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Kinetics of the exchange reaction between two oxidation states of cerium

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KINETICS OF THE EXCHANGE REACTION BETWEEN
TWO OXIDATION STATES OF CERIUM

by

Frank R. Parchen, Jr.

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

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INTRODUCTION

One of the most extensive chemical applications of the artificial radioelements as indicators is in the study of exchange reactions. An isotopic exchange reaction is a chemical reaction in which the atoms of a given element interchange between two or more forms of the element.

Generally, in radioactive exchange studies the atoms of an element, in one of its valence forms or types of chemical combination, are labeled by admixture with some radioactive isotope of the element in the same valence form or type of chemical combination. To this system is added the element in another state of valence or type of chemical combination, containing none of the radioactive isotope. The exchange reaction is then allowed to proceed for a known length of time, the reactants separated by using a suitable analytical technique, the fractions assayed, and the rate of appearance of the radioisotope in the form of the element formerly free of radiotracer determined.

The presence of radioactivity in the second chemical form shows that an effective exchange of atoms between the two different forms has taken place and the rate of appearance of activity in the second chemical form gives a measure of the exchange rate. Complete exchange is attained when

the radioactivity has distributed itself between the two chemical forms in the same ratio as the amounts of the element in the two forms, that is, when the specific activities are the same.

In all exchange reactions, regardless of the number of atomic species participating, the rate varies with time according to the law for first-order reversible reactions, since there is no change in concentration of the reactants. The rate of exchange reactions may, therefore, conveniently be expressed in terms of the half-time, the time necessary for half of the activity to be lost from its original chemical form. It is generally assumed in isotopic exchange studies that the isotopes are chemically identical.

Exchange reactions can provide useful information concerning the nature of chemical linkages, the strength and reactivity of chemical bonds and the effect of solvents on these properties, the extent and nature of solid surfaces, and the reversibility of oxidation-reduction couples. They often have a unique application to the study of reaction mechanisms and the mechanisms of catalysis. In addition, exchange reactions often offer an excellent and convenient means for the introduction of radioactive atoms into compounds.

The present research was undertaken to study the phenomenon of electron transfer occurring in oxidation-reduction reactions. It was hoped the results might give some insight into oxidation-reduction reactions in general. In particular, the cerium(III)-cerium(IV) system, in perchloric acid solution, was chosen and the work carried out with this system was primarily concerned with extending previous investigations and to elucidate further, if possible, the nature of the ionic species existing in the solution, as well as the factors determining the rate of exchange.

LITERATURE REVIEW

In general, oxidation-reduction reactions can be defined as chemical reactions in which electrons are donated to an oxidizing agent by a reducing agent. On this basis, the transfer of electrons between two oxidation states of a single element can be considered to be a very simple form of oxidation and reduction. Such reactions are commonly known as electronic exchange reactions and the possibility of studying the rates of such exchange reactions between various oxidation states of the same element was recognized soon after the discovery of radioactivity (1). It has only been recently, however, that systematic experiments have been carried out to measure the exchange rates and determine the kinetics of such reactions.

This literature review will include not only information concerning the cerium(III)-cerium(IV) exchange reaction but also information concerning certain other exchange reactions between cations, that have been observed to be catalyzed by simple anionic complexing agents. The reviewed exchange reactions are considered to be particularly pertinent to the present investigation.

Cerium(III)-Cerium(IV) Exchange Reaction

Although the cerium(III)-cerium(IV) exchange reaction has been studied under various experimental conditions, the mechanism for the exchange reaction has not been completely formulated. Seiler, Rubinson and Edwards (2) employing a chemical precipitation technique to separate the reactants found the exchange rate to be very rapid and complete.

Linnenbom and Wahl (3), employing an electrical migration method to partially separate the reactants, reported that complete exchange occurred during the separation time. Gryder and Dodson (4) also studied the exchange reaction using a diffusion technique, and they found that complete exchange occurred within two hours after mixing of the reactants.

Gryder and Dodson (4,5), in an attempt to study further the exchange reaction, devised a chemical separation technique involving the extraction of the cerium(IV) ion from a nitric acid solution with diethyl ether. Employing this separation technique, they found the exchange rate in nitric and perchloric acid solutions to be measurable and of the order of minutes.

