product of the decomposition and ignition of such an intermediate material was always PuP_2O_7.

The thermal stability of $PuPO_4$ and PuP_2O_7 was found to be much greater in air than *in vacuo*. Both compounds could be ignited at 950–1000° in air with no detectable loss in weight. At 950° and 5×10^{-5} mm. pressure, however, PuP_2O_7 slowly decomposed to $PuPO_4$. The decomposition rate *in vacuo* was accelerated at 1200–1400°. Significant crystal growth without decomposition resulted when samples of $PuPO_4$ were heated momentarily to 1400° in an induction furnace at 10^{-4} mm. pressure. Longer periods of heating, *e.g.*, 20 min. at 1400–1500°, caused a large proportion of the $PuPO_4$ to decompose, without evidence of melting, to the more stable compound, PuO_2.

Acknowledgment.—The author is indebted to E. Staritzky of this Laboratory for all of the optical measurements, to F. Ellinger for the identifications by X-ray analysis, and to R. D. Baker for many productive discussions and suggestions.

LOS ALAMOS, NEW MEXICO

[CONTRIBUTION FROM THE UNIVERSITY OF CALIFORNIA, LOS ALAMOS SCIENTIFIC LABORATORY]

The Kinetics of the Disproportionation of Plutonium(V)[1]

BY SHERMAN W. RABIDEAU

RECEIVED APRIL 29, 1957

A study has been made of the kinetics of the disproportionation of plutonium(V) in perchlorate solutions of unit ionic strength in which the PuO_2^+ was prepared by the reduction of the plutonyl ion with iodide ion. With this method of preparation, the disproportionation of plutonium(V) was studied in the absence of significant quantities of plutonium(III) and (IV) in the initial phases of the experiments. The rate of disproportionation of plutonium(V) has been found to be directly proportional to the first power of the hydrogen ion concentration, which suggests that the slow step is probably $PuO_2^+ + Pu(O)OH^{++} \rightarrow PuO_2^{++} + Pu(O)OH^+$. An activation energy of 19.6 kcal. has been computed from the temperature dependence of the specific reaction rate constants for the slow step of the disproportionation reaction. The disproportionation of plutonium(V) has also been studied in deuterium oxide to note the influence of a change in solvent upon the reaction rates. It appears from the kinetic results obtained that no evidence has been found which would support the hydrogen atom transfer mechanism in the plutonium(V) disproportionation reaction. Plutonium(V) also has been prepared from the plutonyl ion by the spontaneous α-reduction process. The kinetic data appear to be adequately described by a consideration of previously determined rate and equilibrium constants and the rate constant for the Pu(V)–Pu(V) reaction which was obtained from the experiments in which the plutonyl ion was reduced with iodide.

Introduction

The kinetics of the disproportionation of plutonium(V) has been the subject of previous studies[2,3] in which it was observed that the mechanism of the disproportionation reaction consisted of the slow reaction, $Pu(V) + Pu(III) \rightarrow 2Pu(IV)$, together with the rapid equilibrium reaction, $Pu(V) + Pu(IV) \rightleftarrows Pu(III) + Pu(VI)$. Plutonium(V) is also thermodynamically unstable in moderately acid solution, with respect to the reaction $2Pu(V) \rightarrow Pu(VI) + Pu(IV)$, as has been pointed out[2] and as can be shown from a consideration of the formal potentials[4,5] of the Pu(IV)–Pu(V) and the Pu(V)–Pu(VI) couples. In studies[2] of the disproportionation of plutonium(V) in which the PuO_2^+ was prepared by the electrolytic reduction of plutonyl ion, it appears that the solutions initially contained significant amounts of plutonium in the trivalent state. Connick concluded that the bimolecular rate constant for the disproportionation of plutonium(V) by the Pu(III)–Pu(V) mechanism is at least 35 times greater than that for the Pu(V)–Pu(V) path at room temperature in 0.5 *M* hydrochloric acid; hence, it is somewhat difficult to study the disproportionation of plutonium(V) through the latter reaction in the presence of moderate amounts of plutonium(III). In the present work use was made of the observation[5,6] that plutonium(V) can be prepared by the quantitative reduction of plutonyl ion with iodide ion. Thus, the disproportionation of plutonium(V) could be studied, at least in the initial phases of the reaction, in the absence of significant quantities of plutonium(III). In another series of experiments the PuO_2^+ was prepared by the alpha particle radiation from the plutonium. In these studies, which were of longer duration, it was necessary to consider the disproportionation of plutonium(V) by the Pu(III)–Pu(V) mechanism. An attempt was made to examine some of the details of the disproportionation of plutonium(V) by the proposed Pu(V)–Pu(V) mechanism by noting the influence on the rate of reaction of the substitution of deuterium oxide for ordinary water as the solvent.

