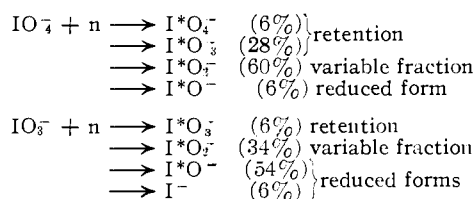


constant. Although this value does not correspond with any of the real or apparent dissociation constants of periodic acid, the complications of simultaneous hydrolytic equilibria obscure the situation.¹⁰

Retention by periodate solutions (Table III) shows some similarities suggestive of the behavior of iodate. The retention as periodate appears to be independent of solution conditions and to have a value (av. = 6%) experimentally indistinguishable from the minimum retention observed with iodate (6%). This observation may be taken to support the previous suggestion that, due to partial cancellation of recoil momenta, insufficient energy is available for rupture of the parent ion. The second similarity is found in the existence of a minimum fraction of reduced form (also 6%) in the presence of an oxidant (periodate itself). That this value should be much smaller than the corresponding value for iodate (60%) is not surprising in view of the greater number of bonds to be broken in periodate. Finally, the third fraction of variable fate again appears, amounting to some 60% (the difference between the two extremes of the

iodate or iodide fractions) and could apparently be described by a relation such as equation (8). A fourth fraction, amounting to approximately 28%, is apparently reduced only as far as iodate, regardless of solution conditions. The approximate equality of this fraction with the variable fraction of 34% in the case of iodate suggests the possibility of the following unified description of the consequences of neutron capture by the two species: Due to partial momentum cancellation or other features of the neutron capture process (such as possible internal conversion) the recoil reactions are divided into the following spectrum: 5%, no bond rupture; 28-34%, loss of one O atom (or ion); 60-54%, loss of two O atoms (or ions); 6%, loss of three or more O atoms (or ions). This possibility may be summarized by the scheme



(10) C. E. Crouthamel, A. M. Hayes and D. S. Martin, *THIS JOURNAL*, **73**, 82 (1951).

NOTRE DAME, INDIANA

[CONTRIBUTION FROM THE CHEMISTRY DIVISION, ARGONNE NATIONAL LABORATORY]

Oxidation Potentials of the Neptunium(III)-(IV) and the Neptunium(V)-(VI) Couples in Perchloric Acid

BY DONALD COHEN AND J. C. HINDMAN

RECEIVED MARCH 14, 1952

The oxidation potentials of the Np(III)-Np(IV) and Np(V)-Np(VI) couples have been measured as a function of temperature in 1 *m* perchloric acid solution. The formal potential for the cell reaction (equation 4) is -0.1551 ± 0.0010 volt at 25°. For this reaction at 25°, ΔH° is -5.7 ± 0.2 kcal. and ΔS° is -31.2 ± 0.8 e.u. For the reaction (equation 1) the formal potential is -1.1373 ± 0.0010 volts at 25°. ΔH° for this reaction at 25° is 28.1 ± 0.2 kcal. and the partial molal entropy change is 6.4 ± 0.6 e.u.

As part of a program to obtain adequate data on which to base calculations of thermodynamic properties of neptunium ions and compounds, measurements have been made of the potentials of the various neptunium couples in 1 *m* perchloric acid as a function of temperature. In this communication the data on the Np(III)-Np(IV) and the Np(V)-Np(VI) couples are summarized. A subsequent publication will deal with the investigation of the Np(IV)-Np(V) couple and the calculations of the partial molal heats and free energies of formation of the neptunium ions.

The oxidation potentials of the neptunium(III)-(IV) and -(V)-(VI) couples in 1.0 *M* HCl at 25° have been measured by Hindman, Magnusson and La Chapelle.¹ They found both couples to be reversible at a platinum electrode. Hindman and Kritchevsky² investigated the polarographic behavior of the Np(III)-Np(IV) couple in hydrochloric and perchloric acids at 25°. This couple was found to be polarographically reversible in hydro-

chloric acid but irreversible in perchloric acid. This irreversible behavior of the Np(III)-Np(IV) couple in perchloric acid is not observed at an inert electrode.