In nitric acid solutions, they found the dependence of the rate of exchange to be first order in both cerium(III)

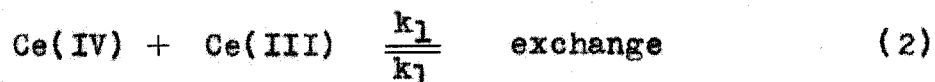
and cerium(IV) concentrations, but the rate appeared to be dependent on the reciprocal hydrogen ion concentration squared. They found the following empirical rate equation to be consistent with their data:

$$R = [\text{Ce(III)}] [\text{Ce(IV)}] \left(k + \frac{k'}{[\text{H}^+]^2} \right) \quad (1)$$

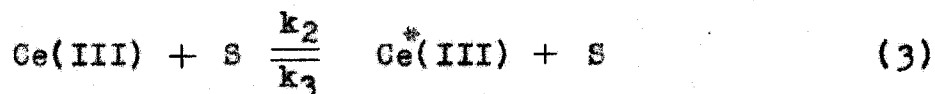
They interpreted the dependence of the exchange rate on the hydrogen ion concentration as indicating the existence of an acid dependent path and an acid independent path by which exchange occurred, and stated that it appeared that the acid dependent path was between an unhydrolyzed species and a substance containing two hydroxyl groups or their equivalent or between two singly hydrolyzed species. They also offered an alternative explanation that a polymeric form of cerium(IV) involving an oxygen bridge might become important as the acidity was decreased. They did not formulate a mechanism for the exchange reaction nor did they speculate any further on the species existing in the nitric acid solution. Moreover, they did not study the dependence of the exchange rate on the nitrate ion concentration. The apparent energies of activation were determined, in the nitric acid system, to be 7.7 kcal./mole for the acid independent path and 24.0 kcal./mole for the acid dependent path.

In perchloric acid, Gryder and Dodson (5) found the dependence of the over-all exchange rate to be first order in the cerium(III) concentration, but an order between zero and one in cerium(IV) concentration, dependent upon the cerium(IV) concentration and on the nature of the medium. They also observed that the rate was a linear function of the reciprocal of the hydrogen ion concentration, but did not study in sufficient detail the dependence of the rate of exchange on the acid concentration to permit an unequivocal interpretation of their results.

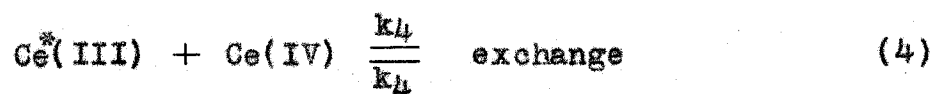
On the basis of their data, Gryder and Dodson (5,6) postulated the following mechanism for the exchange reaction in perchloric acid solutions:



in competition with



where $\text{Ce}^*(\text{III})$ is an excited electronic state of cerium(III) and S is any substance in the solution which is capable of exciting the cerium(III) ion upon collision, and



where k_4 is much greater than k_3 . This leads to the rate equation:

$$R = k [\text{Ce}(\text{III})] + k' [\text{Ce}(\text{III})] [\text{Ce}(\text{IV})] \quad (5)$$

which they found to be consistent with the experimentally determined rate equation.

There are some spectral data (7) and theoretical considerations (8) which indicate the existence of an excited electronic state of cerium(III). Gryder and Dodson (5,6) using a simple Boltzman calculation determined that 10^{-3} per cent of the cerium(III) concentration existed in an excited state at room temperature.

No further attempt was made to elucidate the ionic species existing in perchloric acid solutions. The apparent energies of activation were determined to be 19.4 kcal./mole for the cerium(IV) independent path and 16.8 kcal./mole for the cerium(IV) dependent path.

Hornig and Libby (9) investigated the catalysis of the exchange reaction by fluoride. They found a first order fluoride catalysis reaction existed and, on this

basis, concluded that either cerium(III) or cerium(IV) must form a relatively stable bond with fluoride ion.

They determined the apparent activation energy of the exchange reaction to be 11.7 kcal./mole. They also observed that chloride catalysed the exchange reaction, but to a much smaller extent than fluoride.

