point was heated. The temperature of the uranium compound was measured by placing a thermometer directly in the solid. Samples were removed at various times and analyzed for water, uranium, and oxygen as described in Section F of Part II. The results are shown in Table 10.

Table 10

Thermal Decomposition of Uranyl Peroxide at Atmospheric Pressure

Temp. °C	Total Oxygen to Uranium Ratio				Water to Uranium Ratio			
	After 1 Hour	After 6 Days	Longer Times		After 1 Hour	After 6 Days	Longer Times	
			Days	Ratio			Days	Ratio
98	--	--	12	3.92	--	--	12	1.93
150	3.824	3.215	14	2.99	1.08	0.25	--	--
178	3.350(a)	3.137	14	2.99	0.66(a)	0.20	--	--
230	3.201(b)	3.104	--	--	--	0.09	--	--
295	3.135	3.010	30	3.01	0.08	0.03	30	0.10

(a) Temperature for first hour was 192°C.
(b) Temperature for first hour was 240°C.

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It is apparent that $UO_4 \cdot 2H_2O$ is quantitatively converted to UO_3 at a temperature of 150°C and an oxygen pressure of 0.2 atmospheres. At lower temperatures the rate is less rapid, but even at 98°C the UO_4 is partially decomposed in 12 days. There appears to be no intermediate compound or solid solution which is more stable than UO_3 at temperatures above 150°C and pressures of the order of one atmosphere. This conclusion is probably accurate for lower temperatures too, although the slowness of the rate of conversion makes the experimental verification of this extremely difficult. Thus, the thermodynamic calculation is at least qualitatively correct.

Portions of the samples which had been ignited were dissolved directly in potassium permanganate solution to determine the peroxide oxygen to uranium ratios as described in Section C of Part II. Some typical results are summarized in Table 11.

Table 11

Oxygen to Uranium Ratios in Uranyl Peroxide Samples Ignited for 1 Hour

Temperature °C	Peroxide Oxygen to Uranium Ratio	Total Oxygen to Uranium Ratio, Calculated from Peroxide Oxygen Content	Measured Total Oxygen to Uranium Ratio	"Extra Oxygen" Present Per Atom of Uranium
150	1.39	3.69	3.82	0.13
178	0.33	3.17	3.35	0.18
230	0	3.00	3.20	0.20
295	0	3.00	3.14	0.14

After ignition the samples were found to contain more total oxygen than would be calculated on the basis of the peroxide oxygens present and the hexavalence of uranium. Evolution of gas was noted on immersing the samples in permanganate solution even in those cases in which no reduction of permanganate was noted. This effect was also observed by C. A. Kraus.[6] Since similar evolution of gas occurred on immersing the sample in water in the absence of permanganate, it was evident that immersion of the solid in aqueous solution was responsible for the liberation of the gas. Measurement of the liberated gas gave results which agreed quantitatively with the values calculated for the "extra oxygen". The oxygen might be called "dissolved oxygen", but keeping a sample for 75 hours at room temperature and 10^{-3} mm mercury pressure did not reduce its "extra oxygen" content at all. Ignited samples

of uranyl peroxide contain, therefore, some "extra oxygen" which is bonded in a different manner from either the peroxide oxygen or the normal divalent oxygen, which is not removed by reduced pressures but is liberated immediately on immersion of the dry solid in aqueous solution.

Thermal decomposition curves using short heating times were obtained on four samples. The method was quite similar to that described in Section F, Part II. The sample to be ignited was placed in a quartz tube, and the system was evacuated to a pressure of approximately 10^{-3} mm of mercury. The sample was kept at the designated temperature for 1¼ hours, and then allowed to cool before measuring the evolved oxygen by means of a Toepler pump and a calibrated bulb. The water was trapped and measured as described in Section G of Part II. After the measurement, the oxygen was allowed to diffuse back over the sample which was then ignited to the next higher temperature. The final oxygen pressure on complete ignition to U_3O_8 was approximately 40 mm of mercury. Since the oxygen pressure was initially zero and finally ca. 40 mm, the value during ignition at intermediate points can be calculated from the amount of oxygen evolved, as shown by the formula at the point in question, e.g., the ignition which produced UO_3 was performed at an oxygen pressure of approximately 30 mm of mercury.

The results are shown in Figure 1. It was observed, on ignition of uranyl peroxide samples at temperatures of 150°C or above, that there was an initial fairly rapid decomposition rate (occurring within the first ½ hour), followed by a slow decomposition which eventually results in complete conversion to UO_3. Because of this second slow rate the values shown in Figure 1 and in Section J of Part II (obtained after ignition for 1¼ hours) can be reproduced with considerable precision for any particular sample. The initial rate, which largely determines the value at a particular temperature, appears to be a function of the conditions of preparation of the sample. Thus the samples in experiments 2 and 4 were prepared identically except for the acidity at the time of precipitation. Their decomposition curves are similar but different from those of experiments 13 and 14 which were not prepared in the same manner as experiments 2 and 4.

