state.[16] In this active state tungsten is able to react with oxygen and water forming an unstable adsorption compound. This view is supported by the following experiment: The purest yellow bronze was mixed with anhydrous sodium tungstate and tungsten powder and pressed. Specimens of this mixture behaved in the same way as the sintered bronze specimens.

Acknowledgment.—The above-mentioned work was performed in the State Institute for Metal Chemistry, Marburg a. d. Lahn, Germany. One of the authors (A. Dravnieks) would like to extend his gratitude to Dr. R. Schenck, director, for permission to use the Institute facilities for this investigation.

Summary

The specific conductivity of pure yellow sodium tungsten bronze is about 400 ohm^{-1} and the temperature coefficient is negative. The conductivity is electronic.

The temperature coefficient is definitely negative also for bronzes with up to 20% of tungsten trioxide (in solid solution). The highest specific conductivity (600 ohm^{-1}) is shown by the violet bronze with 38.8% of tungsten trioxide. At higher trioxide contents the resistance of the powder increases.

In the preparation of sintered specimens of sodium tungsten bronzes the $NaWO_3$ decomposes partly upon heating in vacuum, and tungsten, sodium tungstate and similar products are formed. These products cement the powder to a hard, brittle, porous specimen. Tungsten particles form conducting bridges between the crystals of actual bronze. The bridges are interrupted reversibly to some extent by moist oxygen. In this way the peculiar electrical behavior of sintered specimens can be completely explained.

Specimens with more than 35% of trioxide do not contain any free tungsten; therefore, the increase in resistance in moist air does not occur.

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[16] Anhydrous sodium tungstate is quasicubic and the lattice constant is ~5.57 kX.

[CONTRIBUTION FROM THE CHEMISTRY DIVISION OF THE ARGONNE NATIONAL LABORATORY]

The Oxidation States of Neptunium in Aqueous Solution[1,2]

BY J. C. HINDMAN, L. B. MAGNUSSON[3] AND T. J. LACHAPELLE[3a]

The preliminary investigation in 1940 by the discoverers of element 93 (neptunium), McMillan and Abelson,[4] led these authors to the conclusion that there were lower and upper oxidation states of neptunium analogous to the +4 and +6 oxidation states of uranium. These and other experiments,[5] including those by Voigt, Sleight, Hein and Wright,[6] which suggested the possible existence of a +5 oxidation state, were performed by tracer methods using the 2.3 day beta emitting isotope Np^{239}. By use of the long-lived alpha emitting Np^{237} discovered in 1942 by Wahl and Seaborg,[7] it is possible to study neptunium with weighable amounts of material and in July, 1944, Magnusson and LaChapelle[8] succeeded in isolating the first pure compounds of neptunium using as the source of the Np^{237} uranium irradiated with cyclotron neutrons. At this time these investigators definitely established the existence of the +4 and +6 oxidation states by the preparation of microgram quantities of the solid compounds, neptunium(IV) dioxide, NpO_2, and sodium neptunium(VI) dioxytriacetate, $Na_2NpO_2(OOCCH_3)_3$. Zachariasen[9] was able to show by X-ray diffraction studies that these compounds were isomorphous with the analogous compounds of uranium and plutonium.

The isolation and purification of milligram quantities of Np^{237} made possible a more extensive investigation of the chemistry of this element. The first few milligrams were isolated as the result of special runs in the chemical extraction plant of the Clinton Laboratories (now the Oak Ridge National Laboratory) in Tennessee. The Np^{237} from this source was concentrated and isolated in pure form by a group from the Metallurgical Laboratory. This group was headed by J. J. Katz and consisted of Magnusson, LaChapelle, J. R. Gilbreath and W. C. Beard. Larger quanti-

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[1] This work was carried out during 1945 at the Metallurgical Laboratory of the University of Chicago under Contract No. W-7401-eng-37.

[2] Presented in part before the Division of Physical and Inorganic Chemistry at the Chicago Meeting of the American Chemical Society in April, 1948.

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[4] E. M. McMillan and P. H. Abelson, *Phys. Rev.*, **57**, 1185 (1940).

[5] G. T. Seaborg and A. C. Wahl, THIS JOURNAL, **70**, 1128 (1948).

[6] A. F. Voigt, N. R. Sleight, R. E. Hein and J. M. Wright, Manhattan Project report CN-1979, Oct. 10, 1944. To appear as paper No. 15.9 of Vol. 14B, Plutonium Project Record of the National Nuclear Energy Series.

[7] G. T. Seaborg and A. C. Wahl, to be published as paper No. 1.5, Vol. 14B, Plutonium Project Record of the National Nuclear Energy Series, *Phys. Rev.*, **73**, 940 (1948) (written on April 14, 1942).

