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Final Report
No. NYO 6313
August 1957

THERMAL STABILITY OF THE HYDRATES
OF URANYL NITRATE

Project Director: A. J. King

Research Group: Ralph Pfeiffer
William Zeek

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Report CHEM 242-578F

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CHEM242-578F

Date:

August 1, 1957

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ABSTRACT

The purpose of this study was to follow the progress of the thermal decomposition of uranyl nitrate hexahydrate through to the end product, UO_3 , with identification of intermediate phases by appropriate chemical and physical methods.

A number of the compounds which could appear as intermediate phases in the decomposition process and whose existence have been fairly well established were prepared in pure form for use as standards of reference. Among these were $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{UO}_2(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ preparations, and various forms of the monohydrate of UO_3 . X-ray diffraction patterns were prepared for these substances.

Vapor pressure measurements at 0° , 25° and 50.1°C were made of the hydrate pairs, $\text{UN} \cdot 6\text{H}_2\text{O}$ - $\text{UN} \cdot 3\text{H}_2\text{O}$ and $\text{UN} \cdot 3\text{H}_2\text{O}$ - $\text{UN} \cdot 2\text{H}_2\text{O}$. The method of Baxter and Lansing was used with extrapolation to zero flow-rate in order to reduce errors due to non-equilibrium conditions.

A series of studies was made of the end products formed during thermal decomposition of both $\text{UN} \cdot 6\text{H}_2\text{O}$ and $\text{UN} \cdot 3\text{H}_2\text{O}$ at a number of different temperatures.

Preliminary studies of the products present at different stages in the cycle of heating of $\text{UN} \cdot 6\text{H}_2\text{O}$ as practiced by the Mallinckrodt Chemical Works were made by x-ray methods. The only products which were definitely identified were $\text{UN} \cdot 6\text{H}_2\text{O}$, $\text{UN} \cdot 3\text{H}_2\text{O}$ and $\text{UN} \cdot 2\text{H}_2\text{O}$. The end product after heating for four hours and twenty minutes was amorphous.

Unidentified diffraction lines appeared in the intermediate products along with $UN.3H_2O$ and $UN.2H_2O$ respectively. These lines may be due to one or more of the several polymorphic forms of UO_3 or $UO_3.H_2O$. Only one form of each of these has been observed in the course of this investigation, and their patterns did not agree with those of the unknown intermediate.

X-RAY DIFFRACTION STUDIES

As a preliminary to this study it was necessary to obtain a complete set of diffraction patterns of all compounds which might be expected as intermediate products in the decomposition of $UO_2(NO_3)_2.6H_2O$. In all of these preparations Mallinckrodt reagent grade $UO_2(NO_3)_2.6H_2O$ was used as the starting material.

In Table I are listed the $d(hkl)$ values of diffraction pattern of $UO_2(NO_3)_2.6H_2O$. The sample was prepared by moistening it with water before grinding to avoid any loss of water of hydration.

TABLE I

d	Int.	d	Int.	d	Int.	d	Int.
6.70	vvs	2.63	m	2.04	vvw	1.598	m
5.90	vvs	2.55	m	1.98	w	1.576	vw
4.35	vvs	2.49	m	1.96	w	1.540	vvw
3.87	s	2.45	vw	1.89	vs	1.515	mw
3.64	ms	2.37	mw	1.84	w	1.470	mw
3.30	vs	2.28	m	1.83	w	1.405	w
3.18	w	2.24	vvw	1.82	w	1.358	vw
2.94	vw	2.16	mw	1.74	vw	1.320	vw
2.85	w	2.11	mw	1.72	mw	1.272	vvvw
2.76	w	2.09	w	1.645	m	1.242	vvw
						1.140	w

Attempts to prepare the lower hydrates $\text{UO}_2(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ by removal of the required amount of water from UNH in an oven at 120°C resulted in products which were not homogeneous. They were finally obtained by dehydration of UNH at room temperature in vacuo over P_2O_5 . When a given weight of the salt had lost weight corresponding to three and four molecules of water respectively, it was sealed in a glass tube and annealed for several days at 100°C before x-ray diffraction patterns were taken.