In summary, it has been shown that the cerium(III)-cerium(IV) exchange reaction is catalyzed by fluoride, chloride, and hydroxide. In nitric acid, the dependence of the rate of exchange on the cerium(III) and cerium(IV) concentrations has been shown to be first order, while, in perchloric acid, the dependence of the rate of exchange has been shown to be first order with respect to the cerium(III) concentration, but with respect to the cerium(IV) concentration an order between zero and one. Mechanism for the exchange reaction has not been formulated unequivocally, nor have the different species existing in the reaction solutions been completely determined.

Iron(II)-Iron(III) Exchange Reaction

The exchange reaction between iron(II) and iron(III) in acid solution has been the subject of many investigations. Studies (10, 11, 12, 13) employing a diffusion technique to

separate partially the reacting species produced two sets of entirely different and conflicting results. Van Alten and Rice (10) and Kierstead (11) observed half-times of the order of days for the exchange reaction. According to the results of Van Alten and Rice (10), iron(II) diffuses about half as fast as iron(III). Kierstead's results (11), on the other hand, indicate that iron(II) diffuses about three times faster than iron(III).

Linnenbom and Wahl (12) and Betts, Gilmour and Leigh (13) employing the same diffusion technique found that exchange was complete in the hour or so required to effect a partial separation.

Betts, Gilmour and Leigh found that iron(II) diffuses about twenty per cent faster than iron(III). Linnenbom and Wahl obtained data consistent with this later value.

Dodson (14) devised a chemical separation technique, involving the use of dipyridyl, to facilitate separation of the reacting species. Silverman and Dodson (15), using a modification of the chemical separation technique, found the over-all rate of the exchange reaction to be second-order, presumably, first order in iron(II) and first order in total iron(III).

They found the over-all rate constant of the exchange reaction in perchloric acid solution to be a linear function

of the reciprocal of the hydrogen ion concentration. On this basis, the acid dependence was explained by assuming iron(III) to be appreciably hydrolyzed. The exchange reaction then was postulated to proceed through two parallel paths, one independent of the acid concentration and the other involving a hydrolyzed species, probably FeOH^{+2} , the concentration of which would be inversely proportional to the acid concentration.

Silverman and Dodson also found that chloride catalyzed the exchange reaction, but not markedly. They found activation energies of 9.9 kcal./mole for the reaction between the unhydrolyzed ions and 7.4 kcal./mole for the acid-dependent reaction.

Hudis and Wahl (16) observed catalysis of the exchange reaction by fluoride. They interpreted their data in terms of exchange reactions between iron(II) and iron(III) complexes containing one, two, or three fluoride ions.

Europium(II)-Europium(III) Exchange Reaction

Meier and Garner (17, 18) found the exchange reaction of europium(II)-europium(III), in aqueous hydrochloric acid solution, to be first order each with respect to the concentrations of europium(II), europium(III) and chloride.

This, they concluded, indicated that the activated state included a monochloro-complexed europium species. They also found that variation of the hydrogen ion concentration showed little affect on the exchange rate, and they interpreted this as suggesting that hydrolyzed species are of little importance in the rate-determining step. The rate-determining step was proposed as being the exchange between hydrated europium(II) and a hydrated monochloro-complex of europium(III).

Meier and Garner determined the experimental activation energy to be 20.8 kcal./mole. The apparent activation energy includes an unknown contribution from the heat of formation of the chloro-complexed ion and the true activation energy would presumably be appreciably smaller after correction for this factor. Meier and Garner found that neither artificial light nor glass wool catalyzed the exchange reaction.

Antimony(III)-Antimony(V) Exchange Reaction

Bonner (19) studied the kinetics of the exchange reaction between antimony(III) and antimony(V) in hydrochloric acid solutions. He found, in 6 f. hydrochloric acid, half-times in the neighborhood of sixty hours, and

observed the rate to depend critically on the hydrochloric acid concentration.