[8] L. B. Magnusson and T. J. LaChapelle, Manhattan Project CN-2088, Sept. 1, 1944, THIS JOURNAL, **70**, 3534 (1948).

[9] W. H. Zachariasen, Manhattan Project report CN-2091, Sept. 4 (1944). To appear as papers Nos. 20.7, 20.8, Plutonium Project Record of the National Nuclear Energy Series; Symposium on Chemistry of Transuranium Elements, 1948 Spring Meeting, Am. Chem. Soc., Chicago, Ill., *Phys. Rev.*, **73**, 1104 (1948).

ties were obtained during 1945 as the by-product of the operation of the plutonium project plant at the Hanford Engineer Works in the State of Washington. This latter material was isolated as the result of a process designed for the recovery of neptunium at the Hanford Engineer Works by a group at the Metallurgical Laboratory under the direction of F. W. Albaugh and R. C. Thompson.

The initial objective of the work with pure neptunium was the identification of the oxidation states in aqueous solution. In the first part of this paper experiments are described which demonstrate the existence of the +4, +5 and +6 oxidation states of neptunium in solutions of perchloric, hydrochloric and sulfuric acids. That neptunium(III) could exist in aqueous solution was first shown polarographically by Watters.[10]

In the second part of the paper are described experiments on which are based a scheme of oxidation potentials relating the +3, +4, +5 and +6 oxidation states in hydrochloric acid solution.

1. The +4, +5 and +6 Oxidation States of Neptunium

It was expected that the various oxidation states of neptunium like those of uranium and plutonium would have highly characteristic absorption spectra in solution. After establishing the identity of a single oxidation state, one should then be able to titrate the neptunium solution spectrophotometrically with oxidizing or reducing agents and thus to determine the oxidation numbers of any higher or lower states produced.

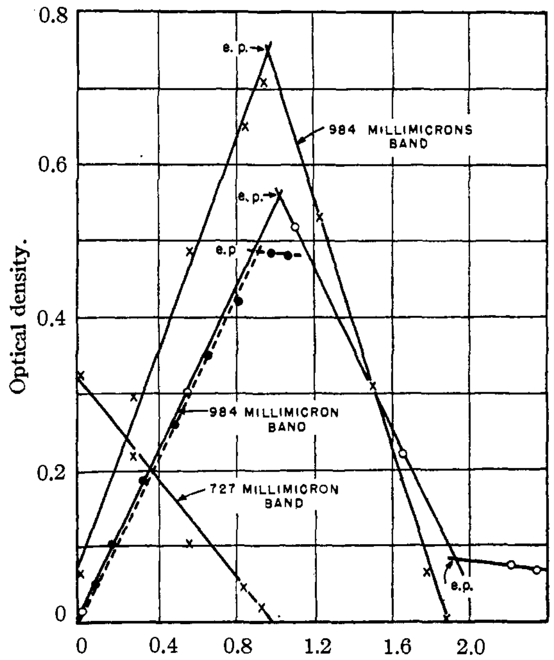

Fig. 1.—Titration of neptunium with oxidizing and reducing agents: ●, reduction of Np(VI) by Sn(II) in 1.0 *M* HCl; ×, oxidation of Np(IV) by Ce(IV) in 0.5 *M* H_2SO_4; ○, reduction of Np(VI) by Fe(II) in 0.5 *M* H_2SO_4.

Experimental

The absorption spectrum measurements were made with a Beckman quartz spectrophotometer. The instrument was operated, in general, at a slit width of 0.01 to 0.02 millimeter. Readings were made at 2 millimicron intervals in the spectral region from 350 to 600 millimicrons, at 2.5 millimicron intervals in the region from 600 to 1000 millimicrons, and at 5 millimicron intervals above 1000 millimicrons except in the vicinity of absorption bands where readings at 1 millimicron intervals were made. In the case of very sharp absorption bands the peak maximum was located by slowly rotating the wave length drum and finding the point of maximum deflection of the galvanometer. Special adapters were made so that Corex absorption cells of 1.000 ± 0.002 cm. and 0.500 ± 0.002 cm. could be used with samples of 1.1 and 0.5 milliliter of solution, respectively.

The first preparation for spectrophotometric examination was made by heating 1.16 mg. of dry, olive-green neptunium hydroxide (later identified as neptunium(IV) hydroxide) in 52 microliters of 9.40 molar perchloric acid. After several hours heating in a water-bath, dilution with water produced a clear, pale green solution, 1.0 molar in perchloric acid. The spectrum of this solution was marked by three sharp, strong absorption bands, at 723, 964 and 984 millimicrons. Later experiments showed this solution contained a mixture of oxidation states.

