TABLE II

INTERPRETATION OF EFFECTS OF ADDED SOLUTES

Substance	Temp., °C.	A_0	10^2 $A_{\min}$	$A_{\max}$	Slope	Intercept	ρ_0	γ
C_2H_5I	20	38.6	25	70	20	0.35	3.6	0.32
	−78	37.0	25					
C_2H_5Br	0	31.8	20	60	9.4	.35	2.5	.47
	−78	34.5	20	60	5.7	.45	1.7	.54
n-C_3H_7Br[a]	25	34.0	22	60	7.2	.38	2.1	.51
n-C_4H_9I[b]	20	37.0	25	56	6.4	.49	1.7	.47
CH_3I[b]	0	56.0	36	95	9.2	.42	2.3	.43
	−46	57.5		95				

[a] Data of Rowland and Libby, ref. 3. [b] Data on the effects of free halogen on the retention were taken from the work of Levey and Willard, ref. 6.

significant. To simplify this evaluation let it be assumed that $P_1 = P_2 = 1$, replace $n_0^{1/2}$ by $\bar{R}_0/L$ and employ the reduced parameters $\rho_0 = \bar{R}_0/d$, $\gamma = L/d$. From the preceding considerations it follows that

$$-\ln(1 - W_\infty(0)) = -\ln(A_{\max} - A_0)/(A_{\max} - A_{\min}) = (\sqrt{2\pi}\rho_0\gamma)^{-1}$$

Combining these results with the slopes of Figs. 4, 5, *viz.* $\sqrt{\pi}\rho_0/\gamma$ we obtain the values of the reduced parameters which are listed in the last two columns of Table II. In view of the uncertainties involved the range of values obtained for the initial separation and mean free path are quite gratifying. It is clearly desirable to test the preceding diffusion equation in a more nearly appropriate system where there is less uncertainty regarding the initial act. Suitable data are, unfortunately, scarce and such a test has thus far been completed only for the photolysis of tribromide ion with bromide ion as the solute[17] and Mn(II) as scavenger.

The primary process is

$$Br_3^- + h\nu \longrightarrow Br_2^- + Br$$

and the effect of the solute in preventing recombination is probably

$$Br + Br^- \longrightarrow Br_2^-$$

followed by

$$Mn(II) + Br_2^- \longrightarrow Mn(III) + 2Br^-$$

We find for this reaction $\rho_0 \simeq 0.6$, $\gamma \simeq 0.5$. Details of this and other related work will be published.

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NOTRE DAME, INDIANA

[CONTRIBUTION FROM THE CHEMISTRY DIVISION, ARGONNE NATIONAL LABORATORY]

Kinetics of Reactions between Neptunium Ions. The Neptunium(IV)-Neptunium(VI) Reaction in Perchlorate Solution

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An investigation of the mechanism of the reaction Np(IV) + Np(VI) $\rightleftarrows$ 2Np(V) has been undertaken in perchlorate media. The rate law for the forward reaction is given by: $-\,d(Np^{+4})/dt = k_1^0[Np^{+4}][NpO_2^{++}][H^+]^{-2}$. At 25° and $\mu = 2.00$, k_1^0 is 2.69 mole l.$^{-1}$ min.$^{-1}$; ΔH^* is 24.6 kcal.; ΔS^* is 17.8 cal./deg. and ΔF^* is 19.3 kcal. At 25° and $\mu = 1.00$, k_1^0 is 3.13 mole l.$^{-1}$ min.$^{-1}$. The effect of ionic strength has been measured. Two alternative mechanisms for the reaction are postulated.

Few quantitative investigations have been made of the kinetics of reactions in which neptunium ions participate. Huizenga and Magnusson[1] have reported that the oxidation of Np^{+4}(aq.) by Fe^{+3}(aq.) appears to proceed by a mechanism involving a hydrolyzed species of neptunium(IV). The exchange reaction between Np^{+4}(aq.) and NpO_2^+(aq.) has been found to be a complex reaction involving two different paths depending on the acid concentration range.[2] Although the disproportionation reaction of neptunium(V) to give neptunium(IV) and -(VI) has been reported[3] at high acid, the experimental conditions make it difficult to interpret the results in any detail. To further extend our information in this field, the investigation of the reaction between Np^{+4}(aq.) and NpO_2^{++}(aq.) was undertaken. Details of this investigation are reported in the present communication.

