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The Exchange of Plutonyl and Solvent Water Oxygen[1]

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Rates of exchange of plutonyl oxygen and H_2O^{18} have been measured in perchloric acid solutions at 23 and 83°. It has been found that the intrinsic exchange reaction is slow, $t_{1/2} > 10^4$ hr. Since the exchange reaction is accelerated in the presence of lower oxidation states of plutonium, chlorine was used in exchange runs to maintain the plutonium in the plutonyl condition. The longer half-times associated with lower plutonyl ion concentrations in the exchange solutions are interpreted in terms of a radiation-induced exchange process.

Introduction

The isotopic exchange reaction between oxygen atoms of UO_2^{++} and water has been shown by Crandall[2] to be very slow. Gordon and Taube[3] have measured an exchange half-time of 3.6×10^4 hr. (25°, 0.939 M $HClO_4$, $\mu = 3.79$) for this system. Further information about the labilities of the oxygenated cations of the series, UO_2^{++}, NpO_2^{++}, PuO_2^{++}, and AmO_2^{++}, would be desirable for the purpose of comparison with other data concerning metal–oxygen bonding in this series. One unusual feature of transuranyl ion bonding is that the decrease in the force constants, $k_{U-O} > k_{Np-O} > k_{Pu-O} > k_{Am-O}$, is accompanied by a decrease in the corresponding metal–oxygen bond distances.[4]

In the present study, the oxygen isotopic exchange rate for the PuO_2^{++}–water system has been examined. This intrinsic exchange reaction was studied in the presence of chlorine to maintain the plutonium in the plutonyl oxidation state. It appeared that in addition to the use of chlorine, it was necessary to make exchange studies at as low concentrations as possible to minimize the radiation-induced exchanges. Sampling of the plutonyl oxygen was accomplished through precipitation of the plutonyl ferricyanide from an aqueous acetone medium, followed by conversion to CO_2 and measurement of the isotope mass ratio $46/(44 + 45)$ with a mass spectrometer.

(1) This work was done under the auspices of the U. S. Atomic Energy Commission.
(2) H. W. Crandall, *J. Chem. Phys.*, **17**, 602 (1949).
(3) G. Gordon and H. Taube, *J. Inorg. Nucl. Chem.*, **16**, 272 (1961); **19**, 189 (1961).
(4) L. H. Jones, *J. Chem. Phys.*, **23**, 2105 (1955).

Experimental

Plutonium(VI) perchlorate solutions were prepared from weighed quantities of the polished, high-purity metal together with the requisite weighed quantity of standardized Baker 70% reagent grade perchloric acid. The diluted perchloric acid stock of Pu(III) was converted to Pu(VI) by chlorination, by electrolysis, or by prolonged ozonization. Sodium perchlorate was prepared from C.P. sodium carbonate and perchloric acid followed by a double recrystallization of the salt from water. This salt was dried at 120° and was used in the preparation of solutions of a desired ionic strength.

Water used in the preparation of solutions was redistilled from an alkaline permanganate medium in an all-Pyrex glass apparatus. The water enriched in the oxygen-18 isotope to the extent of 1.6% was obtained from Yeda Research and Development Co., Ltd., Rehovoth, Israel. To assure removal of possible traces of oxidizable impurities, this enriched water was boiled with alkaline permanganate and distilled slowly on a vacuum line with care being taken to avoid contamination from stopcock grease. Conductivity measurements made with a Barnstead purity meter, Model PM-2, indicated that the water was of good quality after distillation.

Both labeled and unlabeled oxygen in the plutonyl ion have been used in exchange experiments. As a preliminary to the introduction of oxygen-18 into the plutonyl ion, the PuO_2^{++} was reduced with hydrogen gas to Pu^{+3} in the presence of enriched water of known composition. A foil of platinized platinum was placed in the solution to catalyze this reduction. The subsequent reoxidation of the plutonium to form labeled plutonyl ion was accomplished either electrolytically or with chlorine in a sealed tube. Alternatively, it has been found that a plutonyl solution can be equilibrated with solvent water by heating for several days in a sealed tube at 83° in the absence of chlorine. The formation of the lower oxidation states of plutonium as a consequence of α-reduction processes appears to bring about the rapid exchange. The small amount of reduced species formed then was removed by a short period of ozonization.