An excess of argentic oxide was added to the green solution, which turned nearly colorless with a faint pink cast. The strong, sharp absorption bands associated with the initial spectrum had disappeared. A dark brown "hydroxide" was precipitated from the solution by the addition of a slight excess of ammonia. This hydroxide was dissolved in warm 10 molar hydrochloric acid and the solution was diluted to 0.5 molar acid, becoming a yellow green in color. The spectrum was very similar to that of the perchloric acid solution after the argentic oxidation. The spectral identity was taken as evidence that the same oxidation state existed in both solutions.

The first production of a lower oxidation state was carried out by adding small aliquots of Sn(II) to the oxidized neptunium chloride solution. It was found that addition of stannous chloride caused the appearance of an absorption band at 984 millimicrons which increased in optical density until the amount of stannous chloride added was roughly equivalent to one-half mole per mole of neptunium. Further addition of stannous chloride produced only a slight reduction in peak height. A more precise duplication of this titration is illustrated in Fig. 1. An interesting phenomenon observed in the titration was the small growth of the 723 millimicron peak observed in the original perchloric acid solution. The peak disappeared rather quickly.

A neptunium fluoride precipitate (tentatively identified as $KNpF_5$ or K_2NpF_6) was made from the above solution by saturating the solution with sulfur dioxide, then making the solution one molar in potassium fluoride and four molar in hydrofluoric acid. This green precipitate was fumed to dryness with sulfuric acid yielding bright green crystals. An absorption spectrum of the solution produced when the crystals were dissolved in 0.5 molar sulfuric acid showed two prominent peaks at 727 and 971 millimicrons analogous to the peaks at 723 and 964 millimicrons observed in the original neptunium solution in perchloric acid.

Oxidation of the neptunium sulfate solution was carried out by adding aliquots of 0.069 molar Ce(IV) in 0.5 molar sulfuric acid. A peak at 984 millimicrons, corresponding to the peak produced by reduction of an oxidized solution with Sn(II), reached its maximum height when the mole ratio of added Ce(IV) to Np was approximately one. An additional equivalent of Ce(IV) reduced the peak to zero

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[10] J. I. Watters, Manhattan Project memorandum MUC-JIW-53, Feb. 8, 1945.

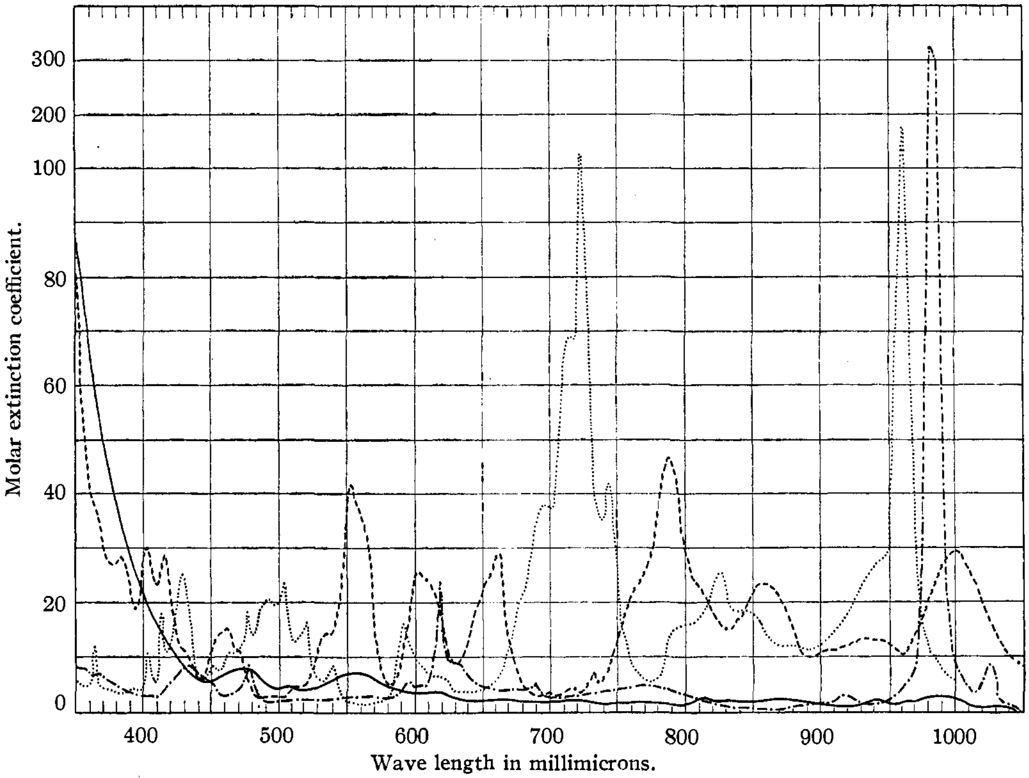

Fig. 2.—Absorption spectra of neptunium ions in aqueous solution: ---, Np(III) in 1.0 M HCl; ..., Np(IV) in 1.0 M HCl; -·-, Np(V) in 1.0 M HCl; —, Np(VI) in 1.0 M HClO$_4$.

optical density (Fig. 1). The spectrum of the latter solution was similar to that of the oxidized perchloric and hydrochloric acid solutions.