Experimental

The apparatus and procedure were essentially those previously described.[7] Neutral solutions of Merck reagent grade sodium iodide were standardized against dried samples of Mallinckrodt reagent grade silver nitrate using a potentiometric method of analysis. After the addition of a given weight of neutral sodium iodide solution to the plutonyl solution, sufficient quantities of standardized perchloric acid and sodium perchlorate were added to maintain the desired acidity and ionic strength. This procedure was used to avoid the air oxidation of the iodide ion which proceeds rapidly in moderately acid solutions. Usually from 25 to 50% of the plutonyl solution was reduced with iodide to PuO_2^+. The sodium perchlorate salt was the recrystallized product obtained by the neutralization of Mallinckrodt reagent grade sodium carbonate with this manufac-

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(1) This work was done under the auspices of the U. S. Atomic Energy Commission. Presented in part at the 131st Meeting of the American Chemical Society, Miami, Florida, April 10, 1957.

(2) R. E. Connick, THIS JOURNAL, **71**, 1528 (1949).

(3) R. E. Connick, "The Transuranium Elements," Natl. Nuclear Energy Ser., Div. IV, Vol. 14-B, 1949, p. 268.

(4) K. A. Kraus, F. Nelson and G. L. Johnson, THIS JOURNAL, **71**, 2510 (1949).

(5) S. W. Rabideau, *ibid.*, **78**, 2705 (1956).

(6) K. A. Kraus and G. E. Moore, ref. 3, p. 550.

(7) S. W. Rabideau, THIS JOURNAL, **75**, 798 (1953).

turer's reagent grade 70% perchloric acid. The cell used was Pt; Pu(V), Pu(VI), $HClO_4(c_1)$, $NaClO_4(c_2)$; $HClO_4(c_1)$, $NaClO_4(c_2)$; Pt, H_2. The concentrations of the plutonium ions in the various oxidation states were obtained from the cell e.m.f., the mean oxidation number and the total plutonium ion concentration. The plutonyl solutions were prepared by dissolving a known weight of oxide-free metallic plutonium in the requisite amount of standardized 70% perchloric acid and oxidizing the plutonium(III) solutions for an extended period with ozone. The temperature of the plutonium solutions was maintained at ±0.01° over a period of several hours and was measured with a type 20D Western Electric thermistor whose resistance-temperature characteristics had been established by comparison with a thermometer calibrated by the U. S. National Bureau of Standards.

Deuterium oxide of 99.9% purity was used in the preparation of the plutonyl solutions in the experiments in which the influence of the change in solvent on the specific reaction rate constant was under investigation. In this series of experiments a liquid junction potential was involved in contrast to the kinetic studies in ordinary water in which the liquid junction potential was essentially zero. However, the liquid junction potential did not appear to interfere in any way although it was necessary to redetermine the formal potentials of the Pu(V)-Pu(VI) couples in each of the various acid–salt solutions used. In the determination of the Pu(V)–Pu(VI) formal potentials the sodium iodide solutions were also prepared in deuterium oxide to introduce as little solvent change as possible. Consistent results were obtained which indicated that the liquid junction potential was little altered during the course of a potentiometric titration.

Results and Discussion

Reduction of Plutonyl Ion with Iodide.—With the iodide method of preparation of PuO_2^+, the disproportionation of plutonium(V) by the Pu(V)–Pu(V) mechanism could be studied, at least in the initial phases of the experiments, without interference from a concomitant reaction involving the Pu(III)–Pu(V) path. The reactions which require consideration in the formulation of the rate law are

$$\mathrm{Pu(V)} + \mathrm{Pu(V)} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{Pu(VI)} + \mathrm{Pu(IV)} \qquad (1)$$

$$\mathrm{Pu(V)} + \mathrm{Pu(IV)} \underset{k_4}{\overset{k_3}{\rightleftharpoons}} \mathrm{Pu(VI)} + \mathrm{Pu(III)} \qquad (2)$$