The procedure used for the sampling of the plutonyl oxygens

was dependent upon the concentration of the plutonium in the exchange solution. For solutions in the concentration range of 0.15 M, 1 ml. of plutonyl solution was added to 1 ml. of distilled water in which was dissolved the stoichiometric quantity of C.P. sodium ferricyanide dihydrate as obtained from the City Chemical Co. Immediately after mixing, 50 ml. of Baker reagent grade acetone was added with vigorous stirring with a magnetic stirrer. A voluminous rust-brown precipitate of plutonyl ferricyanide formed and rapidly settled to the bottom of the precipitation beaker as stirring ceased. A major portion of the clear supernatant was removed by suction and the precipitate was transferred to a filtration tube fitted with 12/30 standard tapered joints at each end and with a medium porosity sintered glass disk in the middle. The precipitate was dried by passing air over it for 1 min. and then placed on the vacuum line. After most of the acetone had been removed, the precipitate was tapped into a combustion bomb (1 cm. o.d. × 36 cm. long fitted with a break seal in the middle of the tube and 12/30 standard tapered joints at each end). Vacuum dried Baker analyzed reagent grade mercuric chloride (100 mg.) was added to the bomb, and the tube was necked down and sealed after a pressure of 3.5×10^{-5} mm. had been attained. The Pyrex tube was heated in an electric tube furnace for 2 hr. at 400°. Gases non-condensable in liquid nitrogen then were removed on the vacuum line; the condensable gas was transferred to a second U-shaped bomb with several grams of a saturated zinc amalgam. The bomb then was sealed and heated to 200° for 2 hr.[3,5] Again, the gas non-condensable in liquid nitrogen was removed on the vacuum line and the CO_2 was fractionated into a mass spectrometer bulb with a Dry Ice–acetone bath.

Some measurements were obtained from exchange solutions containing plutonium(VI) at a concentration of approximately $1.5 \times 10^{-3} M$. Because of the appreciable solubility of plutonyl ferricyanide in water, it was necessary to concentrate the plutonium solution before precipitation. This was accomplished with the cation exchange resin, Bio-Rad 50W-X4, 200–400 mesh, which was obtained from Bio-Rad Laboratories. Dried resin (600 mg.) was placed in a column of 8 mm. i.d. over a medium porosity fritted glass disk. It was found that essentially quantitative removal of the plutonyl ion was possible from a 0.1 M perchloric acid solution. A sample of 100 ml. of the dilute plutonium stock, 1 M in perchloric acid, was diluted to 1 l. with water in a volumetric flask, then passed through the column of cation exchange resin. The elution was carried out with 2 ml. of 1 M perchloric acid which contained an amount of sodium ferricyanide equivalent to the plutonium originally placed on the resin. Fifty ml. of acetone was added to the eluent and the precipitate of plutonyl ferricyanide was treated as described above. The elution procedure and precipitation were repeated a second time to provide a sample of sufficient size for analysis in the mass spectrometer. Although this resin has been observed[3] to promote essentially quantitative reduction of NpO_2^{++}, there was no evidence to indicate that appreciable amounts of reduction of plutonyl ion occurred in our separations.

Anderson[7] has recorded the precipitation of a hydrated plutonyl ferricyanide from aqueous solution. The composition of the precipitate was not well characterized. In the present work, the nature of the plutonyl ferricyanide obtained by precipitation from aqueous acetone solution followed by drying under high vacuum at room temperature has been determined to be in accord with the formula $(PuO_2)_3[Fe(CN)_6]_2 \cdot 2H_2O \cdot 3(CH_3)_2CO$ both by direct analysis and by isotopic dilution experiments. (*Anal.* Calcd.: Pu, 49.5; Fe, 7.7; C, 17.4; H, 1.5; N, 11.6; O, 12.2. Found: Pu, 48.4; Fe, 8.0; C, 17.1; H, 1.4; N, 12.1 from Fe analysis assuming 6N/Fe; O, 13.0 by difference.) The solu-

bility of the plutonyl ferricyanide is reduced considerably upon the addition of acetone to the aqueous solution. From count rate measurements, it has been shown that the solubility approximates 75 mg./l. in the aqueous acetone solution used in the analysis procedures.

