concentration of uranium(V) at acidities greater than 0.01 is negligible. If we let K be the dissociation constant of $UOOH^+$, the above mechanism leads to the rate law

$$-\,d[UO_2^+]/dt = (k'/K)a_{H^+}[UO_2^+]^2 \qquad (8)$$

Comparison with equation (4) shows that the experimentally observed k is then equal to k'/K. From the fact that the uranium(V), uranium(VI) potential is independent of hydrogen ion even in 0.5 M $HClO_4$ (see Table I), the value of K must be greater than 10. On this basis the value of k' must be greater than 1300 (moles/l.)$^{-1}$ sec.$^{-1}$ in the most concentrated perchlorate solutions studied.

Summary

Millimolar solutions of uranium(V) have been prepared by electrolysis of uranyl ion in sodium perchlorate, perchloric acid solutions and studied in this medium by means of the dropping mercury electrode. Diffusion coefficients have been measured for both the penta- and hexavalent ions.

The couple $UO_2^+ = UO_2^{++} + e$ has been shown to be reversible; the constancy of the potential of this couple in 0.01 to 0.5 M perchloric acid solutions of fixed ionic strength has been presented as evidence that the uranium(V) species is UO_2^+.

In sodium perchlorate, perchloric acid mixtures the disproportionation of UO_2^+ obeys the following law from $a_{H^+} = 0.01$ to 0.4 and from $[UO_2^+] = 10^{-5}$ to 10^{-3} M: $-d[UO_2^+]/dt = ka_{H^+}[UO_2^+]^2$. The most probable mechanism for the disproportionation is

$$UO_2^+ + H^+ = UOOH^{++}$$

$$UO_2^+ + UOOH^{++} \longrightarrow UO_2^{++} + UOOH^+ \text{ (slow step)}$$

$$UOOH^+ \longrightarrow \text{stable U(IV) species.}$$

UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA
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[CONTRIBUTION FROM THE CHEMISTRY DIVISION OF THE ARGONNE NATIONAL LABORATORY]

Higher Oxides of the Actinide Elements. The Preparation of Np_3O_8[1]

BY J. J. KATZ AND D. M. GRUEN

The recent elaboration of the actinide hypothesis and the syntheses of the transuranium elements neptunium, plutonium, americium and curium[2] have stimulated interest in the comparative chemistry of these elements. Of particular interest are the structure and properties of the oxide systems of the actinide elements. In addition to the comparative aspects is the bearing these systems have on the general problem of non-stoichiometric compounds, of which these systems are typical examples.[3] Although the three uranium oxides UO_2, U_3O_8, and UO_3 have been known for a hundred years, the uranium–oxygen system did not receive rigorous investigation until 1927.[4] Considerable new data were obtained by various investigators during the course of work carried out for the Metallurgical Project.[5] The situation with respect to the oxide systems of the transuranium elements is less satisfactory. At the time the work reported here was begun, for example, no anhydrous oxide with an oxygen–metal ratio greater than two had been prepared, despite the fact that neptunium, plutonium and americium have higher oxidation states in solution. The broad object of this work, then, was to extend the knowledge of the actinide metal–oxygen systems, while the more immediate task was to search for higher neptunium oxides in order to compare their properties with analogous compounds of other actinide elements.

Since it becomes more difficult to obtain higher oxidation states in going from uranium to the heavier elements, the conditions most likely to yield such states must be chosen with increasing care. Thus, treatment of neptunium dioxide with molecular oxygen even under high temperature and pressure, conditions which result in the conversion of the lower uranium oxides to UO_3, is ineffective in yielding a higher neptunium oxide.[6] A low temperature reaction appeared essential; the higher oxides of the transuranium elements may be expected to show rapidly decreasing thermal stability with increasing atomic number, since the stability of the higher oxidation states decreases in the same manner. The method of Sabatier and Senderens[7] for preparing higher oxides thus seemed of particular interest. Their procedure consisted in treating a metal or lower oxide with anhydrous nitrogen dioxide at 200–400° and at atmospheric pressure. Reactions of the type

$$MO_n + xNO_2 \longrightarrow MO_{n+x} + xNO$$

were observed; they reported for example that V_2O_3 was oxidized to V_2O_5, MnO to Mn_2O_3, and UO_2 to $3UO_3{\cdot}UO_2(NO_3)_2$. Because of the relatively mild temperature conditions required and the evidently strong oxidizing power of nitrogen dioxide, this reaction was applied to neptunium.

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(1) Reported in part at the Spring, 1948, Meeting of the American Chemical Society.

(2) G. T. Seaborg, *Chem. Eng. News*, **23**, 2190 (1945); **24**, 1192 (1946); **25**, 358 (1947); *American Scientist*, **36**, 361-376 (1948).

