aldehyde, as drawn in Fig. 2, increasing the temperature may cause an increase in the permitted *s-trans* conformations for which transitions are no longer possible, and consequently the absorption intensity may decrease. *Alternatively*, increasing the temperature may cause an increase in the permitted *s-cis* conformations, so that transitions, which previously were not possible, are now possible for these conformations. The latter transitions may in this way give rise to an overall intensity increase, or a combination of the two opposing effects may lead to results which cannot be predicted *a priori*.

The Effective Interference Values of Atoms in Solution.—If steric interactions cause the observed spectral effects in β-methylcrotonaldehyde (III), they may be expected to be greater in the *s-trans* conformation (III A). Using scale drawings, the distance between the centers of the methyl group and the hydrogen atom in the coplanar *s-trans* form and the distance between the methyl group and the carbonyl oxygen atom in the *s-cis* form are both found to be 2.6 Å. From the previously suggested interference radii for H, 0.95 ± 0.1 Å.; O(in C=O), 1.0 ± 0.15 Å.; and CH_3, 1.7 ± 0.2 Å.[1,6]; it follows that if a hydrogen atom and a methyl group approach each other to within a distance of *ca.* 2.65 Å., one would expect spectral effects to be caused by these steric interactions. Precisely these spectral effects are observed. It may be noted that since the spectral effects ascribed to steric interactions are appreciable for β-methylcrotonaldehyde, it is probable that yet smaller steric interactions between non-bonded atoms may also be detected by this method.

It may finally be noted that throughout the discussion, by using the obvious important resonance forms, it has been assumed that the transitions involve an electron transfer in which a π-electron is transferred from one part of the molecule to another part of the molecule. This type of transition has been described as occurring to electron transfer (E.T.) states,[22] in order to distinguish it from transitions occurring to locally excited (L.E.) states in which the π-electrons remain associated with the C=C and C=O groups, respectively. Steric effects in spectra leading to E.T. states have also been discussed from a theoretical viewpoint by Murrell,[23] who tentatively concludes that steric hindrance for compounds of that type results in a decreased absorption intensity without displacement of the band position. This agrees with our conclusions. The reason why the absorption bands are ascribed by us to transitions leading to E.T. states, or at least to excited states in which electron transfer plays an important part, is based on the observation that for α,β-unsaturated carbonyl compounds large bathochromic wave length displacements are observed compared with the C=C and the C=O absorptions. In addition, not only for these, but also for other examples particularly in the aromatic series, displacements to longer wave length are greatest whenever the excited state is hybrid involving electron mobility along an extended conjugated system. Further, in this particular example, since the absorption band at 240 mμ for acetophenone is associated with transitions to an E.T. excited state,[23] it seems highly probable that a similar transition accounts for the absorption of ultraviolet light of α,β-unsaturated aldehydes.

Acknowledgments.—The authors gratefully acknowledge the receipt of research grants from the National Research Council of Canada and the Research Corporation of New York.

(22) H. C. Longuet-Higgins and J. N. Murrell, *Proc. Phys. Soc.*, **68A**, 601 (1955); *cf.* also ref. 10.

(23) J. N. Murrell, *J. Chem. Soc.*, 3779 (1956).

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[CONTRIBUTION FROM E. I. DU PONT DE NEMOURS AND CO., SAVANNAH RIVER LABORATORY, AIKEN, SOUTH CAROLINA]

Kinetics of HNO_2 Catalyzed Oxidation of Neptunium(V) by Aqueous Solutions of Nitric Acid[1]

BY T. H. SIDDALL, III, AND E. K. DUKES

RECEIVED MAY 13, 1958

It was shown that the rate-controlling step of the oxidation reaction in the system occurs by reaction 1. Succeeding steps are suggested by reactions 2 and 3. Reaction 1 has an activation energy of 12 kcal. The number of hydrogen ions, *n*, which are involved may be as large as four. The rate of the reaction depends on the fourth power of the concentration of nitric acid. The rate of reaction 2 does not become comparably slow until the concentration of nitrous acid in the aqueous phase is reduced to less than 5×10^{-5} *M*. Equilibrium data were obtained for the over-all reaction 4. The over-all reaction is slightly endothermic. Equilibrium data are given in Table IV. Depending on the composition of the aqueous phase, the major fraction of the neptunium may be in the hexavalent state at equilibrium.

