

TABLE IV

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

Time, hr.	Pu(III), <i>M</i>	Pu(IV), <i>M</i>	Pu(V), <i>M</i>	Pu(VI), <i>M</i>	d(Pu(V))/dt - d(Pu(IV))/dt × 10 <sup>6</sup>	
					Obsd.	Calcd.
8.01	.....	.....	8.38 × 10 <sup>-6</sup>	1.85 × 10 <sup>-2</sup>	1.15	1.15
18.00	.....	.....	1.96 × 10 <sup>-4</sup>	1.83	0.98	0.98
28.18	3.25 × 10 <sup>-6</sup>	1.59 × 10 <sup>-5</sup>	2.91	1.82	.79	.72
47.21	1.57 × 10 <sup>-5</sup>	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 <sup>-4</sup>	4.03	1.79	-.74	-.56

The values of  $K_{\text{disprop}}$ ,  $k_6$  and  $K_{3456}$  in molar perchloric acid at 25° have been reported in previous communications<sup>5,7</sup> and are  $8.4 \times 10^{-3}$ , 0.12 l./mole/hr. and 13, respectively. The value of  $k_\alpha$  was obtained from observations of the rate of  $\alpha$ -reduction and is equal to  $6.25 \times 10^{-4}$  hr.<sup>-1</sup>. 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  $\alpha$ -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<sup>1</sup>

BY PAUL B. SIGLER AND B. J. MASTERS

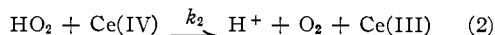
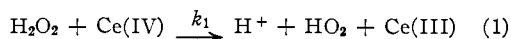
RECEIVED MAY 3, 1957

The technique of isotopic exchange in non-stable systems has been applied to study the kinetics of the reaction between Ce(IV) and H<sub>2</sub>O<sub>2</sub> in 0.8 *N* H<sub>2</sub>SO<sub>4</sub> 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)]/

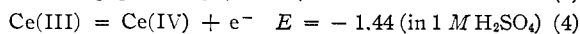
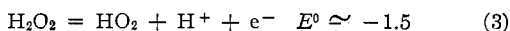
[Ce(IV)]. The results are consistent with the mechanisms  $\text{H}_2\text{O}_2 + \text{Ce(IV)} \xrightleftharpoons{k_1} \text{HO}_2 + \text{Ce(III)} + \text{H}^+$  and  $\text{HO}_2 + \text{Ce(IV)} \xrightarrow{k_1 k_2} \text{Ce(III)} + \text{O}_2 + \text{H}^+$ .

### Introduction

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



These investigators claim that HO<sub>2</sub> 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<sup>3</sup> for the following couples

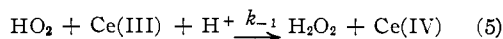


(1) This work was performed under the auspices of the Atomic Energy Commission. Inquiries about the manuscript may be addressed to B. J. M.

(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.

suggest that the reverse of reaction 1



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<sup>4</sup> 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<sub>2</sub>O<sub>2</sub> 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

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

tracer measurements of the rate constant ratio  $k_{-1}/k_2$ . (iii) The isotopic exchange data obtainable from this system are necessary for the interpretation of the more complex radiation-induced cerium exchange system,<sup>5</sup> in which reaction of Ce(IV) with the water decomposition product  $H_2O_2$  may provide one of the induced-exchange paths.

The rate laws for the ordinary electron-exchange reaction between Ce(III) and Ce(IV) in nitric acid<sup>6</sup> and in perchloric acid<sup>6,7</sup> solutions have been reported previously. In the course of the present investigation, it became necessary to determine the kinetics of this reaction in sulfuric acid solution. This electron-exchange process will be referred to hereafter as the "thermal" exchange reaction.

### Experimental

**Materials.**—The stock solutions used throughout most of this work were prepared from Baker and Adamson C.P. sulfuric acid and distilled water. However, for the set of induced exchange runs in which "high purity" reagents were employed, the sulfuric acid was distilled from  $K_2Cr_2O_7$  before use, and dilutions were performed with water which had been redistilled from alkaline permanganate solution.

