

interpretation of the magnetic properties of manganese, technetium and rhenium. According to this theory, d-orbitals may be involved in bonding in the metallic state, and usually one or more orbitals, termed "metallic orbitals," are available for the unsynchronized resonance of the bonds. Manganese may be assumed on this view to possess valences of six and four. The electronic structure (A) of the first is presumed to consist of six electrons forming covalent bonds while one unpaired electron is placed in an atomic orbital. The other structure (B) then consists of four bonding electrons with three unpaired electrons in atomic orbitals. Both structures have two "metallic" orbitals.

Structure	d	s	p	Valence	Un-paired electrons
A	↑ . . . .	.	. o o	6	1
B	↑ ↑ ↑ . .	.	. o o	4	3
C	. . . . .	.	. o o	7	0

The proper "valence" of technetium and rhenium metals may be derived from their structures and interatomic spacings. From a study of the variation of atomic radii with position in the Periodic Table, Pauling has derived a simple empirical relation between the radius for a given coordination number and the average valence. Using this relation, a valence of six is predicted for Tc and Re. The assignment of a higher valence to technetium and rhenium than to manganese seems to be consistent with the magnetic observations, for a higher valence implies fewer unpaired electrons, and hence a lower susceptibility (*cf.* Table VI). On the basis of the magnetic susceptibilities rhenium must have the highest valence. Further, from the suscepti-

bilities it would appear that electron structure A is more important for Tc than for Mn. Another structure, C, may also contribute to a small extent to the resonating structures. Although C may be more important for rhenium than for either manganese or technetium, it seems likely that A is the predominant structure for all three metals.

TABLE VI  
MAGNETIC SUSCEPTIBILITIES OF THE ELEMENTS

Element	T, °K.	Gram susceptibility $\times 10^6$	Atomic susceptibility $\chi_A \times 10^6$
Mn	298	. .	527 <sup>a</sup>
Tc	402	2.5	250
	298	2.7	270
	78	2.9	290
Re	402	0.37	69
	298	.37	69
	78	.35	66
Independent of T			68.2 <sup>b</sup>

<sup>a</sup> M. A. Wheeler, *Phys. Rev.*, **41**, 331 (1932). <sup>b</sup> N. Perakis and L. Capatos, *J. phys. radium*, **6**, 462 (1935).

In some cases, as Pauling has pointed out, the valences assumed for the metallic state are the same as those for the compounds of the element. This similarity may be seen to exist in the cases of Mn, Tc and Re. Lower valences such as four and two are more stable in manganese compounds, while the valence of seven seems to be more stable in technetium and rhenium compounds. The melting points of the metals increase from manganese to rhenium. This indicates stronger binding which in terms of Pauling's theory, would mean a higher valence.

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## Isotopic Exchange Reactions of Neptunium Ions in Solution. I. The Np(V)-Np(VI) Exchange

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The isotopic exchange reaction between  $\text{NpO}_2^+$  and  $\text{NpO}_2^{++}$  in 1 M  $\text{HClO}_4$  at 0 and 10° has been measured. At 0°  $k = 29 \text{ mole}^{-1} \text{ liter sec.}^{-1}$ . The energy of activation,  $E_{a,p}$ , has been found to be 8.3 kcal. and the entropy of activation,  $\Delta S^\ddagger$ , to be  $-24 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ . This result is discussed in terms of an electron transfer mechanism for a homogeneous exchange reaction.

The isotopic exchange reactions between the various oxidation states that neptunium exhibits in perchloric acid solutions are of considerable interest. It is feasible to study the exchange between the two oxygenated species,  $\text{NpO}_2^+$  and  $\text{NpO}_2^{++}$ , between an oxygenated ion,  $\text{NpO}_2^+$ , and a tetrapositive ion and between a tri- and a tetrapositive ion in such solutions. The analytical problem is simplified because of the two available isotopes of neptunium;  $\text{Np}^{237}$  is an  $\alpha$ -emitter with a  $2.20 \times 10^6$  year half-life while  $\text{Np}^{239}$  is a  $\beta$ -emitter with a 2.33 day half-life. Therefore the measurements of alpha to beta ratios furnish sufficient analytical data for determining the fraction exchanged.

This communication represents the first of a series of such studies and concerns itself with the exchange between Np(V) and Np(VI) in perchloric acid.

### Experimental

The  $\text{Np}^{239}$  was prepared by bombarding uranium in the Argonne National Laboratory pile and was purified by standard radiochemical methods.<sup>1</sup> The purity of the tracer was checked by following the decay of a suitably mounted aliquot. The tracer was found to be radiochemically pure. The  $\text{Np}^{237}$  solutions were spectroscopically pure.

