trast, lithium appears to behave more like calcium in that no trimethylboron has been found among the reaction products, and the dimethylborohydrides of both of these metals have been isolated.

The explanation of the differences in the apparent stabilities of these salts is not obvious, although the lattice energies of the calcium and lithium salts would certainly be greater than those of the sodium and potassium salts, and the lattice energy may well serve to stabilize the dimethylborohydride ion in the solid state. In solution it could be postulated that ion aggregation, also dependent upon change density, would serve to stabilize the calcium and lithium salts.

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[CONTRIBUTION FROM THE CHEMISTRY DIVISION, ARGONNE NATIONAL LABORATORY]

Kinetics of Reactions Involving Neptunium(IV), Neptunium(V) and Neptunium(VI) Ions in Sulfate Media[1]

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The rates of the forward and reverse reactions involved in the equilibrium Np(IV) + Np(VI) $\rightleftarrows$ 2Np(V) have been measured in sulfate solution. Both forward and reverse reactions involve multiple parallel reaction paths. The rate of the forward reaction can be expressed in the form $R = k_0'[\mathrm{Np}^{+4}][\mathrm{NpO_2}^{++}][\mathrm{H}^+]^{-2} + \{k_1[\mathrm{NpSO_4}^{++}][\mathrm{NpO_2}^{++}] + k_2[\mathrm{NpSO_4}^{++}][\mathrm{NpO_2SO_4}]\}\{k_3[\mathrm{H}^+]^{-2} + k_4[\mathrm{H}^+]^{-3}\}$. At 25° and $\mu = 2.2$, $k_0' = 2.69$ mole l.$^{-1}$ min.$^{-1}$, $k_1 = 4.27$ mole^{-1} l. min.$^{-1}$, $k_2 = 7.12$ mole^{-1} l. min.$^{-1}$, $k_3 = 3.6$ mole^2 l.$^{-2}$ and $k_4 = 1.7$ mole^3 l.$^{-3}$. The rate of the disproportionation reaction may be represented by $R = \{k_5[\mathrm{NpO_2}^+]^2[\mathrm{HSO_4}^-] + k_6[\mathrm{NpO_2}^+]^2[\mathrm{HSO_4}^-]^2\}\{k_7 + k_8[\mathrm{H}^+]\}$. At 25° and $\mu = 2.2$, $k_5 = 0.30$ mole^{-2} l.^{2} min.$^{-1}$, $k_6 = 0.090$ mole^{-3} l.^{3} min.$^{-1}$, $k_7 = 0.74$, and $k_8 = 0.14$ mole l.$^{-1}$. Apparent activation energies are given. Probable restrictions on the geometrical configurations for the transition state complexes and the mechanism of the electron transfer processes are considered. Relationships of the reactions in sulfate solution to similar reactions occurring in perchlorate media are discussed.

Three prior investigations of the kinetics of the neptunium(IV)–neptunium(VI) reaction have been reported.[2-4] In perchloric acid solution the mechanism of the reaction appears to involve hydrolysis products of neptunium(IV).[2] In mixed ethylene glycol–water media the mechanism is altered, ethylene glycol apparently being present in the activated complex.[3] In sulfate solution the only measurements made were in one molar sulfuric acid.[4] The present research has been carried out to see if alternate paths involving complex ion species are available. The sulfate system has been selected for further investigation for two reasons. First, data on the complexity constants of neptunium(IV) and sulfate are now available.[5] Second, measurement of the reverse reaction, the disproportionation of neptunium(V), is possible in this medium. Interest in the latter reaction is due to the apparent difference in reaction mechanism deduced from kinetic and equilibrium data in perchlorate solution[2] and the reaction which would be expected if the behavior of neptunium(V) paralleled that of uranium(V).

Experimental

The stock solutions of the neptunium ions in perchloric acid were prepared according to previously described methods. The sulfuric acid was reagent grade standardized by titration with sodium hydroxide.

The experimental technique also has been previously described.[2] The only major modification of that technique used in this investigation was the preparation of calibration curves necessary to determine the concentration of Np(IV) in the sulfuric acid–perchloric acid mixtures. The interaction between Np(IV) and bisulfate is reflected in the lowering and slight shift in wave length of the band at 724 mμ which is most useful for analytical purposes.