The following empirical rate expression was found to describe the rate of the exchange reaction:

$$R_{25^{\circ}\text{C}} = 8.8 \times 10^{-11} [\text{Sb(III)}]^{0.6} [\text{Sb(V)}]^{1.1} [\text{H}^+]^4 [\text{Cl}^-]^9 \quad (6)$$

Bonner made no attempt to formulate a mechanism for the exchange reaction due to the general lack of accurate knowledge concerning the nature of the ionic species existing in solutions of antimony in hydrochloric acid.

He determined the experimental activation energy to be 27 kcal./mole, and also observed that glass beads did not catalyze the exchange reaction.

Thallium(I)-Thallium(III) Exchange Reaction

Two groups of workers, Harbottle and Dodson (20) and Prestwood and Wahl (21), simultaneously reported on the kinetics of the thallium(I)-thallium(III) exchange reaction in acid solutions. Further work by both groups (20, 22) found the rate of the exchange reaction to be dependent on the first power of both the thallium(I) and thallium(III) concentrations. They also found the rate, in perchloric

acid solutions, decreased as the hydrogen ion concentration was increased.

On the basis of this Prestwood and Wahl (21) assumed that the exchange reaction proceeded via two independent paths, two electrons being transferred slowly from the thallium(I) ion to the thallium(III) ion and the more rapid exchange being between the thallium(I) ion and the hydrolyzed thallium(III) ion, presumably $TlOH^{+2}$.

Harbottle and Dodson (20) found their data to be consistent with the assumption that two thallium(III) species (e.g., Tl^{+3} and $TlOH^{+2}$) were present, and that only the more highly hydrolyzed form accepted electrons from the thallium(I) ion.

Both nitrate (22) and chloride (20) were observed to catalyze the exchange reaction, chloride being the more effective. It was observed (20) that at low concentrations, approximately 0.01 f., chloride inhibited the reaction. Prestwood and Wahl (22) also observed that platinum black catalyzed the exchange, but that silica gel did not.

Prestwood and Wahl (22) determined the experimental activation energies to be 17.6 kcal./mole for the hydrogen ion independent path and 10.3 kcal./mole for the hydrogen ion dependent path.

METHODS AND MATERIALS

Cerium Tracer

The radioactive cerium(III) (Ce^{144} having a 275 day half-life) was obtained from the Oak Ridge National Laboratory on allocation from the U. S. Atomic Energy Commission through the Institute for Atomic Research, Iowa State College. The radio-cerium was incorporated in the cerium(III) valence state and measurements made on the transfer of radioactivity to the cerium(IV) state.

The active cerium was purified (23, 24) by precipitation of the fluorides of cerium and lanthanum in the presence of zirconium holdback carrier. The fluorides were dissolved in a solution of boric and nitric acids, oxidized with sodium bromate, and cerium(IV) iodate precipitated. The precipitate was dissolved with nitric acid and hydrogen peroxide, and cerium(IV) iodate reprecipitated after oxidation with sodium bromate. The latter step was repeated twice. The precipitate was again dissolved with nitric acid and hydrogen peroxide, zirconium carrier added, and then zirconium iodate precipitated in the presence of cerium(III) ion. Cerium(III) hydroxide was then precipitated by the addition of sodium hydroxide. The cerium(III)

hydroxide precipitate was dissolved with hydrochloric acid, sulfurous acid added to reduce the iodate to iodide, and cerium(III) reprecipitated with ammonium hydroxide. Finally, this precipitate was dissolved with hydrochloric acid and cerium(III) oxalate precipitated by the addition of oxalic acid. The cerium(III) oxalate was dissolved with perchloric acid and the solution fumed to destroy the oxalate ion. In this process some of the cerium(III) may have been oxidized, therefore, a drop of hydrogen peroxide was added and this was decomposed by heating the solution. The resulting solution was used as the stock reagent for introducing activity into the reaction materials.

Measurement of Radioactivity

All radioassays were made on solutions, using a Nuclear model D-52 dipping Geiger tube with Nuclear Instrument and Chemical Corporation scalers either model 165 or model 183.