In the majority of the instances in which plutonyl perchlorate solutions were prepared, the final acidity in the 0.5 to 1.0 M range could be computed from the initial weights of metal and acid which were used. However, at lower acidities with the relatively large amount of plutonium metal to be dissolved, *ca.* 0.3 g. in 10 ml., a sufficient amount of insoluble residue formed to introduce an appreciable uncertainty in the computed hydrogen ion concentration. Since it was found that the potentiometric titration procedure developed by Ahrland[8] for the determination of acidity in the presence of uranyl ion also was applicable in the presence of plutonyl ion, this method was used to determine the acidity in experiments in which more than a trace of residue was formed on dissolution of the plutonium metal.

The isotopic compositions of CO_2 samples from a given series of exchange measurements were determined on the same day together with a standard sample of normal CO_2 which served as a reference. It was felt that this procedure would eliminate possible small instrumental variations. A Consolidated-Nier mass spectrometer, Model No. 21–201, was used and the isotope ratios were obtained directly from the dials provided with the instrument for this purpose. The isotope ratio readings were used in the calculation of the fractional exchange values. These values were computed relative to measurements obtained from "zero time" and "complete exchange" samples which had been subjected to the separation procedure, in order to eliminate any possible errors introduced by isotope fractionation, isotopic dilution, or separation induced exchange which might have occurred during the manipulations. The slopes of the McKay plots were determined by least squares methods and the reported uncertainties of these slopes are equal to the standard deviations.

In a series of experiments in which an enhanced α-radiation flux was desired, the plutonyl solutions were prepared from 117 mg. of plutonium enriched in the Pu^{238} isotope. This material was obtained in the form of a plutonium(IV) nitrate solution in nitric acid. The acid solution was saturated with HCl gas and passed through a Dowex-1 × 10 resin column of 100 to 200 mesh. The plutonium was eluted from the resin with 0.1 M HCl, and these eluents were concentrated by vacuum distillation. A few ml. of 70% perchloric acid then was added and the solution was heated to fuming, nearly to dryness. The brownish solid was dissolved in 1 ml. of normal water and ozonized overnight to prepare the plutonyl ion for use in exchange experiments.

Results

In a series of experiments at 23° designed to measure the rate of exchange of oxygen between plutonyl ion and solvent water, a 0.14 M solution of unlabeled plutonyl ion in 0.34 M perchloric acid was prepared in 1.6% labeled water. Lower oxidation states of plutonium are gradually formed in the perchloric acid solution as a consequence of the α-particle radiation.[9] Although the solution was ozonized to remove these lower oxidation states prior to analysis and a suitable correction was applied to take into account the dilution with ozone-derived oxygen, a non-linear McKay[10] plot of the type shown in Fig. 1a was obtained.

It appeared that in order to measure the intrinsic exchange reaction, an oxidant would have to be present in the plutonium solution to inhibit the formation of

(5) M. Anbar and S. Guttmann, *Intern. J. Appl. Radiation Isotopes*, **5**, 233 (1959).

(6) J. C. Sullivan, D. Cohen, and J. C. Hindman, *J. Am. Chem. Soc.*, **77**, 6203 (1955).

(7) H. H. Anderson in G. Seaborg, J. Katz, and W. Manning (Ed.), "The Transuranium Elements," National Nuclear Energy Series, IV-14B, McGraw-Hill Book Co., Inc., New York, N. Y., 1949, p. 801.

(8) S. Ahrland, *Acta Chem. Scand.*, **14**, 2035 (1960).

(9) See, *e.g.*, S. W. Rabideau, *J. Am. Chem. Soc.*, **75**, 798 (1953).