Results

I. The Np(IV) + Np(VI) $\longrightarrow$ 2Np(V) Reaction

Effect of Metal Ion.—The stoichiometry of the reaction with respect to each of the metal ions was determined by experiments in which the concentration of Np(IV) and Np(VI) were varied in the reaction mixture. Data were obtained at total sulfuric acid concentrations of 0.0865 and 1.00 molar. At zero bisulfate the reaction is bimolecular.[2] In the bisulfate solutions the data were also found to be consistent for a bimolecular process. The rate constants, k_{obsd}, were computed from the experimental data both by graphical evaluation of the initial rate[6] and by means of the integrated equation for a bimolecular reaction

$$k_{\mathrm{obsd}} = \frac{2.303}{([\mathrm{Np(IV)}]^0 + [\mathrm{Np(VI)}]^0)t} \log \frac{[\mathrm{Np(VI)}]^0}{[\mathrm{Np(IV)}]^0}\left(\frac{[\mathrm{Np(VI)}]^0 - x}{[\mathrm{Np(IV)}]^0 - x}\right) \quad (1)$$

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[1] Based on work performed under the auspices of the U. S. Atomic Energy Commission.

[2] J. C. Hindman, J. C. Sullivan and D. Cohen, THIS JOURNAL, **76**, 3278 (1954).

[3] D. Cohen, E. S. Amis, J. C. Sullivan and J. C. Hindman, *J. Phys. Chem.*, **60**, 701 (1956).

[4] L. B. Magnusson, J. C. Hindman and T. J. LaChapelle, "The Transuranium Elements," edited by G. T. Seaborg, J. J. Katz and W. M. Manning (McGraw-Hill Book Co., New York, N. Y., 1949), National Nuclear Energy Series, Plutonium Project Record, Div. IV, Vol. 14B, paper 15.11, p. 1134.

[5] J. C. Sullivan and J. C. Hindman, THIS JOURNAL, **76**, 5931 (1954).

[6] *Cf.* R. Livingston, "Technique of Organic Chemistry," Vol. VIII, Interscience Publishers, Inc., New York, N. Y., 1953, p. 182.

where $[\mathrm{Np(IV)}]^0$ and $[\mathrm{Np(VI)}]^0$ represent the initial total concentrations of reactants, and x the concentration of Np(IV) at time t. In the calculations involving equation 1 only the data for the first 10% of the reaction were used in order to minimize the correction for the back reaction. The data are summarized in Table I.

TABLE I

DETERMINATION OF METAL ION DEPENDENCE FOR THE REACTION Np(IV) + Np(VI) → 2Np(V)

$t = 25°$, $\mu = 2.2$

Initial $[H_2SO_4]$, mole l.$^{-1}$	Initial $[H^+]$, mole l.$^{-1}$	$10^3 \times [\mathrm{Np(IV)}]^0$, mole l.$^{-1}$	$10^3 \times [\mathrm{Np(VI)}]^0$, mole l.$^{-1}$	Apparent rate k_{obsd}, l. mole^{-1} min.$^{-1}$
0.0865	1.96	2.64	18.78	3.87
.0865	1.95	5.26	15.65	4.01
.0865	1.92	13.36	6.26	3.55
.0865	1.94	10.70	9.08	3.70
1.00	1.04	9.82	9.27	2.20
1.00	1.04	12.60	6.26	2.39
1.00	1.04	5.27	15.65	2.28

Effect of $[HSO_4^-]$.—Table II summarizes the data on the effect of bisulfate on the apparent rate of the reaction. Examination of the data in this table shows that the rate increases to a maximum and then decreases as the bisulfate concentration is further increased. The maximum in the rate occurs when $\bar{n}_{\mathrm{IV}}$ is close to one, that is, where the average number of sulfate groups attached to a neptunium(IV) ion is unity[5] (see Fig. 1). It would therefore appear that the rate is increased by the addition of a single sulfate ion to the Np(IV). At the point where the maximum in the rate is observed the Np(VI) is presumably largely NpO_2^{++}. Thus far successful measurements of the complex constants for the Np(VI) sulfate system have not been made.[7] The degree of complex formation was therefore estimated using the constants for the U(VI) system.[8] Calculations of the solution composition have been made using the above complexing data and a value of 0.080 for the dissociation constant of $[HSO_4^-]$ at $\mu = 2.2$.[9] These calculations have been made as

TABLE II

EFFECT OF $[HSO_4^-]$ ON THE RATE OF THE REACTION
Np(IV) + Np(VI) ⇄ 2Np(V)