Introduction

Half cell potentials[2] show that nitrate ion should significantly oxidize Np(V) to Np(VI). However, the nitrate ion is known to be inert even when a thermodynamic potential exists. The first objective of the work covered in this paper was to investigate the kinetics of the oxidation of tracer concentrations (10^{-6} to 10^{-5} *M*) of Np(V) to Np(VI) in the system: HNO_3–HNO_2–H_2O–Np–1.09 *M*[3] tri-*n*-butyl phosphate in *n*-dodecane. A second objective was to determine the equilibrium constants for the oxidation reaction in the same system.

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(1) The information contained in this report was developed during the course of work under contract AT(07-2)-1 with the Atomic Energy Commission, whose permission to publish is gratefully acknowledged.

(2) G. T. Seaborg and J. J. Katz, "The Actinide Elements," National Nuclear Energy Series IV-14A, McGraw-Hill Book Co., New York, N. Y., 1954.

(3) Thirty volume per cent.

Experimental

Purification of Neptunium-237.—The neptunium used in this work was purified by extraction with TTA (thenoyl trifluoroacetone). A solution of neptunium in 1.0 *M* nitric acid was adjusted to 0.2 *M* in ferrous sulfamate, which reduced neptunium to the IV state. The solution of neptunium(IV) was agitated for 10 minutes with an equal volume of a 0.5 *M* solution of TTA in benzene. The solution of TTA was scrubbed with an equal volume of 0.5 *M* nitric acid and then neptunium was extracted back into 5.0 *M* nitric acid.

Preparation and Purification of Np-239.—Neptunium-239 was prepared by short irradiations of solid uranyl nitrate hexahydrate in the Standard Pile at the Savannah River Laboratory. The Np-239 was separated from uranium and fission products by carrying with lanthanum fluoride followed by further purification by TBP or TTA extraction. Decay curves and scans with the γ-ray spectrometer confirmed the purity of the Np-239.

Preparation of TBP.—All TBP used in this work was first purified by recrystallization of the addition compound with uranyl nitrate. Crude TBP was saturated with uranyl nitrate and recrystallized from *n*-hexane three times. The addition compound of uranyl nitrate with TBP started to crystallize at −20° and filtration was carried out at −40°. After the final recrystallization, uranium was removed from the TBP by washing with Na_2CO_3 and water. Hexane was removed from the TBP by steam distillation and water was removed by evaporation at a reduced pressure.

TBP was made up to 30% by volume in olefin-free *n*-dodecane and was scrubbed with caustic and water immediately before use. Olefin-free *n*-dodecane was obtained from Humphrey-Wilkerson and was used without further treatment.

Preparation of Np(VI).—Neptunium(VI) was prepared by oxidizing small aliquots from the stock solution of purified neptunium. A 100-microliter aliquot which contained 1.6×10^6 d./(min.)(ml.) of Np was added to a solution which contained 3.0 *M* nitric acid and 0.03 *M* potassium permanganate. This solution was allowed to stand at room temperature for 10 minutes and was then held at 70° for 10 minutes. An excess of manganous nitrate was added to destroy the permanganate. The manganese dioxide cake was discarded after centrifugation and the supernate was extracted with an equal volume of 30% TBP in *n*-dodecane. The organic phase which contained the Np(VI) was scrubbed with an equal volume of 3.0 *M* nitric acid.

Preparation of Np(V) Tracer.—Np(V) tracer was prepared from the Np(VI) by reduction with nitrous acid in nitric acid. An equal volume of water was added to an aliquot of 1.09 *M* TBP in dodecane which contained the Np(VI) and some extracted nitric acid. Enough sodium nitrite was added so that its concentration was 0.02 to 0.05 *M*. The solutions were agitated and the extraction coefficient of Np was determined at regular intervals. When a distribution coefficient of 0.1 or less was obtained, the organic phase was discarded. Fresh organic phase was added to remove nitrous acid and Np(VI) from the aqueous phase. The aqueous phase was put aside for use as Np(V) tracer. In low concentrations of nitric acid Np(V) was found to be very stable.