(3) For a comprehensive review of the non-stoichiometric compounds, see J. S. Anderson, *Ann. Reports Chem. Soc.*, **43**, 104-120 (1946).

(4) W. Biltz and H. Müller, *Z. anorg. Chem.*, **163**, 261-295 (1927).

(5) R. E. Rundle, N. C. Baenziger, A. S. Wilson and R. B. McDonald, THIS JOURNAL, **70**, 99-105 (1948).

(6) S. Fried and N. R. Davidson, THIS JOURNAL, **70**, 3539 (1948).

(7) P. Sabatier and J. B. Senderens, *Ann. chim. phys.*, [7] **7**, 356, 384, 396 (1896).

Because of the nature of the reaction product reported by Sabatier and Senderens for UO_2, it also appeared desirable to reinvestigate the case of uranium.

Experimental

The apparatus is shown in Fig. 1. It consisted of a nitrogen dioxide generator and a quartz reactor. A hollow quartz finger served as the sample holder; a thermocouple inserted in the finger permitted the temperature to be read in the immediate vicinity of the reaction boat. Both the nitrogen dioxide generator and the quartz reaction vessel were heated with electric furnaces controlled by Variacs. The temperature in the reaction tube was maintained constant to within ±10°.

Although we employed nitrogen dioxide from cylinders for some experiments, for the most part, anhydrous nitrogen dioxide was generated from lead nitrate (previously dried for several days at 115°) by heating to 450°. Nitrogen dioxide prepared in this way contains oxygen

$$Pb(NO_3)_2 \longrightarrow PbO + 2NO_2 + {}^1/_2O_2$$

The reactions described here, however, can be attributed unambiguously to nitrogen dioxide, since oxygen is either known or was shown to have no effect under the reaction conditions used here. In the case of U_3O_8 and NpO_2, oxidation with molecular oxygen at atmospheric pressure has never been observed; with NpO_2, even high pressures of oxygen are still ineffective in causing oxidation. In the majority of the experiments described here, nitrogen was used as a carrier gas; if the nitrogen is replaced by oxygen, products identical within experimental error result. Under our experimental conditions, then, oxygen is an inert diluent.

For each experiment, approximately 100-mg. samples in the case of the uranium experiments were weighed into clean, dry, platinum boats; a glass piggy was used to exclude moisture. The boat was then inserted into the reaction vessel which had previously been swept with dry nitrogen. Reaction with nitrogen dioxide was then allowed to proceed, and the time, temperature and color of the sample were noted. At the end of each run, the boat and sample were reweighed and the weight changes noted.

All solid starting materials and products were submitted to Professor W. H. Zachariasen for X-ray analysis.

Materials.—The uranium compounds employed in this work were spectroscopically pure. U_3O_8 was prepared by ignition of uranyl nitrate at 700° in air. UO_2 was obtained by hydrogen reduction of UO_3. The neptunium employed in the work was a highly purified sample; it was supplied to us as a solution of Np(V) (10 mg./ml.) in 1 *M* $HClO_4$.

Results and Discussion

Reaction of Uranium Oxides with Nitrogen Dioxide.—Nitrogen dioxide reacts with U_3O_8 at 250–350° to form a brick-red solid, rather than the ordinary yellow UO_3. The results of a number of experiments are summarized in Table I. The composition of the product was established by comparing the observed weight changes with values calculated for the reaction

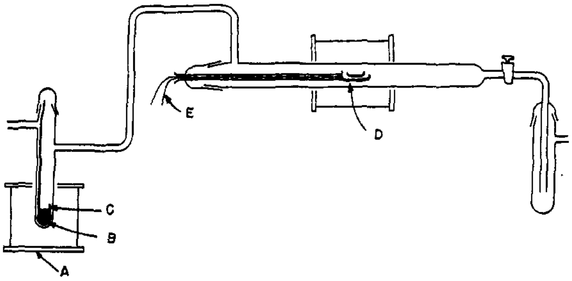

Fig. 1.—Apparatus for nitrogen dioxide oxidations: A, furnace; B, platinum boat; C, lead nitrate; D, reaction vessel; E, thermocouples.

$$U_3O_8 + NO_2 \longrightarrow 3UO_3 + NO$$

The close agreement between the calculated and observed weight changes together with the X-ray data indicate that anhydrous UO_3 is indeed obtained, but that it differs crystallographically from yellow UO_3 obtained by thermal decomposition of uranyl nitrate. The approximate rate of the reaction was determined by noting the time required for the black U_3O_8 to be fully converted to the brick-red UO_3. The reaction is initiated at 250°, and its rate increases rapidly to 350° where it levels off. A plot of log $1/t$ *vs.* $1/T$ (t = time in minutes for complete change of color, T = absolute temperature) yields an estimated value for the activation energy of 10 ± 3 kcal. for this reaction.