(10) H. A. C. McKay, *Nature*, **142**, 997 (1938).

the lower oxidation states. Linear McKay plots of the type shown in Fig. 1b were obtained in the presence of chlorine. Spectrophotometric examinations of solutions stored under these conditions did not reveal the presence of plutonium species other than the plutonyl ion.
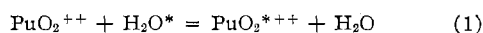
The results of a typical exchange experiment are given in Table I. Each of eight Pyrex glass ampoules of 7 ml. volume was sealed with 1 ml. of 0.1565 M unlabeled plutonyl ion in oxygen-18 enriched water containing molar perchloric acid and 0.38 mmole of chlorine. The solutions were degassed on a vacuum line before adding the chlorine and sealing. Each ampoule was opened after a timed interval, flushed with nitrogen to remove dissolved chlorine, and the enrichment of the plutonyl fraction was determined. A complete exchange sample was obtained by allowing the contents of one ampoule to equilibrate in the absence of scavenger, after which the ampoule was resealed with chlorine, heated to 83° in order to ensure complete oxidation of the sample, and treated in the usual manner.

Fig. 1.—McKay plot for plutonyl–water exchange: (a) unscavenged plutonyl solution in 0.34 M HClO$_4$ at 23°, instantaneous half-time of 123 hr. at 240 hr.; (b) chlorine-scavenged plutonyl solution in 1.0 M HClO$_4$ at 83°, half-time of 4.39 × 10^3 hr.

TABLE I

RATE OF EXCHANGE OF PLUTONYL AND SOLVENT WATER OXYGENS AT 23° IN MOLAR PERCHLORIC ACID, μ = 1.45, [PuO$_2^{++}$] = 0.15 M

Exchange time, hr.	(46/(44 + 45)) mass ratio	% exchange
0	0.00441	0
240	.00451	1.1
575	.00469	3.0
935	.00476	3.7
1416	.00483	4.5
2011	.00495	5.7
3116	.00483	4.5
∞	.01384	100

The slow formation of a small amount of white, insoluble flocculent material shown to contain plutonium, silicon, and boron as major constituents by spectrographic analysis, possibly a plutonium borosilicate formed as a result of attack of the Pyrex glass, may explain the introduction of a small amount of normal oxygen in the sample at the 3116 hr. point. Samples were centrifuged and an effort was made to remove this material, but the solubility is unknown, and some small amount of the product may have been included in the analyzed sample. A least squares analysis of the data in Table I resulted in a value of −1.52 × 10⁻⁵ hr.⁻¹ for the slope of the plot of ln (1 − F) vs. time with a standard deviation of 0.51 × 10⁻⁵ hr.⁻¹. This slope corresponds to a half-time of 4.55 × 10⁴ hr. The slope of the McKay plot should be equal in magnitude to the specific rate constant for the intrinsic exchange reaction

$$PuO_2^{++} + H_2O^* = PuO_2^{*++} + H_2O \qquad (1)$$

$$R_{xc} = k[PuO_2^{++}] = -[PuO_2^{++}]\,d[\ln(1 - F)]/dt \qquad (2)$$

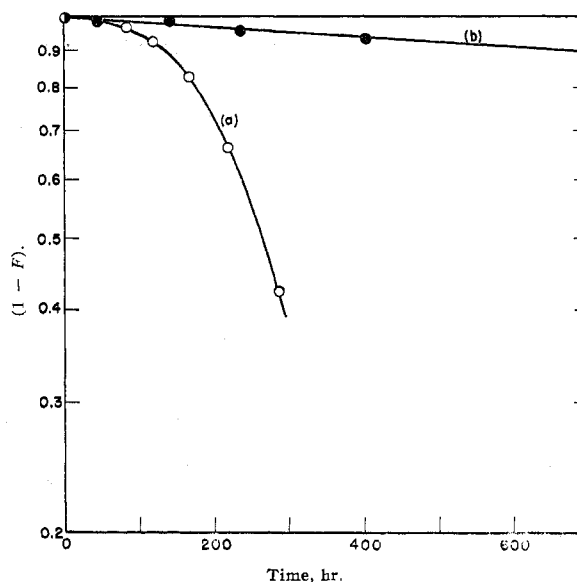provided that reaction 1 were solely responsible for the observed exchange. However, it appears that a contribution to the observed exchange is made as a consequence of the α-induced radiation effects as shown later in this paper.