Rate Experiments.—The rate of oxidation of Np(V) to Np(VI) in the presence of nitric acid and nitrous acid was measured in the following way. Np(V) tracer was added to nitric acid of the desired concentration and one-milliliter aliquots of this aqueous solution were combined with an equal volume of 1.09 *M* TBP in *n*-dodecane. Sodium nitrite was added and the two phases were agitated for a given period of time. After agitation the amount of Np was determined in each phase, and the distribution coefficient of Np was calculated. This procedure was repeated with separate samples for each different time interval. In other experiments a large volume (10 ml.) of each phase was used. At desired time intervals aliquots of each phase were sampled and counted. Counting was done to a standard error of 3% in all cases. Analyses were made of each sample for nitric and nitrous acid.

Measurements on the rate of reduction of Np(VI) to Np(V) were carried out by a similar procedure. An aliquot of Np(VI) was added to fresh 1.09 *M* TBP *n*-dodecane which was mixed with solution of nitric acid and nitrous acid. Mixing and sampling were done in the way described above.

Analysis for Nitrous Acid.—Nitrous acid was determined by the colorimetric method described by B. F. Rider.[4] In this method nitrous acid reacts with sulfanilic acid to form a diazonium salt which can be coupled with α-naphthylamine to form a red dye. In the present work, absorbance was measured on a Beckman model DU spectrophotometer at 540 mμ.

In most cases the aqueous phase could not be analyzed for nitrous acid directly since the samples that are required are too large at nitrous acid concentrations of 5×10^{-4} *M* and less. Instead, the concentration of nitrous acid in the organic phase was determined and the concentration of nitrous acid in the aqueous phase was calculated from previously prepared data on the distribution of nitrous acid. Errors were introduced by these steps which reduced the precision to about 20%.

Results and Discussion

Rate Studies.—Scouting work showed that Np(V) extracts very little from solutions of nitric acid into TBP. The exact values were difficult to establish because of the presence of small quantities of Np(VI). However, distribution coefficients[5] at least as low as 0.01 were obtained for the distribution of Np(V) between 1.09 *M* TBP in *n*-dodecane and solutions which contained up to 4 *M* nitric acid.

On the other hand Np(VI) was shown to extract quite well, with distribution coefficients up to about 20, in 4 *M* HNO_3. The distribution coefficients for Np(VI) are shown in Fig. 1 as a function of the concentration of nitric acid at 24.5, 35 and 50°. Cerium(IV) was used as a holding oxidant.

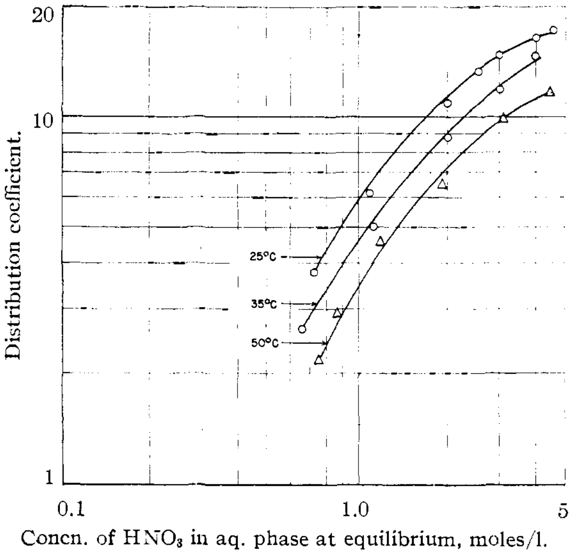

Fig. 1.—Distribution of neptunium(VI).

The difference in the extraction behavior of Np(V) and Np(VI) was used as the basis for analyzing for these two oxidation states of the element in all the subsequent work that is described in this paper.

Preliminary investigations showed that Np(V) was only very little oxidized if at all when no nitrous acid was present. In a typical experiment Np(V) in 3.60 *M* HNO_3 was stirred overnight at room temperature with 1.09 *M* TBP in *n*-dodecane. The distribution coefficient for Np decreased slightly to 0.04 from an initial value of 0.06.