Crystalline $\text{UO}_2(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ was also prepared by dissolving fifty grams of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in 80 ml. of 16N. HNO_3 and evaporating the solution to about one-half its original volume. On cooling large tabular crystals separated, yellow in color with a strong greenish fluorescence. The diffraction pattern was the same as that prepared by the method outlined above.

The data for the tri- and di-hydrates are given in Table II and Table III.

TABLE II

d	Int.	d	Int.	d	Int.	d	Int.
6.30	vs	2.82	mw	1.98	mw	1.510	vvvw
5.50	vvs	2.75	vw	1.93	m	1.412	m
5.15	m	2.69	vw	1.86	s	1.383	m
4.90	m	2.55	w	1.835	m	1.340	vw
4.71	m	2.47	m	1.770	vw	1.325	vw
4.04	vs	2.37	ms	1.745	s	1.295	w
3.71	m	2.29	m	1.705	m	1.280	w
3.48	vvs	2.23	s	1.660	mw	1.255	w
3.11	s	2.18	ms	1.622	w	1.238	mw
3.03	vw	2.07	vvvw	1.585	ms	1.082	m
2.95	m	2.04	m	1.560	vw	0.995	mw
				1.530	m	0.919	mw

TABLE III

d	Int.	d	Int.	d	Int.
6.6	s	2.91	m	2.035	w
5.10	vs	2.72	w	1.988	m
5.00	w	2.55	vw	1.898	ms
4.75	s	2.53	s	1.805	vw
4.40	vs	2.43	w	1.720	m
4.10	vvvw	2.37	vw	1.700	m
3.75	vs	2.27	ms	1.628	m
3.50	m	2.21	vw	1.622	m
3.25	w	2.19	ms	1.495	vvw
2.97	s	2.14	m	1.480	vvw

The bright yellow modification of $\text{UO}_3\text{H}_2\text{O}$ was prepared by the method of Lebeau (1). Orange amorphous UO_3 was dissolved in uranyl nitrate, the

(1) Lebeau, Bull. soc. Chim. (4) 11,800 (1912)

solution evaporated to dryness at 100°C and the residue extracted with ether. The data given in Table IV were obtained from the ether insoluble portion of the residue. Although this should be $\text{UO}_3\text{H}_2\text{O}$ according to Lebeau, analysis showed that it contained only 66.5% uranium as compared with the theoretical value of 78.28% U for this compound.

TABLE IV

Lebeau $\text{UO}_3\text{H}_2\text{O}$

d	Int.	d	Int.	d	Int.
9.7	m	3.80	vw	2.34	vw
7.4	s	3.58	vs	2.14	m
5.6	vw	3.50	vvw	2.07	vw
5.1	vw	3.41	vvw	2.03	vw
4.4	m	3.22	vvs	1.96	m
4.3	m	2.78	vvw	1.89	w
4.05	vvw	2.70	vw	1.84	vw
4.00	vvw	2.55	w	1.80	vvw
		2.43	vw	1.62	vvw

In Table V are shown the data from M. C. W. orange UO_3 which on analysis was found to contain 0.92% NO_3 and traces of U_3O_8 .

TABLE V
M. C. W. Orange UO_3

d	Int.	d	Int.	d	Int.	d	Int.
4.90	vvw	1.98	w	1.270	vvw	0.909	w
4.28	vw	1.96	w	1.252	vvw	0.875	w
3.38	s	1.88	mw	1.220	vvw	0.872	w
3.20	m	1.82	s	1.212	vvw	0.862	w
2.99	m	1.81	ms	1.190	vw	0.836	mw
2.75	s	1.73	vs	1.166	vw	0.834	mw
2.59	vvw	1.71	s	1.113	vw	0.825	mw
2.37	vvw	1.528	ms	1.092	vw	0.786	m
2.17	w	1.363	w	1.006	vvw	0.784	w
2.09	mw	1.300	vw	0.995	w	0.782	w
2.08	w	1.295	vw				

A sample of "Green" UO_3 marked "Oak Ridge" which analysis proved to contain no NO_3 was found to contain 5.10% H_2O which was not removable by Karl Fischer reagent. The theoretical H_2O content of $\text{UO}_3 \cdot \text{H}_2\text{O}$ is 5.91%.