Experimental

E.m.f. measurements were made on cells of the type



where Np(O) and Np(R) refer to the oxidized and reduced form of the neptunium ion for the particular couple. The potentials of the cells were measured at various neptunium ratios in molal perchloric acid at three temperatures. The ratios of Np(V) to Np(VI) and Np(III) to Np(IV) were prepared electrolytically using a continuous-control type potentiostat. Blank determinations showed that at the potentials used in these electrolyses secondary reactions such as oxygen or hydrogen deposition did not occur. In addition, the coulometer readings agreed with the total neptunium content of the solutions as determined by alpha assay. From this it was concluded that the current efficiency was 100%.

The starting material, in all cases, was a solution of pure Np(V) in 1.0 molal HClO₄ prepared by a procedure similar to that previously described.³ The electrolysis cell and the potentiostat have been described by Wehner and Hindman.⁴

(1) J. C. Hindman, L. B. Magnusson and T. J. La Chapelle, *THIS JOURNAL*, **71**, 687 (1949).

(2) J. C. Hindman and E. S. Kritchevsky, *ibid.*, **72**, 953 (1950).

(3) R. Sjöblom and J. C. Hindman, *ibid.*, **73**, 1744 (1951).

(4) P. Wehner and J. C. Hindman, *ibid.*, **72**, 3911 (1950).

The three-compartment electrolysis cell also served as the measuring cell, with the large spiral platinum electrode serving as the inert measuring electrode. The usual electrical measuring circuit was used with a Leeds and Northrup Type K potentiometer. The sensitivity of the galvanometer was 7×10^{-9} ampere per mm. The standard cell was checked against a cell certified by the National Bureau of Standards. Three hydrogen electrodes of conventional design checked each other within 0.1 millivolt. The constant temperature-bath was controlled to $\pm 0.02^\circ$.

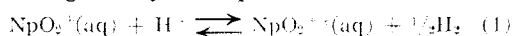
The oxidation state of the solution during the course of the electrolysis was determined by means of a gas coulometer of the type described by Lingane.⁵

The Np(V)-Np(VI) Potential.—A sample of Np(V) was placed in the center compartment of the electrolysis cell. The two end compartments of the cell were filled with the stock molal perchloric acid. The solutions in the anode and cathode compartments were stirred with prepurified nitrogen. This also served to remove oxygen from the solutions. The nitrogen was first bubbled through molal perchloric acid which was also kept in the constant temperature-bath. The Np(V) was oxidized to Np(VI) at a platinum anode at -1.4 v. using the potentiostat. Several times during the course of the oxidation, the electrolysis was stopped to permit e.m.f. measurements to be made. A hydrogen electrode was inserted into the "bridge" compartment of the cell. A constant potential was reached in five to ten minutes. The hydrogen electrode was then removed and the electrolysis was continued. After the oxidation was completed, the Np(VI) solution was reduced at the platinum cathode at -0.95 v. Again, as before, the electrolysis was interrupted several times to permit e.m.f. measurements to be made. Barometric readings were taken during the run.

The Np(III)-Np(IV) Potential.—The technique for measuring this couple was essentially the same as described above for the Np(V)-Np(VI) couple. A mercury cathode at $+0.1$ v. was used to reduce Np(V) to Np(III). The high overvoltage⁶ for the electrolytic reduction of Np(V) prevented the preparation of pure Np(IV) by direct reduction of Np(V). The electrolysis cell was modified to contain a mercury pool to serve as the cathode for the reduction of Np(V) to Np(III). Prepurified nitrogen was bubbled through the mercury cathode to facilitate the reduction and to remove all traces of oxygen. Np(III) is very sensitive to air oxidation. The Np(III) solution was then oxidized to the (IV) state at -0.4 v. with a platinum anode which did not touch the mercury pool. This platinum electrode was also used as the inert measuring electrode for this couple. Several potential measurements were made during the oxidation of Np(III) to Np(IV) and also during the reduction of Np(IV) back to Np(III) at a potential of $+0.05$ v.