$t = 25.1°$, $\mu = 2.2$, $[H^+]_i = 2.20\ M$

Initial $[HSO_4^-]$, mole l.$^{-1}$	Total [Np(IV)], mole l.$^{-1}$ × 10^3	Total [Np(VI)], mole l.$^{-1}$ × 10^3	Apparent rate k_{obsd}, l. mole^{-1} min.$^{-1}$
0.00	6.86	7.30	0.59[b]
0.00	...	...	0.61
1.02×10^{-3}	6.86	7.30	0.776
3.07×10^{-3}	6.86	7.30	1.26
3.22×10^{-3}	10.52	9.21	1.64
3.11×10^{-3}	6.86	7.42	1.13
6.14×10^{-3}	6.86	7.30	1.61
1.02×10^{-2}	6.86	7.30	2.12
1.64×10^{-2}	6.86	7.30	2.58
2.02×10^{-2}	10.50	9.21	2.21
3.07×10^{-2}	6.86	7.30	3.11
5.12×10^{-2}	6.86	7.30	3.38
9.21×10^{-2}	6.86	7.30	3.36
0.1228	6.86	7.30	3.20
.168	10.98	10.70	2.51
.2075	6.86	7.42	2.65
.311	6.86	7.42	2.17
.498	6.86	7.42	1.57
.504	10.88	10.70	1.36
.942	10.70	10.70	0.716
.942	9.64	9.27	0.760
1.93[a]	10.84	10.70	0.320

[a] $H^+ = 2.11$. [b] Reference 2.

$$[\Sigma HSO_4^-]_i = [HSO_4^-]_{\mathrm{free}} + [SO_4^{--}]_{\mathrm{free}} + [\Sigma \bar{n}_i Cm_i] \tag{2}$$

where

$$\bar{n} = \frac{\beta_1[HSO_4^-] + 2\beta_2[HSO_4^-]^2}{1 + \beta_1[HSO_4^-] + \beta_2[HSO_4^-]^2} \tag{3}$$

and

$$Cm_i = [\Sigma \mathrm{Np(IV)}] \text{ or } [\Sigma \mathrm{Np(VI)}] \tag{4}$$

combining with

$$0.080 = \frac{[H^+][SO_4^{--}]}{[HSO_4^-]} \tag{5}$$

and

$$[H^+] = [H^+]_i + [SO_4^{--}]_f + [\Sigma n_i Cm_i] \tag{6}$$

where

$$[H^+]_i = \text{initial hydrogen ion concn.} \tag{7}$$

and solving for $[HSO_4^-]_f$, we get

$$[HSO_4^-]_f^2 - [HSO_4^-]_f(2[\Sigma HSO_4^-]_i + [H^+]_i + 0.080 - [\Sigma \bar{n}_i Cm_i]) + ([H^+]_i[\Sigma HSO_4^-]_i + [\Sigma HSO_4^-]_i^2 - [H^+]_i[\bar{n}_i Cm_i] - [\Sigma HSO_4^-]_i[\bar{n}_i Cm_i]) = 0 \tag{8}$$

The quadratic is solved for $[HSO_4^-]_f$. To obtain a final value for the bisulfate concentration it is necessary to make successive approximations. This is done as follows. The $\bar{n}_i Cm_i$ terms are obtained using $\bar{n}$ values taken from a plot of $\bar{n}$ *versus* free bisulfate or by solution of equation 3. The plot is obtained using $\beta_1 = 270/[H^+]$ and $\beta_2 = 2970/[H^+]^2$ for the constants of the Np(IV) system at a given acidity and $\beta_1 = 6.25/[H^+]$ and $\beta_2 = 7.6/[H^+]^2$ for approximating the constants of the Np(VI) sulfate system. In the first approximation the free $[HSO_4^-]$ is set equal to the total sulfuric acid concentration and the $\bar{n}$ values read from the plot. $[HSO_4^-]_f$ values are then calculated from equation 8 and the process repeated.

The degree of formation of the individual complex is computed from the relation

$$a_i = \frac{[MA_i]}{Cm} = \frac{\beta_i[A_i]^i}{1 + \sum_{i=1}^{J} \beta_i[A]^i} \tag{9}$$

whence concentrations of the individual complex species are calculated readily.

The decrease in k_{obsd} (Table II) at high bisulfate concentration is coincident with the formation of the complexes $Np(SO_4)_2$ and $NpO_2(SO_4)_2^{--}$, suggesting that these complexes do not contribute appreciably to the reaction. The general rate equation that would take into account the complex de-

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(7) J. C. Sullivan, D. Cohen and J. C. Hindman, THIS JOURNAL, **77**, 6263 (1955).

(8) R. A. Day, Jr., and R. M. Powers, *ibid.*, **76**, 3895 (1954).