A six microliter sample (10 micrograms of neptunium) was removed from the ceric oxidized solution and precipitated in a capillary by making the solution four molar in sodium ion and two molar in acetate ion. An X-ray diffraction pattern of the precipitate was found by Zachariasen[9] to be identical with that of the salt he had previously identified as sodium neptunyl acetate, NaNpO$_2$(OOCCH$_3$)$_3$. On the basis of this evidence, it was concluded that the highest oxidation state obtained was +6. The oxidation numbers of the other two states are, therefore, +4 and +5. Data on the stoichiometric reduction of Np(VI) in 0.5 molar sulfuric acid by ferrous ion are also given in Fig. 1.

Discussion

Differences in absorption spectra have led to the identification of three oxidation states of neptunium in aqueous solution. The lowest state obtained is characterized by two strong, sharp absorption bands at 723 and 964 millimicrons in chloride or perchlorate solution. Figure 2 shows the spectrum of Np(IV) in 1.0 M hydrochloric acid solution. These bands are shifted to 727 and 971 millimicrons in 0.5 molar sulfuric acid solution. This shift is presumably caused by complex ion formation involving neptunium(IV) and sulfate ions. The next higher oxidation state, which differs in oxidation number by one unit from both the lowest state and highest state obtained as determined by stepwise spectrophotometric titration with oxidizing or reducing agents, has a spectrum characterized by a sharp, strong band at 984 millimicrons in perchlorate, chloride or sulfate solutions. Figure 2 shows the spectrum of the +5 oxidation state in 1.0 molar hydrochloric acid solution. Isolation of the salt NaNpO$_2$(OOCCH$_3$)$_3$ from the solution of highest oxidation number has been used to identify this state as the +6 oxidation state. The oxidation numbers of the other two states are +4 and +5. The spectrum of the +6 state shown in Fig. 2 has no marked absorption bands in the visible region of the spectrum. The spectrum of the +6 perchlorate is given rather than the chloride because of the difficulty in correcting the chloride spectrum for the presence of chlorine.

2. The Oxidation Potentials of Neptunium Couples

The Np(III)-Np(IV) Potential.—A preliminary attempt to prepare Np(III) by reduction of Np(IV) in 1.0 molar hydrochloric acid at a platinum cathode was unsuccessful, leading to the conclusion that the potential for the Np(III)–Np(IV) couple was more positive than zero. It has been found, however, that the failure to obtain Np(III) may be attributed to the extremely rapid oxidation of Np(III) in the presence of air. Watters[10] showed with the polarograph that Np(III) could be formed in solution; and, although the Np(III)-Np(IV) couple appeared to be irreversible at the dropping mercury electrode, Watters[10] estimated the formal oxidation potential of the couple in 0.25 molar sulfuric acid to be approximately +0.1 volt. Further experiments by the authors revealed that Np(III) could be obtained in fair yield in hydrochloric acid by reduction of Np(IV) with a mercury pool cathode and that Np(III) is stable with respect to oxidation by hydrogen ion in one molar hydrochloric acid.

Experimental

Gross neptunium concentrations were determined by radiometric assay. Assays of concentrations of the individual oxidation states were made spectrophotometrically. All potential measurements were made at 25 ± 1°, using a Rubicon precision potentiometer and galvanometer of 0.003 microampere per mm. sensitivity.

The micro-scale reduction cell employed for the preparation of Np(III) consisted of a 1-cm. corex spectrophotometer absorption cell with air-tight connections. Details of its construction are given elsewhere.[11] The complete electrolytic apparatus was mounted in a cell holder for convenient transfer to the Beckman spectrophotometer.

1.5 ml. of 0.00752 molar Np(IV) solution in 1.63 molar hydrochloric acid was placed in the cell and the cork sealed with ceresin wax. Oxygen was removed by bubbling pure nitrogen, saturated with water vapor, through the solution for ten minutes before the electrolysis. The solution was reduced by electrolyzing with a current density of *ca.* 8 milliamperes/sq. cm. Nitrogen was continuously bubbled through to stir the solution and to assist in maintaining an oxygen-free atmosphere. The reduction was stopped periodically and the nitrogen inlet and vent disconnected and sealed to permit insertion of the holder into the spectrophotometer. The extent of reduction was determined by observing the decrease in the 723 millimicron absorption band of Np(IV). The change in hydrochloric acid concentration was computed from the total number of coulombs passed through the cell. The solution was electrolyzed for a total of 1278 milliampere-minutes, resulting in a reduction of the hydrochloric acid concentration to 0.96 molar (no volume change perceptible). The optical density of the 723 millimicron band had been reduced to 16% of the value before electrolysis. The nitrogen inlet and vent were sealed and the complete absorption spectrum of the solution was measured over the range 350–1050 millimicrons. Over a period of two hours during the measurement of the absorption spectrum the optical density at 723 millimicrons increased by only 1% of the peak value.