Results and Discussion

The Np(V)-Np(VI) Couple.—The reaction for this cell is given by the equation



The e.m.f. for this reaction is

$$E = E' - \frac{RT}{F} \ln \frac{[\text{H}_2]^{1/2}[\text{Np(VI)}]}{[\text{H}^+][\text{Np(V)}]} \quad (2)$$

where E' is defined by the equation

$$E' = E^\circ - \frac{RT}{F} \ln \frac{\gamma_{\text{H}_2}^{1/2} \gamma_{\text{Np(VI)}}}{\gamma_{\text{H}^+} \gamma_{\text{Np(V)}}} + E_L \quad (3)$$

E_L is the unknown liquid junction potential. This has been shown to be small, (see later discussion). E' , as defined by equation (3), is the formal potential of the cell with the hydrogen ion at unit concentration, with the hydrogen at one atmosphere pressure and with the two neptunium ion concentrations equal and small (each, $0.005 M$).

The hydrogen gas pressure was obtained by subtracting the vapor pressure of the perchloric acid from the barometric reading. The vapor pressure of molal perchloric acid at 25° was taken from the

data of Pearce and Nelson.⁷ This value was compared with the vapor pressures of hydrochloric acid to allow estimation of the vapor pressures of the perchloric acid at the other temperatures. Table I gives the estimated values for the vapor pressures of $1.0 m \text{ HClO}_4$ used in the calculations.

TABLE I

VAPOR PRESSURES OF $1.0 m \text{ HClO}_4$ AT VARIOUS TEMPERATURES				
Temp., $^\circ\text{C}$.	15.2	25.0	35.4	47.4
V.p., mm.	12.3	22.9	41.5	78.5

Table II gives the results of one of the experiments at 25° . The precision of the data obtained during oxidation is much better than that found during reduction. The data given are typical of all the experiments. In addition to a larger scatter it was generally noted that the first value in the reduction run was considerably more positive than the rest of the values. The reason for this is not entirely clear. The principal source of error in the present experiments lies in the evaluation of the neptunium ratios.

TABLE II

E.M.F. OF THE CELL: $\text{Pt}:\text{H}_2:\text{HClO}_4:\text{HClO}_4, \text{Np(V)}, \text{Np(VI)}:\text{Pt}$ AT 25° AND $1.027 m \text{ HClO}_4$			
Electrolytic process	$\frac{\text{Np(VI)}}{\text{Np(V)}}$	$-E$, volts	$-E'$, volts
Oxidation	0.3175	1.1067	1.1375
	0.6207	1.1239	1.1375
	1.336	1.1434	1.1373
	2.448	1.1591	1.1375
Reduction	5.024	1.1721	1.1320
	1.681	1.1501	1.1381
	0.883	1.1336	1.1381
	0.574	1.1233	1.1389

Despite the scatter in the data, with a large number of measurements the average deviation of the formal potential was found to be less than 1.0 millivolt. A summary of all the e.m.f. measurements for the Np(V)-Np(VI) couple is given in Table III.

TABLE III

E.M.F. OF THE CELL: $\text{Pt}:\text{H}_2:\text{HClO}_4:\text{HClO}_4, \text{Np(V)}, \text{Np(VI)}:\text{Pt}$ $1.027 m \text{ HClO}_4$ AT VARIOUS TEMPERATURES				
Temp., $^\circ\text{C}$.	$-E'$, volts	Average deviation, volt	Number of measurements	$\Delta E'/\Delta T$, volts/deg.
15.20	1.1403	± 0.0008	31	0.00030
25.05	1.1373	± 0.0008	77	0.00023
35.35	1.1349	± 0.0007	21	

The formal potential for the Np(V)-Np(VI) couple at 25° in molal perchloric acid is -1.1373 ± 0.0010 volt. Hindman, Magnusson and La Chapelle¹ found the formal potential of this couple in molal hydrochloric acid to be -1.14 volt. Using the Gibbs-Helmholtz equation, $\Delta \bar{H}$ for reaction (1) at 25° is 28.1 ± 0.2 kcal. For this reaction, the partial molal entropy change at 25° is therefore 6.4 ± 0.6 e.u.

The magnitude of the junction potential, E_L , (equation 3) was estimated by measuring the po-

(5) J. J. Lingane, *THIS JOURNAL*, **67**, 1916 (1945).