The X-ray results are of interest. All of the products obtained with anhydrous NO_2 on U_3O_8 gave identical X-ray diffraction patterns, indicating that only one particular phase of UO_3 was being produced. This phase was identical with the "phase I" prepared by the oxidation of U_3O_8 with nitric acid vapors by Gates, Pitt and Andrews.[8] These workers, however, appeared to have obtained a second UO_3 phase (designated then as "phase II") by using U_3O_8 prepared in a different manner from that yielding UO_3 "phase I." The complete absence of "phase II" from our products led us to repeat the experiment using nitric acid vapors prepared by bubbling nitrogen through nitric acid at 70°, and U_3O_8 samples prepared in accordance with the directions of Gates, Pitt and Andrews. From the results given in Table I, (Expt. 28 and 29c) it can be seen that, depending upon the method of preparation of U_3O_8, either anhydrous UO_3 or hydrated UO_3 is obtained with nitric acid vapors, and that the "phase II" of Gates, Pitt and Andrews is in reality a UO_3 hydrate. A comparison of the X-ray patterns indicates conclusively that only one UO_3 phase (phase I) is produced by the reaction of anhydrous NO_2

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[8] J. Gates, R. B. Pitt and L. O. Andrews, Manhattan Project Report CD.495 (1945).

TABLE I

REACTIONS OF URANIUM OXIDES WITH NITROGEN DIOXIDE

Experiment	Oxidizing agent	Temp., °C.	Time, min.	Starting material, g.	Product, g.	Formula of product[c]	X-Ray report
					U_3O_8		
2	NO_2	200	120	0.0824	0.0825	$UO_{2.68}$	U_3O_8
3	NO_2	250	120	.0838	.0854	$UO_{3.00}$	UO_3 Phase I
7a	NO_2	275	40	.0807	.0824	$UO_{3.05}$	UO_3 Phase I
4	NO_2	300	20	.0855	.0871	$UO_{2.99}$	UO_3 Phase I
12	NO_2	325	15	.0726	.0739	$UO_{2.98}$	UO_3 Phase I
5	NO_2	350	13	.0701	.0715	$UO_{3.01}$	UO_3 Phase I
29c	HNO_3[a] vapor	350	60	.0960	.1017	$UO_3·0.5H_2O$	UO_3 Hydrate
28	HNO_3[b] vapor	325	30	.0630	.0641	$UO_{2.92}$	Like UO_3 Phase I
					UO_2		
11	NO_2	350	40	0.1469	0.1547	$UO_{2.86}$	$U_6O_{17}(UO_{2.83})$
13	NO_2	300	15	.0987	.1040	$UO_{2.91}$	Very similar but not identical with UO_3 Phase I
110a	NO_2	350	90	.2711	.2855	$UO_{2.89}$	
110a	NO_2	350	12 hr.	.2711	.2860	$UO_{2.93}$	
16	O_2	300	180	.0861	.0887	$UO_{2.51}$	U_3O_8 Struct.
17b	Air	120	30	.0935	.0935	UO_2	UO_2
109	Air	300	180	.2891	.2999	$UO_{2.63}$	
121	NO_2	150	90	1.1793	1.1938	$UO_{2.20}$	

[a] U_3O_8 made from $UO_4·2H_2O$ by ignition at 600°. [b] U_3O_8 made from uranyl nitrate hexahydrate by ignition at 800°. [c] Phase I of UO_3 is a brick-red solid; $UO_{2.91}$ is orange, and compositions between $UO_{2.5}$ and $UO_{2.86}$ are black or very dark brown.

on U_3O_8.[9] That oxidation of U_3O_8 with nitric acid vapors can yield a hemihydrate stable at 300° is not unexpected in view of the work of Hüttig and Schroeder[10] on the stability of the UO_3 hydrates.

The reaction of nitrogen dioxide with UO_2 appears to be considerably more complex than with U_3O_8, and is not yet fully understood. The results of a number of experiments are given in the lower portion of Table I. Sabatier and Senderens[7] reported a product from this reaction which they characterized as $3UO_3·UO_2(NO_3)_2$. However, none of the X-ray patterns of any of the reaction products obtained in the present series of experiments or any analytical data indicate that the mixture $3UO_3·UO_2(NO_3)_2$ was ever obtained. At 300°, UO_2 reacts with nitrogen dioxide to form an oxide which is very similar to, but not identical with UO_3(Phase I). The principal product at high temperature apparently is a relatively stable oxide with a uranium to oxygen ratio of approximately 1:2.9. From the weight changes, it will be noted that oxides of composition intermediate between $UO_{2.2}$ and $UO_{2.9}$ can be obtained depending on the temperature. Products in the vicinity of $UO_{2.9}$ appear to be undistinguishable by ordinary X-ray methods from UO_3, since very nearly the same lattice constants are obtained in the region $UO_{2.8}$ to $UO_{3.0}$; in this case, the gravimetric results probably reflect the situation more accurately than do the X-ray data.