Experimental

The neptunium stock solutions in perchloric acid were prepared electrolytically from a neptunium(V) stock in perchloric acid according to previously described methods.[4] The reaction solutions were prepared volumetrically using standardized solutions of sodium perchlorate, perchloric acid and neptunium(IV). A two-centimeter silica absorption cell was used for the reaction vessel. After spectrophotometric measurement of the density of the neptunium(IV) band at 724 mμ[3] to give a value for the initial optical density, the neptunium(VI) was added. The progress of the reaction was followed by monitoring the neptunium (IV) band at 724 mμ. Small corrections were made for the absorption of the neptunium(V) produced in the reaction. The temperature in the thermostatic cell compartment of the Cary recording spectrophotometer was maintained to ±0.1°.

The acid concentration in the reaction solution was checked after completion of the reaction by titration with standard alkali.[2]

Results and Discussion

Effect of Metal Ion.—The stoichiometry of the reaction with respect to each of the metal ions was determined by experiments in which the concentra-

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(1) J. R. Huizenga and L. B. Magnusson, THIS JOURNAL, **73**, 3202 (1951).

(2) J. C. Sullivan, D. Cohen and J. C. Hindman, *ibid.*, in press (1954).

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

(4) D. Cohen and J. C. Hindman, *ibid.*, **74**, 4679, 4682 (1952).

tions of neptunium(IV) and neptunium(VI) were varied in the reaction mixture. Graphical analyses showed that the data were most consistent for a bimolecular process. The results of a typical experiment are summarized in Table I. The precision of the data as in all cases reported is given in terms of standard deviation. The apparent rate constant, k', was calculated by the integrated equation for a bimolecular process

$$k_1' = \frac{2.303}{([\mathrm{Np(IV)}]^\circ - [\mathrm{Np(VI)}]^\circ)t} \log \frac{[\mathrm{Np(VI)}]^\circ}{[\mathrm{Np(IV)}]^\circ} \left(\frac{[\mathrm{Np(IV)}]^\circ - x}{[\mathrm{Np(VI)}]^\circ - x}\right) \quad (1)$$

TABLE I

THE RATE OF REACTION OF Np(IV) WITH Np(VI) AT 25°

$\mu = 2.00$; $[\mathrm{H}^+] = 1.000M$; $[\mathrm{Np(IV)}]^\circ = 4.99 \times 10^{-3} M$; $[\mathrm{Np(VI)}]^\circ = 1.024 \times 10^{-2} M$

Time, min.	d_{724}, cor.	Moles/l. × 10^4	k_1', l. mole^{-1} min.$^{-1}$
0	1.374		
5.00	1.221	5.57	2.39
10.00	1.070	11.1	2.61
15.00	0.969	14.7	2.46
18.00	.911	17.0	2.49
20.00	.875	18.3	2.48
25.00	.778	21.6	2.51
30.00	.700	24.6	2.57
35.00	.628	27.1	2.59
40.00	.567	29.3	2.61
45.00	.520	31.1	2.60
50.00	.467	32.9	2.63
55.00	.438	34.0	2.56
60.00	.387	35.8	2.65
70.00	.334	37.8	2.61
80.00	.273	40.0	2.67
		Av.	2.56 ± 0.08

where $[\mathrm{Np(IV)}]^\circ$, $[\mathrm{Np(VI)}]^\circ$, represent the initial concentrations of reactants, and x the concentration of Np(IV) that has reacted at time, t. The back reaction can be neglected in the calculations of the forward rate constants since at equilibrium the concentrations of Np(IV) and Np(VI) are negligible.

The results of experiments at varying neptunium (IV) and neptunium(VI) concentrations are summarized in Table II. The k_1^0 values are corrected for the effect of hydrogen ion concentration as discussed in the next section.