A few bubbles of air were blown through the solution. Alternate measurements of the optical density of the 723 millimicron absorption band and the e.m.f. of the neptunium cell were made. The e.m.f. measurements were made using the Hg^0 cathode as the indicator electrode and a saturated potassium chloride–calomel electrode as the reference electrode. The 723 millimicron absorption band optical density was observed to increase steadily over a period of five hours to the maximum value observed in the pure Np(IV) solution before the electrolysis. The measured potentials were very stable, shifting slowly to less positive values as the oxidation proceeded. At the completion of the experiment radiometric assays showed the concentration of the neptunium to be the same as before the electrolysis.

Results

The color of the Np(III) solution was pale purple, similar to that of U(III) and Pu(III). From a plot of the complete absorption spectrum measured immediately after the electrolysis, the amount of Np(IV) present in the solution was estimated by a series of approximations. It was concluded that the Np(IV) had been approximately 87% reduced to Np(III). The Np(III) absorption spectrum reproduced in Fig. 2 was obtained by correcting the observed spectrum for the Np(IV) contribution.

The optical density of the solution at the times of e. m. f. measurements was obtained by interpolation from a density–time plot. The Np(III) and Np(IV) concentrations were derived from the equation

$$D - E_{\text{III}}C/E_{\text{IV}} - E_{\text{III}} = C_{\text{IV}} \qquad (1)$$

where C = total neptunium concentration in moles liter^{-1}; D = measured optical density at 723 millimicrons; E_{III} = molar extinction coefficient of Np(III) at 723 millimicrons; E_{IV} = molar extinction coefficient of Np(IV) at 723 millimicrons; C_{III} = concentration of Np(III) in moles liter^{-1}; C_{IV} = concentration of Np(IV) in moles liter^{-1}.

The molar extinction coefficients, E_{III} and E_{IV}, were evaluated as follows: The measured optical density of the Np(IV) 723 millimicron band has been found from independent measurements to conform to Beer's law over the range of concentrations of Np(IV) in this experiment, the molar extinction coefficient being equal to 126.[12] A value for the molar extinction coefficient, E_{III}, of 4.2 was obtained by subtracting the estimated peak height at 723 millimicrons contributed by Np(IV) in a complete spectrum measured after reduction. Concentrations of Np(III) and Np(IV) at the times of e. m. f. measurement were calculated directly from the interpolated density at 723 millimicrons using equation 1. The formal potential, E_f, of the Np(III)–Np(IV) couple was calculated by the use of equation 2.

$$E_f = -E_{\text{measured}} + E^0(\text{Hg–HgCl}) + 0.05914 \log (C_{\text{IV}}/C_{\text{III}}) \qquad (2)$$

The E^0 of the saturated calomel reference electrode was taken as −0.245 volt. The formal potential as defined by equation 2 is the potential of the Np(III)–Np(IV) couple in 1 molar hydrochloric acid at equal concentrations of Np(III) and Np(IV).

Although the precision of the measurements is higher, the measured potentials are not considered to be more accurate than ±0.005 volt. On this basis the potential of the couple

$$\text{Np(III)} \rightleftharpoons \text{Np(IV)} + e^- \qquad (3)$$

is −0.137 ± 0.005 volt.

The Np(IV)–Np(V) Potential.—The potential of a bright platinum electrode inserted in a solution containing Np(IV) and Np(V) in one molar hydrochloric acid drifts to less positive values with no indication of approaching constancy

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(11) L. B. Magnusson, T. J. LaChapelle and J. C. Hindman, to be published as paper No. 15.3, Vol. 14B, Plutonium Project Record of the National Nuclear Energy Series.

(12) J. C. Hindman, L. B. Magnusson and T. J. LaChapelle, paper to appear as No. 15.2 of Vol. 14B, Plutonium Project Record of the National Nuclear Energy Series.