Effect of Acidity, 0.15 M PuO$_2^{++}$.—The observed rate of exchange of plutonyl and solvent water oxygen is increased in solutions of greater acidity as is shown by the results in Table II. This result is in contrast to the reported inverse first power acidity dependence for the uranyl system[3]; however, because of the α-induced radiation effects present in addition to the intrinsic exchange reaction in these 0.15 M plutonyl solutions, the comparison of hydrogen ion concentration order should not be drawn between these systems on the basis of these experiments.

Influence of Chlorine Pressure.—Incorporated with the samples of plutonyl ion in 0.21 M perchloric acid as shown in Table II were two measurements which were included to permit observation of the possible effect of an increased chlorine pressure upon the exchange rate. The same quantity of chlorine used with the

TABLE II

INFLUENCE OF ACIDITY ON EXCHANGE RATE AT 83° IN HClO$_4$ SOLUTION, [PuO$_2^{++}$] = 0.15 M; μ = 1.45

[H⁺] = 0.21 M			[H⁺] = 1.0 M		
Exchange time, hr.	(46/ (44 + 45))	% exchange	Exchange time, hr.	(46/ (44 + 45))	% exchange
0	0.00516	0.0	0	0.00448	0.0
120	.00515	−.1	138	.00461	1.1
696	.00521	.4	234	.00498	4.5
1388	.00577	4.9	402	.00518	6.4
1632ᵃ	.00598	6.3	695	.00560	10.1
2495	.00665	11.9	∞	.01546	100
2496ᵃ	.00703	14.9			
∞	.01771	100			

Slope = −5.98 ± 0.81 × 10⁻⁵ hr.⁻¹   Slope = −1.58 ± 0.16 × 10⁻⁴ hr.⁻¹

($t_{1/2}$ = 1.16 × 10⁴ hr.)   ($t_{1/2}$ = 4.39 × 10³ hr.)

ᵃ High pressure Cl$_2$ samples.

TABLE III

EXCHANGE OF 1.33 × 10⁻³ *M* PLUTONYL OXYGEN WITH SOLVENT WATER IN PERCHLORIC ACID SOLUTIONS, $\mu = 1$

⌐——— $t = 23°$; [H⁺] = 1 *M*———			⌐——— $t = 83°$; [H⁺] = 1 *M*———			⌐——— $t = 83°$; [H⁺] = 0.1 *M*———		
Exchange time, hr.	(46/(44 + 45))	% exchange	Exchange time, hr.	(46/(44 + 45))	% exchange	Exchange time, hr.	(46/(44 + 45))	% exchange
0	0.01466	0	0	0.01457	0	0	0.01295	0
97.5	.01419	4.3	47.4	.01352	9.7	380	.01198	10.4
288	.01474	−0.7	144.3	.01378	7.3	548	.01406	−12.1
1128	.01508	−3.8	475	.01379	7.2	719	.01418	−13.4
1585	.01435	2.8	1008	.01427	2.8	1003	.01256	4.5
1921	.01415	4.7	1489	.01340	10.8			
			∞	.00378	100			

Slope = −1.01 ± 1.96 × 10⁻⁵ hr.⁻¹   Slope = −2.29 ± 3.44 × 10⁻⁵ hr.⁻¹   Slope = +4.30 ± 13.0 × 10⁻⁵ hr.⁻¹

other samples, 0.38 mmole, was added to two heavy-walled glass tubes which had only one-third the volume of the other tubes as gas space above the exchange solution. The sample taken at 1632 hr. was indistinguishable on the McKay plot from the samples with the lower chlorine pressures.