Cerous sulfate and ceric sulfate stock solutions were prepared from G. Frederick Smith reagent grade chemicals, except in the case of the "high purity" reagents, which were prepared from spectroscopically analyzed cerium metal as described elsewhere.<sup>8</sup> All of the stock solutions were made up to 0.8 *N*  $H_2SO_4$  concentration. The solutions were analyzed periodically for ceric cerium and total cerium by standard volumetric methods. No detectable reduction of the ceric sulfate stock solution occurred over a period of several months duration.

The  $Ce^{144}$  tracer was obtained from the Carbide and Carbon Chemicals Co., Oak Ridge, Tennessee, in the form of carrier-free  $CeCl_3$  in HCl solution. This material was purified by Boldridge and Huine's method,<sup>9</sup> after which the resulting high specific activity  $Ce^*(OH)_3$  product was dissolved in sulfuric acid. By diluting the specific activity of this tracer preparation approximately 100-fold with unlabeled cerous sulfate, stock solutions of the desired specific activity were obtained.

Three per cent. "Baker Analyzed" hydrogen peroxide, which contains a trace (0.013%) of acetanilide as a stabilizer, was diluted with 0.8 *N*  $H_2SO_4$  stock solution for use in most of the induced exchange experiments. In the case of the exchange runs with "high purity" reagents, 30% Baker and Adamson A.C.S. reagent grade inhibitor-free hydrogen peroxide was used.

Eastman "White Label" tri-*n*-butyl phosphate was used in the Ce(III)-Ce(IV) separations,<sup>10</sup> usually without further purification. A tolerable amount of Ce(IV) reduction by this solvent occurred during the time required for the extractions. Reduced pressure distillation of the tri-*n*-butyl phosphate prior to use brought about little, if any, reduction in Ce(IV) loss during the separation procedure.

All other chemicals were of laboratory reagent quality, and were used without further purification.

**Run Procedure.**—Thermal exchange runs were carried out in a thermostated 250-ml. flask fitted with a mechanical stirring device. Calculated amounts of ceric sulfate stock solution and 0.8 *N*  $H_2SO_4$  solution were added to the flask and allowed to come to thermostat temperature. The cerous\* sulfate stock solution, also at the correct temperature was then added. After the exchange solution was

thoroughly mixed, a 25-ml. aliquot was removed for separation and counting of the Ce(IV)-fraction. This "zero time" sample was followed by the removal of successive aliquots at periodic time intervals. Finally, an "infinite exchange" sample was obtained by removing one aliquot, warming it to  $\sim 70^\circ$  for a period of time sufficient to ensure complete exchange, cooling the sample, and extracting the Ce(IV)-fraction in the usual manner.

Preliminary induced exchange experiments were carried out using a consecutive sampling procedure similar to that employed for the thermal exchange runs. An exchange solution of  $Ce^*(III)$  and Ce(IV) in 0.8 *N*  $H_2SO_4$  was placed in a 250-ml. reaction cell and subjected to stirring. A synchronous motor was then started, causing a dilute solution of  $H_2O_2$ , also in 0.8 *N*  $H_2SO_4$ , to be driven from a 100-ml. ground glass syringe at the constant rate of  $4.73 \times 10^{-5}$  liters-sec.<sup>-1</sup> through a capillary tube and into the rapidly stirred exchange solution. The solutions were allowed to contact no surfaces other than Pyrex, and both reaction cell and syringe were thermostated during the course of the measurements. Successive samples of the exchange solution were withdrawn at four-minute intervals for separation of the Ce(IV)-fractions, the first such sample to be removed being designated as the "zero time" sample. When approximately two-thirds of the original Ce(IV) present had been reduced, the syringe drive mechanism was stopped and a final aliquot was removed for treatment as an "infinite exchange" sample. In addition to these counting samples, it was necessary to remove aliquots of the exchange solution at "zero time" and at the end of the run. These samples were used directly in a spectrophotometric determination of the total amount of Ce(IV)-reduction that had occurred during the experiment.

