perchlorate solutions is attributed in part to the formation of a weak chloride complex of U(IV).

The potential of the reaction

$$UO_2^+ \rightleftarrows UO_2^{++} + e^-$$

is −0.063 ± 0.004 v. in 1 *M* perchloric acid at 25°. Chloride ion also appears to form a weak complex with the uranyl ion.

The reduction of UO_2^+ at the dropping mercury electrode is hydrogen ion dependent in the absence of the maximum suppressors thymol and gelatin.

Chicago 80, Illinois Received August 30, 1948

[Contribution from the Chemical Laboratory of the University of California]

The Potential of the Uranium(V), Uranium(VI) Couple and the Kinetics of Uranium (V) Disproportionation in Perchlorate Media[1,2]

By D. M. H. Kern and E. F. Orlemann

Introduction

The disproportionation of pentavalent uranium into the four and six states in aqueous solutions has long been known to be very rapid. Herasymenko[3] reported that the formation and disproportionation of uranium(V) could be detected during reduction of uranyl ion at the dropping mercury electrode (d. m. e.). His evidence for these conclusions was meager, but they have since been completely confirmed by the polarographic studies of Kolthoff and Harris[4] and the unpublished work of Heal.[5] Heal estimated the rate of disproportionation of uranium(V) by observing the rate at which a platinum electrode came to equilibrium after a small amount of uranium(V) was formed in a uranium(VI) solution; his data indicated that the rate of disproportionation in sulfate solutions was second order in uranium(V) and first order in hydrogen ion, but the precision of the measurements was very limited.

In the present investigation millimolar solutions of uranium(V) have been prepared by a controlled reduction of uranium(VI) in sodium perchlorate, perchloric acid solutions at a mercury cathode, a method used previously by Kraus[6] in chloride media. The potentials of the uranium(V), uranium (VI) couple and the rate of disproportionation of uranium(V) have been determined in solutions of varying acidity, and these measurements have served to establish the nature of the uranium(V) species and the most probable mechanism of disproportionation in these solutions.

Experimental

Reagents.—Merck reagent grade uranyl nitrate was converted to the perchlorate by evaporation with perchloric acid, and also by precipitation of ammonium diuranate, which was dissolved in perchloric acid, reprecipitated, and redissolved. The uranium content of the stock solutions was determined gravimetrically as (U_3O_8).

Reagent grade sodium perchlorate and perchloric acid were used without further purification; they were found to be free of chloride.

The Cell.—The electrolysis cell is shown in Fig. 1. The volume of the anode compartment, 2.5 ml., was sufficiently small compared to the total solution volume of 250 ml. so that diffusion of material through the sintered glass disc after electrolysis could be neglected. Thus current voltage (c. v.) curves could be obtained and the disproportionation of uranium(V) could be followed by means of the d.m.e. in the cathode compartment immediately after an electrolysis. Purified nitrogen or hydrogen was used to free the body of the solution of air and to sweep oxygen out of the anode compartment during electrolysis.

Electrolysis Procedure.—Solutions containing 0.1 to 0.5 *M* $NaClO_4$, 0.002 *M* $UO_2(ClO_4)_2$ and about 0.002 *M* $HClO_4$ were freed of oxygen and electrolyzed for thirty minutes or less at a rate of between twenty and forty milliamps. The vigorously stirred mercury cathode was maintained at a potential of −0.55 v. against a saturated calomel reference electrode (S. C. E.) by an adaptation of the potential controlling device described by Lingane.[7] Such electrolyses usually produced 0.001 *M* uranium(V).

Dropping Mercury Electrode Measurements.—Current-voltage curves were obtained with a manual apparatus of the type described by Kolthoff and Lingane.[8] All measurements were made at a temperature of 25.00 ± 0.05°.

Results

Diffusion Current Constant of Uranium(V).—In the kinetic studies, the uranium(V) concentrations were obtained from the diffusion currents of the uranium(V) oxidation wave at the d. m. e. A well-defined diffusion current region is available for such measurements as shown in Fig. 3.

In order to calculate uranium(V) concentrations from the observed currents, the diffusion current constant was determined by amperometric titrations of uranium(V) with ferric ion. An air-free solution of 0.02074 *M* $Fe(ClO_4)_3$, was added in small amounts to 250 ml. of millimolar uranium(V) in a 0.4 *M* $NaClO_4$ solution and the decrease in the diffusion current of uranium(V) at +0.1 v. (*vs.* the S.C.E.) was determined. The ob-

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[1] This paper is based on work performed under Contract Number W-7405-eng-48B with the Atomic Energy Commission in connection with the Radiation Laboratory of the University of California, Berkeley, California.