The tracer was mixed with a solution of  $\text{Np}^{237}$ , and a Np(V) solution in 1 M perchloric acid was prepared by a pro-

(1) P. Fields, Vol. 14B Div. IV NNES, "The Transuranium Elements," McGraw-Hill Book Co., Inc., New York, N. Y., 1949, p. 1128.

cedure similar to that previously described.<sup>2</sup> A Np(VI) solution, containing only Np<sup>237</sup>, was prepared by electrolytic oxidation.<sup>3</sup>

A solvent extraction technique was used to separate the ionic species. Blanks were run against pure neptunium(V) solutions to see if oxidation occurred in the separation process. In all cases this was found to be negligible. The solvent for the extraction process was commercially pure tributyl phosphate which was scrubbed with sodium hydroxide and then washed with water.

The perchloric acid solution was prepared from G. Frederick Smith double vacuum-distilled 72% perchloric acid. The aluminum nitrate and ammonium nitrate solutions were made up from reagent grade salts.

A standard Geiger tube with sufficient absorber present to screen out the Np<sup>237</sup> alphas was used for the beta counting. A methane proportional alpha counter was used to determine the Np<sup>237</sup> concentration. All counting was done to a statistical accuracy of  $\pm 1\%$  (standard deviation).

The experimental separation procedure was as follows: The Np(VI) and Np(V) solutions were added to the Teflon reaction vessel and after a definite time interval, two ml. of tributyl phosphate was added directly to the neptunium solution in the reaction vessel and contacted for 1 minute. The two phases were then separated by centrifugation and an aliquot of the tributyl phosphate was plated and counted.

### Results

At neptunium concentrations of  $2 \times 10^{-4} M$  or less, the exchange is slow enough at 0° to be readily measurable. Figure 1 shows some representative experimental curves. The kinetics of the exchange was studied as a function of metal ion concentration, hydrogen ion concentration and temperature. The results of these measurements are given in Table I. Each value of  $t_{1/2}$  and  $k$  represents a mean value computed from the five to seven separate experiments involved in each run. To obtain these values correction was made by graphical methods for the zero time exchange.

TABLE I

Np(V)-Np(VI) EXCHANGE AS A FUNCTION OF METAL ION CONCENTRATION, HYDROGEN ION CONCENTRATION AND TEMPERATURE

[Np(V)] $\times 10^4$	[Np(VI)] $\times 10^4$	[H <sup>+</sup> ]	Temp., °C.	$t_{1/2}$ , sec.	$k$ , l. mole <sup>-1</sup> sec. <sup>-1</sup>
10.40	9.27	0.99	0.0	122	28.9
5.20	9.27	.99	.0	155	30.9
5.20	9.27	.99	.0	155	30.9
2.60	9.04	.99	.0	193	30.8
10.40	3.62	.99	.0	180	27.5
10.40	1.81	.99	.0	245	23.2
					29.8 <sup>a</sup>
10.40	3.62	.32 <sup>b</sup>	.0	152	32.5
5.20	1.81	.99	9.9	192	51.5
10.40	3.62	.99	9.9	97	51.0
					51.2

<sup>a</sup> Run 6 was omitted for this average. <sup>b</sup> NaClO<sub>4</sub> was added to keep ionic strength at 1 M.

Table I shows that the rate has a first-order dependence on the Np(V) concentration, a first-order dependence on the Np(VI) concentration and a zero-order dependence on the hydrogen ion concentration. From the temperature dependence, one calculates the heat of activation to be 8.3 kcal. This value can be used to obtain the value for the

entropy of activation by means of the usual rate equation

$$k = \frac{eKT}{\eta} e^{-E^\ddagger/RT} e^{\Delta S^\ddagger/R} \quad (1)$$

at 0°,  $\Delta S^\ddagger = -24$  e.u.