The four-minute time interval between successive sample removals was designed to allow sufficient time for complete separation of the Ce(IV) fraction of each preceding sample. However, it was found that the thermal exchange contribution during this time interval was usually so large that measurements of the induced exchange reaction were somewhat lacking in precision. It therefore became desirable to reduce the time interval between samples, at the same time increasing the rate of peroxide addition, so that the induced exchange reaction would predominate. Consequently, in all of the later induced exchange measurements, an individual run technique was employed in place of the consecutive sampling procedure used throughout the preliminary work. In the case of the individual exchange runs, the apparatus was modified by the substitution of a 100-ml. reaction cell for the 250-ml. reaction flask previously employed. About 50 ml. of exchange solution, made up in the usual manner, was placed in the reaction cell. After allowing the syringe drive mechanism to run for a carefully timed interval, the entire contents of the reaction cell were treated by the usual separation procedure. The run was then repeated, using the same initial composition for the exchange solution and varying only the syringe driving time. A series of runs, including a "zero time" run and an "infinite exchange" run, were thus performed. The Ce(IV)-reduction rate, which remained constant throughout the series of experiments, was obtained from independent spectrophotometric measurements.

**Separation of the Cerium Oxidation States.**—A modification of Warf's extraction procedure<sup>10</sup> was employed. At the start of each series of experiments, a number of separatory funnels, each containing 5 ml. of tri-*n*-butyl phosphate and 10 ml. of concentrated nitric acid, were cooled to  $0^\circ$ . As each successive sample of exchange solution was obtained, it was immediately transferred to a funnel and shaken in order to separate the Ce(IV)-fraction into the organic layer. This procedure resulted in a small, reproducible amount of "separation-induced exchange." After washing the organic layer twice with 10-ml. portions of 6 *M*  $HNO_3$ , the Ce(IV)-fraction was re-extracted into the aqueous phase by shaking with 25 ml. of 1 *M*  $H_2SO_4$  solution.

**Specific Activity Determinations.**—Each of the Ce(IV)-1 *M*  $H_2SO_4$  counting samples was treated with potassium persulfate and silver ion catalyst in order to ensure complete oxidation, after which one aliquot was taken for spectrophotometric measurement of the Ce(IV) present. A second aliquot was removed to a 10-ml. Pyrex culture tube and allowed to stand for at least two hours in order to permit the 17.5 minute  $Pr^{144}$  daughter to attain equilibrium concentration. Counting was done with a side-window  $\beta$ - $\gamma$  pro-

(5) (a) G. E. Challenger and B. J. Masters, *THIS JOURNAL*, **77**, 1063 (1955); (b) G. E. Challenger and B. J. Masters, to be published.

(6) J. W. Gryder and R. W. Dodson, *ibid.*, **73**, 2890 (1951); see also H. C. Hornig and W. F. Libby, *J. Phys. Chem.*, **56**, 869 (1952); W. D. Armstrong and L. Singer, *Anal. Chem.*, **26**, 1047 (1954).

(7) F. R. Duke and F. R. Parchen, *THIS JOURNAL*, **78**, 1540 (1956).

(8) B. J. Masters and G. E. Challenger, *J. Phys. Chem.*, **59**, 1093 (1955).

(9) National Nuclear Energy Series, Division IV, 9, "Radiochem. Studies: The Fission Products," Book 3, McGraw-Hill Book Co., Inc., New York, N. Y., 1951, p. 1699.

(10) J. C. Warf, *THIS JOURNAL*, **71**, 3257 (1949).

portional counter, the sample tube being mounted in a reproducible vertical position directly in front of the window. Empirically determined corrections for counting efficiency variations among the sample tubes were applied. Although the over-all counting efficiency of this arrangement was only about 1%, sufficient activity was present in each sample so that, within reasonable counting times, a statistical counting error of less than one or two per cent. was realized. By combining the spectrophotometric and counting measurements, the specific activity (counts per minute per unit concentration) of each Ce(IV) sample was obtained.