[2] Presented at the Symposium on the Transuranic Elements at the meeting of the American Chemical Society, Chicago, Illinois, April, 1948.

[3] P. Herasymenko, *Trans. Faraday Soc.*, **24**, 272 (1928).

[4] I. M. Kolthoff and W. E. Harris, This Journal, **68**, 1175 (1946); **67**, 1484 (1945).

[5] H. G. Heal, *Nature*, **157**, 225 (1946), and private communications.

[6] K. A. Kraus, private communication.

[7] J. J. Lingane, *Ind. Eng. Chem., Anal. Ed.*, **17**, 332 (1945).

[8] I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1941, p. 215 ff.

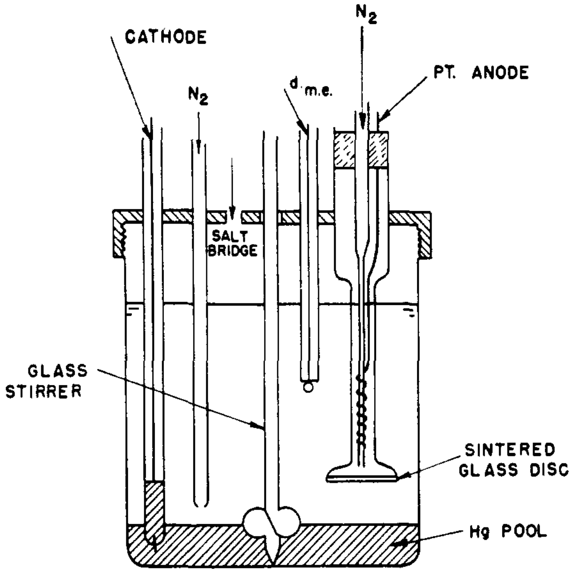

Fig. 1.—Combined electrolysis and polarographic cell.

served currents were corrected for the residual current and the change in volume; the acidity was sufficiently low and the titration sufficiently rapid, so that a significant amount of disproportionation did not occur during the experiments.

A typical plot of the corrected diffusion currents against the volume of added ferric perchlorate is shown in Fig. 2. From this figure it is evident that the relation $i_d = K[U(V)]$ is followed. Experimental values of the diffusion current constant, K, in 0.4 M $NaClO_4$ at 25° are

pH	2.9	3.1	3.5
K in μamp. (mmol./l.)$^{-1}$	3.07	3.06	3.18
$m^{2/3}t^{1/6}$ in mg.$^{2/3}$ sec.$^{-1/2}$	1.925	1.925	1.945

There is no trend with pH over this small interval.

The Diffusion Coefficients of Uranium(V) and Uranium(VI).—The diffusion current constant is related to the diffusion coefficient, D, the rate of flow of mercury, m, the drop time, t, and the number of electrons transferred per molecule, n, by the Ilkovic equation[9]

$$K = 605nm^{2/3}t^{1/6}D^{1/2} \tag{1}$$

Substitution of the experimental data into this equation leads to a value of 0.70 ± 0.02 × 10^{-5} cm.^{2} sec.$^{-1}$ for the diffusion coefficient of U(V) in 0.4 M $NaClO_4$ at 25°.

Measurement of the diffusion currents of 1.8 and 3.6 × 10^{-3} M UO_2^{++} in 0.09 M $NaClO_4$, 0.01 M $HClO_4$ (with a capillary with $m^{2/3}t^{1/6}$ = 2.145 mg.$^{2/3}$ sec.$^{-1/2}$) gave a value of 3.38 ± 0.01 μamp. (mmol./l.)$^{-1}$ for the diffusion current constant and a calculated value of 0.68 × 10^{-5} cm.^{2} sec.$^{-1}$ for the diffusion coefficient of uranium(VI). Kolthoff and Harris[2] reported a value 0.62 × 10^{-5} in 0.1 M KCl, 0.01 M HCl at 25°. The difference between these values is possibly due to complexing by chloride ion in the latter case.

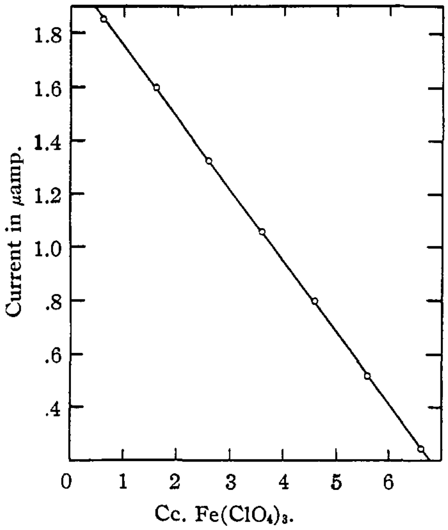

Fig. 2.—Amperometric titration of uranium(V) with $Fe(ClO_4)_3$ at the d. m. e.