The counting tube was held vertically in a test tube of such a size that 20 ml. of solution exactly filled the annular space. The test tube was modified by attachment of a number 2 stopcock at the bottom. This facilitated emptying the test tube and allowed for permanent positioning of the counter tube with respect to the test tube so as to

give reproducible geometry. The counting tube assembly was housed in a light-tight box. The background count for this tube was approximately 45 c.p.m. The input voltages of the scaling units were held constant with a Sorensen model 1750 voltage regulator.

Since the solutions to be counted were of constant chemical composition, absorption and scattering corrections were unnecessary. All the counting rates were below 1000 c.p.m., thus corrections for coincidence were unnecessary. In all cases the samples were allowed to stand at least three hours before counting to permit the 17-minute praseodymium daughter to grow into equilibrium concentration. Each sample was counted at least in duplicate and sometimes in triplicate to check the reproducibility of geometry and each count was for a time sufficient to reduce the statistical counting error to 1 per cent or less standard deviation. The fraction of exchange was obtained by comparing the observed count with the experimentally determined counting rate of an "infinite time" sample.

Chemicals

Reagent grade cerium(III) perchlorate was obtained from the G. Frederick Smith Chemical Company and was used

without further purification. The cerium(IV) perchlorate used was obtained from two sources. Cerium(IV) perchlorate in 6 f. perchloric acid was obtained from the G. Frederick Smith Chemical Company and was used without further purification. Cerium(IV) perchlorate also was prepared in this laboratory by electrolytic oxidation of pure cerium(III) perchlorate. Cerium(III) chloride was dissolved in dilute perchloric acid and the cerium(III) ion precipitated with oxalate. The insoluble cerium(III) oxalate was washed several times with dilute perchloric acid. The cerium(III) oxalate precipitate was then boiled in excess 72 percent perchloric acid to oxidize the oxalate ion to carbon dioxide. The resulting solution was evaporated to near dryness to expel any chloride formed in the oxidation of oxalate ion. The resulting solution was diluted and cerium(IV) perchlorate was prepared by electrolytic oxidation. No difference was noted in the rate of the exchange reaction when the two different cerium(IV) perchlorates were employed. G. Frederick Smith Chemical Company vacuum distilled 70 percent perchloric acid was used directly. The acid was analyzed by titration with standard alkali. Commercial Solvents Corporation tri-n-butyl phosphate was employed in the extraction technique. All other chemicals were standard chemically pure reagents.

The water used in this investigation was redistilled from an all-glass still and the nitrogen used was scavenged of oxygen by passage through a vanadous sulfate solution (25).

Separation of Reactants

The separation procedure used was essentially that of Gryder and Dodson (4, 5), the only change being that tri-n-butyl phosphate (26) was substituted for diethyl ether in the extraction of cerium(IV). An aliquot of the reaction mixture was delivered into a 250 ml. separatory funnel containing 50 ml. of a solution 1.0 f. each in nitric acid and ammonium nitrate. Then an equal volume, 70 ml., of tri-n-butyl phosphate was added, extraction of the cerium(IV) taking place. After separation, the solvent layer was scrubbed one or two times with 70 ml. of a solution 1.0 g. each in nitric acid and ammonium nitrate. The cerium(IV) was quantitatively recovered from the tri-n-butyl phosphate by re-extraction with water after reduction of cerium(IV) to cerium(III) by hydrogen peroxide. This second aqueous phase was diluted to a constant volume of 100 ml. for counting. It was found that the amount of cerium(III)

extracted was insignificant, and that the extraction of cerium(IV) nitrate was essentially complete.

Experimental Procedure

Appropriate volumes of all component solutions of a reaction mixture except the active cerium(III) solution, which in all cases was less than a few per cent of the total volume, were added to a 500 ml. low actinic glass erlenmeyer flask, the exchange vessel. The reaction solution was allowed to reach temperature equilibrium, as were all solutions used in the exchange run, by being placed in a large refrigerated constant temperature bath, the maximum temperature variation of which was $\pm 0.05^{\circ}$.

The exchange was started by the rapid addition of tagged cerium(III) perchlorate at room temperature to the exchange vessel. The exchange solution was agitated by removal and re-injection of an aliquot and further by gentle rotation of the reaction vessel. Approximately 20 ml. aliquots of the exchange solutions were removed from the reaction vessel at timed intervals. Separation of cerium(IV) from cerium(III) was carried out as previously described. In each experimental run samples were taken at times spaced evenly over two to three half-times.