(9) E. L. Zebroski, H. W. Alter and F. K. Heumann, *ibid.*, **73**, 5646 (1951).

pendence of the rate on the bisulfate concentration can be written as

$$R = [\mathrm{Np(IV)}][\mathrm{Np(VI)}]k_{\mathrm{obsd}} = k_0'[\mathrm{Np}^{+4}][\mathrm{NpO_2}^{++}] + k_1[\mathrm{NpSO_4}^{++}][\mathrm{NpO_2}^{++}] + k_2[\mathrm{NpSO_4}^{++}][\mathrm{NpO_2SO_4}] + k_3[\mathrm{Np(SO_4)_2}][\mathrm{NpO_2}^{++}] + k_4[\mathrm{Np}^{+4}][\mathrm{NpO_2SO_4}] + \ldots \quad (10)$$

Analysis of the data shows that the rate may be reproduced within the experimental uncertainties by a rate equation involving only the first three terms on the right-hand side of equation 10. Using a value of $k_0 = 0.59$ for the 2.2 molar acid solution, the least square value for $k_1 = 4.27$ mole^{-1} l. min.$^{-1}$ and for $k_2 = 7.12$ mole^{-1} l. min.$^{-1}$. The agreement between the calculated and experimental data is shown in Fig. 1. The calculated values of the rate constant were obtained using the equation

$$k_{\mathrm{obsd}} = k_0\left[1 - \sum_{i=1}^{J} a_{\mathrm{i}}\right]_{\mathrm{Np(IV)}}\left[1 - \sum_{i=1}^{J} a_{\mathrm{i}}\right]_{\mathrm{Np(VI)}} + k_1[a_{\mathrm{NpSO_4^{++}}}] \times \left[1 - \sum_{i=1}^{J} a_{\mathrm{i}}\right]_{\mathrm{Np(VI)}} + k_2[a_{\mathrm{NpSO_4^{++}}}][a_{\mathrm{NpO_2SO_4}}] \quad (11)$$

valid for a given condition of acidity. In equation 11 and subsequent equations, the terminology

$$\left[1 - \sum_{i=1}^{J} a_{\mathrm{i}}\right] = \frac{[\mathrm{Np}^{+4}]}{[\mathrm{Np(IV)}]},\ [a_{\mathrm{NpSO_4^{++}}}] = \frac{[\mathrm{NpSO_4}^{++}]}{[\mathrm{Np(IV)}]}, \text{ etc.}$$

is used for simplicity.

The Effect of Hydrogen Ion Concentration.—The effect of varying the hydrogen ion concentration at constant bisulfate concentration is summarized in Table III. Two initial bisulfate concentrations were used. One corresponds approximately to the concentration at which the rate of reaction is at a maximum. The second, higher concentration is for the region in which the rate has again decreased to a relatively low value. Examination of the data shows that k_{obsd} for both regions is inversely proportional to a value between the second and third power of the hydrogen ion concentration.

TABLE III

EFFECT OF HYDROGEN ION CONCENTRATION ON THE RATE OF THE Np(IV)-Np(VI) REACTION IN SULFATE SOLUTION

$\mu = 2.2, t = 25°$

Original $[H^-]$, mole l.$^{-1}$	Original $[HSO_4^-]$, mole l.$^{-1}$	[Np(IV)] $\times 10^3$, mole l.$^{-1}$	[Np(VI)] $\times 10^3$, mole l.$^{-1}$	k_{obsd}, l. mole^{-1} min.$^{-1}$	k_{calcd} l. mole^{-1} min.$^{-1}$
1.96	0.0865	2.64	18.78	3.87	3.71
1.95	.0865	5.26	15.65	4.01	3.77
1.94	.0865	10.70	9.08	3.70	3.84
1.92	.0865	13.36	6.26	3.55	3.87
1.09	.0865	10.00	9.08	11.1	12.0
0.680	.0865	10.00	9.08	34.0	29.8
0.288	.0865	10.00	9.08	138	146
2.20	.943	9.64	9.27	0.67	0.80
1.55	1.00	10.35	9.08	1.30	1.18
1.04	1.00	10.27	9.08	1.76	1.79
0.651	1.00	10.18	9.08	2.84	2.60
0.285	1.00	10.26	9.08	4.77	4.95

The variation of the reaction rate with variation in hydrogen ion concentration can be represented as a combination of five hydrogen ion dependent paths as represented by the equation