(6) Donald Cohen and J. C. Hindman, manuscript in preparation.

(7) J. N. Pearce and A. F. Nelson, *THIS JOURNAL*, **55**, 3075 (1933).

tential of the cell as a function of the neptunium ion concentration. The formal potential became more negative as the neptunium concentration was increased as shown in Fig. 1. However, the results at neptunium concentrations below 0.01 M were scattered and not reproducible. It appears that reduction is occurring since the potential decreases with time in these solutions. Extrapolation to zero neptunium concentration was therefore made from measurements at neptunium concentrations 0.01 M or above. From this extrapolation we would estimate the value of E_L to be approximately 0.2 mv. Since this correction is small relative to the total uncertainty in the value for the couple it has been neglected in the calculations.

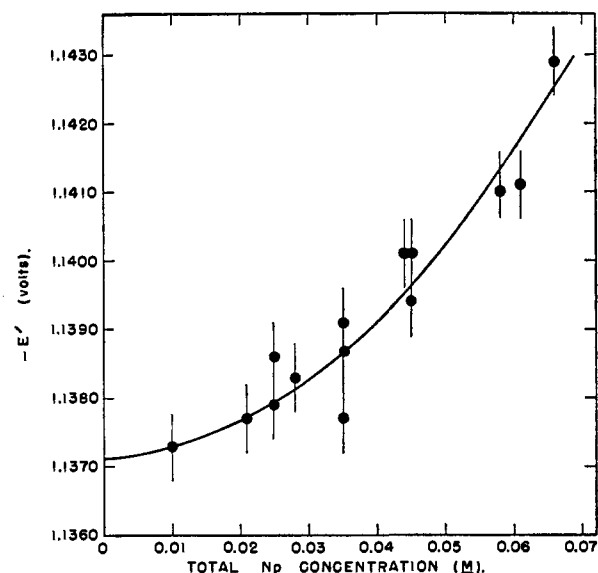
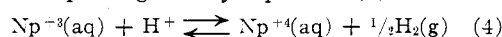


Fig. 1.—The effect of total neptunium concentration on the potential of the Np(V)-Np(VI) couple.

The Np(III)-Np(IV) Couple.—The cell reaction for this couple is given by equation (4)



The e.m.f. for this reaction is given by

$$E = E' - \frac{RT}{F} \ln \frac{[\text{H}_2]^{1/2}[\text{Np}(\text{IV})]}{[\text{H}^+][\text{Np}(\text{III})]} \quad (5)$$

where E' the formal potential is defined by an equation analogous to equation (3).

Table IV gives the results of one of the experiments at 25°. The formal potentials from the re-

TABLE IV

E.M.F. OF THE CELL: Pt:H₂:HClO₄:HClO₄, Np(III), Np(IV):Pt AT 25° AND 1.027 M HClO₄

Electrolytic process	$\frac{\text{Np(IV)}}{\text{Np(III)}}$	-E, volt	-E', volt
Oxidation	0.279	0.1216	0.1556
	0.656	.1428	.1548
	1.028	.1546	.1547
	1.725	.1676	.1548
	2.300	.1746	.1544
Reduction	6.874	.2039	.1556
	3.032	.1830	.1558
	1.778	.1694	.1558
	1.058	.1563	.1563
	0.488	.1364	.1560

duction run are more negative than those from the oxidation run. Nevertheless, the agreement is good.

Table V summarizes the results of the measurements on this couple. In the experiments the total neptunium concentration was approximately 0.01 M.