TABLE VI
"Oak Ridge" Green Oxide

d	Int.	d	Int.	d	Int.
7.10	m	1.82	vvw	1.425	mw
5.05	vs	1.765	s	1.375	w
3.75	vvvs	1.730	m	1.345	mw
2.83	s	1.720	vw	1.295	vw
2.52	w	1.700	vw	1.290	vw
2.46	s	1.690	vw	1.240	vvw
2.12	m	1.628	ms	1.178	vvw
2.03	m	1.518	w	1.148	w
1.97	vs	1.470	w	1.048	w

Although a number of hydrates of UO_3 have been described (2)

(2) Katz, J., and Rabinowitch, E., "The Chemistry of Uranium," Part I, McGraw-Hill Book Co., 1951

in the literature, namely $\text{UO}_3 \cdot 2\text{H}_2\text{O}$, $\text{UO}_3 \cdot 1.5\text{H}_2\text{O}$, $\text{UO}_3 \cdot \text{H}_2\text{O}$, $\text{UO}_3 \cdot 0.5\text{H}_2\text{O}$, it is probable that only $\text{UO}_3 \cdot \text{H}_2\text{O}$ and $\text{UO}_3 \cdot 0.5\text{H}_2\text{O}$ have sufficient thermal stability to withstand the temperatures attained in the MCW process. According to Hüttig et al (3) both $\text{UO}_3 \cdot \text{H}_2\text{O}$ and $\text{UO}_3 \cdot 0.5\text{H}_2\text{O}$ are the

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- (3) Hüttig, G., and Von Schroeder, E., Zeit. Anorg. U. Allgem. Chem. 12, (1922) 251.
-

only hydrates which are stable above 100°C .

$\text{UO}_3 \cdot \text{H}_2\text{O}$ has been reported (2) to exist in at least four different

-
- (2) Katz, J., and Rabinowitch, E., "The Chemistry of Uranium, Part I, McGraw-Hill Book Co., 1951.
-

crystalline forms and an amorphous form. Only one form, which was definitely shown to be $\text{UO}_3 \cdot \text{H}_2\text{O}$ was observed in this investigation; Oak Ridge "green" oxide, which may have undergone hydration before received by us and a product obtained by digestion of MCW active orange oxide which was subjected to digestion with water at 100°C . Both of these gave the same diffraction pattern and their analysis agreed with $\text{UO}_3 \cdot \text{H}_2\text{O}$. A sample of so-called Lebeau (1) monohydrate gave an entirely different

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- (1) Lebeau, Bull. soc. Chim. (4) 11,800 (1912)
-

diffraction pattern and analysis showed it to contain 66.5% U as compared with the theoretical value of 78.28% U. Its true identity was not established.

METHODS OF ANALYSIS

Uranium: Determination of uranium by ignition to U_3O_8 was found to be reproducible to within 0.05% U upon repeated analysis of compounds of known purity.

Nitrate: Determination of nitrate by precipitation of UO_4 with hydrogen peroxide (4) and subsequent titration of the acid was investi-

(4) Anal. Chem., Manhattan Project VIII, 1, 214.

gated and found to be satisfactory for pure uranyl nitrate hydrates. This method is not applicable, however, in the presence of other acids. The method depends upon the following reaction:

The determination of nitrate by the Kjeldahl method, although more time consuming, proved to be more satisfactory for our purpose.

Water: It was found that the water content in the uranyl nitrate hydrates could be determined accurately by the Karl Fischer method as described by Mitchell (5). This method can be applied only where the

(5) Mitchell, Aquametry, Interscience Publishers.

water is weakly bound in the compound and cannot be used to determine strongly bonded water such as the fifth water in $CuSO_4 \cdot 5 H_2O$. In this work it was found that all six waters in UNH could be determined, but the water in the "Green oxide" which agrees by analysis with $UO_3 \cdot H_2O$

could not be removed by the reagent.

An alternate method used for the determination of water was ignition of the compound U_3O_8 with simultaneous collection of the water in a weighed drying tube.

PART II - VAPOR PRESSURE STUDIES

A knowledge of the vapor pressures of various compositions in the range $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ - $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ was considered as being fundamental to a study of the decomposition process.