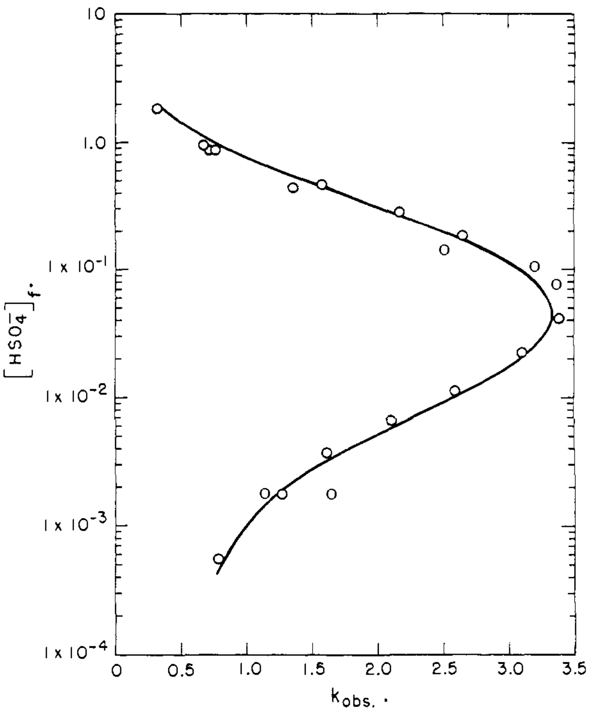


Fig. 1.—Variation of k_{obsd} with free bisulfate at constant hydrogen ion; $[\mathrm{H}^+] = 2.2\,M$; $\mu = 2.2$; $t = 25.0°$. Solid line calculated from equation 11.

$$k_{\mathrm{obsd}} = k_0\,\frac{[a_{\mathrm{Np}^{+4}}][a_{\mathrm{NpO_2^{++}}}]}{[\mathrm{H}^+]^2} + \left\{k_1\,[a_{\mathrm{NpSO_4^{++}}}][a_{\mathrm{NpO_2^{++}}}] + k_2[a_{\mathrm{NpSO_4^{++}}}][a_{\mathrm{NpO_2SO_4}}]\right\}\left\{\frac{k_3}{[\mathrm{H}^+]^2} + \frac{k_4}{[\mathrm{H}^+]^3}\right\} \quad (12)$$

It is not possible to reproduce the data by a simpler equation involving only two sulfate dependent paths with different hydrogen ion dependencies. The four sulfate containing activated complexes implied by equation 12 are formally the same as the principal activated complexes found in sulfate solution for the disproportionation reaction of Np(V) (see later Discussion).

The least squares values of the constants are $k_3 = 3.6$ mole^2 l.$^{-2}$ and $k_4 = 1.7$ mole^3 l.$^{-3}$ for the low bisulfate region and $k_3 = 3.8$ mole^2 l.$^{-2}$ and $k_4 = 2.8$ mole^3 l.$^{-3}$ for the high bisulfate region. At the 95% confidence level the uncertainties in the precision of the constants are approximately 20%. Within the experimental uncertainties the k_3 values are the same for both sets of data. It is by no means certain that the apparent differences in k_4 values are significant. The variation in solution composition is so great that appreciable deviations in the activity coefficients of the various species would not be unexpected.

Temperature Effect.—The variation of the reaction rate with temperature was determined for solutions initially 0.084 and 0.943 M in $\mathrm{HSO_4^-}$. The temperatures were 15.1, 25.0 and 35.2°. The apparent activation energies were $\Delta E = 23.1 \pm 3.3$ kcal./mole and $\Delta E = 23.3 \pm 3.2$ kcal./mole for the 0.084 and 0.943 M bisulfate solutions, respectively.

The activation energy previously found for 1 M $HClO_4$ was $\Delta E = 25.2$ kcal./mole.

II. The Disproportionation Reaction

$$2\ Np(V) \rightarrow Np(IV) + Np(VI)$$

Effect of Metal Ion.—The stoichiometry of the disproportionation reaction with respect to the Np(V) concentration was determined by a series of experiments in which the initial concentration was varied over approximately a ten-fold range at constant initial bisulfate and hydrogen ion. The rate constant, k_{obsd}, was calculated from the experimental data by the same methods used for the Np(IV)–Np(VI) reaction. Table IV summarizes the data, which are consistent with a second-power dependence on the concentration of Np(V).

TABLE IV

THE EFFECT OF VARIOUS FACTORS ON THE DISPROPORTIONATION OF Np (V) AT 25.1° AND $\mu = 2.2$

Initial $[HSO_4^-]$, mole l.$^{-1}$	Initial $[H^+]$, mole l.$^{-1}$	[Np(V)], mole l.$^{-1}$	k_{obsd}, l. mole^{-1} min.$^{-1}$	k_{calcd} l. mole^{-1} min.$^{-1}$
2.00	2.18	0.0207	1.08	0.980
2.00	2.18	.0104	1.08	.980
2.00	2.18	.00288	0.940	.980
2.00	2.18	.00196	.890	.980
1.00	2.18	.0214	.380	.385
0.466	2.18	.0214	.154	.164
.938	1.18	.0218	.342	.327
.895	0.583	.0218	.287	.284
.823	0.184	.0218	.232	.241

The Effect of Bisulfate and Hydrogen Ion.—The rate of the disproportionation reaction is a monotonic increasing function of the bisulfate concentration. Analysis of the data in Table IV by standard methods results in a non-integral bisulfate dependence of 1.3 over the range of concentration $2.00 \leq [HSO^{4-}] \leq 0.466\ M$.