**Calculation of Exchange Results.**—The thermal exchange data were treated by the method of Prestwood and Wahl<sup>11</sup> in order to correct for the separation-induced exchange effect. For each set of runs performed under identical experimental conditions, the individual fractional exchange values were calculated by means of the equation

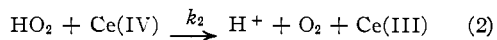
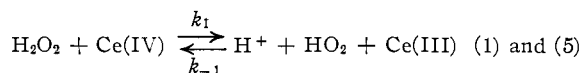
$$F = \frac{S - S_0}{S_\infty - S_0} \quad (6)$$

in which  $F$  represents the fractional exchange achieved at the time  $t$  (seconds),  $S$  the specific activity of the sample removed at time  $t$ , and  $S_0$  and  $S_\infty$  the specific activities of the "zero time" and "infinite exchange" samples. A plot of  $\ln(1 - F)$  vs.  $t$  was then made for each set of runs, and from the least squares slope of the resulting plot, the thermal exchange rate was calculated according to the classical equation<sup>12</sup>

$$R_1 = - \frac{ab \ln(1 - F)}{v(a + b)t} \quad (7)$$

in which  $R_1$  is the thermal exchange rate (moles-l.<sup>-1</sup>-sec.<sup>-1</sup>),  $v$  is the original volume (liters) of the exchange solution, and  $a$  and  $b$  are the amounts (moles) of Ce(III) and of Ce(IV), respectively, originally present in the exchange solution.

In order to obtain a quantitative mathematical treatment of the induced exchange data, it was necessary to assume a tentative reaction mechanism. An examination of the raw experimental data from the induced-exchange runs indicated that the induced-exchange effect increased with increasing [Ce(III)]/[Ce(IV)] ratio, in agreement with the probable mechanism



The assumption of this mechanism was subsequently justified by the general agreement of the final results obtained through this treatment. However, it should be borne in mind that the present study was carried out at a single sulfuric acid concentration, and that no attempt has been made to distinguish the above set of reactions from other equivalent mechanisms differing from (1), (5) and (2) only in the number of  $\text{H}^+$ ,  $\text{HSO}_4^-$  and  $\text{SO}_4^{2-}$  ions considered to be complexed in the hydrogen peroxide, hydroperoxo, or cerium species. In order that the following kinetic treatment may represent equally well all such possible variations in the assumed mechanism, all hydrogen ion and sulfate ion concentration terms shall be considered to be implicit in the appropriate rate constants.

With the syringe mechanism delivering  $\text{H}_2\text{O}_2$ -0.8  $N$   $\text{H}_2\text{SO}_4$  solution to the exchange system at the constant rate  $s$  (liters-sec.<sup>-1</sup>), so that the constant rate of  $\text{H}_2\text{O}_2$  addition is  $r$  (equiv.-sec.<sup>-1</sup>), the following steady-state situation should prevail.

$$- \frac{d}{dt} [\text{H}_2\text{O}_2] = 0; \frac{r}{2(v + st)} + k_{-1}[\text{HO}_2][\text{Ce(III)}] = k_1[\text{H}_2\text{O}_2][\text{Ce(IV)}] \quad (8)$$

$$- \frac{d}{dt} [\text{HO}_2] = 0; k_2[\text{HO}_2][\text{Ce(IV)}] + k_{-1}[\text{HO}_2][\text{Ce(III)}] = k_1[\text{H}_2\text{O}_2][\text{Ce(IV)}] \quad (9)$$

Equations 8 and 9 may be combined and solved for the

(11) R. J. Prestwood and A. C. Wahl, *THIS JOURNAL*, **71**, 3137 (1949).