Nitrogen dioxide appears to be strongly adsorbed on uranium oxides at room temperature. Treatment of UO_2, U_3O_8 and UO_3 with pure nitrogen dioxide at room temperature and atmospheric pressure for twelve hours gave weight increases of 2.16, 2.00 and 2.06%, respectively. No significant weight loss was observed on pumping in a high vacuum for several hours. Heating in the absence of nitrogen dioxide at 150° resulted in removal of practically all of the nitrogen dioxide in the case of U_3O_8 and UO_3, but in the case of UO_2, oxidation to $UO_{2.20}$ resulted. This indicates that nitrogen dioxide is more strongly adsorbed by UO_2 than by U_3O_8 or UO_3 at moderate temperatures and this may be significant for the mechanism of nitrogen dioxide oxidations. It is interesting to note that the amount of oxygen introduced in forming the compound $UO_{2.20}$ from the UO_2–NO_2 complex corresponds very closely to the removal of one oxygen from the amount of nitrogen dioxide adsorbed. No significant amounts of nitrogen dioxide are retained at 300°. This is shown by the presence of only a few parts per thousand of nitrogen in the products on chemical analysis.

Oxidation of UO_2 with O_2 at 300° (Experiment 16, Table I) gave a product of composition $UO_{2.51}$ which had the orthorhombic U_3O_8 structure. This may be the lower limit of a monophasic range extending from $UO_{2.66}$ down to $UO_{2.5}$.[3] We observed no oxidation of our sample of UO_2 with oxygen at 150° in contra-distinction to the results of Gronvold and Haraldsen.[11] This disagreement is

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[9] A total of four distinct UO_3, phases thus are now known. The others, one of which is hexagonal (yellow) UO_3 were discovered by S. Fried and N. R. Davidson, and identified by W. H. Zachariasen. These results will be reported by them in a subsequent communication.

[10] G. F. Hüttig and E. V. Schroeder, *Z. anorg. Chem.*, **121**, 251 (1922).

[11] F. Gronvold and H. Haraldsen, *Nature*, **162**, 69 (1948).

certainly associated with the fact that susceptibility of UO_2 to oxidation is strongly dependent upon its previous history and especially the method employed in its preparation.

Reactions of Neptunium Compounds with Nitrogen Dioxide.—The preliminary experiments with the uranium oxides indicated the probable applicability of the nitrogen dioxide reaction to the neptunium–oxygen system. Essentially the same apparatus was used, but the platinum boats were made much smaller. The experiments were carried out on the 100 microgram to one milligram scale; all of the experiments described here were performed with a total of 10 mg. of neptunium.

Employed in this work was the long-lived α-emitting neptunium isotope $_{93}Np^{237}$, discovered by Seaborg and Wahl.[12] The small amount of neptunium used in each experiment made it difficult to obtain significant gravimetric results, and for the most part it was necessary to rely on X-ray data.

The reaction of nitrogen dioxide on a variety of neptunium compounds was studied; and a number of observations on the chemistry of neptunium compounds were made which have hitherto not been reported. It was found that reaction of nitrogen dioxide on dried neptunium hydroxides yields the compound Np_3O_8, and that this compound can also be prepared in a number of other ways.

In general, the preparation of the neptunium hydroxides which were the starting materials for most of the experiments was carried out on the 100 microgram to one milligram scale in microcones by ammonia precipitation from Np(IV), Np(V) or Np(VI) perchlorate solutions. The Np(V) solution is easily reduced to Np(IV) by treatment with sulfur dioxide, and is readily oxidized to Np(VI) by treatment with chlorine. Addition of ammonia to these solutions yields, in the case of Np(IV) and Np(V), the corresponding neptunium hydroxides; in the case of Np(VI), ammonium di-neptunate (see below) appears to be the principal product. The flocculent hydroxide precipitates were centrifuged in a high speed centrifuge, dissolved in dilute hydrochloric acid, reprecipitated and washed twice with distilled water. They were then dried for six hours at 70°, transferred to small platinum boats and treated with nitrogen dioxide (or other reagent) in the apparatus described above. Precautions were taken to prevent the spread of alpha activity.

The results obtained with neptunium are summarized in Table II.

In every case, oxidation of Np(IV), Np(V), Np(VI) hydroxide precipitates with nitrogen dioxide at 300–450° yielded a product from which an X-ray pattern was obtained resembling that of orthorhombic U_3O_8 very closely. In addition, heating Np(V) and Np(VI) compounds in air at temperatures of 275–450° yielded Np_3O_8; no oxidation of Np(IV) was observed with either air or oxygen. The most satisfactory method of preparing Np_3O_8 is by oxidation of Np(V) hydroxide with nitrogen dioxide at 300° (see Exp. 30a, Table II). Oxidation of Np(V) or Np(VI) compounds with air or oxygen seems in general to lead to a less pure product. Np_3O_8 is a chocolate-brown solid, easily soluble in nitric acid. Some chemical properties of Np_3O_8 will be reported at a later time.