Empirical analysis of the data in Table IV also reveals that the rate of the reaction is dependent on the 0.1 power of the hydrogen ion concentration over the acid range $2.18 \leq [H^+] \leq 0.184\ M$. The empirical form of the rate equation is then

$$R = [Np(V)]^2 k_{obsd} = k[Np(V)]^2[HSO_4^-]^{1.32\pm0.02} \times [H^+]^{0.092\pm0.002} \quad (13)$$

The value of $k = 0.364 \pm 0.022$ at the 95% confidence level.

As in the case of the Np(IV)–Np(VI) reaction, the non-integral bisulfate and hydrogen ion dependencies indicate that the Np(V) disproportionation reaction is complex. It is possible to express the results in the equation

$$k_{obsd} = \{k_5[HSO_4^-] + k_6[HSO_4^-]^2\}\{k_7 + k_8[H^+]\} \quad (14)$$

The least squares values for the specific constants are $k_5 = 0.300$ mole^{-2} l.^{2} min.$^{-1}$, $k_6 = 0.0877$ mole^{-3} l.^{3} min.$^{-1}$, $k_7 = 0.739$ and $k_8 = 0.135$ mole^{-1} l. Calculated values of k_{obsd} using this equation are given in Table IV, column 5. It is possible to reproduce the results if the hydrogen ion dependent terms are neglected; however, the fit to the data is not quite as good. This might be justified on the basis that the environmental conditions are altered sufficiently to give an effect of this magnitude. The resulting equation then would be

$$k_{obsd} = k_5'[HSO_4^-] + k_6'[HSO_4^-]^2 \quad (15)$$

with $k_5' = 0.26$ mole^{-2} l.^{2} min.$^{-1}$ and $k_6' = 0.14$ mole^{-3} l.^{3} min.$^{-1}$.

It should be pointed out that the four paths indicated by equation 14 yield stoichiometric formulas for the activated complexes identical with three of those obtained for the four bisulfate dependent paths of the Np(IV)–Np(VI) reaction. The principle of detailed balancing requires that all possible paths exist for the disproportionation reaction. The applicability of the simpler equation is therefore indicative of the relative rates of reaction for the several paths and the limited precision of the data.

The Effect of Temperature.—The temperature coefficient of the reaction rate was measured for solutions initially 2.18 M in $[H^+]$ and 2.00 M in $[HSO_4^-]$. Temperatures were 15.15, 25.1 and 35.15°. The apparent activation energy was $\Delta E = 14.3 \pm 3.1$ kcal./mole. The activation energy previously measured for 1 M $HClO_4$ solutions was 17.1 ± 1.6 kcal./mole.

Discussion

The stoichiometric formulas for the activated complexes derived from the rate data can be written

$$A = [NpO_2NpOOHSO_4^{+1}]^{\ddagger}$$
$$B = [NpO_2Np(OH)_2(SO_4)_2]^{\ddagger}$$
$$C = [NpO_2Np(OH)_2SO_4^{+2}]^{\ddagger}$$
$$D = [NpOOHNp(OH)_2(SO_4)_2^{+1}]^{\ddagger}$$
$$E = [NpO_2Np(OH)_3(SO_4)_2^{-1}]^{\ddagger}$$

Representation of the stoichiometry as above does not necessarily imply the existence of the given entities in the actual configurations of the activated complexes. Alternate representations can be given. The transition states A and B represent those for the predominant reaction paths for the Np(V) disproportionation. C and D also represent activated complexes for the disproportionation reaction. The states A, B and C are common to both the disproportionation reaction and the Np(IV)–Np(VI) reaction. Since it is a requirement of the principle of microscopic reversibility that the transition state be the same for both the forward and reverse reaction, the fact that the state D is derived only from the rate equation for the disproportionation and the state E only from the rate equation for the Np(IV)–Np(VI) reaction is therefore only indicative of the relative rates of reaction for the several paths of these two reactions.