Two "infinite-time" samples, the specific activity corresponding to complete exchange, were taken in each run. In each experimental run, after the six timed samples had been taken, four aliquots of the exchange mixture were collected, and analyses were performed to determine the total cerium and cerium(IV) concentrations. Duplicate analyses were run for each and the results averaged.

Cerium Analyses

Cerium(III) and cerium(IV) concentrations were determined independently for each exchange run. An aliquot of the reaction mixture was taken, added to 75 ml. of a 13.3 per cent sulfuric acid solution, and the cerium(IV) concentration determined directly by titration with standard iron(II) solution.

In order to obtain the total cerium concentration another aliquot of the reaction mixture was taken and 10 ml. of concentrated sulfuric acid added. The solution was diluted to 200 ml. Five ml. of a solution containing 2.5 grams of silver nitrate per liter, and 5 grams of solid ammonium persulfate were added. This solution was boiled for 10 minutes, cooled to room temperature and a second titration made using standard iron(II) solution. The

cerium(III) concentrations were determined as the differences between the cerium(IV) and total cerium concentrations. The standard iron(II) sulfate solution employed was standardized using ferrous ethylenediamine sulfate.

Errors

Slight errors exist in the determined concentrations because corrections were not made for volume changes that occurred with temperature changes and because of the assumption that solution volumes were additive. Also in experimental runs where the cerium(IV) concentration was relatively high compared to the cerium(III) concentration it was necessary in performing the calculation to subtract two numbers of approximately the same magnitude to obtain the cerium(III) concentration.

The temperature of the exchange solution fluctuated every time a sample was taken, although the temperature of the bath was constant to $\pm 0.05^\circ$. Even though the exchange reactions were fairly rapid, half-times of 5 to 60 min., errors in the rate constants due to inaccuracies in timing the reactions were probably no more than a few per cent. This was because aliquots of the exchange mixture were separated in a reproducible way so that although the

exact time of separation might have been uncertain by five to ten seconds, the time interval between the separation of any two aliquots was known to within a few seconds. The time intervals between samples affected the slope of the exchange curve and therefore the measured rate and rate constants. Errors in the absolute time of separation, or the zero time, merely shifted the exchange curve affecting the apparent zero-time exchange but not the slope.

One principal source of error was the statistical fluctuations in the counting rate. As noted previously all samples were counted sufficiently to reduce this error to one per cent or less.

EXPERIMENTAL RESULTS

The following reaction was under study in this investigation:



The asterisks indicate radioactive atoms. For this particular reaction, the exponential exchange law (27, 28) in its logarithmic form is:

$$Rt = - \frac{[\text{Ce}(\text{III})] [\text{Ce}(\text{IV})]}{[\text{Ce}(\text{III})] + [\text{Ce}(\text{IV})]} \ln (1-F) \quad (8)$$

The exchange rate, R , is the rate at which cerium(III) becomes cerium(IV) and at which cerium(IV) becomes cerium(III). R is a constant when cerium(III) and cerium(IV) are uniformly dispersed in the same phase and all conditions, except the distribution of the radioactive atoms, are held constant. Further, if any of the reacting chemical species contain more than one cerium atom, the atoms must be chemically equivalent. Bracketed quantities indicate gross concentrations expressed in gram atoms per liter of solution, and t is the time the exchange of radioactive atoms is followed, that is, the time after addition of tagged cerium(III)

to the rest of the reaction mixture. The fraction exchange, F , is a measure of the extent of the exchange of radioactive atoms and it approaches an equilibrium value of one.

Since cerium(IV) was initially inactive, F may be expressed as:

$$F = \frac{S(\text{IV})}{S_{\infty}} = \frac{S(\text{III}) - S(\text{III})_0}{S_{\infty} - S(\text{IV})_0} \quad (9)$$

where the specific activity, S , is defined as the ratio of radioactive to total cerium atoms in the indicated oxidation state or chemical fraction, subscripts (III) and (IV) referring to the oxidation states of cerium, and subscripts 0 and ∞ referring to the time the specific activity was measured. As can be seen from equation 8, the quantity $(I-F)$ should decrease exponentially with respect to time, so that if 50 per cent exchange occurred in time t , 75 per cent exchange would occur in time $2t$, etc., and a semi-logarithmic plot of $(I-F)$ against time should be a straight line with an ordinate value of one at zero time regardless of the reaction mechanism. Figure 1 shows three typical exchange curves.