TABLE I

THE FORMAL OXIDATION POTENTIAL OF THE Np(III)–Np(IV) + e^- COUPLE IN 1.0 MOLAR HYDROCHLORIC ACID

Optical density at 723 millimicrons	Np(IV) moles/liter × 10^3	$\frac{\text{Np(IV)}}{\text{Np(III)}}$	$E_{\text{meas.}}$ volt	E_f, volt
0.157	1.03	0.162	0.154	−0.138
.184	1.26	.205	.146	− .140
.236	1.68	.293	.140	− .136
.266	1.93	.352	.136	− .136
.274	2.00	.370	.135	− .136
.315	2.33	.459	.128	− .137
.334	2.49	.506	.126	− .136
.360	2.70	.574	.123	− .136
.387	2.92	.651	.121	− .135
.438	3.34	.821	.115	− .135
.487	3.75	1.02	.108	− .136
.589	4.58	1.62	.096	− .137
.639	4.99	2.06	.089	− .137
.661	5.17	2.31	.083	− .140
.707	5.55	2.98	.080	− .137
.743	5.85	3.75	.074	− .137
.781	6.16	4.92	.065	− .139
.812	6.41	6.41	.060	− .137
.814	6.43	6.56	.058	− .138
.817	6.46	6.87	.056	− .139
.849	6.72	9.75	.049	− .138
.852	6.74	10.05	.047	− .139
.856	6.78	10.8	.045	− .139

within a period of several hours. For this reason, an indirect method was used to obtain the potential of this couple. Preliminary experiments showed that the reduction of Np(V) by Fe(II) was not quantitative in one molar hydrochloric acid. Estimates of the potential were therefore obtained from measurements on solutions containing Np(V), Np(IV), Fe(III) and Fe(II) in equilibrium.

Experimental

In the first experiment, 2.0 ml. of a 0.0042 molar Np(VI) solution in 1.00 molar hydrochloric acid was titrated with a 1.00 molar Fe(II) solution in 1.00 molar hydrochloric acid. The Fe(II) solution was prepared by dissolving a weighed quantity of Fe^0 in hydrochloric acid. The reduction was followed spectrophotometrically. Although the reduction of the Np(VI) to Np(V) was instantaneous the further reduction to Np(IV) took approximately eighty minutes to reach equilibrium after each addition of Fe(II). The concentration of Np(IV) was calculated from the optical density of the 723 millimicron band and the concentration of the Np(V) by difference. The electrode system used consisted of a bright platinum indicator electrode and a Ag^0–AgCl reference electrode.

TABLE II

POTENTIAL MEASUREMENTS ON Np(IV)–Np(V) COUPLE IN 1.00 *M* HCl (0.00423 *M* Np; *t* = 25°)

$\frac{\text{Np(V)}}{\text{Np(IV)}}$	*E* obs., volt	E_f, volt
5.04	0.530	−0.734
2.01	.510	− .737
0.790	.487	− .738
0.447	.471	− .732
0.0944	.440	− .746
	Av.	−0.737

TABLE III

POTENTIAL MEASUREMENTS ON Np(IV)–Np(V) COUPLE IN 1.00 *M* HCl (*t* = 25°)

Np, mole/liter	$\frac{\text{Np(V)}}{\text{Np(IV)}}$	*E* obs., volt	E_f, volt
0.00366	0.167	0.453	−0.739
.00366	.0388	.423	− .750
.00274	.676	.491	− .746
.00274	.129	.430	− .727
.00396	.247	.474	− .737
.00396	.0883	.436	− .725
		Av.	−0.737

In two additional experiments, potential measurements were taken at two ratios of Np(IV) to Np(V).

Calculations and Results

The formal oxidation potential of the Np(IV)–Np(V) couple was calculated from the equation

$$E_f = -E_{\text{measured}} + E_{\text{Ag}^0-\text{AgCl}} + 0.05914 \log a_{\text{Cl}^-} + 0.05914 \log \frac{C_{\text{V}}}{C_{\text{IV}}} \quad (4)$$

In this equation C_{V} and C_{IV} represent the molar concentrations of Np(V) and Np(IV), respectively. The *E* value of the Ag^0–AgCl electrode is taken as −0.222 volt and the value of a_{Cl^-} as 0.84 (the mean activity of a one molar hydrochloric acid solution).

The data are summarized in Tables II and III. The accuracy of the measurements is not considered to be greater than ±10 millivolts. The potential of the couple

$$\text{Np(IV)} \longrightarrow \text{Np(V)} + e^- \quad (5)$$

is −0.74 ± 0.01 volt in one molar hydrochloric acid at 25°.

The Formal Potential of the Np(V)–Np(VI) Couple.—The couple was measured in 1.00 molar hydrochloric acid solution during the course of a stannous ion reduction of Np(VI).

Experimental

The cell consisted of a bright platinum wire indicator electrode and a silver–silver chloride reference electrode. The neptunium was reduced by adding an aliquot of 0.05 molar stannous chloride in 1.0 molar hydrochloric acid and measuring the potential after equilibrium was established as judged by a constant optical density for the 984 millimicron Np(V) absorption band. Reduction of Np(VI) by chloride caused a slow falling off of the measured potential so the first reading obtained upon inserting the electrode was taken as most nearly representing the true potential.