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[4] B. F. Rider, Knolls Atomic Power Lab., KAPL-890, April 30, 1953, (Classified Report).

[5] Concentration in the organic phase divided by concentration in the aqueous phase.

However, when nitrous acid was added to the system, Np(V) was oxidized to Np(VI) at measurable rates. Qualitatively the rate of fractional oxidation was the same when 10^{-12} M Np-239 was substituted for 2×10^{-5} M Np-237. Further, the rate of oxidation was observed to increase greatly as the concentration of nitric acid was increased.

From these preliminary experiments it was evident that the oxidation reaction was first order in concentration of neptunium at least up to 2×10^{-5} M in neptunium, that nitrous acid was necessary as a catalyst or perhaps as the oxidant and that the rate expression must contain the concentration of nitric acid to some high power.

An equation is derived below to describe the oxidation of Np(V) to Np(VI) in the two-phase system: nitric acid–nitrous acid–water–Np(V)–Np(VI)–TBP in n-dodecane. The total concentration of neptunium, Np(V) plus Np(VI), the concentrations of all other components, the temperature and the ratio of phases are kept constant for a single experiment. The extraction of Np(V) is taken to be negligibly small and is set equal to zero. Any reactions which take place in the organic phase are assumed to be negligibly slow. The transfer of Np(VI) between phases is assumed to be rapid compared to the oxidation of neptunium. The organic phase then acts only as a source or a sink for neptunium.

For these conditions

$$\ln [z(1 + y) - y] = -k(1 + y) \times t + \ln [z_0(1 + y) - y]$$

where

$$z = \frac{E - F}{F(g - 1) + E}$$

$$y = \frac{E - F_e}{gF_e}$$

g = 1 + (E × the volume ratio, organic/aqueous)
E = distribution coefficient (o/a) for Np(VI)
F = distribution coefficient (o/a) for the mixed states of neptunium
The subscript 0 is for zero time
The subscript e is for equilibrium
t = time in minutes
k = reaction rate constant for the oxidation of Np(V)

A plot of $\ln [z(1 + y) - y]$ against time should give a straight line. The straight line should have a slope which is equal to $-(1 + y)k$.

The distribution coefficients for neptunium were measured as a function of time at 20° when the aqueous phase contained 2.94 M HNO_3, 5.2×10^{-4} M HNO_2 and initially 1×10^3 d./(min.)(ml.) (or 6×10^{-6} M) of Np-237. The organic and aqueous phases were kept in equal volume. The data are given in Table I and Fig. 2. As required by the mathematics a straight line was obtained to well within the experimental accuracy. The half time of oxidation was 24 minutes.

TABLE I

DATA FROM A RATE EXPERIMENT

Time, min.	Distribution coefficient for Np
0	0.01
5	.23
10	.27
20	.70
30	1.17
40	1.41
60	2.11
Equilibrium	3.00

This experimental technique and method of data analysis were then employed to examine the kinetics of oxidation over a range of conditions. The data in Table II show that the rate of oxidation of neptunium(V) is independent of the concentration of nitrous acid above 5×10^{-5} M. The data in Table III show that for the concentrations of Np-237 in the range used in this work the rate of the oxidation reaction does not become dependent on the concentration of nitrous acid until nitrous acid is lowered to below 6×10^{-5} molar.

TABLE II

HALF TIME OF OXIDATION AT DIFFERENT CONCENTRATIONS OF NITROUS ACID AT 20°

Concn. of HNO_3 in aq. phase, moles/l.	Approximate concn. of HNO_2 in aq. phase, mole/l.	Half time, min.
2.4	5×10^{-5}	45
2.4	2×10^{-4}	45
2.4	1×10^{-3}	51
2.9	5×10^{-5}	22
2.9	2×10^{-4}	21
2.9	1×10^{-3}	17
2.9	1×10^{-2}	16
4.0	5×10^{-5}	5.8
4.0	2×10^{-4}	5.7
4.0	1×10^{-3}	5.9
4.0	1×10^{-2}	5.7

TABLE III

EFFECT OF NITROUS ACID ON THE OXIDATION OF NEPTUNIUM(V) AT 24.5° AND 2.8 M NITRIC ACID

Concn. of HNO_2 in aq. phase, moles/l.	Distribution coefficient of Np after 6 min.[a]
6×10^{-5}	0.38
2.5×10^{-5}	.24
6×10^{-6}	.15
5×10^{-6}	.13
4×10^{-6}	.11
6×10^{-7}	.06
4×10^{-7}	.03
6×10^{-7}	.02

[a] Distribution coefficient at zero time was 0.02 for the stock solution of Np(V) used in the experiment.