Since reaction 1 is much removed from an equilibrium condition, the contribution of the back reaction is negligible. Reaction 2 is the rapid reversible equilibrium among the four oxidation states of plutonium which is maintained at all times.[2] The rate of decrease of plutonium(V) from reactions 1 and 2 is

$$-\mathrm{d}(\mathrm{Pu(V)})/\mathrm{d}t = 2k_1(\mathrm{Pu(V)})^2 + k_3(\mathrm{Pu(V)})(\mathrm{Pu(IV)}) - k_4(\mathrm{Pu(VI)})(\mathrm{Pu(III)}) \qquad (3)$$

During that portion of an experiment in which the (Pu(V))/(Pu(VI)) ratio is essentially constant, the (Pu(III))/(Pu(IV)) ratio is given by

$$r = K_{3456}(\mathrm{Pu(V)})/(\mathrm{Pu(VI)}) \qquad (4)$$

where K_{3456} is the equilibrium constant for reaction 2. The rate law can then be written

$$-\mathrm{d}(\mathrm{Pu(V)})/\mathrm{d}t = \left(2 + \frac{r}{r+1}\right) k_1(\mathrm{Pu(V)})^2 \qquad (5)$$

Thus, a plot of the reciprocal of the plutonium(V) concentration *versus* time should give a straight line with a slope equal to $(2 + r/(r + 1))k_1$. Linear plots have been obtained from the experimental data treated in this manner.

Effect of Acidity on Rate of Plutonium(V) Disproportionation.—The hydrogen ion concentration dependence of the rate of disproportionation of plutonium(V) by the Pu(V)–Pu(V) mechanism has been studied at 25° by varying the perchloric acid concentration from 0.20 to 1.00 *M* with sodium perchlorate added to maintain the ionic strength at unity. The results are given in Table I, and it appears that the rate of disproportionation of plutonium(V) is directly proportional to the first power of the hydrogen ion concentration. This result is analogous to that observed[8] in the disproportionation of uranium(V), and the disproportionation of plutonium(V) can be expressed in a similar series of reactions[9]

$$PuO_2^+ + H^+ \rightleftharpoons Pu(O)OH^{++} \qquad (6)$$

$$PuO_2^+ + Pu(O)OH^{++} \longrightarrow PuO_2^{++} + Pu(O)OH^+ \text{ (slow step)} \qquad (7)$$

$$Pu(O)OH^+ \longrightarrow \text{stable Pu(IV) species} \qquad (8)$$

Influence of Solvent on Disproportionation Rate.—Duke and Pinkerton[10] have examined the influence of the substitution of deuterium oxide for ordinary water upon the rate of disproportionation of UO_2^+ in perchlorate solutions of ionic strength 0.5 at 25°. Since uranium(V) disproportionates at a much greater rate than plutonium(V), these authors were required to use somewhat lower acidities than was the case in the present work. In these uranium studies, the conclusion was reached that since the rate constants for the disproportionation of uranium(V) in deuterium oxide were about 1.7-fold greater than those in ordinary water, a mechanism which involved a hydrogen atom transfer appeared to be highly improbable.

It would appear that both uranium(V) and plutonium(V) might be expected to participate in a similar reaction mechanism in their disproportionation reactions since the reaction rates are second order in the metal(V) ion and first order in hydrogen ion. It was of interest to determine the influence of a change in solvent upon the rate of disproportionation of plutonium(V). In Table II are given the values of the rate constants in deuterium oxide as a function of acidity.[10a] As can be noted from a comparison of the results of Tables I and II, with equal weight given to the experiments at each acidity, the ratio of the rate constants, $k_{D_2O}/k_{H_2O} = 1.17$. Thus, the rate of disproportionation of plutonium(V) appears to be somewhat greater in deuterium oxide than in ordinary water. Rule and LaMer[11]

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

(9) A parenthesis is placed around the oxygen to indicate that peroxide linkage is not intended.

(10) F. R. Duke and R. C. Pinkerton, *ibid.*, **73**, 2361 (1951).

(10a) NOTE ADDED IN PROOF.—In the analysis of the kinetic data for the disproportionation of plutonium(V) in D_2O it was considered that K_{3456} was not appreciably altered upon changing the solvent from ordinary water to D_2O. A precise determination of the value of this quotient was not made because of the unknown magnitude of the liquid junction potential of the cell. However, values of K_{3456} in D_2O recently have been obtained from spectrophotometric measurements (S. W. Rabideau and R. J. Kline, to be published). These results indicate that the equilibrium quotient is significantly larger in D_2O than in H_2O. However, since the values of the quantity $(2 + r/(r + 1))$ remain very nearly equal to three, the values of k_1 in Table II are essentially unchanged.