(12) H. A. C. McKay, *Nature*, **142**, 997 (1938); R. B. Duffield and M. Calvin, *THIS JOURNAL*, **68**, 557 (1946).

steady-state hydroperoxo radical concentration.

$$[\text{HO}_2] = \frac{r}{2k_2(v + st)[\text{Ce(IV)}]} \quad (10)$$

The steady-state rate of conversion of cerous ions (tagged and untagged) to the ceric state is

$$R_2(t) = k_{-1}[\text{HO}_2][\text{Ce(III)}] = \frac{rk_{-1}[\text{Ce(III)}]}{2k_2(v + st)[\text{Ce(IV)}]} \quad (11)$$

In addition to chemical conversion by the process described above, a transfer of cerium atoms from one oxidation state to the other takes place as a result of the thermal exchange reaction. From independent thermal exchange measurements, this reaction was shown to occur at the rate

$$R_1(t) = k[\text{Ce(III)}][\text{Ce(IV)}]$$

$k$  being the bimolecular rate constant for thermal exchange.

The quantitative exchange law describing non-stable exchange systems of this general type has been derived elsewhere.<sup>4</sup> The general equation is

$$\ln(1 - F_B) = - \int_0^t \frac{(a + b)R(t) dt}{(a + \rho(t))(b - \rho(t))} \quad (12)$$

in which the subscript on  $F$  indicates that the fractional exchange values must be obtained from specific activity measurements of the species whose population is decreasing, i.e., Ce(IV), and  $a$  and  $b$  represent the initial amounts (moles) of Ce(III) and Ce(IV), respectively, present in the system. The function  $\rho(t)$  represents in the present case the net amount (moles) of ceric ion reduction occurring in the time  $t$ . The instantaneous volume of the system is given by the relation  $v(t) = v + st$ , and the instantaneous net rate (moles-l.<sup>-1</sup>-sec.<sup>-1</sup>) of ceric ion reduction is  $r(t) = r/v(t)$  or  $r/(v + st)$ , so that

$$\begin{aligned} \rho(t) &= \int_0^t r(t)v(t) dt \\ &= \int_0^t r dt \\ &= rt \end{aligned} \quad (13)$$

The quantity  $R(t)$  used in eq. 12 represents the total rate (moles-sec.<sup>-1</sup>) at which cerous ions are converted to the ceric state (either by  $\text{HO}_2$  radicals or *via* the thermal exchange process), and may be expressed by the equation

$$\begin{aligned} R(t) &= R_1(t)v(t) + R_2(t)v(t) \\ &= k(v + st)[\text{Ce(III)}][\text{Ce(IV)}] + \frac{rk_{-1}[\text{Ce(III)}]}{2k_2[\text{Ce(IV)}]} \\ &= \frac{k(a + rt)(b - rt)}{(v + st)} + \frac{rk_{-1}(a + rt)}{2k_2(b - rt)} \end{aligned} \quad (14)$$

Substituting 13 and 14 into 12 and integrating

$$\ln(1 - F_B) = - \frac{(a + b)k}{s} \ln \frac{v + st}{v} + \frac{(a + b)k_{-1}}{2k_2(b - rt)} - \frac{(a + b)k_{-1}}{2k_2b}$$

This solution may be rearranged to give

$$\frac{k_{-1}}{k_2} = - \frac{2b(b - rt)}{rt(a + b)} [\ln(1 - F_B) + \frac{a + b}{s} k \ln \frac{v + st}{v}] \quad (15)$$

Equations 6 and 15 were used directly for the conversion of data obtained by the individual exchange run procedure into the tabulated  $k_{-1}/k_2$  values. However, in the case of the runs performed by the consecutive sampling procedure in which counting samples were removed at the successive times  $t_0, t_1, t_2, \dots, t_n$ , an abrupt change in the quantities  $(v + st)$ ,  $(a + rt)$  and  $(b - rt)$  occurred each time a sample was removed. Consequently, it was necessary to calculate a  $k_{-1}/k_2$  value for the interval between each successive pair of samples. First, the ratio  $k_{-1}/k_2$  for the interval  $t_0 \rightarrow t_1$  was computed in the obvious manner and tabulated. Next,  $t_1$  was designated as a new "zero time" in order to calculate  $F_B$  for the interval  $t_1 \rightarrow t_2$  by means of eq. 6. This  $F_B$  value was then used in eq. 15, together with the new values of  $a$ ,

$b$  and  $v$  corresponding to the "initial conditions" prevailing at  $t_1$ . The arithmetical average of the  $k_{-1}/k_2$  values for the intervals  $t_0 \rightarrow t_1$  and  $t_1 \rightarrow t_2$  was then tabulated. The process was repeated for succeeding intervals, in each case the resulting  $k_{-1}/k_2$  value being averaged together with the values thus obtained for all preceding intervals. The tabulated results obtained by this averaging process were directly comparable to the measurements obtained from the individual exchange runs.