The Uranium(V), Uranium(VI) Potential and the Effect of Hydrogen Ion.—In connection with the mechanism of uranium(V) disproportionation it was necessary to establish the nature of the uranium(V) species in perchlorate medium. To this end, the effect of hydrogen ion on the potential of the uranium(V), uranium(VI) couple was determined with the d. m. e. since uranium (V) disproportionates too rapidly to allow direct e. m. f. measurements except at very low acidities.

In the polarographic literature it is customary to have the cell reaction correspond to reduction at the d. m. e. and oxidation at the reference electrode. With this convention the current voltage equation for a reversible reduction of uranium(VI) to uranium(V) at 25° is[10]

$$E = E_{1/2} + 0.0591 \log (i_d - i)/i \tag{2}$$

$$E_{1/2} = E^0 + 0.0591 \log \frac{\gamma(\mathrm{VI})}{\gamma(\mathrm{V})} \left[\frac{D(\mathrm{V})}{D(\mathrm{VI})}\right]^{1/2} \tag{3}$$

In these equations E^0 is the standard potential of the couple referred to a specified reference electrode; $E_{1/2}$ is the potential measured when i equals one-half the diffusion current, i_d; the symbols (V) and (VI) refer to uranium(V) and uranium(VI); and the other symbols have their usual significance.

Before these equations can be applied to uranium(VI) reduction waves, it must be shown that the couple is reversible at the d. m. e., and that the disproportionation of uranium(V) does not contribute significantly to the uranium(VI) diffusion current. That the latter condition is met can be shown from the data in Table II. In the most severe case, (0.4 M $HClO_4$), the half life of millimolar uranium(V) is about twenty-five seconds as compared to the three second lifetime of a drop. That the couple is reversible is demon-

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[9] See ref. 6, p. 55.

[10] See ref. 6, p. 144.

strated by the c. v. curves of mixtures of uranium(V) and uranium(VI); the curve shown in Fig. 3 is a typical one. This curve is analyzed in Fig. 4, where log $(i_d - i)/i$ is plotted against E after shifting the current origin from zero to the uranium(V) diffusion current. The observed slope in Fig. 4 is 0.062 v. in satisfactory agreement with the theoretical value of 0.059 v. Equally important, Fig. 4 shows that the c. v. curve is continuous as the net process changes from an oxidation of uranium(V) to a reduction of uranium(VI). These facts are definite proof that the couple is reversible at the dropping mercury electrode, and confirm the assumption of reversibility by previous investigators.[2,3] It should be noted that a linear relation between E and log $(i_d - i)/i$ of the theoretical slope, for the c. v. curves of uranium (VI) alone, is a necessary but not a sufficient condition for reversibility.

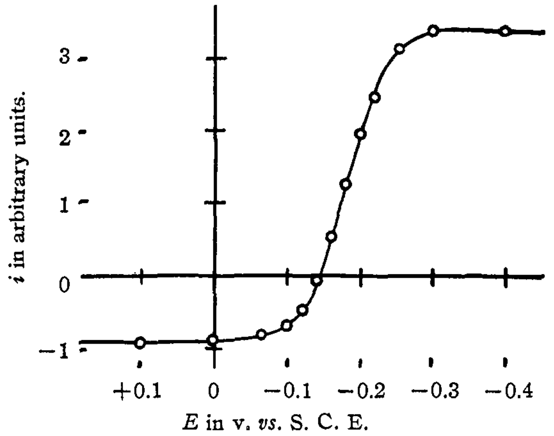

Fig. 3.—C. v. curve of a U(V)-U(VI) mixture in perchlorate medium.

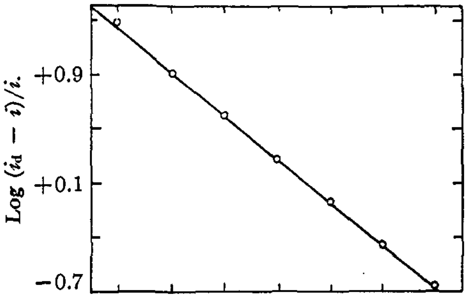

Fig. 4.—Analysis of the c. v. curve of Fig. 3.