TABLE II

EFFECT OF METAL ION CONCENTRATION ON THE RATE OF REACTION OF NEPTUNIUM(IV) AND NEPTUNIUM(VI) AT 25°

$\mu = 2.00$

$[\mathrm{Np(IV)}]^0$, moles/liter × 10^3	$[\mathrm{Np(VI)}]^0$, moles/liter × 10^3	$[\mathrm{H}^+]$, moles/l.	k_1', l. mole^{-1} min.$^{-1}$	k_1^0, mole l.$^{-1}$ min.$^{-1}$
2.42	4.89	1.046	2.63	2.88
4.85	4.89	1.046	2.60	2.84
4.99	10.24	1.000	2.56	2.56
6.47	3.07	1.022	2.35	2.45

Effect of Hydrogen Ion.—The hydrogen ion order of the reaction was determined by measuring the rate of the reaction as a function of hydrogen ion concentration at constant and equal Np(IV) and Np(VI) concentrations. The data are summarized in Table III. The k_1' values were calculated from the relation for a bimolecular reaction

$$k' = \frac{x}{[\mathrm{Np(IV)}]^0([\mathrm{Np(IV)}]^0 - x)t} \quad (2)$$

and k^0 from the relation

$$k^0 = k'[\mathrm{H}^+]^n \quad (3)$$

As can be seen from Table III, the best fit of the data is given with $n = 2$.

TABLE III

EFFECT OF HYDROGEN ION CONCENTRATION ON RATE OF REACTION OF NEPTUNIUM(IV) AND NEPTUNIUM(VI) AT 25°

$\mu = 2.00$, $[\mathrm{Np(IV)}]^\circ = [\mathrm{Np(VI)}]^\circ = 5.00 \times 10^{-3} M$

$[\mathrm{H}^+]$, moles/l.	k', l. mole^{-1} min.$^{-1}$	k^0 $n = 1$	$n = 2$	$n = 3$
1.994	0.581	1.16	2.31	4.61
1.046	2.60	2.69	2.84	2.94
0.532	10.47	5.57	2.96	1.58
0.227	54.5	12.4	2.81	0.64

Effect of Ionic Strength.—Very little effect of ionic strength on the reaction rate is indicated by the data in Table IV. There is a slight trend in k° with increasing ionic strength.

TABLE IV

EFFECT OF IONIC STRENGTH ON RATE OF REACTION OF NEPTUNIUM(V) AND NEPTUNIUM(VI) AT 25°

$[\mathrm{Np(IV)}] = [\mathrm{Np(VI)}] = 5.00 \times 10^{-3} M$

$[\mathrm{H}^+]$, moles/l.	μ	k_1^0, mole l.$^{-1}$ min.$^{-1}$
0.494	0.55	3.54
.502	0.55	3.35
.511	1.00	3.11
.520	1.00	3.16
1.046	2.00	2.84
0.532	2.00	2.96

The Effect of Temperature.—In Table V are summarized the data on the temperature coefficient of k_1^0. From the data in Table V, which are plotted in Fig. 1, the Arrhenius energy of activation, ΔE, for the reaction was calculated to be 25.2 ± 1.6 kcal. using the method of least squares.

TABLE V

EFFECT OF TEMPERATURE ON THE RATE OF REACTION OF NEPTUNIUM(IV) AND NEPTUNIUM(VI)

$\mu = 2.00$ $[\mathrm{Np(IV)}]^\circ = [\mathrm{Np(VI)}]^\circ = 5.00 \times 10^{-3} M$

$[\mathrm{H}^+]$, moles/l.	k_1', l. mole min.$^{-1}$	k_1^0 mole l.$^{-1}$ min.$^{-1}$	Temp., °C.
1.009	10.01	10.19 ± 0.35	34.8
1.017	9.79	10.13 ± .31	34.7
. . .	. . . .	2.69 ± .23	25.0[a]
1.004	0.609	0.614 ± .03	15.5
1.013	0.614	0.630 ± .03	15.4

[a] Mean of data for 25° (metal and hydrogen ion effects).

The heat and entropy of activation for the reaction were calculated from the rate expressions for the transition state theory[5] in the form

$$k_1^0 = e^{\frac{kT}{h}} e^{\frac{-\Delta E}{RT}} e^{\frac{\Delta S^*}{R}} = e^{\frac{kT}{h}} e^{\frac{-(\Delta H^* + RT)}{RT}} e^{\frac{\Delta S^*}{R}} \quad (4)$$

The computed values of $\Delta H^* = 24.6 \pm 1.6$ kcal.,

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(5) S. Glasstone, K. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, pp. 197–199.