TABLE II

REACTIONS OF NEPTUNIUM COMPOUNDS WITH NITROGEN DIOXIDE

Expt.	Starting material[a]	Oxidizing agent	Temp., °C.	Time, min.	X-Ray report[b]
32b	Np(IV) hydroxide	NO_2	300	90	Np_3O_8
35b	Np(IV) hydroxide	NO_2	300	180	Np_3O_8
33b	Np(IV) nitrate	NO_2	300	90	Np_3O_8
30a	Np(V) hydroxide	NO_2	300	120	Np_3O_8
30b	Np(V) hydroxide	Air	450	120	Np_3O_8
53	$(NH_4)_2Np_2O_7.H_2O$	NO_2	400	16 hours	Np_3O_8
36b	$(NH_4)_2Np_2O_7.H_2O$	Air	275	120	Np_3O_8
36c	$(NH_4)_2Np_2O_7.H_2O$	Air	425	180	Np_1O_8 type
36d	$(NH_4)_2Np_2O_7.H_2O$	Air	550	120	May be transition phase
36e	$(NH_4)_2Np_2O_7.H_2O$	Air	770	60	NpO_2
36f	$(NH_4)_2Np_2O_7.H_2O$	NO_2	100	60	New unidentified pattern

[a] All of the starting compounds were dried at 70°.

[b] These results are due to Dr. R. C. L. Mooney and Mr. W. H. Koehler.

The oxidation of certain other neptunium compounds under various conditions was examined in an attempt to follow changes in phase from Np_3O_8 to NpO_2. It was also of interest to look for evidence for the formation of higher oxides such as NpO_3. The starting material in this series of experiments was an Np(VI) hydroxide precipitate, air dried at 70°. This material yielded poor X-ray patterns, but comparison with patterns of authentic $(NH_4)_2U_2O_7{\cdot}H_2O$ indicates that the compound is the analogous $(NH_4)_2Np_2O_7{\cdot}H_2O$.

Ammonium dineptunate was heated in air at various temperatures and the products examined by X-rays (Table II). Indications of a phase intermediate between Np_3O_8 and NpO_2 were obtained from the product heated at 550° (Expt. 36c); however, the Np_3O_8 structure seems to persist, over a fairly large range of composition. A number of products were obtained, the compositions of which are still undetermined. Treatment of $(NH_4)_2Np_2O_7{\cdot}H_2O$ with NO_2 at 100° gave a pattern not previously observed, but its identification is still in doubt; this material is converted to Np_3O_8 on heating in nitrogen dioxide at 350°. Still another unidentified pattern was obtained from an ammonia precipitate of an Np(VI) solution dried at 70° and treated with nitrogen dioxide at 100° for one hour. The product in this case appears to be a neptunyl compound.

In the course of all of this work, no pattern analogous to any one of the four UO_3 modifications was observed.

A number of experiments were performed with neptunium oxides obtained by treatment of Np-

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(12) G. T. Seaborg and A. C. Wahl, *Phys. Rev.*, **73**, 940 (1948).

(IV) and Np(V) solutions with hydrogen peroxide. Hydrogen peroxide gives a light-grey precipitate with Np(IV) and Np(V) solutions. Neptunium appears to be in the (IV) oxidation state in its peroxide. This conclusion is based on the similarity of X-ray patterns of neptunium and uranium peroxide; the latter is known to be $UO_4 \cdot 2H_2O$ and to contain U(IV). Neptunium peroxide dried at 70° possesses an X-ray pattern similar to NpO_2, but differences in the oxygen periodicities exist. Such a substance thus appears to be representative of transition states intermediate between the peroxide and NpO_2. No reaction occurred on treatment of this intermediate oxide with NO_2 at 250°.

Determination of the Formula and Stability of Np_3O_8.—Although the X-ray crystallographic results show the higher neptunium oxide to be isomorphous with U_3O_8, this unfortunately is not sufficient to establish the formula of the higher neptunium oxide unambiguously. This circumstance arises from the fact that the volume of the unit cell of the neptunium compound is found to be 110.7 cu. Å., whereas that of U_3O_8 is 110.4 cu. Å. It might be expected that the volume of the unit cell of the neptunium compound would be smaller than that of uranium because of the "actinide contraction" effect. At least two explanations for this discrepancy may be advanced. First, that the Np_3O_8 represents a less closely packed structure than U_3O_8, or secondly, that the composition of the higher neptunium oxide is actually in the vicinity of Np_6O_{17} ($NpO_{2.83}$), by analogy to the known oxide U_6O_{17}. Consequently, a direct determination of the formula was desirable in view of the difficulty in arriving at a decision on the basis of purely crystallographic considerations.