Calculations and Results

The formal potential of the Np(V)–Np(VI) couple in 1.00 molar hydrochloric acid was calculated in two ways from the data obtained. The first method involved the determination of the Np(V) concentration spectrophotometrically and the concentration of the Np(VI) by difference. Observation has shown that the Np(V) band at 984 millimicrons does not obey Beer's law. Since accurate calibration curves were not available the spectrophotometric densities were disregarded except for determination of equilibrium after each addition of stannous chloride. The amount of Np(VI) in the solution was obtained by subtraction according to the reaction equivalence

$$2\text{Np(VI)} + \text{Sn(II)} \rightleftharpoons 2\text{Np(V)} + \text{Sn(IV)} \quad (6)$$

This method of calculation gave more consistent results. The potentials were calculated by an equation analogous to equation 4. The data are summarized in Table IV.

TABLE IV

FORMAL OXIDATION POTENTIALS FOR THE Np(V)–Np(VI) COUPLE in 1 *M* HCl, 0.00556 *M* Np; $t = 25°$

$\frac{\text{NpVI}}{\text{NpV}}$	$E_{\text{meas.}}$, volt	E_f, volt
1.90	0.912	−1.135
1.50	.904	−1.134
1.21	.900	−1.135
0.771	.891	−1.138
.487	.875	−1.134
.281	.863	−1.136
.130	.842	−1.135

Although it is believed that the cell behaved reversibly, two complicating factors reduced the precision of measurement: (1) Np(VI) is slowly reduced by chloride in the presence of platinum, and (2) the reduction of Np(VI) by Sn(II) is rather slow, so that attainment of equilibrium is somewhat uncertain. The formal oxidation potential for the reaction

$$\text{Np(V)} \rightleftharpoons \text{Np(VI)} + e^- \quad (7)$$

is −1.14 ± 0.02 volt in one molar hydrochloric acid at 25°.

Discussion

Although the oxidation potentials of the couples given in this paper are not thermodynamic E^0 values, they are nevertheless quite useful in predicting the stabilities of the different oxidation states and their probable reactions with various oxidizing and reducing agents.

Direct observation of the stabilities of the various oxidation states is in agreement with what would be expected on the basis of the reported oxidation potentials. Np(III) in one molar hydrochloric acid is extremely unstable to air oxidation and can be maintained in solution only by using precautionary measures to exclude oxygen. Both the +4 and +5 states have been found to be stable in one molar hydrochloric acid over periods of days. From the potential of the couple of −0.74 v., air oxidation of Np(IV) to Np(V) can occur, although the reaction is slow. Np(V) solutions exhibit the expected stability in one molar hydrochloric acid solution. Np(VI) is not stable in hot one molar hydrochloric acid, being slowly reduced to Np(V). Although the reaction with cold hydrochloric acid is very slow at room temperatures, contact with platinum catalyzes the reduction in some manner so that Np(V) is produced at an appreciable rate at the platinum surface. Np(III) undoubtedly cannot be maintained in a nitrate solution, and Np(IV) is slowly oxidized to Np(V) in nitric acid. Np(V) solutions have been prepared in one molar nitric acid with no evidence of disproportionation into Np(IV) and Np(VI). It is expected that the Np(IV)–Np(V) potential in one molar nitric acid is close to that in hydrochloric acid.

Np(V) disproportionates to a considerable extent in one molar sulfuric acid because of preferential complexing of Np(IV) and Np(VI) by the sulfate ion. In high concentration of sulfuric acid, Np(V) would be unstable since, in addition to the sulfate effect, the disproportionation reaction probably has a hydrogen ion dependence.

Considerable evidence has been accumulated to show that the ions of the +3, +4, +5 and +6 oxidation states of neptunium, like those of the corresponding oxidation states of the elements uranium and plutonium, are Np^{+3}, Np^{+4}, NpO_2^{+} and NpO_2^{++} in molar acid solution in the absence of complexing agents. Details of this evidence will appear in subsequent publications.

The reversibility of the Np(III)–Np(IV) and the Np(V)–Np(VI) couples is probably connected with the fact that only electron transfers are involved, whereas the irreversibility of the Np(IV)–Np(V) couple would appear to arise from the fact that oxygen transfer must also occur, a process which would appear to be slow at a noble metal electrode. The sluggishness of reactions involving the oxidation of Np(IV) or the reduction of Np(V), as by ferrous ion or stannous ion, would also presumably be attributable to the slowness of the oxygen transfer process.