A flow method of determining vapor pressures as described by G. Baxter and J. Lansing (6) was chosen as best suited for our purposes.

(6) J. Am. Chem. Soc., 42, 419 (1920)

The flow method in theory depends simply on determining the amount of water vapor contained in a measured amount of air passed over the hydrated salt under equilibrium conditions. Some difficulty arises in practice, however, in attaining and maintaining equilibrium among the hydrated phases and the sweeping gas. This can be largely overcome by thoroughly grinding of the salt and mixing it with glass beads before filling the saturation tube.

The apparatus in Figure 1 was constructed with these requirements in mind. At A + A' the incoming air is dried by either calcium chloride or calcium chloride and magnesium perchlorate, depending on the approximate range of vapor pressures being determined. A further improvement might be introduced by determining the approximate vapor pressure by the present method, and then controlling the humidity of the entering air to closely approximate this vapor pressure for subsequent determinations for that particular composition. In this way

APPARATUS FOR DETERMINING VAPOR PRESSURES

FIG I

equilibrium would be established very rapidly and without seriously affecting the composition of the mixture even after many determinations.

The dried air passes through preheating coils (B) immersed in a constant temperature bath, controlled to $\pm 0.05^{\circ}\text{C}$, and then through the saturation tube (C) which contains the salt mixed with glass beads. The saturation tube (C) was constructed from 15 mm. tubing of sufficient length to provide a column of sample 30 cms. long. The moist air flows through a short connection into a U-tube (D) filled with magnesium perchlorate. The short connection between the saturation tube (C) and the absorption tube (D) was heated by a blast of hot air in experiments where condensation of water could occur at room temperature. A second drying tube (E) prevents possible backing-up of water vapor from the aspirator bottle (F). This bottle had a capacity of about 5 liters and was fitted with a long exit tube and a manometer. Placement of the manometer at this position was justified as there was no measurable pressure drop through (D) and (E), so that the manometer reading gave the pressure of the H_2O laden air in the outlet side of (C).

The displaced water passing through the siphon (G) was collected in narrow-necked flasks and weighed.

Calculations were made in the following manner:

$$\text{vapor pressure} = \frac{\text{volume vapor}}{\text{volume (vapor + air)}} \times \text{pressure (vapor + air)}$$

$$\text{vapor pressure} = \frac{V_w \cdot \frac{760}{P_I} \cdot \frac{T_B}{273.1}}{V_A \cdot \frac{P_C}{P_I} \cdot \frac{T_B}{T_C} + (\text{numerator})} \cdot P_I$$

$$= V_A \times \frac{\frac{V_w}{273.1} \cdot \frac{P_C}{T_C} + V_w}{\frac{760}{P_I}} \times P_I$$

V_w = volume of the vapor at S.T.P., as determined from the weight of H_2O collected in D. V_A = total volume of air as obtained from the weight of displaced water. P_I = pressure of the saturated air as given by the manometer. P_C = pressure of air in aspirator, corrected for vapor pressure above the water. T_C = absolute temperature of the collected water and of the air in the aspirator. T_B = absolute temperature of the bath.

In following Baxter and Lansing's method more accurate results were obtained by measuring the vapor pressure at a number of different flow-rates and extrapolating to a zero flow-rate. In this manner errors due to non-equilibrium conditions were mainly eliminated.

A series of measurements at flow-rates between 0.4 and 4.5 liters per hour were made on three different samples at several temperatures. That the results were satisfactorily reproducible was shown by duplicate runs of the given composition under the same conditions.

The results are shown in Figures 2, 3, 4, and 5, with extrapolated vapor pressures as follows:

TABLE VII

VAPOR PRESSURES OF UN-HYDRATE PAIRS

25% hexahydrate + 75% trihydrate

Temp. °C	0°	25°	50.1°
V. P. (mm)	1.32	8.03	53.2

25% trihydrate + 75% dihydrate

Temp. °C	0°	25°	50.1°
V. P. (mm)	--	1.03	7.25

70% hexahydrate + 30% trihydrate

Temp. °C	0°	25°	50.1°
V. P. (mm)	--	9.02	--

It may be seen that the isotherm for the hexahydrate-trihydrate pair is somewhat removed from the ideal case as there is a drop in vapor pressure of about 1 mm over the range between 75% hex. to 25% hex. in the mixture.