An apparatus was therefore constructed in which the amount of oxygen liberated on thermal decomposition by 2–3 mg. of higher neptunium oxide could be accurately measured. This apparatus is shown in Fig. 2. It consists of a small quartz vessel connected to a differential manometer made of capillary tubing. The volume of the quartz vessel to the calibration mark of the manometer was 1.26 cc. The tip of the quartz vessel could be heated by a platinum wound stainless steel furnace fitted with a chromel–alumel thermocouple. In operation, a sample of oxide (2–3 mg.) is placed in the quartz vessel and weighed in a micro-balance. The vessel is attached to the line with apiezon wax. The apparatus is then thoroughly evacuated and the sample pumped on for six to ten hours. Mercury is then allowed to rise in the capillary manometer to the calibration mark and the sample heated at a high enough temperature to ensure decomposition. The resultant pressure is determined by admitting argon to the system until the capillary manometer shows no pressure differential. The pressure is then read on the auxiliary manometer; we believe that our pressure determinations have a precision of 0.5 mm. To correct for the fact that a portion of the apparatus is at a high temperature, a series of calibration curves were prepared by heating oxygen at various initial pressures at a series of temperatures. From these curves it is possible to determine the increase in the pressure reading due to the high temperature zone. Alternatively, the entire apparatus may be allowed to cool to room temperature before reading the pressure. Pressures determined by both procedures agreed well. The apparatus was checked by determining the formula of a uranium trioxide sample of high purity. Assuming U_3O_8 to be the product of decomposition, the formula deduced for the starting material, based on a number of experiments on samples ranging from 1 to 10 mg. was $UO_{2.989}$. The observed values were all within 5 per cent. of the calculated value for uranium trioxide.

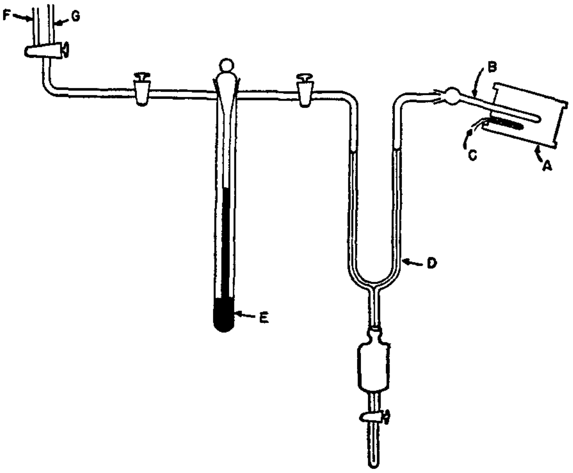

Fig. 2.—Apparatus for measuring decomposition pressures and determining formulas of oxides: A, furnace; B, reaction bulb; C, thermocouple well; D, capillary manometer; E, manometer; F, vacuum line; G, argon line.

The formula of the higher neptunium oxide was established in the same manner. A 2.56-mg. sample of the neptunium oxide was heated to 700°; the total pressure developed in the apparatus was 45 mm. (reduced to room temperature). (On cooling to room temperature, a small fraction (about 8%) of the oxygen is reversibly adsorbed by the quartz and the NpO_2. The adsorbed gas is readily evolved on re-heating.) The formula calculated for the higher oxide prepared by NO_2 oxidation of Np(IV) hydroxide (Exp. 35b, Table II) is thus $NpO_{2.64 \pm 0.03}$ based on the reaction

$$Np_3O_8 \longrightarrow 3NpO_2 + O_2$$

The apple-green product of the decomposition was shown by precision X-ray measurements to be very pure NpO_2. The formula Np_6O_{17}($NpO_{2.83}$) considered as a possible formula in the light of the crystallographic data (see above) is therefore excluded.

The apparatus lends itself to a comparison of the ease of decomposition of Np_3O_8 and UO_3. Decomposition curves were obtained by heating the samples at 100° temperature intervals until the pressure was constant for at least one hour. The composition of the solid phase in "equilibrium" with that particular pressure at a given temperature could then be calculated. Equilibrium in this case refers to a greatly decreased rate of oxygen evolution. Since the range UO_3–U_3O_8 is monophasic, equilibrium dissociation pressures are not observed in this case; the irreversibility of the decomposition reaction makes the thermodynamic significance of these pressure–temperature relations difficult to evaluate. Nevertheless, certain features of the decomposition curves (Fig. 3 and Fig. 4) are perfectly reproducible. Thus, in the case of the uranium oxides, a plateau between 450–550° corresponding to an oxide composition $UO_{2.92}$ is observed. A similar plateau is implicit in the results of Biltz and Müller[4] and of N. W. Taylor.[13] It will be recalled that oxidation of UO_2 by nitrogen dioxide yielded products of composition between $UO_{2.86}$ and $UO_{2.91}$. Thus it would seem that the composition $UO_{2.91}$, although not a new phase, is distinguished by a particularly stable configuration.