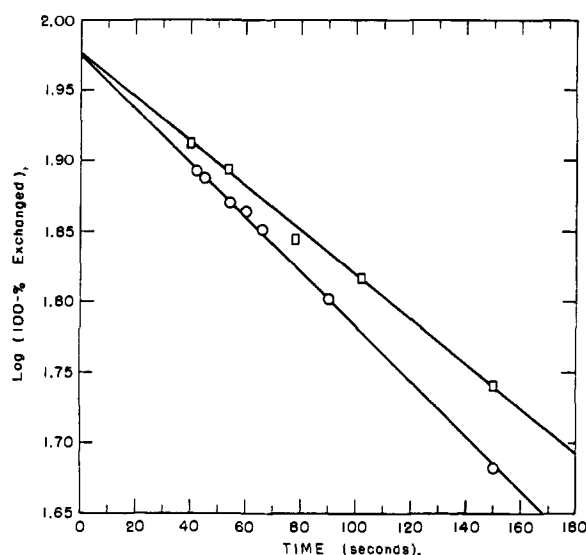


Fig. 1.—Typical rate data for Np(V)-Np(VI) exchange in 1 M HClO<sub>4</sub> at 0°; [H<sup>+</sup>] = 0.99 M; □,  $9.04 \times 10^{-5} M$  Np(VI),  $2.60 \times 10^{-5} M$  Np(V); ○,  $9.27 \times 10^{-5} M$  Np(VI),  $5.20 \times 10^{-5} M$  Np(V).

### Discussion

In discussing the exchange reaction between Np(V) and Np(VI) in terms of a homogeneous electron transfer mechanism, several points are of interest. First, a variety of spectral evidence indicates that Np(V) and Np(VI) exist as doubly oxygenated ions in perchloric acid solutions.<sup>2,4</sup> The infrared spectra indicate that both ions are of the linear O-Np-O type with the respective interatomic distances (M-O) reasonably close ( $\sim 0.06$  Å). In this case one would expect that the hydration spheres are also very nearly identical. Calculation indicates that within the amplitude of the zero point energy vibration, the structures of the two ions will match. By application of the Franck-Condon principle,<sup>5</sup> this structural similarity is concomitant with a high probability for the electron transfer process.

The comparatively small difference between the heat and entropy of activation in the present case and that for the Fe(II)-Fe(III)<sup>6</sup> exchange (Table II) is surprising in view of this expected diminution in the barrier for exchange. An explanation cannot be found in the repulsion energy since the lower net charge in the case of the neptunium system should further increase the probability of exchange.

The possible effect of the electronic configuration may be considered as follows: Assume that the bonding between the neptunium and oxygen atoms, as well as the presence of the field of the H<sub>2</sub>O dipoles does not perturb the energetically close lying 5 f

(2) R. Sjolom and J. C. Hindman, *THIS JOURNAL*, **73**, 1744 (1951).

(3) Donald Cohen and J. C. Hindman, *ibid.*, **74**, 4679 (1952).

(4) L. H. Jones and R. A. Penneman, *J. Chem. Phys.*, **21**, 524 (1953).

(5) W. F. Libby, *J. Phys. Chem.*, **56**, 863 (1952).

(6) J. Silverman and R. W. Dodson, *ibid.*, **56**, 846 (1952).

TABLE II  
ENERGIES AND ENTROPIES OF ACTIVATION FOR THE EXCHANGE REACTIONS OF  $\text{NpO}_2^+$  AND  $\text{NpO}_2^{++}$ , AND OF FERROUS ION WITH VARIOUS FERRIC SPECIES

	$E_{\text{act.}}$ kcal./mole	$\Delta S^\ddagger$ cal./deg./mole
$\text{NpO}_2^+ - \text{NpO}_2^{++}$	8.3	-24
$\text{Fe}^{++} - \text{Fe}^{+++}$	9.9	-25
$\text{Fe}^{++} - \text{Fe}(\text{OH})^{++}$	7.4	-18
$\text{Fe}^{++} - \text{FeCl}^{++}$	8.8	-24

and 6 d levels. Then the remaining electrons at the highest energy level at  $5f^1$  and  $5f^2$  for  $\text{NpO}_2^{+2}$  and  $\text{NpO}_2^+$ , respectively. Calculations based on the Fermi-Thomas model<sup>7</sup> indicate that the  $5f$  electron will have a second maximum in its radial distribution function at a distance of  $\sim 5 \text{ \AA}$ . from the nucleus. Since the effective potential energy of the second minimum is small there is a high probability for barrier penetration. Therefore, even if the somewhat naive assumptions made previously do hold, qualitatively there should be no decrease in the degree of probability for the exchange.

If the bonding and/or environment interaction does lead to promotion of the  $5f$  electrons to  $6d$

(7) M. Mayer, *Phys. Rev.*, **60**, 184 (1941).

electrons, then the argument becomes more straightforward due to the greater extension of the  $6d$  orbitals.