(11) C. K. Rule and V. K. LaMer, *ibid.*, **60**, 1974 (1938).

TABLE I

ACIDITY DEPENDENCE OF PLUTONIUM(V) DISPROPORTIONATION RATE AT UNIT IONIC STRENGTH AND 25°

(H^+), moles/l.	$(NaClO_4)$, moles/l.	k_1, l./mole/hr.	$k_1/(H^+)$
1.000	0.000	14.1	14.1
1.000	.000	14.7	14.7
0.750	.250	9.7	12.9
.500	.500	6.1	12.2
.200	.800	2.5	12.6
		Mean	13.0 ± 0.7

TABLE II

DEPENDENCE OF PLUTONIUM(V) DISPROPORTIONATION RATE CONSTANTS UPON CHANGE OF SOLVENT FROM ORDINARY WATER TO DEUTERIUM OXIDE AT 25°

Mole fraction, D_2O	(H^+), moles/l.	$(NaClO_4)$, moles/l.	k_1, l./mole/hr.	$k_1/(H^+)$
0.94	1.000	0.000	18.9	18.9
.94	0.750	.250	13.6	18.1
.96	.500	.500	6.5	12.9
.97	.200	.800	2.4	12.0
			Mean	15.4 ± 4

have shown that the dissociation constants of the deutero acids are somewhat smaller than the corresponding proto acids; however, the ratio of the acid dissociation constants in the two media becomes more nearly unity with increased strength of the acid. Since $Pu(O)OH^{++}$ would have to be considered a fairly strong acid, a large change in the acid dissociation constant would not be expected as the solvent is changed from H_2O to D_2O, and the increase in the reaction rate in deuterium oxide from this effect would be predicted to be small. The mass and solvent effects for this solvent change in a hydrogen atom transfer reaction would be expected to be in the direction of lowered rates of reaction. Thus, it would seem that no evidence has been obtained on the basis of these kinetic studies which would support a hydrogen atom transfer mechanism for the disproportionation of plutonium(V).

Temperature Dependence of Plutonium(V) Disproportionation.—From measurements of the rates of disproportionation of plutonium(V) between 10 and 35° a value of 19.6 kcal. was computed for the activation energy of the slow step in the disproportionation of plutonium(V) in molar perchloric acid solutions from the data of Table III. The heat and entropy of activation for the disproportionation reaction were calculated from the rate expressions for the transition state theory.[12] The computed values of ΔH^* and ΔS^* are 19.0 kcal. and −5.8 cal./deg., respectively.

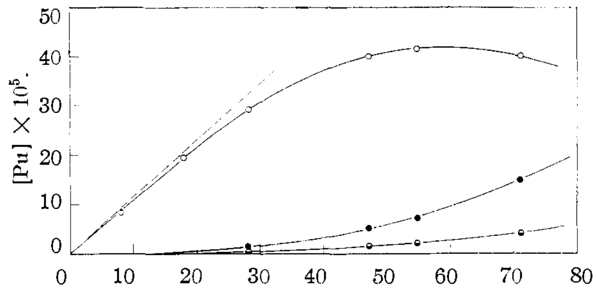

Fig. 1.—α-Reduction of plutonyl ion and subsequent disproportionation of plutonium(V) in molar perchloric acid at 25°: dashed line, α-reduction rate; ◒, Pu^{+++}; ●, Pu^{++++}; ○, PuO_2^+.

TABLE III

TEMPERATURE DEPENDENCE OF RATE CONSTANTS IN THE DISPROPORTIONATION OF PLUTONIUM(V) IN MOLAR PERCHLORIC ACID

(H^+), moles/l.	T, °K.	$1/T \times 10^3$	k_1, l./mole/hr.	2.303 log k_1
1.000	307.99	3.2469	46.3	3.835
1.000	298.16	3.3539	14.4	2.668
1.000	289.02	3.4600	5.6	1.723
1.000	283.28	3.5301	3.6	1.281