TABLE V

E.M.F. OF THE CELL: Pt:H₂:HClO₄:HClO₄, Np(III), Np(IV):Pt 1.027 M HClO₄ AT VARIOUS TEMPERATURES

Temp., °C.	-E', volt	Av. dev., volt	Number of measurements	$\Delta E'/\Delta T$, volt/deg.
15.20	0.1421	±0.0008	38	-0.00132
25.05	.1551	±.0010	34	-0.00139
35.35	.1694	±.0008	29	

Again, as with the Np(V)-Np(VI) couple, the average deviations of the formal potential are 1.0 millivolt or less. Figure 2 illustrates the effect of total neptunium concentration on the potential of the couple. The unusually large change in formal potential with increasing neptunium content might be due to a change of the neptunium species in the solution. The extrapolation to zero neptunium concentration would give an E_L value of approximately 0.2 millivolt. Since this correction is much less than the probable error of the potentials it has been neglected in the calculations. The formal potential of the Np(III)-Np(IV) couple in molal perchloric acid at 25° is -0.1551 ± 0.0010 volt. For reaction (4) at 25°, ΔH is -5.7 ± 0.2 kcal. and ΔS is -31.2 ± 0.8 e.u.

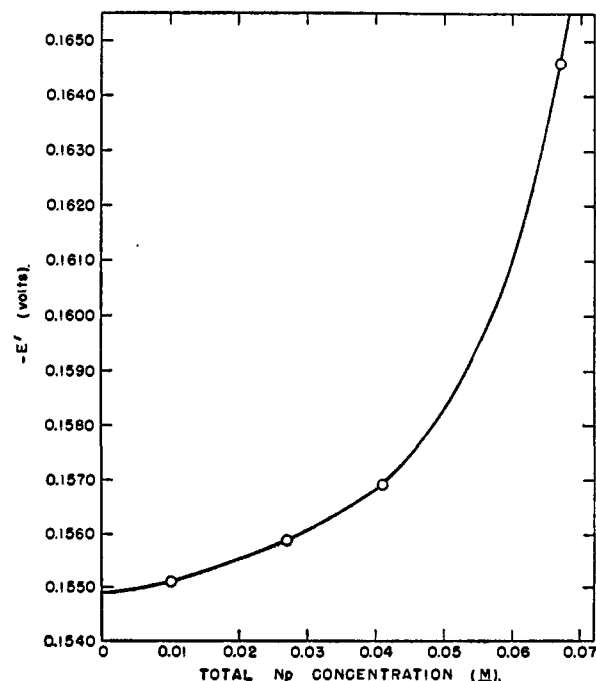


Fig. 2.—The effect of total neptunium concentration on the potential of the Np(III)-Np(IV) couple.

This couple has been found to be reversible at an inert electrode in perchloric acid as contrasted

to the work of Hindman and Kritchevsky² who found this couple to be polarographically irreversible in perchloric acid. This phenomenon is not unique. Jones and Colvin⁸ found the V(III)–V(IV) couple to behave reversibly at a platinum electrode, while Lingane⁹ found this couple to be

(8) G. Jones and J. H. Colvin, *THIS JOURNAL*, **66**, 1563 (1944).

(9) J. J. Lingane, *ibid.*, **67**, 182 (1945).

irreversible at the dropping mercury electrode. This behavior can most probably be attributed to a measurable slowness of the electrode reaction.

The ΔS for the cell reaction of -31.2 e.u. is very close to that found by Connick and McVey¹⁰ (-30.6 e.u.) for the corresponding plutonium reaction.

(10) R. E. Connick and W. H. McVey, *ibid.*, **73**, 1798 (1951).

CHICAGO 80, ILLINOIS

[CONTRIBUTION FROM THE CHEMISTRY DIVISION, ARGONNE NATIONAL LABORATORY]

The Neptunium(IV)–Neptunium(V) Couple in Perchloric Acid. The Partial Molal Heats and Free Energies of Formation of Neptunium Ions

BY DONALD COHEN AND J. C. HINDMAN

RECEIVED MARCH 14, 1952

The formal oxidation potential for the cell reaction (equation 1) has been determined to be -0.7391 ± 0.0010 v. in 1 *m* perchloric acid at 25°. ΔH for this reaction is 35.6 ± 0.3 kcal. and ΔS is 62.3 ± 1 e.u. Based on these and previously reported measurements a potential scheme for the neptunium ions in 1 *m* perchloric acid is given. Calculations have been made of the partial molal heats and free energies of formation of the various neptunium ions. Entropies of these ions are given.