Current voltage curves of *ca.* 0.002 M UO_2^{++} were obtained in sodium perchlorate, perchloric acid solutions of ionic strength 0.5. A mercury pool of large area served as an anode; a hydrogen electrode was used in the cell solution as a reference for all measurements of the potential of the d. m. e. In this way a possible iR correction was avoided and liquid junction potentials were eliminated. The latter were found to be serious in 0.1–0.5 M $HClO_4$ when a S. C. E. reference electrode was tried. Reduction of uranium at the platinum surface was found too slight to interfere with the measurements; in two of the runs, the platinum electrode was separated from the d. m. e. by a sintered glass barrier. The observed $E_{1/2}$ values reported in Table I were obtained by plotting $\log(i_d - i)/i$ *vs.* E, as in Fig. 4; they include the change in potential of the hydrogen electrode due to the change in pH of the solutions. The potential of the hydrogen electrode in each of these solutions was then calculated and subtracted from the observed $E_{1/2}$ to obtain values of $E_{1/2}$ *vs.* the standard hydrogen electrode (column four of Table I). At the high acidities (0.1–0.5 M $HClO_4$) the concentration of acid was determined by titration and a mean activity coefficient of 0.75 was used to calculate the corresponding hydrogen ion activities. The value 0.75 is an arbitrary average based on the data given by Latimer,[11] from which it is found that $\gamma \pm$ of perchloric acid changes only by a few hundredths of a unit in going from 0.1 to 0.5 M $HClO_4$. The assumed activity coefficient affects the apparent constancy of $E_{1/2}$ from 0.003 to 0.096 M $HClO_4$ and the absolute value of $E_{1/2}$ *vs.* the N. H. E. It does not alter the observed constancy of $E_{1/2}$ from 0.096 to 0.482 M $HClO_4$. An error of 10% in the assumed activity coefficient makes an error of 2.4 mv. in the reported value of $E_{1/2}$; we believe the value used is correct within 10%.

TABLE I

HALF-WAVE POTENTIAL OF URANIUM(VI), URANIUM(V) COUPLE AT 25° AND IONIC STRENGTH 0.5 IN $NaClO_4$–$HClO_4$ SOLUTIONS

Obs. $E_{1/2}$, v.	$HClO_4$, M	a_{H^+}	$E_{1/2}$ (N. H. E.), v.
0.214	...	0.0028[b]	0.063
.130	0.096	.072	.062
.101	.289	.22	.062
.088	.482	.36	.062

[b] Measured with a quinhydrone electrode.

Since the uranium(VI) species is known to be UO_2^{++} at these acidities[12] and the reversible potential of the couple has been shown to be independent of pH, the principal uranium(V) species from 0.003 M to 0.48 M $HClO_4$ must be UO_2^+ (or a hydrated UO_2^+).

Substitution of the value of $E_{1/2}$ and the previously given values of the diffusion coefficients of uranium(V) and uranium(VI) into equation (3) leads to the result

$$UO_2^+ = UO_2^{++} + e^-$$

$$E^0\ (25°,\ \text{N. H. E.}) = -0.062 \pm 0.002 + 0.059 \log (\gamma_{UO_2^{++}}/\gamma_{UO_2^+})$$

in $NaClO_4$–$HClO_4$ solutions of $\mu = 0.5$.

Kinetics of Disproportionation of Uranium(V).—The acidity of sodium perchlorate, perchloric

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[11] W. M. Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 1938, p. 323.

[12] W. E. Harris, Ph.D. Thesis, University of Minnesota, 1944.

acid solutions of ionic strength 0.4 was varied from 0.02 to 0.4. The rate of disproportionation of uranium(V) was then determined in these solutions by measuring the uranium(V) diffusion current at +0.1 v. *vs.* S. C. E. at thirty second intervals. After uranium(V) had been prepared by electrolysis of uranium(VI) in a slightly acid solution of the required sodium perchlorate concentration, the desired amount of oxygen free perchloric acid was added by buret, and the solution was mixed by a stream of purified hydrogen or nitrogen. Oxygen reacts very rapidly with uranium(V); the rate is comparable to the rate of disproportionation of uranium(V) at the higher acidities. Since the uranium(V) concentration was always millimolar or less, even traces of oxygen caused difficulty. At low acidities the initial uranium(V) concentration was only a fraction of millimolar to avoid changes of hydrogen ion concentration during the reaction. At high acidities the initial measurements were made at small concentrations because the disproportionation was too fast to be followed until most of the uranium(V) had reacted.