α-Particle Reduction of Plutonyl Ion.—It has been observed that the rate of reduction of plutonyl ion by the α-particles from the plutonium is about 1.5% per day. From both spectrophotometric and potentiometric data it is found that in pure plutonyl solutions the plutonium(V) concentration initially increases at a rate equal to the rate of α-reduction. However, as the plutonium(V) concentration increases, the rate at which disproportionation occurs becomes greater since the rate is proportional to the square of the plutonium(V) concentration. Also, the concentrations of Pu(III) and Pu(IV) gradually increase thereby providing the possibility for disproportionation through the Pu(III)–Pu(V) path. The reactions which have been considered in the analysis of the kinetic data are

$$\text{Alpha} + \text{Pu(VI)} \xrightarrow{k_\alpha} \text{Pu(V)} \qquad (9)$$

$$\text{Pu(V)} + \text{Pu(V)} \underset{k_2}{\overset{k_1}{\rightleftarrows}} \text{Pu(IV)} + \text{Pu(VI)} \qquad (10)$$

$$\text{Pu(V)} + \text{Pu(IV)} \underset{k_4}{\overset{k_3}{\rightleftarrows}} \text{Pu(VI)} + \text{Pu(III)} \qquad (11)$$

$$\text{Pu(V)} + \text{Pu(III)} \underset{k_6}{\overset{k_5}{\rightleftarrows}} \text{Pu(IV)} + \text{Pu(IV)} \qquad (12)$$

The rate law can be written as

$$\begin{aligned} \mathrm{d}(\text{Pu(V)})/\mathrm{d}t - \mathrm{d}(\text{Pu(IV)})/\mathrm{d}t = k_\alpha\, \Sigma\text{Pu} - {} \\ 3k_1(\text{Pu(V)})^2 + 3k_2(\text{Pu(IV)})(\text{Pu(VI)}) - {} \\ 3k_5(\text{Pu(V)})(\text{Pu(III)}) + 3k_6(\text{Pu(IV)})^2 \end{aligned} \qquad (13)$$

However, since at equilibrium

$$k_1(\text{Pu(V)})^2 = k_2(\text{Pu(IV)})(\text{Pu(VI)}) \qquad (14)$$

$$k_2 = k_1 K_{\text{disprop}}/K^2{}_{3456} \qquad (15)$$

and

$$k_5 = k_6 K^2{}_{3456}/K_{\text{disprop}} \qquad (16)$$

where $K_{\text{disprop}} = (\text{Pu(III)})^2(\text{Pu(VI)})/(\text{Pu(IV)})^3$ and $K_{3456} = (\text{Pu(III)})(\text{Pu(VI)})/(\text{Pu(IV)})(\text{Pu(V)})$. With these substitutions in eq. 13 it is possible to write

$$\begin{aligned} \mathrm{d}(\text{Pu(V)})/\mathrm{d}t - \mathrm{d}(\text{Pu(IV)})/\mathrm{d}t = k_\alpha \Sigma\text{Pu} - {} \\ 3k_1(\text{Pu(V)})^2\{1 - K_{\text{disprop}}\, (\text{Pu(IV)})(\text{Pu(VI)})/ \\ K^2{}_{3456}(\text{Pu(V)})^2)\} + 3k_6(\text{Pu(IV)})^2\, \{1 - {} \\ K_{3456}(\text{Pu(III)})(\text{Pu(V)})/K_{\text{disprop}}\, (\text{Pu(IV)})^2\} \end{aligned} \qquad (17)$$

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[12] S. Glasstone, K. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941.

TABLE IV

ALPHA REDUCTION OF PLUTONYL ION AND DISPROPORTIONATION OF PLUTONIUM(V) IN MOLAR PERCHLORIC ACID AT 25°

Time, hr.	Pu(III), *M*	Pu(IV), *M*	Pu(V), *M*	Pu(VI), *M*	$d(Pu(V))/dt - d(Pu(IV))/dt \times 10^5$ Obsd.	Calcd.
8.01	....	....	8.38×10^{-5}	1.85×10^{-2}	1.15	1.15
18.00	....	....	1.96×10^{-4}	1.83	0.98	0.98
28.18	3.25×10^{-6}	1.59×10^{-5}	2.91	1.82	.79	.72
47.21	1.57×10^{-5}	5.27	4.02	1.80	.03	.09
54.79	2.19	7.30	4.17	1.80	− .26	− .14
71.17	4.36	1.50×10^{-4}	4.03	1.79	− .74	− .56

The values of K_{disprop}, k_6 and K_{3456} in molar perchloric acid at 25° have been reported in previous communications[5,7] and are 8.4×10^{-3}, 0.12 l./mole/hr. and 13, respectively. The value of k_α was obtained from observations of the rate of α-reduction and is equal to 6.25×10^{-4} hr.$^{-1}$. In Table IV the results of a typical experiment in molar perchloric acid at 25° are given in which the plutonium(V) was produced by the α-reduction of the plutonyl ion. A value of 15 l./mole/hr. was used for k_1 in eq. 17. This value is in fairly good agreement with the rate constant obtained in the experiments in which the plutonium(V) was prepared by the iodide reduction of plutonyl ion. The experimentally observed changes in plutonium concentrations with time are shown in Fig. 1. The plutonyl ion concentration is not shown since its value is essentially constant throughout the experiment.