### Results and Discussion

**Thermal Exchange Experiments.**—The results of the thermal exchange experiments are summarized in Table I. Each entry in this table represents a set of at least six fractional exchange measurements.

TABLE I  
THERMAL Ce(III)-Ce(IV) EXCHANGE IN 0.8 N H<sub>2</sub>SO<sub>4</sub>

$T$ (°C.)	$a/v =$ [Ce(III)] $\times 10^3$	$b/v =$ [Ce(IV)] $\times 10^3$	$t_{1/2}$ (sec.)	$k = R_{1/2}/ab$ (l. mole <sup>-1</sup> sec. <sup>-1</sup> )
0.0	9.270	1.068	154	0.435
.0	0.1030	1.068	1380	.428
.0	1.030	1.068	786	.420
.0	1.030	10.68	147	.403
.0	1.030	0.1068	1428	.427
10.0	0.4682	0.4855	630	1.16

It would be interesting to compare these results with the kinetic behavior observed for the thermal exchange reaction in perchloric acid medium. Unfortunately, somewhat conflicting results have been reported for the latter system. Gryder and Dodson,<sup>6</sup> observing an exchange rate dependence first order in [Ce(III)] and between zero and first order in [Ce(IV)], have proposed, in addition to a simple bimolecular exchange path, a second path involving electronic excitation of Ce(III) as the rate-determining step. On the other hand, Duke and Parchen<sup>7</sup> report a first-order dependence upon [Ce(III)] and a [Ce(IV)] dependence between first and second order, presumably due to a second exchange path involving a dimeric Ce(IV) species. No evidence for the occurrence of either of these postulated exchange paths in 0.8 N H<sub>2</sub>SO<sub>4</sub> solution is apparent from the results of Table I, in which the thermal exchange rate constant, calculated on a simple bimolecular basis, exhibits remarkable constancy over hundred-fold variations in concentration of Ce(III) and Ce(IV).

Whereas Ce(III) migrates to the cathode and Ce(IV) migrates to the anode in 1 M sulfuric acid solution,<sup>13</sup> both species exist as cations in perchloric acid media. Considering only the electrostatic interactions involved, the thermal exchange rate of these species might be expected to be orders of magnitude greater in sulfuric acid than in perchloric acid. However, the half-time values in Table I are quite comparable to the values observed for perchloric acid solutions of about the same acidity although somewhat higher ionic strength.

**Induced Exchange Experiments.**—The results of the individual exchange runs are presented in Table II, in sufficiently complete form so that re-interpretation of the raw data according to alternate mechanisms may be attempted. In addition, the  $k_{-1}/k_2$  values resulting from the present inter-

(13) V. J. Linnenbom and A. C. Wahl, THIS JOURNAL, 71, 2589 (1949).

TABLE II  
H<sub>2</sub>O<sub>2</sub>-INDUCED Ce\*(III)-Ce(IV) EXCHANGE IN 0.8 N H<sub>2</sub>SO<sub>4</sub><sup>a</sup>

$a$ (moles) $\times 10^3$	$b$ (moles) $\times 10^3$	$r$ (equiv. sec. <sup>-1</sup> ) $\times 10^3$	$t$ (sec.)	$F_B$ $\times 100$	$k_{-1}/k_2$
10.38	21.28	0.0847	30	2.08	0.136
			60	4.11	.115
			90	7.59	.137
			120	9.83	.109
			150	15.56	.122
10.46	21.36	.0717	150 <sup>b</sup>	16.72	.133
			30	2.74	.161
			60	5.14	.131
			90	8.49	.137
			120	12.10	.134
20.05	20.57	.0845	150	15.91	.124
			150 <sup>b</sup>	15.50	.119
			30	2.70	.129
			60	6.61	.132
			90	9.81	.129
20.03 <sup>c</sup>	20.59	.0775	120	14.83	.128
			150	21.90	.127
			30	2.82	.147
			60	5.08	.115
			90	8.00	.109
10.46 <sup>d</sup>	21.36	.0845	120	12.63	.121
			150	19.41	.133
			30	4.82	.165
			60	9.20	.134
			90	15.11	.150
			120	19.66	.125