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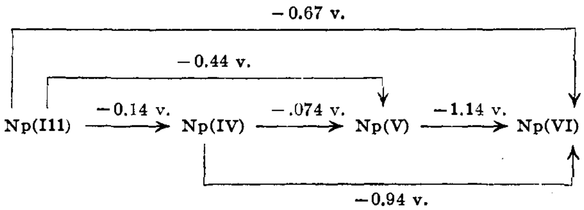
Summary

Spectrophotometric titrations of neptunium solutions with oxidizing and reducing agents have been used, together with the isolation of the salt $\text{NaNpO}_2(\text{OOCCH}_3)_3$ from the solution of the highest oxidation state obtained, to establish the existence of the +4, +5 and +6 states of neptunium. In contrast to both uranium and plutonium, the +5 state of neptunium has been found to be quite stable in acid solution.

The formal oxidation potentials for the various neptunium couples have been measured in one molar hydrochloric acid. These may be represented schematically as follows:



The Np(III)–Np(IV) and Np(V)–Np(VI) couples have been found to behave reversibly while the Np(IV)–Np(V) couple is irreversible. In the latter case measurements of the potential in a system in equilibrium with Fe(II) and Fe(III) have been used to obtain the value of the couple.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Supported Oxides of Manganese[1]

BY P. W. SELWOOD, T. E. MOORE,[2] MARYLINN ELLIS AND KATHRYN WETHINGTON

The applicability of the susceptibility isotherm method has already been described for supported oxides of chromium, and of copper. The present paper describes exploratory studies on the use of the method for supported oxides of manganese. Similar papers on nickel and on iron and other elements will shortly be forthcoming from this Laboratory.[3]

Experimental Part

X-Ray, magnetic susceptibility and surface area studies were made by standard methods previously described.[3]

One of the objectives of all this work is the relation of inorganic structure to catalyst activity. The various supported oxide systems are, therefore, referred to as catalysts, even though their applicability as catalysts may not be obvious.

Preparation of Catalysts.—Manganese oxides supported on alumina were prepared as follows: a water solution made from recrystallized manganous nitrate was impregnated in excess on γ-alumina. The area of the alumina was about 200 m.^{2} g.$^{-1}$ (BET nitrogen). The susceptibility of the alumina was -0.3×10^{-6} and was independent of temperature. The impregnated alumina was filtered with suction, then dried and heated to 150–160° for forty-eight hours under slightly reduced pressure. The product was removed, ground, screened and reheated for twenty-four hours at 200°. This procedure would normally be expected to yield a layer of manganese dioxide in the *pyrolusite* structure covering the alumina. A series of catalysts was prepared in this way. Variations in manganese content was obtained by changing the concentration of the impregnating solution. Manganese concentrations ran from about 1 to over 20%. The color of all the finished catalysts ranged from pale tan to black. Analytical and other data are given below.

Prolonged heating of manganese dioxide results in the quantitative formation of the sesquioxide in the *bixbyite* structure. Some of the catalysts described above were subjected to thermal decomposition at 600°. The properties of this series are also described below.

During the course of this work it became obvious that manganese oxides supported on high-area *rutile* would be an interesting system for study. Considerable difficulty was experienced in obtaining this support, but finally a laboratory prepared sample was obtained from the National Lead Company, Titanium Division. This titania was all in the *rutile* structure, had a surface area of about 129 m.^{2} g.$^{-1}$ (BET nitrogen), and had a susceptibility of -0.3×10^{-6}, which was substantially independent of temperature.

A series of supported manganese catalysts was prepared on the titania by procedures identical with those described for the alumina support, except that heating was not carried over 200°. Somewhat more concentrated impregnating solutions were found to be required to obtain equivalent concentrations of manganese on titania as compared with alumina.

One catalyst was made containing rhenium supported on alumina. γ-Alumina was impregnated with a hot saturated solution of potassium perrhenate. The mixture was kept hot for twenty minutes, then filtered and dried at 110°. The sample was then ignited in vacuum to 350°. After magnetic and other measurements had been made the sample was further heated in hydrogen at 350° for twenty-four hours. Before reduction the sample was white, and afterward gray. A few miscellaneous preparations are briefly indicated below.

Analytical Procedures.—The analytical data required were (1) manganese, and (2) "active" oxygen. For the manganese determination the sample was dissolved in sulfuric acid containing ferrous sulfate. The manganese was then oxidized with sodium bismuthate in nitric acid. The resulting permanganate was titrated with ferrous sulfate.

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(1) This paper describes, in part, work performed under contract with the Squier Signal Laboratory, Signal Corps Engineering Laboratories, as part of their program for the improvement of dry cells.

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(3) This is the fifth paper on the susceptibility isotherm from this Laboratory. The third and fourth appeared in THIS JOURNAL, **70**, 2145, 2271 (1948).