The sample analyzed at 2496 hr. displayed a little greater exchange than would correspond to the least squares line through the other six points. Insofar as the effectiveness of chlorine as a scavenger in these solutions is concerned, the lower pressures of chlorine (0.38 mmole in 5 ml.) seem to have been adequate for the removal of water decomposition products.

Effect of Chloride Ion.—A sample of plutonyl ion was sealed in an ampoule in the 0.21 *M* perchloric acid series without chlorine but with sufficient sodium chloride to provide a 0.5 *M* solution. Since an exchange of 83.2% was observed after 43 hr. at 83°, it appears that chloride ion is ineffectual for the prevention of the catalysis of the PuO_2^{++}–water exchange by the lower oxidation states of plutonium.

Radiation-Induced Exchange.—A distinction can be made between two types of radiation processes occurring within these self-irradiated exchange solutions. First, the scattering of α-particles by solvent molecules produces chemically active decomposition products. In the present studies, these radiolytic products are assumed to be removed by chlorine scavenger before they can react with plutonyl ions. On the other hand, when scattering occurs within the plutonyl molecule-ion itself (or perhaps within the first hydration sphere of the ion), rupture of the metal–oxygen bond probably results. This latter process, hereafter referred to as the hot-atom exchange contribution, in general cannot be eliminated by the scavenger.

In order to investigate the hot-atom exchange effect, a 0.15 *M* plutonyl stock in molar perchloric acid was prepared from a sample of plutonium which was 87% Pu^{238} ($t_{1/2}$ = 86.4 yr.).[11] Three 1-ml. samples were sealed in glass ampoules with 0.38 mmole of chlorine and were placed in an electrically heated oven at *ca.* 80°. Samples taken at zero time, 17, and 24 hr. provided results which indicated a half-time for exchange of 58 hr. This is in contrast to the results which were obtained under similar experimental conditions with

Pu²³⁹ in which a half-time of 4.39 × 10³ hr. was observed. The energy input in the Pu²³⁸ solution was calculated from measurements taken with a 100-channel α-pulse analyzer on an aliquot of the exchange solution. It was computed to be 7 × 10¹⁸ e.v./min./ml. This radiation flux was about 216-fold greater than was usual with the 0.15 *M* Pu²³⁹ solutions. It appears to have been demonstrated that the hot-atom contribution to the observed exchange also must be taken into consideration in the 0.15 *M* Pu²³⁹ exchange experiments.

Dilute Plutonyl Exchange Solutions.—The usual plutonyl ion concentration in the exchange solutions was 0.15 *M*. This concentration was as large as was conveniently possible, and a 1-ml. aliquot of this stock would provide a surplus of gas for mass spectrometric analysis. However, it was concluded that a result which would more nearly correspond to the intrinsic exchange rate probably could be obtained by a reduction of the plutonyl ion concentration about 100-fold in order to minimize the hot-atom contribution. An analytical problem was posed by the use of these dilute solutions because a gas sample of sufficient size for mass spectrometric analysis could not be obtained without concentration of the plutonyl exchange solution prior to precipitation as plutonyl ferricyanide. This concentration was accomplished as outlined in the Experimental section of this paper by the use of a cation-exchange resin. In Table III are given the results of exchange experiments performed both at 23 and 83° in 1 and 0.1 *M* perchloric acid with 1.33 × 10⁻³ *M* plutonyl ion. In these experiments, the plutonyl ion fraction was initially labeled and the solvent was of normal isotopic composition. It is evident from the results in Table III that with the dilute plutonyl solutions, long half-times again are observed. However, because the precision of the results is less in these experiments than was observed in the more concentrated plutonyl solutions, presumably because of the smaller sample sizes, statistically the slopes of the McKay plots are not significantly different from zero.

Discussion

The deviation from linearity of the McKay plots obtained in the analysis of the exchange behavior of solutions initially composed of plutonyl ions, but without added chlorine, Fig. 1a, can be attributed to the growth of the lower oxidation states of plutonium

(11) D. Hoffman, G. Ford, and F. Lawrence, *J. Inorg. Nucl. Chem.,* **5**, 6 (1957).

which are formed as a consequence of the α-reduction process. This result has been alluded to in the present paper to emphasize the necessity of assuring that the plutonium is present as PuO_2^{++} if measurements are to be made of the intrinsic exchange rates.