Using the above procedure, a sample of $UO_4 \cdot 2H_2O$ was ignited to $UO_{3.5}$, UO_3, and U_3O_8. Portions of the sample at each stage were removed for X-ray analysis. The remainder of the sample was then heated to 1150°C while a pressure of approximately 10^{-5} cm was maintained by continuous pumping with a mercury diffusion pump. The sample was cooled in the presence of oxygen and was then submitted for X-ray analysis also. The X-ray analyses were performed by Dr. W. H. Zachariasen.

The results are shown in Table 12. They indicate a complete change from the orthorhombic structure of uranyl peroxide to an amorphous phase at $UO_{3.5}$. Amorphous UO_3 is also formed, and on ignition at 720° the familiar orthorhombic pattern of U_3O_8 was observed. The ignition at 1150° and 10^{-3} mm pressure followed by cooling in the presence of oxygen did not affect the crystal structure of the U_3O_8.

Table 12

Effect of Thermal Decomposition on Crystal Structure

Temperature °C	Time hours	Uranium to Oxygen Ratio	Water to Uranium Ratio	Crystal Structure
Room Temp.	--	4.005	2.3	alpha
310	1.5	3.53	0.85	amorphous
502	1.5	2.988	0.00	amorphous
720	1.5	2.666	--	U_3O_8
1150(a)	4.0(a)	2.666	--	U_3O_8

(a) Heated at 10^{-3} mm of mercury but air allowed to come in contact with sample before cooling started.

IV. SUMMARY

Samples of uranyl peroxide were prepared under widely varied conditions of precipitation and drying. It was found that the conditions of precipitation do not affect the composition of the precipitate but do affect its physical characteristics and its rate of thermal decomposition. The drying conditions affect the composition only when the conditions are extreme, i.e., when large lumps are dried for short intervals or when the temperature is high enough to cause thermal decomposition. The formula of the compound is $UO_4 \cdot 2H_2O$. Two of the oxygens are peroxide oxygens, and no sulfate or nitrate ions were found in the molecule. Except for the water to uranium ratio, wet samples have the same composition as dry samples.

A very rough thermodynamic calculation indicates that $UO_4 \cdot 2H_2O$ is unstable with respect to UO_3 (anhydrous) even at 25°C. The uranyl peroxide is completely converted to UO_3 at 150°C and can probably be so converted at lower temperatures, although the rate of conversion decreases rapidly with decreasing temperature. Because of the slow rate of conversion, reproducible values for compositions between $UO_4 \cdot 2H_2O$ and UO_3 can be obtained on heating for short intervals, but these values do not correspond to equilibrium conditions. The initial rate of thermal decomposition appears to be affected by the conditions of preparation of the sample.

On thermally decomposing the uranyl peroxide, some oxygen is found to be present which is neither peroxide oxygen nor normal divalent oxygen. This oxygen is liberated as molecular oxygen immediately on immersing the sample in water.

Two crystal forms of $UO_4 \cdot 2H_2O$ exist, an orthorhombic structure and another distinct yet unidentified phase. The transition from the beta (unidentified) crystal structure to the alpha (orthorhombic) crystal structure is accelerated by standing at reduced pressures.

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REFERENCES

1. Biltz and Muller, Zeit. Anorg. Alleg. Chem. 163, 257 (1927)
2. Huttig and Von Schroeder, Zeit. Anorg. Alleg. Chem. 121, 243 (1922)
3. Sieverts and Muller, Zeit. Anorg. Alleg. Chem. 173, 297 (1926)
4. Rosenheim and Daehr, Zeit. Anorg. Alleg. Chem. 206, 81 (1932)
5. Biltz, Zeit. Anorg. Alleg. Chem. 244, 281 (1940)
6. Kraus, Report No. A-360 (October 1942)
7. Kolthoff and Lingane, J.A.C.S. 55, 1871 (1933)
8. Hoffpauir and Guthrie, Ind. and Eng. Chem., Anal. Ed., 16, 391 (1944)
9. Tanford and Larson, C-3.385.3 (August 1945)
10. S. W. Rasmussen, Unpublished, Notebook CL-941
11. W. H. Zachariasen, CC-2768 (March 1945)
12. W. H. Zachariasen, MUC-FWHZ-161 (November 1945)
13. Bichowsky and Rossini, The Thermochemistry of Chemical Substances, Reinhold Publishing Corp., New York (1936)
14. Brewer, Bromley, Gilles, and Lofgren, CC-3234 (September 1945)
15. Lewis and Randall, Thermodynamics, McGraw-Hill Book Company, New York (1923)
16. Wenner, Thermochemical Calculations, McGraw-Hill Book Co., New York (1941)
17. Latimer, J.A.C.S., 43, 818 (1921)

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