Examination of the stoichiometric formulas for the activated complexes suggests certain conclusions as to the probable geometrical configurations of the transition states and probable restrictions on the mechanism for the electron transfer process. First, the data suggest that the neptunium ions must attain a configuration close to that of a O–Np–O$^+$ ion before the electron transfer can occur. As a corollary, it would further appear that it is unlikely that the mechanism can involve the rupture of a Np–O bond of the linear complex in the rate-determining step. That these conditions should be met is not surprising. The O–M–O structure for the ions of the penta- and hexapositive oxidation states of the actinide elements is very stable, persisting both in solution and in the solid state as an entity.[10–13]

The principal experimental observation supporting the idea that the neptunium ions attain a configuration that readily yields NpO_2^+ before electron transfer occurs is the hydrogen ion dependencies observed for those reactions involving oxidation of Np(IV). For the Np(IV)–Np(VI) reaction in perchlorate solution the dominant reaction path yields a stoichiometry for the activated complex that may be represented as $[NpO_2Np(OH)_2^{+4}]^{\ddagger}$.[2] Similarly, the oxidation of Np(IV) to Np(V) by Fe(III) involves a hydrogen ion dependence that yields the stoichiometric formula, $[Fe(OH)Np(OH)_2^{+4}]^{\ddagger}$.[14] Analogous results have been found for the disproportionation reaction of Pu(IV), where similar species are involved.[15–17] In this case the transition state for the slow step[16] may be represented as $[Pu(OH)_2PuOH^{+5}]^{\ddagger}$. For the reactions in the present research, the importance of the hydrogen ion dependence is emphasized by the participation of sulfate in the reaction. That is, the equivalent of the reaction occurs despite the fact that this equilibrium

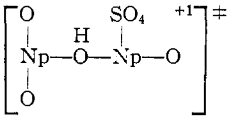
$$Np^{+4}(aq.) + 2H_2O \rightleftharpoons Np(OH)_2^{++} + 2H^+ \quad (16)$$

rium, which lies far to the left in perchlorate solutions of equivalent acidity, will be further shifted in this direction by the presence of sulfate attached to the Np(IV). The same general argument would apply whether the hydrogen ion is split off in a pre-equilibrium similar to reaction 16 or in the process of formation of the activated complex. The fact that Np(IV) sulfate complexes containing more than one sulfate group do not participate in the reaction to an appreciable extent undoubtedly is partially explicable on the basis that the more sulfate groups attached, the less favorable are conditions for removal of hydrogen ions.

A second factor that may affect the number of sulfate groups involves the question of whether or not the sulfate acts as a bridging ligand in the activated complex. Considering the available data on the relative effectiveness of different bridging groups,[18,19] it appears likely that if there is a choice between bridging through sulfate or hydroxyl, the hydroxyl would be highly favored. In this connection it might be mentioned that in the solid compounds $Th(OH)_2SO_4$ and $Th(OH)_2CrO_4 \cdot H_2O$, the structure appears to consist of chains of thorium ions linked by hydroxide bridges with the sulfate or chromate ions acting to hold these chains together in the form of a layer structure.[20,21] Formation of similar structures in the hydrolysis–polymerization reactions of uranium and thorium have been proposed.[22]

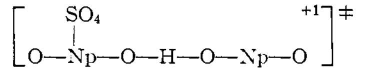
Considering that it is unlikely that the function of the sulfate is that of a bridging group, the catalytic effect of limited concentrations of sulfate can probably be attributed to a charge reduction for the activated complex.

Assuming that the hydroxyl is the most likely bridging anion the question arises as to the actual geometrical configurations in the activated complex and the probable mechanisms for the electron transfer. Consider for example the transition state complex, A. We can write two possible configurations



X

and



$$\left[O{-}\overset{\overset{\displaystyle SO_4}{|}}{Np}{-}O{-}H{-}O{-}Np{-}O\right]^{+1\,\ddagger}$$

Y

The mechanism of charge transfer for the configuration X could be considered either as an electron transfer through a hydroxyl bridge or as a hydroxy atom transfer. If we accept our argument that the tendency is to form and maintain the O–M–O structure, then we can rule out the hydroxyl atom transfer mechanism. There is no *a priori* way of deciding whether an electron transfer or a hydrogen atom transfer mechanism, corresponding to the configuration Y, is the correct one. It might be pointed out, however, that formation of complexes corresponding to the general configuration Y involves no rearrangement of the hydration spheres of the reacting ions in the formation of the bridge. The transition state is also more symmetrical for those complexes with the Y configuration.