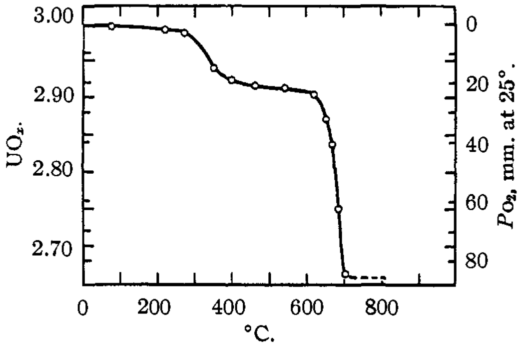

Fig. 3.—Decomposition curve of uranium trioxide.

The thermal decomposition curve of Np_3O_8 is given in Fig. 4. No plateau indicative of a stable oxide intermediate between NpO_2 and Np_3O_8 is observed. Oxygen is lost at 500° and the decomposition is essentially complete at 600°. The lack of true equilibrium makes application of the phase rule to these observations difficult. Although few X-ray data are as yet available, Np_3O_8 probably behaves similarly to U_3O_8 in that a continuous region may exist between Np_3O_8 and Np_2O_5, passing into a diphasic region between Np_2O_5 and NpO_2. Some support is furnished by the observation that in one instance a sample of supposedly pure Np_3O_8 yielded on decomposition half the expected amount of oxygen. X-Ray analysis showed that this sample actually consisted of a mixture of approximately equal parts of Np_3O_8 and NpO_2, with no evidence for the presence of an intermediate phase.

We thus find a marked similarity between the thermal stability of Np_3O_8 and UO_3. Since oxides higher than Np_3O_8 may be expected to be even less stable, the prospect of preparing compounds such as NpO_3 now appears rather remote.

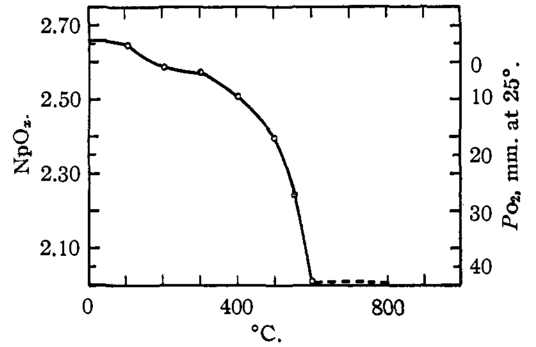

Fig. 4.—Decomposition curve of Np_3O_8.

NpO_2 shows no decomposition on heating in vacuum to 1100°. The ignited oxide is exceedingly refractory. It does not react with nitrogen dioxide, and can be satisfactorily dissolved only by such vigorous procedures as pyrosulfate fusion.

Plutonium, Americium and Protactinium Oxides with Nitrogen Dioxide.—These experiments were carried out using the capillary technique described by Fried and Davidson.[6] In each case, about 10–50 micrograms of dried hydroxide precipitate, *e. g.*, hydrated plutonium(IV) oxide, americium(III) oxide, and protactinium(V?) oxide were treated with nitrogen dioxide in X-ray capillaries in the temperature range 100–500°. X-Ray examination showed no oxidation in the case of plutonium and americium beyond the dioxide stage, and was inconclusive for protactinium. (The small amount of protactinium at our disposal precluded further chemical studies.) Since no evidence was found for higher oxidation states, these experiments need not receive detailed discussion, except to point out that the difficulty in attaining higher oxidation states of these elements in the solid state seems to be in agreement with the relative difficulties experienced in obtaining the higher oxidation states of these actinides in solution.

Some Remarks on the Mechanism of Nitrogen Dioxide Oxidations.—Nitrogen dioxide is of course a complex reagent. Some N_2O_4 is always present in equilibrium with the NO_2, and the slow, reversible reaction

$$NO_2 \rightleftarrows NO + {}^1/_2O_2$$

takes place to a significant extent even at 400°.[14] Since the rate of oxidation increases with increasing temperature where the equilibrium concentration of N_2O_4 becomes vanishingly small, N_2O_4 is presumably not the active reagent, although it may be important in the adsorption phenomena. Likewise, the oxygen liberated by decomposition of nitrogen dioxide cannot be important under our

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(13) N. W. Taylor, THIS JOURNAL, 53, 4459 (1931).