A satisfying explanation for the observed results is difficult to propose. If a direct electron transfer mechanism is postulated, it would appear that the probability for the penetration of the barrier is not primarily determined by the symmetry of the species (Franck-Condon principle). Furthermore, the small difference in the observed free energy of activation for the neptunium and iron cases is difficult to reconcile with the relatively large difference in free energy of rearrangement of the hydration spheres expected in the two cases. An explanation of the observed results can be made in terms of electron transfer if it is assumed that the determining factor is the low probability for the transfer of an electron through the intervening water molecules. Alternatively, an atom transfer mechanism could be proposed.<sup>8,9</sup> Decision as to the probable mechanism will have to await further investigation.

(8) H. Taube, H. Myers and R. L. Rich, *THIS JOURNAL*, **75**, 4119 (1953).

(9) J. Hudis and A. C. Wahl, *ibid.*, **75**, 4153 (1953).

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## The Solubility of Uranium(VI) Orthophosphates in Phosphoric Acid Solutions

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The solubility behavior of uranium(VI) orthophosphates has been determined in aqueous solutions containing 0.001 to 15  $M$  total phosphate. Identification of the equilibrium solid phases has been made microscopically, chemically and by X-ray diffraction analysis.

### I. Introduction

The solubility data on uranium(VI) phosphates in pure phosphoric acid reported previous to the present work cover a limited range of molarities and in some cases the equilibrium solid phase is in question.

Lord, Andrews and Gates<sup>1</sup> studied the solubility of  $\text{UO}_2\text{HPO}_4 \cdot x\text{H}_2\text{O}$  as a function of phosphate concentration at  $p\text{H}$  1 and 2. The  $p\text{H}$  of their solutions was adjusted with ammonia and nitric acid which suggests that their solubility data were probably for uranyl ammonium phosphate.<sup>2</sup> Their measurements were made without control of temperature, and data showing the attainment of equilibrium conditions were not presented.

Leader<sup>3</sup> reported the solubility behavior of  $\text{UO}_2\text{HPO}_4 \cdot 4\text{H}_2\text{O}$  in  $\text{HNO}_3$  and  $\text{H}_3\text{PO}_4$  over a range of 0.3 to 3.0  $M$   $\text{H}_3\text{PO}_4$ . Phosphate determinations were made by precipitation of bismuth phosphate and were reported to be 5-10% high.

For the current solubility measurements, it was

(1) E. J. Lord, L. J. Andrews and J. W. Gates, Jr., Report CD-4035, June 16, 1945.

(2) W. B. Schaap and J. W. Gates, Jr., Report C-0.375.3, March 12, 1946.

(3) G. R. Leader, Report CN-2195, 1944.

necessary to prepare several pure uranium(VI) phosphate salts in order to establish the range of stability of each solid phase. Three uranyl orthophosphates have been reported previously; they are  $\text{UO}_2\text{HPO}_4 \cdot 4\text{H}_2\text{O}$ ,  $(\text{UO}_2)_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$  and  $\text{UO}_2(\text{H}_2\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ . Zachariasen<sup>4</sup> examined  $\text{UO}_2\text{HPO}_4 \cdot 4\text{H}_2\text{O}$  by X-ray methods and showed this compound to be tetragonal with a calculated density of 3.41. Harris and Scott<sup>5</sup> discussed the optical properties of  $\text{UO}_2\text{HPO}_4 \cdot 4\text{H}_2\text{O}$  and  $(\text{UO}_2)_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ . They reported that both these compounds are tetragonal, and  $\text{UO}_2\text{HPO}_4 \cdot 4\text{H}_2\text{O}$  was said to crystallize as tabular plates, usually four sided but occasionally as truncated squares. The  $(\text{UO}_2)_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$  was said to crystallize in needle-like crystals. They gave the density values of  $\text{UO}_2\text{HPO}_4 \cdot 4\text{H}_2\text{O}$  and  $(\text{UO}_2)_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$  as 3.399 and 3.213, respectively. Werther<sup>6</sup> reported the preparation of crystals of  $\text{UO}_2(\text{H}_2\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$  by heating small amounts of  $\text{H}_3\text{PO}_4$  with  $\text{UO}_3$  to boiling and allowing to stand over  $\text{H}_2\text{SO}_4$ . The crystal structure of this latter compound has not been previously determined.

(4) W. H. Zachariasen, Report CC-2768, March 12, 1945.

(5) W. W. Harris and Roberta H. Scott, Report AECD-2746, September 30, 1949.

(6) G. Werther, *J. prakt. Chem.*, [1] **43**, 321 (1848).