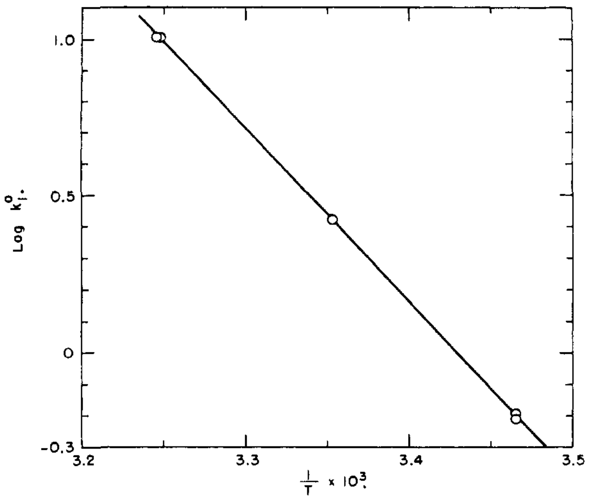

Fig. 1.—Effect of temperature on k_1^0.

$\Delta S^* = 17.8 \pm 2.7$ cal./deg. and $\Delta F^* = 19.3 \pm 1.6$ kcal.

From the free energy, heat and entropy data[4] for the over-all reaction (equation 5) and the data for the forward reaction given above, $\Delta F^* = 28.5 \pm 1.6$ kcal., $\Delta H^* = 17.1 \pm 1.6$ kcal. and $\Delta S^* = -38.1 \pm 2.9$ cal./deg. for the disproportionation reaction of neptunium(V). In these calculations the effect of the difference in ionic strength at which the data were obtained was neglected.

The Disproportionation Reaction.—From the published data[4] on the potentials of the neptunium couples, the constant, K, for the over-all reaction

$$Np^{+4}(aq.) + NpO_2^{++}(aq.) + 2H_2O \rightleftarrows 2NpO_2^{+}(aq.) + 4H^+ \quad (5)$$

is 5.45×10^6 at 25° in 1 M perchloric acid. Using the data for k_1^0 at unit ionic strength

$$Np(IV) + Np(VI) \underset{k_2}{\overset{k_1}{\rightleftarrows}} 2Np(V) \quad (6)$$

the value of $k_2^0 = k_1^0/K = 5.74 \pm 0.55 \times 10^{-7}$ $l.^3$ $mole^{-3}$ $min.^{-1}$.

It is of interest to note that the simplest molecularity for the neptunium(V) disproportionation that can be deduced from the stoichiometry of the over-all reaction 5, *i.e.*

$$-d[NpO_2^+]/dt = k[NpO_2^+]^2[H^+]^2 \quad (7)$$

differs from that found for the analogous uranium (V) reaction.[6,7] In the latter case the rate law is given as

$$-d[UO_2^+]/dt = k[H^+][UO_2^+]^2 \quad (8)$$

Why the stoichiometry should be different in the two cases is not readily explained.

Mechanism of the Reaction.—Based on the observed metal ion dependencies and hydrogen ion dependence, a number of mechanisms can be postulated for this reaction. Two of these are

$$Np^{+4}(aq.) + H_2O \rightleftarrows NpO^{++} + 2H^+ \quad \text{rapid equilibrium} \quad (9)$$

followed by

$$NpO^{++} + NpO_2^{++} \rightleftarrows [O\text{-}Np\text{-}O\text{-}Np\text{-}O]^{+4} \longrightarrow NpO_2^+ + NpO^{+++} \quad (10)$$

and then

$$NpO^{+++} + H_2O \rightleftarrows NpO_2^+ + 2H^+ \quad \text{rapid equilibrium} \quad (11)$$

Alternatively, we may write

$$Np^{+4}(aq.) + 2H_2O \rightleftarrows Np(OH)^{+2}{}_2 + 2H^+ \quad \text{rapid equilibrium} \quad (12)$$

$$Np(OH_2)^{+2} + NpO_2^{++} \rightleftarrows [O\text{-}Np\text{-}O\text{---}H\text{-}O\text{-}Np\text{-}O\text{-}H]^{+4} \longrightarrow 2NpOOH^{+2} \quad (13)$$

and

$$NpOOH^{+2} \rightleftarrows NpO_2^+ + H^+ \quad \text{rapid equilibrium} \quad (14)$$

With the data available at present, preference for either the oxygen transfer or the hydrogen transfer mechanism is a matter of individual insight.

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(6) D. M. H. Kern and E. F. Orlemann, THIS JOURNAL, **71**, 2102 (1949).

(7) H. G. Heal and J. G. N. Thomas, *Trans. Faraday Soc.*, **45**, 11 (1949).