If we assume that the bridging is by way of either hydroxyl or hydrogen, then the fundamental mechanism for the electron transfer process is probably the same in the presence or absence of sulfate. We can then advance a reasonable explanation for the apparent anomalies previously discussed for experiments in perchlorate media.[2,23] For example, it was found that the Np(IV)–Np(VI) reaction in perchlorate solution could be adequately represented by

$$-\frac{d[Np^{+4}]}{dt} = k_0'[Np^{+4}][NpO_2^{++}][H^+]^{-2} \quad (17)$$

Combining this with the equation for the over-all equilibrium involving Np(IV), Np(V) and Np(VI), it was deduced that the Np(V) disproportionation reaction could be written as a mechanism which

$$-\frac{d[NpO_2^+]}{dt} = k_1'[NpO_2^+]^2[H^+]^2 \quad (18)$$

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differed in stoichiometry with respect to hydrogen ion from the analogous U(V) reaction.[24] On the other hand, one of the paths for the Np(IV)–Np(V) exchange reaction had the stoichiometry of the U(V) disproportionation.

$$-\frac{d[NpO_2^+]}{dt} = k_1''[NpO_2^+]^2[H^+] \qquad (19)$$

It was found further that the energetics for the overall equilibrium was not in accord with the energetics for the two reactions, (19) and (17). It appears likely from the present observations that the explanation for the disparities is that multiple reaction paths are involved. With this possibility in mind the data for the Np(IV)–Np(VI) reaction were re-examined. Least squares analysis showed that the hydrogen ion dependence was $[H^+]^{-2.08 \pm 0.06}$ (95% confidence level). From this it is possible to write a kinetic expression involving two hydrogen ion dependent paths as

$$k_{obsd} = k_1[H^+]^{-2} + k_2[H^+]^{-3} \qquad (20)$$

with $k_1 = 2.59$ and $k_2 = 0.074$. Although it is clear that the predominant reaction involves only two hydrogen ions these computations lend some support to the hypothesis that more than a single reaction path is involved in perchlorate solution.

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Anodic Stripping Voltammetry with Mercury Electrodes—Potential-step and Current-step Methods

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An amalgam forming metal is deposited on a stationary mercury electrode and then is anodically oxidized. Anodic stripping is carried out either by sudden switching of potential (potential-step method) or by passing a constant current through the cell (current-step method). A theoretical analysis is developed for both methods for conditions of semi-infinite linear diffusion. The following derivations are given: equations for current–time, current–potential and potential–time curves; diffusion current and transition time for the stripping process; sensitivity gain. Detailed experimental results are discussed for the anodic stripping of cadmium from a hanging mercury drop, and theory and experiment are compared. Sensitivity gains with respect to voltammetry with stirred solution can be larger than 100. Application to concentrations as low as 10^{-7}–10^{-9} molar appears feasible. The two methods are compared with anodic stripping at continuously varying potential (Nikelly and Cooke).

Anodic stripping methods which have been known for years[2] recently have been applied again to the analysis of traces of metals.[3–5] The metal to be determined in a solution is first deposited on a solid[3,5] or amalgamated[4] electrode, and then is stripped from this electrode by anodic oxidation. The amount of metal ion in solution is determined from the quantity of electricity consumed in the stripping process. Nikelly and Cooke[6] recently modified the method and used a mercury pool electrode for deposition of the metal to be analyzed. They reoxidized the metal at continuously varying potential and obtained current–potential curves not unlike those of oscillographic polarography. These curves exhibit a peak from the height of which the concentration of metal is deduced directly. The method of Nikelly and Cooke is a voltammetric procedure whereas previous methods belong to coulometry. These authors coined the expression "anodic stripping polarography" for their method, but we prefer to call it "anodic stripping voltammetry," thus reserving the term "polarography" for methods involving the use of the dropping mercury electrode.[7]

In addition to the method of Nikelly and Cooke, two other simple methods can be conceived: (a) the "potential-step" method in which the metal is oxidized by sudden variation of potential to a more anodic value; and (b) the "current-step" method in which the stripping process is carried out at constant current. These methods are discussed and compared in this paper for the case of stationary mercury electrodes.

Potential-step Method

Diffusion Stripping Current.—A metal M is deposited at constant potential on a stationary mercury electrode in stirred solution. The conditions are such that the electrolysis current is constant; *i.e.*, the volume of solution is so large and the plating time so short that depletion of ions M^{+n} in solution can be neglected. Electrolysis is carried out at a potential corresponding to the limiting current range. Mercury is not stirred, and M is supposed to diffuse in the bulk of mercury under conditions of semi-infinite linear diffusion. After τ seconds, the potential is changed abruptly to a sufficiently anodic value at which metal M is oxidized at a rate that is solely diffusion controlled. The resulting *diffusion stripping current* will now be derived. This current is obtained by deriving the flux of metal M at the electrode surface, *e.g.*, by solving

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