This study was not completed. Further studies should be made of compositions higher in uranium content than the dihydrate.

X-RAY STUDIES OF THE MCW PROCESS

Preliminary x-ray studies were made of the products obtained at various intervals, following approximately the time-temperature program of the MCW process.

VAPOR PRESSURE OF URANYL NITRATE HYDRATES

FIG 2

VAPOR PRESSURE OF URANYL NITRATE HYDRATES

T 25.0°C

FIG. 3

VAPOR PRESSURE OF URANYL NITRATE HYDRATES

25% HEXAHYDRATE - 75% TRIHYDRATE

AT 50.1°C

FIG 4

FIG 5

Two hundred-gram samples of UNH were heated in a furnace designed to provide an even distribution of heat over the entire wall of the porcelain reaction vessel. The sample was stirred during the heating cycle until the "doughy" stage was reached. Beyond this point the stirring device was inadequate to provide thorough mixing of the products of reaction.

Figure 6 illustrates the course of one particular series as compared with the MCW process. The intervals at which samples were taken are indicated by arrows on the curve.

The x-ray pattern of Sample 1 corresponded to a mixture of the hexahydrate and the trihydrate.

Sample 2 contained lines of the trihydrate and in addition, ten lines out of the forty observed, which could not be accounted for on the basis of patterns of any reference compounds which might be expected in this series.

Sample 3 gave a pattern, the major portion of which agreed with the dihydrate. The balance was different from anything heretofore observed in this study.

Sample 4 gave only the diffuse diffraction rings characteristic of a substance in the amorphous condition.

The x-ray study of this system is complicated by the tendency of the uranium compounds to exist in a number of polymorphic forms, by the possibility that intermediate compounds, as yet unidentified, seem to be produced in the process, and that near the end of the cycle the products tend to be amorphous.

FIG 6

DECOMPOSITION STUDIES OF $\text{UN} \cdot 6\text{H}_2\text{O}$ AND $\text{UN} \cdot 3\text{H}_2\text{O}$

The solid products produced during the thermal decomposition of both $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{UO}_2(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ were investigated at a series of different temperatures.

Samples of the pure UN hydrates contained in open Pyrex tubes were heated in a bath of Wood's metal, the temperature of which was maintained at the desired value. At the end of the heat-treatment, the samples were analysed and the solid phases identified by diffraction methods.

The data given in Tables VIII and IX show the results of heating $\text{UN} \cdot 6\text{H}_2\text{O}$ and $\text{UN} \cdot 3\text{H}_2\text{O}$ respectively for a period of twenty-four hours at the indicated temperatures.

TABLE VIII

$\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ DECOMPOSITION SERIES

T°	Chemical Analysis		X-Ray
	<u>U (%)</u>	<u>H₂O (%)</u>	
100°	54.95	9.05	$\text{UN} \cdot 3\text{H}_2\text{O}$ only
120°	55.37	8.36	$\text{UN} \cdot 3\text{H}_2\text{O}$ + $\text{UN} \cdot 2\text{H}_2\text{O}$
140°	55.67	7.86	Chiefly $\text{UN} \cdot 2\text{H}_2\text{O}$; trace $\text{UN} \cdot 3\text{H}_2\text{O}$
160°	58.98	2.43	$\text{UN} \cdot 2\text{H}_2\text{O}$ dihydrate
180°	60.91	2.15	$\text{UN} \cdot 2\text{H}_2\text{O}$ dihydrate, trace UO_3
200°	71.53	--	$\text{UN} \cdot 2\text{H}_2\text{O}$ and some UO_3 . Unidentified lines. <u>Not</u> $\text{UO}_3 \cdot \text{H}_2\text{O}$
240°	83.01	--	UO_3

TABLE IX
 $\text{UO}_2(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ DECOMPOSITION SERIES