<sup>a</sup> Individual exchange run procedure;  $v = 0.05209$  liters;  $s = 4.73 \times 10^{-5}$  liters-sec.<sup>-1</sup>; all runs at 0° except as noted.  
<sup>b</sup> One-half normal stirring speed. <sup>c</sup> "High purity" reagents.  
<sup>d</sup> Temp., 10°.

pretation are summarized graphically in Fig. 1. The results obtained by the consecutive sampling procedure, being somewhat less reliable than the individual exchange measurements, are presented only in the graphical form.

In Fig. 1, all of the  $k_{-1}/k_2$  values obtained through both the consecutive sampling procedure and the individual exchange run procedure are plotted against the [Ce(III)]/[Ce(IV)] ratios prevailing in the exchange solution at the time of sample withdrawal. These values show no significant trends over a rather wide range in [Ce(III)]/[Ce(IV)] ratio. In addition, the results appear to have been unaffected by minor alterations in temperature, rate of stirring and reagent purity. It should also be noted that the rate of hydrogen peroxide addition, which was varied by a threefold factor in the case of the consecutively sampled experiments, appears to exert no appreciable influence upon the results. An average value of  $k_{-1}/k_2 = 0.136$  with a standard deviation of  $\pm 0.019$  is calculated from these 41 independent observations. Considering only the 22 individual exchange run measurements at 0°, an average value of  $k_{-1}/k_2 = 0.129 \pm 0.013$  is obtained.

Consideration must be given to a number of alternative mechanisms through which this induced exchange reaction might possibly occur. One such exchange path, involving anionic catalysis of the bimolecular electron exchange reaction, appears to be particularly plausible. Assuming the anions to be derived from the ionization of hydrogen peroxide

or of hydroperoxo radical, it may be shown that an induced exchange rate proportional to the cerous ion concentration should probably result. However, rather poor agreement results when this rate law is applied in the standard manner<sup>4</sup> in an attempt to fit the observed  $F_B$  values. From this, and from similar consideration of other simple exchange mechanisms, the present interpretation, represented by eq. 1, 2 and 5, is concluded to be the one most consistent with the observed data.

This purely mathematical treatment of the exchange results does not, of course, uniquely determine the chemical identity of the intermediate species responsible for the induced exchange reaction. However, hydroperoxo radical is probably to be favored for this position, since it does appear to be capable both of oxidizing cerous ion and of reducing ceric ion, without interfering in the stoichiometry of the over-all reduction process.

Since the over-all reduction of ceric ion by hydrogen peroxide appears to take place very rapidly, the question may be raised as to whether or not the rate of stirring during the hydrogen peroxide addition was sufficient to insure uniform concentrations of reactants and intermediates throughout the exchange solution. The results of the two experiments performed at reduced stirring speed would seem to indicate that mixing was indeed adequate.

From the observed temperature independence of the rate constant ratio  $k_{-1}/k_2$ , it may be concluded that the difference in activation energy between reaction steps 2 and 5 is small. Since the activation energy for reaction 2 is probably small (very rapid reaction) and since both reactions proceed at about equal rates, this result is not entirely unexpected.

At equal concentrations of cerous and ceric ions, the rate of reaction step 2 is seen to be approximately eight times that of reaction step 5. From the estimated<sup>3</sup> potentials of the half-reactions 3 and 4, it may further be concluded that the rate constants  $k_1$  and  $k_{-1}$  are of roughly the same order of magnitude. Care must therefore be exercised in attempting to simplify the kinetics of the over-all reduction mechanism by assuming any single stage to be rate determining.