If all or some of the cerium(IV) can be separated free of cerium(III) and if no exchange occurs during this separation, then the specific activity of the cerium(IV)

Figure 1. Typical exchange curves as semi-logarithmic plots of (1-Fraction Exchange) against time at concentrations

Curve A: 3.92 mf. $\text{Ce}(\text{ClO}_4)_3$, 0.770 mf.

$\text{Ce}(\text{ClO}_4)_4$, 5.04 f. HClO_4 ,

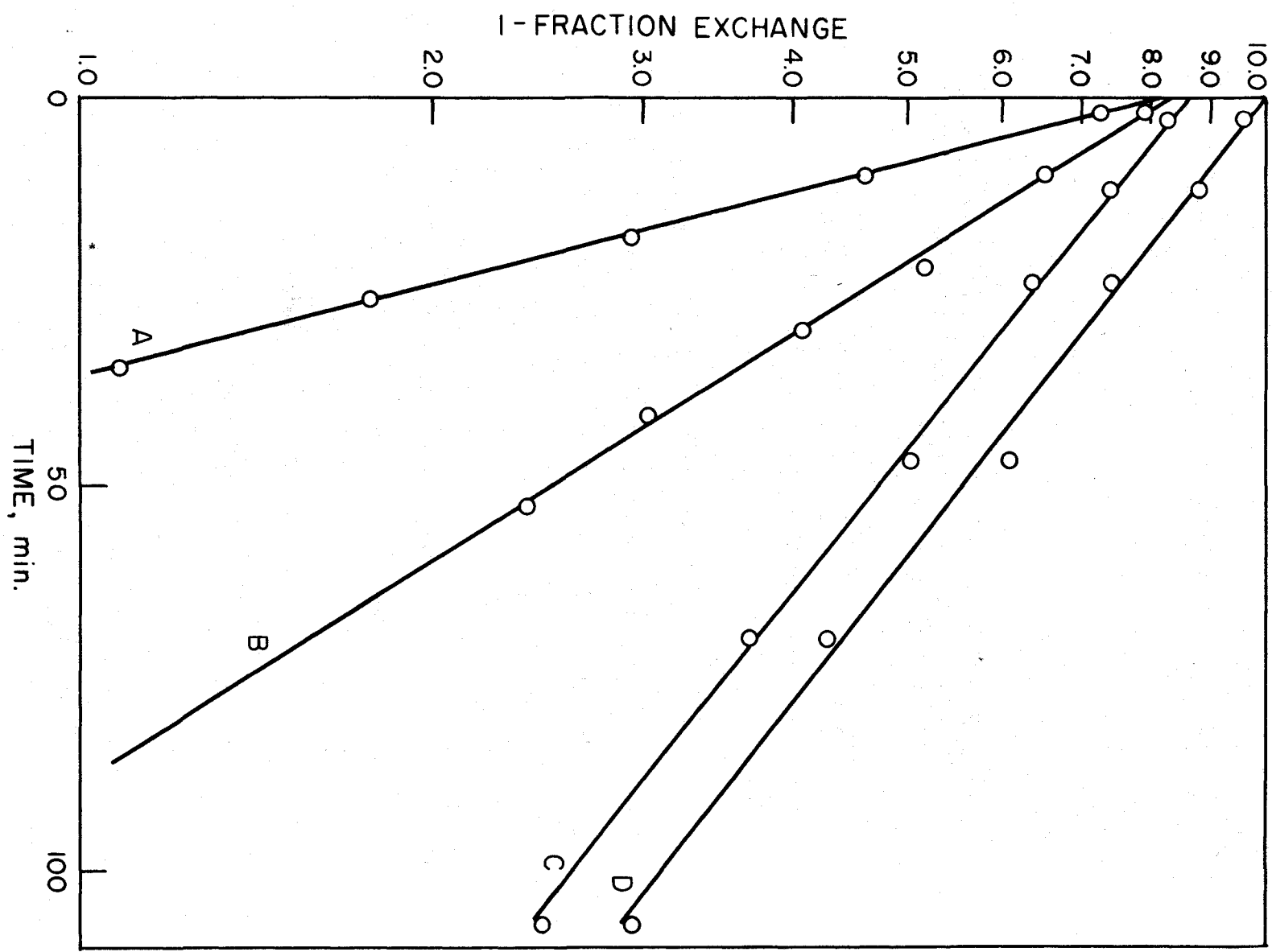
$\mu = 5.85$

Curve B: 2.95 mf. $\text{Ce}(\text{ClO}_4)_3$, 0.550 mf.

$\text{Ce}(\text{ClO}_4)_4$, 5.85 f. HClO_4

Curve C and D: 1.53 mf. $\text{Ce}(\text{ClO}_4)_3$, 1.28 mf.

$\text{Ce}(\text{ClO}_4)_4$, 6.0 f. HClO_4



fraction is equal to the specific activity of the cerium(IV) in the reaction mixture just prior to the separation, and this may be used to calculate the fraction exchange that occurred in solution. However, if the cerium(IV) fraction contains some cerium(III) and if exchange occurs during the separation, the specific activity of the cerium(IV) fraction will not be equal to the specific activity of the cerium(IV) in solution prior to the separation. As a matter of fact, the specific activity of the cerium(IV) will be some function of the amounts of cerium(IV) and cerium(III) in the separated fractions, the specific activities of cerium(III) and cerium(IV) prior to separation, and the extent of the separation-induced exchange. The same thing applies to the cerium(III) specific activity.

It has been shown (22, 28) that when separation-induced exchange and the incomplete separation effects are reproducible that the following relationships are true:

$$F = \frac{S - S_0}{S_\infty - S_0} = \frac{F' - F'_0}{1 - F'_0} \quad (10)$$

where S and S_0 are the specific activities of one chemical fraction, containing essentially one of the exchange