T°	Chemical Analysis		X-Ray
	U (%)	H ₂ O (%)	
120°	54.85	9.21	UN.3H ₂ O and UN.2H ₂ O
140°	55.99	7.32	UN.2H ₂ O with some UN.3H ₂ O but no UO ₃ pattern
160°	61.02	3.35	UN.2H ₂ O and UO ₃
180°	75.19	1.0	UO ₃ + trace of UN.2H ₂ O
200°	76.89	--	UO ₃
240°	82.91	--	UO ₃

Only three solid phases can be positively identified in the end products of these treatments. No diffraction lines of $\text{UO}_3 \cdot \text{H}_2\text{O}$ were observed among the products although this compound might reasonably be expected to be present since it is stable up to 300°C. However, the diffraction patterns are very complex and in view of the tendency of $\text{UO}_3 \cdot \text{H}_2\text{O}$ to exist in an amorphous state, its presence could easily escape detection. The unidentified lines in the sample of UN.6H₂O at 200° could be due to one or more of the several modifications of either $\text{UO}_3 \cdot \text{H}_2\text{O}$ or UO₃ which have been described in the literature (2).

A comparison of the analysis of the end product versus the

(2) Katz, J., and Rabinowitch, E., "The Chemistry of Uranium," Part I, McGraw-Hill Book Co., 1951.

products identified in its diffraction pattern, as shown in Tables VIII and IX is indicative of the shortcomings of the diffraction method. As can be seen by referring to Table X, showing the

TABLE X

<u>Compound</u>	<u>U (%)</u>	<u>H₂O (%)</u>
UO ₂ (NO ₃) ₂ ·6H ₂ O	47.41	21.52
UO ₂ (NO ₃) ₂ ·3H ₂ O	53.14	12.07
UO ₂ (NO ₃) ₂ ·2H ₂ O	55.36	8.38
UO ₂ (NO ₃) ₂	60.42	--
UO ₃ ·H ₂ O	78.28	5.91
UO ₃	83.22	

theoretical analysis of the several hydrates and oxides, the chemical composition of the end product is not in accord with the apparent amount of these phases appearing in the diffraction pattern. This is particularly evident in the results obtained after heating UN·6H₂O for 24 hours at 160° and 180° respectively. The x-ray patterns indicate that the end product in each case is essentially UN·2H₂O whereas the analysis agrees more nearly with anhydrous UO₂·(NO₃)₂ or a mixture of UN·2H₂O and UO₃. Even at 200° the pattern of UN·2H₂O still persists. These results can be justified only on the assumption that UN·2H₂O decomposes to form an intermediate phase which is amorphous and does not give a characteristic diffraction pattern. This phase may be UO₃ or UO₃·H₂O which are known

to exist in the amorphous state. The crystalline pattern of UO_3 began to appear in the $\text{UN} \cdot 6\text{H}_2\text{O}$ series at 180° and in the $\text{UN} \cdot 3\text{H}_2\text{O}$ series at 160°C , at which temperature the chemical analyses show 60.9% U, 2.15% H_2O and 61.02% U, 3.35% H_2O respectively. It would appear that little amorphous intermediate product ($\text{UO}_3?$) is formed during the decomposition of $\text{UN} \cdot 3\text{H}_2\text{O}$. The data on $\text{UN} \cdot 3\text{H}_2\text{O}$ therefore indicate that only the three intermediate phases - $\text{UN} \cdot 3\text{H}_2\text{O}$, $\text{UN} \cdot 2\text{H}_2\text{O}$ and UO_3 - are involved in its thermal decomposition to UO_3 , under the conditions of this investigation. It is also possible that this is the case with $\text{UN} \cdot 6\text{H}_2\text{O}$. The trace of unidentified material found in the sample heated at 200°C may be one of the several polymorphic forms of UO_3 for which no reference patterns were available.

SUMMARY

1. Methods of analysis have been devised and tested.
2. Compounds which are expected to appear in the course of the reaction have been prepared and x-ray patterns obtained for identification purposes.
3. Vapor pressure studies over the ranges UNH-UNT and UNT-UND have been made at 0°, 25° and 50.1°.
4. Studies of the products in the system at particular time intervals in the MCW process have been initiated.
5. The decomposition products of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and of $\text{UO}_2(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ after heating for twenty-four hours at a number of different temperatures were investigated by analytical and x-ray diffraction methods.

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