Cahill and Taube,<sup>14</sup> using heavy oxygen tracer, have shown that the oxygen gas liberated by the  $H_2O_2$ -Ce(IV) reaction in water solution is derived exclusively from the hydrogen peroxide molecule, no detectable amounts of oxygen having been found to originate from the solvent. Baxendale<sup>15</sup> has reported the oxidation of hydrogen peroxide by Ce(IV) to be complete within a few seconds at room temperature, even at micromolar concentrations, and has concluded that the reaction proceeds through two consecutive single electron transfer steps. The results of the present study are fully consistent with both of these previous investigations, as well as with the stoichiometric measurements of Baer and Stein.<sup>2</sup>

**Induced Exchange Experiments with Additives Present.**—A number of hydrogen peroxide-induced exchange runs were performed in the presence

(14) A. E. Cahill and H. Taube, *THIS JOURNAL*, **74**, 2312 (1952).

(15) J. H. Baxendale, *J. Chem. Soc. (London)*, Spec. Publ. No. 1, 40 (1954).

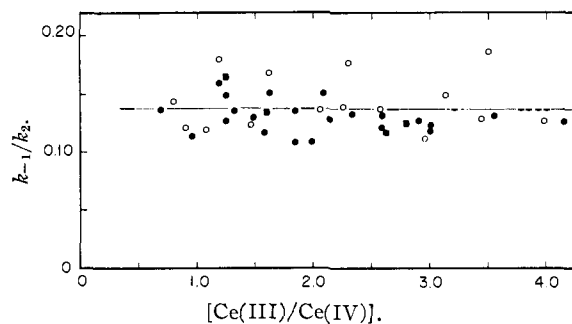
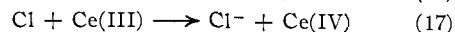
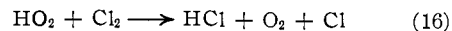
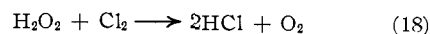


Fig. 1.— $H_2O_2$ -induced Ce\*(III)-Ce(IV) exchange in 0.8  $N$   $H_2SO_4$ : O,  $0^\circ$  results obtained by the consecutive sampling procedure; ●,  $0^\circ$  results obtained by the individual run procedure, including two runs at one-half normal stirring speed and five runs with "high purity" reagents; ■,  $10^\circ$  results obtained by the individual run procedure.

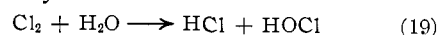
of dissolved silver ions, thallose ions, ferric ions and chlorine gas, in order to determine the efficiency of these additives as scavengers for  $HO_2$  radical. In the case of the  $Ag^+$ ,  $Tl^+$  and  $Fe^{+++}$  additives, each present at concentrations about equal to the concentration of cerous ion in the exchange solutions, no significant alteration was noted in the ceric ion reduction stoichiometry, in the thermal exchange rate, or in the observed amount of induced exchange. Presumably, none of these additives react with hydroperoxo radical at a sufficiently rapid rate to provide competition with reactions 2 and 5. The results obtained with dissolved chlorine present are more difficult to interpret. In this case, considerably less than the stoichiometric amount of ceric ion reduction was found to have occurred, while a slight increase in the thermal exchange rate was noted. A somewhat reduced amount of induced exchange was actually observed, however, the alteration was proportionately much smaller than in the case of the ceric reduction stoichiometry, so that the ratio of radioceric ion production to over-all ceric ion reduction was considerably enhanced by the presence of chlorine. It appears quite likely that a reaction sequence of the type



may account for at least part of the observed decrease in ceric ion reduction stoichiometry as well as the relative increase in radioceric ion production. However, the measurements obtained from this system cannot be regarded as really conclusive evidence for the occurrence of a reaction between chlorine and hydroperoxo radical, for the system is greatly complicated by other reactions such as the direct reaction between hydrogen peroxide and chlorine



and the hydrolysis reaction



**Acknowledgment.**—The authors wish to thank Prof. Henry Taube and Dr. T. W. Newton for several interesting and helpful discussions of this problem.

LOS ALAMOS, NEW MEXICO