The rate of the oxidation reaction depends on the fourth power of the nitric acid concentration. The half time for the oxidation reaction was determined as a function of the concentration of nitric acid at 20°. The logarithm of reaction half time is plotted as a function of the logarithm of the concentration of nitric acid in Fig. 3. The slope of the line is four, which indicates the fourth-power dependence.

It appears probable that the rate expression does contain hydrogen ion to a high power and that the fourth-power dependence is not due to the salting effect of nitric acid. The half time of the reaction at 20° for an aqueous solution which contained 2.5 M HNO_3 and 1.5 M $NaNO_3$ was 46 minutes. The half time at 20° in 2.4 M HNO_3 with no sodium nitrate was 47 minutes.

The activation energy of the oxidation reaction is 12 kcal. over the range 10 to 47° when the concentration of nitric acid is 2.9 M. Interpolation and

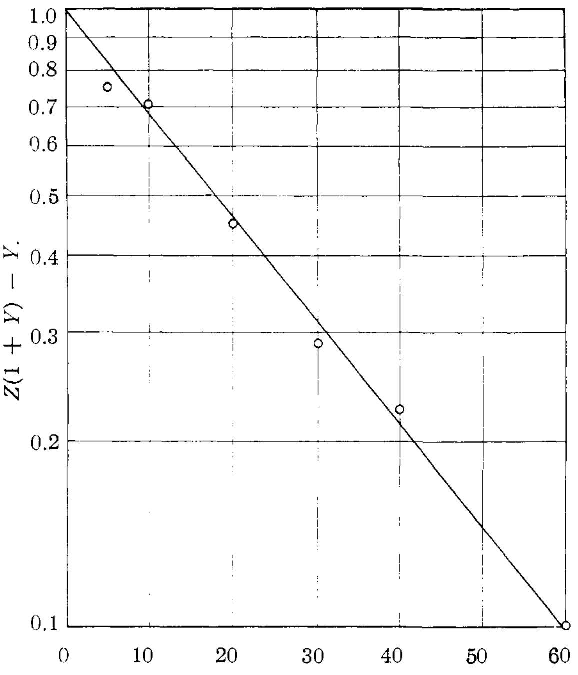

Fig. 2.—Treatment of data from a rate experiment.

extrapolation of the data in Fig. 1 were used to take into account the change in the distribution coefficients of Np(VI) with temperature. The rate constant in 2.9 M acid was determined as a function of temperature and was then plotted in Fig. 4.

The data from 27 determinations of the half time of oxidation for temperatures ranging from 10 to 48° and concentrations of nitric acid from 2.0 to 4.0 molar were treated by the method of least squares to obtain

$$\log t_{1/2} = -5.994 - 3.280 \log \mathrm{HNO_3} + 2.598 \times 10^3 \times \frac{1}{\text{temp., °K.}}$$

The average deviation of the experimental points from this formula was 14%.

The coefficient, −3.280, would indicate that the half time depends on the 3.3 power of the concentration of nitric acid rather than the 4th power as obtained in Fig. 3. The difference is probably not real, but is due to the statistical weight thrown on acidity between 2.8 and 3.0 M. A large number of the 27 determinations were in this range.

All of the above experiments were performed by starting with all or nearly all of the neptunium as Np(V). As a test of the validity of this procedure one experiment was performed by starting with the neptunium as neptunium(VI). For 2.80 M HNO_3 and 1 × 10^{-4} M HNO_2 at 24.5° the reaction half time was 15 minutes, which agrees roughly with the value of 25 minutes which was obtained by interpolation from data when all of the neptunium was Np(V) at zero time. Starting with all the neptunium as Np(VI) is very unfavorable in terms of propagation of error. If a high concentration of nitrous acid is used, the rate of reduction of Np(VI) is very fast and the change in the distribution coefficient of neptunium is too rapid to measure. If a low concentration of nitrous acid is used, the change in distribution coefficient occurs at a measurable rate, but the difference between the distribution coefficient at any time and at equilibrium is small. Since the data analysis depends on the small difference of a function of the distribution coefficient at time t and at equilibrium, experimental error is multiplied in the calculation of half time.