The amperometric titrations of uranium(V) previously described showed a linear dependence of the diffusion current on the uranium(V) concentration. In view of this fact, a linear relation between the reciprocal of the diffusion current and the time, as shown for a typical run in Fig. 5, demonstrates that the rate is proportional to the second power of the uranium(V) concentration. In all cases from 10^{-3} to 10^{-5} *M* UO_2^+ and from 0.02 to 0.5 *M* $HClO_4$ this second order dependence was found. The observed rate constants corresponding to the expression

$$-\frac{d[UO_2^+]}{dt} = k''[UO_2^+]^2$$

are tabulated in Table II. Unless otherwise indicated, the hydrogen ion activities a_{H^+} in column two were obtained from the potentials of a quinhydrone electrode. The last column shows the first order dependence on the hydrogen ion activity. The accuracy of the results is probably less than might be concluded from the precision.

TABLE II

RATE OF DISPROPORTIONATION OF URANIUM(V) AT 25° AND IONIC STRENGTH 0.4 IN $NaClO_4$–$HClO_4$ SOLUTIONS

k'', (moles/l.)$^{-1}$ sec.$^{-1}$	a_{H^+}	k''/a_{H^+}, (moles/l.)$^{-1}$ sec.$^{-1}$
2.77	0.0216	128
4.69	.0365	128
6.76	.0555	122
9.64	.0711	135
10.8	.0843	128
25.9	.197[b]	131
35.2[a]	.260[b]	135
43.8[a]	.318[b]	137
40.5[a]	.322[b]	126
		Av. 130 ± 4

[a] Ionic strength = 0.5. [b] Activity calculated as described in connection with Table III.

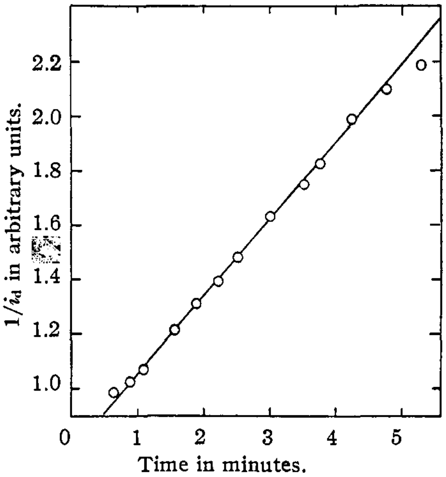

Fig. 5.—Typical plot of the reciprocal of the U(V) current against time.

It follows from the data in Table II that the rate law is

$$-d[UO_2^+]/dt = ka_{H^+}[UO_2^+]^2 \quad (4)$$

$k = 130 \pm 4$ (moles/l.)$^{-1}$ sec.$^{-1}$ at 25.0° in $NaClO_4$–$HClO_4$ of $\mu = 0.4$.

The effect of ionic strength, over a limited range, is shown in Table III. The rate of disproportionation was determined as before, but in 0.1 *M* $NaClO_4$ solutions of varying perchloric acid concentration. The data show an increase in rate with an increase in ionic strength as would be predicted by the Brönsted theory for the proposed reaction mechanism, in which the activated complex is $(UO_2UOOH)^{+++}$. However, the experimentally possible ionic strength range is too high to permit a detailed analysis of this point.

TABLE III

THE EFFECT OF IONIC STRENGTH ON THE RATE OF URANIUM(V) DISPROPORTIONATION IN $NaClO_4$–$HClO_4$ SOLUTIONS AT 25°

μ	k'', (moles/l.)$^{-1}$ sec.$^{-1}$	a_{H^+}	k''/a_{H^+}, (moles/l.)$^{-1}$ sec.$^{-1}$
0.119	1.67	0.0214	78
.137	3.08	.0383	80
.156	4.61	.0577	80
.174	6.41	.0725	88
.192	8.29	.0852	97
.281	18.9	.158	120
.40	...	.02–0.3	130

Mechanism of Disproportionation.—The most probable mechanism of disproportionation in acid perchlorate solutions is

$$UO_2^+ + H^+ = UOOH^{++} \quad (5)$$

$$UO_2^+ + UOOH^{++} \xrightarrow{k'} UO_2^{++} + UOOH^+ \quad (6)$$

$$UOOH^+ \longrightarrow \text{Stable U(IV) species} \quad (7)$$

In calculating a rate law corresponding to this mechanism of disproportionation the reverse reaction can be neglected because the equilibrium 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
RECEIVED DECEMBER 6, 1948

[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).