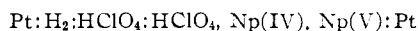
Measurements on the potentials of the neptunium(III)–(IV) and neptunium(V)–(VI) couples in molal perchloric acid have been reported previously.¹ The present communication deals with the potential data on the neptunium(IV)–(V) couple and the calculations of the partial molal heats and free energies of the neptunium ions in this medium.

Prior measurements on this couple were made in molar hydrochloric acid at 25°.² The couple was not reversible at a bright platinum electrode; the potential was therefore evaluated from a cell containing an equilibrium mixture of Np(V), Np(IV), Fe(III) and Fe(II). More recently, Magnusson and Huizenga³ measured the potential of this couple in perchloric acid at several temperatures using this same technique.

Investigation of the overvoltage behavior exhibited in the electrolytic oxidation and reduction of neptunium ions⁴ suggested that a direct measurement of the potential of the couple might be feasible at higher temperatures. Actually, a reinvestigation of the couple has shown that a formal potential can be obtained without a mediator at 25° as well as at higher temperatures. The time required for electrode equilibrium to be reached rapidly decreases with increasing temperature.

Experimental

The formal potential of the Np(IV)–Np(V) couple was measured using the cell



The three temperatures used were 47, 35 and 25°. The ratios of Np(IV) to Np(V) were prepared from stock solutions of the pure oxidation states. Two separate stock solutions of each state were used.

(1) D. Cohen and J. C. Hindman, *THIS JOURNAL*, **74**, 4679 (1952).

(2) J. C. Hindman, L. B. Magnusson and T. J. La Chapelle, *ibid.*, **71**, 687 (1949).

(3) L. B. Magnusson and J. R. Huizenga, paper presented before the Division of Nuclear Chemistry, XII International Congress of Pure and Applied Chemistry, New York, September, 1951.

(4) D. Cohen and J. C. Hindman, manuscript in preparation.

The Np(V) stock solution was prepared by dissolving Np(V) hydroxide in perchloric acid. The Np(IV) stock solution was prepared electrolytically using a potentiostat. Np(V) perchlorate solution was first reduced to Np(III) and this solution was then oxidized to Np(IV). Care was taken to keep the Np(IV) solution under an atmosphere of nitrogen to prevent its slow oxidation by air to the (V) state. The stock solutions were analyzed for neptunium content by radiometric assay.

The measuring cell was an "H" type cell with the two compartments separated by a 10-mm. fine sintered glass disc. The tops of the cell were fitted with standard taper joints, one for the hydrogen electrode and the other for a delivery tube to bubble prepurified nitrogen through the neptunium solution. Twenty-one inches of 51 mil platinum wire in the form of a spiral served as the inert measuring electrode.

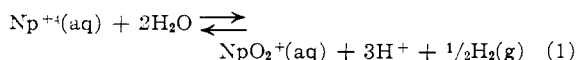
The usual electrical measuring circuit was used with a Leeds and Northrup Type K potentiometer. The constant temperature bath was controlled to $\pm 0.03^\circ$.

The following procedure was used to measure the potential for this couple. A mixture of Np(IV) and Np(V) was added to the thermostated cell and nitrogen was bubbled through this solution. The other compartment of the measuring cell containing a hydrogen electrode of conventional design was filled with the stock molal perchloric acid. Both the hydrogen and the nitrogen were first bubbled through molal perchloric acid solutions which were kept in the constant temperature-bath. E.m.f. readings were taken until a constant potential was attained after which the neptunium ratio was changed and again, e.m.f. measurements were taken until the potential became constant.

As a check on the effect of electrode surface compositions on the cell potentials, measurements were also made using platinumized platinum and gold for the inert electrode.

Results and Discussion

Magnusson and Huizenga³ have shown the fourth power hydrogen ion dependence of the Np(IV)–Np(V) couple. These data, combined with other evidence⁵ that Np(IV) exists as Np^{+4} in acid solution leads to the cell reaction



The e.m.f. for this reaction is given by equation (2)

$$E = E^\circ - \frac{RT}{F} \ln [H^+]^3 [H_2]^{1/2} \frac{[\text{Np(V)}]}{[\text{Np(IV)}]} \quad (2)$$

(5) J. C. Sullivan and J. C. Hindman, manuscript in preparation.