Acknowledgments.—The author wishes to express his appreciation for helpful discussion and interest in this research to Professor Robert E. Connick, consultant to L.A.S.L., and to Dr. J. F. Lemons, under whose general direction this work was performed. Also, it is a pleasure to acknowledge the assistance of Miss Mildred Bradley in some of the reagent standardization analyses.

LOS ALAMOS, NEW MEXICO

[CONTRIBUTION FROM THE UNIVERSITY OF CALIFORNIA, LOS ALAMOS SCIENTIFIC LABORATORY]

The Hydrogen Peroxide-induced Ce*(III)–Ce(IV) Exchange System[1]

BY PAUL B. SIGLER AND B. J. MASTERS

RECEIVED MAY 3, 1957

The technique of isotopic exchange in non-stable systems has been applied to study the kinetics of the reaction between Ce(IV) and H_2O_2 in 0.8 *N* H_2SO_4 solution. In addition to the bimolecular electron exchange reaction between Ce*(III) and Ce(IV), an induced exchange reaction is found to occur at a rate proportional to the concentration ratio [Ce(III)]/[Ce(IV)]. The results are consistent with the mechanisms $H_2O_2 + \text{Ce(IV)} \overset{k_1}{\rightleftarrows} HO_2 + \text{Ce(III)} + H^+$ and $HO_2 + \text{Ce(IV)} \xrightarrow{k_1k_2} \text{Ce(III)} + O_2 + H^+$.

Introduction

The reduction of ceric ion by hydrogen peroxide in sulfuric acid solution has been studied by Baer and Stein,[2] who propose a mechanism consisting of two irreversible reaction steps.

$$H_2O_2 + \text{Ce(IV)} \xrightarrow{k_1} H^+ + HO_2 + \text{Ce(III)} \quad (1)$$

$$HO_2 + \text{Ce(IV)} \xrightarrow{k_2} H^+ + O_2 + \text{Ce(III)} \quad (2)$$

These investigators claim that HO_2 radicals, if they are in fact formed as postulated above, are incapable of reoxidizing cerous ions. However, since only stoichiometric oxidation–reduction data rather than rate measurements are reported, this interpretation is very much open to question. Furthermore, the oxidation potentials[3] for the following couples

$$H_2O_2 = HO_2 + H^+ + e^- \quad E^0 \simeq -1.5 \quad (3)$$

$$\text{Ce(III)} = \text{Ce(IV)} + e^- \quad E = -1.44 \text{ (in 1 } M\, H_2SO_4) \quad (4)$$

suggest that the reverse of reaction 1

$$HO_2 + \text{Ce(III)} + H^+ \xrightarrow{k_{-1}} H_2O_2 + \text{Ce(IV)} \quad (5)$$

may indeed be of kinetic importance. Consequently, a further investigation of this reaction system appears to be in order.

An isotopic tracer method, involving measurement of the rate of appearance of labeled ceric ions when hydrogen peroxide reacts with a solution originally containing labeled cerous ions and unlabeled ceric ions, was chosen for use in the present study because of the following reasons: (i) This system readily lends itself to quantitative interpretation in the manner previously described[4] for non-stable exchange systems, and provides an excellent example of the non-stable exchange technique. (ii) The over-all reduction of Ce(IV) by H_2O_2 in sulfuric acid solution takes place so rapidly that measurable rates of chemical change may be obtained only by resorting to flow techniques. On the other hand, preliminary experiments indicated that a relatively simple reaction apparatus would suffice for

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[1] This work was performed under the auspices of the Atomic Energy Commission. Inquiries about the manuscript may be addressed to B. J. M.

[2] S. Baer and G. Stein, *J. Chem. Soc.*, 3176 (1953).

[3] W. Latimer, "Oxidation Potentials," 2nd ed., Prentice-Hall, Inc., New York, N. Y., 1952, pp. 47, 294.

[4] C. P. Luehr, G. E. Challenger and B. J. Masters, THIS JOURNAL, **78**, 1314 (1956).