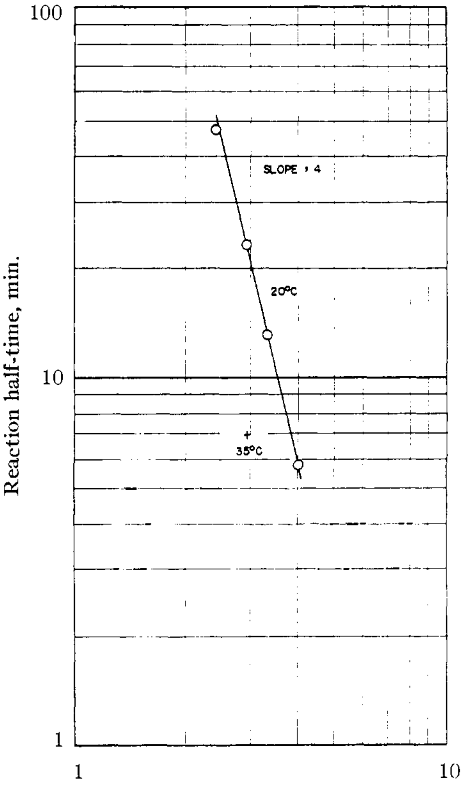

Fig. 3.—Reaction half-time for the oxidation of Np(V).

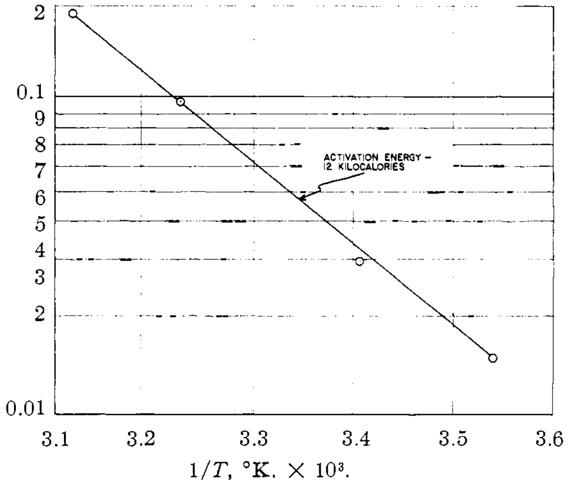

Fig. 4.—Effect of temperature on oxidation of Np(V) to Np(VI): system 2.9 M HNO_3 in H_2O, 30% TBP in dodecane.

An experiment also was performed to test the conclusion that the reactions of neptunium occur exclusively in the aqueous phase. Starting with Np(V) in 2.86 M HNO_3 and 8 × 10^{-4} M HNO_2 the aqueous phase was allowed to stand alone at 20°. Periodically, aliquots were withdrawn and rapidly mixed with 1.09 *M* TBP at 0° and the phases were separated. A half time of 35 minutes was obtained, which compares well with the value of 28 minutes interpolated from Fig. 3. This procedure is experimentally less favorable than the usual procedure because of the small changes in distribution coefficient of the neptunium. Since the organic phase is not available as a sink for Np(VI), the reverse reaction to reduce Np(VI) is important even at short time intervals, and the reaction cannot proceed as far in the oxidation of Np.

A mechanism for the oxidation of Np(V) can be developed which is consistent with the experiments described above.

$$NpO_2^+ + nH^+ \underset{\text{slow}}{\leftrightarrows} Np(V)^* \text{ (``activated state'')} \qquad (1)$$

$$Np(V)^* + HNO_2 \underset{\text{fast}}{\leftrightarrows} NpO_2^{++} + NO + n - 1\,H^+ + H_2O \qquad (2)$$

$$H_2O + 2NO + NO_3^- + H^+ \underset{\text{fast}}{\leftrightarrows} 3HNO_2 \qquad (3)$$

Reaction 1 is rate controlling except at very low concentrations of nitrous acid when reaction 2 becomes comparably slow. According to Abel,[6] reaction 3 is rapid. Reaction 1 implies that neptunium-to-oxygen bonds are broken, or modified, since it is difficult to imagine what other role the hydrogen ions could play in this reaction.