The observation that chloride ion is ineffective in the prevention of the catalysis of the PuO_2^{++}–water oxygen exchange is not surprising in view of earlier measurements[12] which demonstrated that $HClO_4$–HCl solutions of approximately the same concentration as used in these exchange experiments did not completely inhibit the formation of lower oxidation states of plutonium though they did reduce the rate at which these appeared. Presumably in molar HCl the exchange rate would be much less since under these conditions chlorine is formed slowly by the oxidation of the chloride ion and the rate of decrease of the mean oxidation number is essentially zero at 25°.

The observed exchange rates in chlorine-scavenged 0.15 M plutonyl solutions appear to be of the expected order of magnitude for the hot-atom exchange contribution alone. For example, in the Pu^{238} experiment, the flux rate of 7×10^{21} e.v./min./l. should give rise to about 1×10^{19} ionizations/min./l. within the first coördination sphere of the plutonyl ion. If each of these events ruptures the metal–oxygen bond, an exchange half-time of the order of 100 hr. results. This value appears to be in reasonable agreement with the observed exchange half-time of 58 hr. if the assumptions involved in the calculation are taken into consideration. Similarly, an expected half-time of about 10^4 hr. is calculated for the exchange solutions 0.15 M in Pu^{239}, whereas half-times between 4×10^3 hr. and 4×10^4 hr. were observed for these solutions. For the 1.33×10^{-3} M Pu^{239} solutions, the hot-atom contribution to the exchange should be very small, and an improved measurement of the intrinsic exchange reaction rate should have been obtained from these dilute solutions. Apart from the very long times involved, in principle the intrinsic exchange for the plutonyl–water system could best be measured by an extrapolation of measured half-times to infinite dilution. Unfortunately, the techniques employed in the analysis of these dilute solutions produced experimental uncertainties which rendered the observed exchange rates statistically indistinguishable from zero. Hence, on

the basis of the present investigation, the qualitative conclusion may be drawn that the intrinsic exchange between plutonyl ion and water is extremely slow. A lower limit of about 10^4 hr. can be assigned to the intrinsic exchange half-time, although it may be many orders of magnitude greater than this.

The results obtained from 0.15 M plutonyl solutions (Tables I and II) exhibit a temperature and acidity dependence. Since sensitivity to these factors would not be predicted for a hot-atom exchange process, this might be taken as evidence for the contribution of an intrinsic exchange path. However, the solubility of chlorine is decreased both by increased acidity and elevated temperatures, and it appears possible that scavenging action may have been incomplete in the molar perchloric acid solution at 83°. The difficulty of the measurement of an intrinsic exchange in the Pu^{239} solutions could be lessened with the use of the relatively long-lived isotope Pu^{242} ($t_{1/2} = 3.8 \times 10^5$ yr.); however, this isotope is not currently available in macro quantities.

The lower limit exchange half-time observed in the plutonyl system is of the same order of magnitude as the exchange half-time (10^4 hr.) reported for the uranyl system.[3] It appears possible that this latter value also may be considered as a lower limit intrinsic exchange half-time; the exchange of uranyl ion with water is known to be catalyzed by the presence of uranium(V) and a steady state concentration of approximately 10^{-9} M UO_2^+ can be shown to account for this observed exchange rate.

The extremely non-labile behavior observed for the oxygen complexes of hexavalent uranium and plutonium ($t_{1/2} \geq 10^4$ hr.), is in marked contrast to the extreme lability ($t_{1/2} \leq 0.004$ sec.) inferred[3] for uranium(V) in molar $HClO_4$. Further measurements of other actinides would be of value in the determination of whether non-lability is characteristic of the hexavalent actinide species or whether electronic structure plays a dominant role in the ease of substitution. The exchange behavior of NpO_2^{++}, which is isoelectronic with UO_2^+, is currently under study.

(12) S. W. Rabideau, M. J. Bradley, and H. D. Cowan, LAMS-2236 (1959).