(14) For a review of the chemistry of the nitrogen oxides, see D. M. Yost and H. Russell, "Systematic Inorganic Chemistry," Prentice-Hall, New York, N. Y., 1944, p. 27 *et seq.*

conditions, since pure oxygen itself will not lead to oxidation. In other experiments, to be reported later, we have found that atomic oxygen acting on U_3O_8 gives rise to the same crystal modification of UO_3 (Phase I) as does nitrogen dioxide. As mentioned above, nitrogen dioxide is strongly adsorbed by the lower oxides. We would therefore like to suggest that the active reagent in the nitrogen dioxide oxidations is atomic oxygen, which originates from the adsorbed nitrogen dioxide when sufficient thermal energy is imparted to the molecule. In the absence of reliable adsorption and kinetic data, further speculation does not appear warranted. Assuming atomic oxygen mechanisms for reactions of the type discussed here, nitrogen dioxide reactions will be more favorable than molecular oxygen reactions by an amount corresponding to the difference in the heats of adsorption and heats of dissociation between nitrogen dioxide and molecular oxygen.

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Summary

1. Nitrogen dioxide oxidation of U_3O_8 above 250° results in a brick-red anhydrous UO_3 with a crystal structure distinct from other known phases of UO_3.

2. Nitrogen dioxide oxidation of UO_2 results in products varying in composition from $UO_{2.2}$ to $UO_{2.9}$, depending on the temperature.

3. Treatment of Np(IV, V, VI) hydroxide precipitates (dried at 70°) with nitrogen dioxide at 300–450° yields Np_3O_8, isomorphous with U_3O_8. Direct analysis of the product leads to the formula $NpO_{2.64 \pm 0.03}$.

4. Thermal decomposition curves of UO_3 and Np_3O_8 have been compared. The former shows a region of stability corresponding to the formula $UO_{2.91}$. The curve for Np_3O_8 shows no plateau but indicates a marked similarity in the thermal stabilities of UO_3 and Np_3O_8.

5. Attempts at the preparation of NpO_3 and higher oxides of plutonium, americium and protactinium were unsuccessful.

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[CONTRIBUTION FROM COATES CHEMICAL LABORATORY, LOUISIANA STATE UNIVERSITY]

The Alkaline Hydrolysis of Ethyl Acetate from the Standpoint of Ion-Dipole Theory

BY JAMES EDWARD POTTS, JR.,[1] AND EDWARD S. AMIS[2]

We have been interested in the rates of reaction between ions and dipolar molecules. Among the reactions which have been studied have been the inversion of sucrose by hydrochloric acid,[3] the hydrolysis of ethylene acetal by perchloric acid,[3] and the hydroxide ion–diacetone alcohol reaction.[4] These reactions, the first two of which were of the positive ion–dipolar molecule type and the third of which was of the negative ion–dipolar molecular type, were discussed in relation to an equation derived[3] to explain ion–dipolar molecule reaction rates from a theoretical standpoint.

The alkaline hydrolysis of ethyl acetate was chosen for the purpose of further investigating the ion–dipolar molecule type of reaction. The velocity of the reaction is favorable for study and there are no complications, the strictly second order rate equation holding throughout.

Experimental

The ethyl acetate used in these experiments was a colorless sample purified as described by Weissberger and Proskauer.[5] The ethyl acetate was dried with anhydrous potassium carbonate and one gram of water added for each 250 g. of ester, after which it was distilled through a 36 inch column packed with $^1/_8$ inch single turn stainless steel helices and equipped with a total reflux partial take-off still head. Any alcohol remaining in the mixture passed off as a water–alcohol–ester azeotrope. The ethyl acetate which distilled at 77.1° under pressure of 760 mm. was stored in a pyrex erlenmeyer flask fitted with a ground glass stopper. One-gram samples of the material were analyzed, by adding twice the theoretical amount of standard sodium hydroxide solution, allowing the mixture to stand one hour at 70°, and titrating the excess alkali with standard acid. The average of four analyses gave the ratio of moles of sodium hydroxide per mole of ethyl acetate reacting to be 1.0025.

The ethyl alcohol was purified by the method of Young as described by Weissberger and Proskauer.[5] One liter of 95% grain alcohol was refluxed for four hours with 300 g. of calcium oxide and distilled. A large middle fraction from this distillation was refluxed with calcium metal and distilled, yielding absolute alcohol. A middle fraction comprising about two-thirds of the material was retained for use.

Freshly boiled distilled water was used in the preparation of solutions containing water.

Carbonate-free sodium hydroxide stock solutions were prepared by dissolving chemically pure sodium hydroxide in water in a one to one weight ratio. The concentrated solution was allowed to stand in a covered container for twenty-four hours, after which the clear supernatant liquid

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(1) Present address: Bakelite Corporation, Bloomfield, New Jersey.

(2) Present address: Chemistry Department, University of Arkansas, Fayetteville, Arkansas.

(3) Amis and Jaffe, *J. Chemical Phys.*, **10**, 598 (1942).

(4) Amis, Jaffe and Overman, THIS JOURNAL, **66**, 1823 (1944).

(5) Weissberger and Proskauer, "Organic Solvents," Oxford University Press, London, 1935.