Equilibrium Studies.—Equilibrium values were obtained for the over-all reaction which is

$$NpO_2^+ + 3/2H^+ + {}^1/_2NO_3^- \leftrightarrows NpO_2^{++} + {}^1/_2HNO_2 + H_2O \qquad (4)$$

The equilibrium distribution coefficients which were obtained experimentally and the equilibrium constants which were calculated from the distribution coefficients and composition of the aqueous phase are given in Table IV. No attempt was made to compensate for activity coefficients or for nitrate complexing of neptunium.

TABLE IV

EQUILIBRIUM CONSTANTS FOR THE REACTION

$NpO_2^+\ 3/2H^+ + {}^1/_2NO^-_3 \leftrightarrows NpO_2^{++} + {}^1/_2HNO_2 + H_2O$

Concn. of HNO_3 in aq. phase, moles/l.	Concn. of HNO_2 in aq. phase, moles/l.	Equilibrium distribution coefficient for Np	Temp., °C.	Equilibrium constant
2.01	8.0×10^{-5}	1.67	24.5	3.6×10^{-4}
2.04	7.0×10^{-5}	2.55	24.5	5.6×10^{-4}
2.21	2.5×10^{-4}	2.00	24.5	5.9×10^{-4}
2.26	9.0×10^{-5}	2.44	24.5	4.3×10^{-4}
2.66	9.5×10^{-5}	4.09	24.5	5.4×10^{-4}
2.98	2.9×10^{-4}	3.03	24.5	4.6×10^{-4}
3.11	5.0×10^{-5}	6.6	24.5	5.1×10^{-4}
3.52	4.5×10^{-4}	5.1	24.5	7.1×10^{-4}
		Av.	24.5° =	5.2×10^{-4}
1.98	7.0×10^{-5}	2.27	35	7.4×10^{-4}
2.06	7.0×10^{-5}	2.19	35	6.1×10^{-4}
2.70	2.4×10^{-4}	2.37	35	5.5×10^{-4}
2.76	1.2×10^{-4}	3.04	35	5.0×10^{-4}
2.83	1.6×10^{-4}	3.31	35	6.0×10^{-4}
2.86	7.0×10^{-5}	5.4	35	8.2×10^{-4}
2.88	1.1×10^{-4}	4.35	35	7.0×10^{-4}
3.26	2.9×10^{-4}	4.85	35	9.3×10^{-4}
3.39	8.0×10^{-5}	6.4	35	6.9×10^{-4}
3.59	1.2×10^{-4}	5.2	35	4.9×10^{-4}
		Av.	35° =	6.6×10^{-4}
1.99	7.4×10^{-5}	0.97	50	3.5×10^{-4}
2.20	3.2×10^{-5}	2.89	50	7.0×10^{-4}
2.39	6.7×10^{-5}	1.89	50	4.3×10^{-4}
2.39	2.0×10^{-4}	1.32	50	4.7×10^{-4}
2.88	1.7×10^{-4}	3.30	50	8.4×10^{-4}
2.90	1.7×10^{-4}	3.37	50	8.4×10^{-4}
3.00	3.4×10^{-5}	4.62	50	5.7×10^{-4}
3.20	2.0×10^{-5}	6.1	50	6.1×10^{-4}
		Av.	50° =	6.0×10^{-4}

The average equilibrium constant at 24.5° agrees well with the value which can be calculated from the data in the literature.[2] The average at 24.5° is 5.2×10^{-4}; the literature value is 4.0×10^{-4} at 25°. Considering the neglect of activity coefficients the agreement is better than might be expected.

AIKEN, S. C.

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(6) D. M. Yost and H. Russell, Jr., "Systematic Inorganic Chemistry of the Fifth and Sixth Group Nonmetallic Elements," Prentice-Hall, Inc., New York, N. Y., 1944.