reactants separated at time t and time zero. Combining equations 8 and 10, gives:

$$\ln (1-F') = - \frac{[\text{Ce(III)}] + [\text{Ce(IV)}]}{[\text{Ce(III)}][\text{Ce(IV)}]} Rt + \ln (1-F'_0) \quad (11)$$

$$\ln (S_\infty - S) = - \frac{[\text{Ce(III)}] + [\text{Ce(IV)}]}{[\text{Ce(III)}][\text{Ce(IV)}]} Rt + \ln (S_\infty - S_0) \quad (12)$$

Semi-logarithmic plots of $(1-F')$ against time and $(S_\infty - S)$ against time should be straight lines with intercepts of $(1-F'_0)$ and $(S_\infty - S_0)$ at time zero. The slopes and half-values of these plots will be the same as those of a semi-logarithmic plot of $(1-F)$ against time. Curve D, see Figure 1, is a plot of $(1-F)$ against time, F having been calculated using equation 10 from F' and F'_0 values obtained from curve C.

The uncertainty in the time a reaction was started relative to the times of separation may in part be responsible for some of the apparent zero-time exchange. A very rigid experimental procedure was followed and in all cases the apparent zero-time exchange was reproducible for a given run and therefore would not affect the slope of the exchange curve.

When 50 per cent exchange has occurred, $F = 0.5$, $(1-F) = 0.5$ and $t = t_{\frac{1}{2}}$ by definition. At this point:

$$R = \frac{[\text{Ce(III)}] [\text{Ce(IV)}]}{[\text{Ce(III)}] + [\text{Ce(IV)}]} \times \frac{\ln 2}{t_{\frac{1}{2}}} \quad (13)$$

and since in any given experiment the cerium(III) and cerium(IV) concentrations are known, and $t_{\frac{1}{2}}$ can be obtained from the plot of $\log(1-F)$ against time, it is then possible to calculate the value of R , the rate of exchange, for each experiment.

The specific activity values used in calculations of the fraction of exchange were in units of counts per min./20 ml. of solution counted and not the ratio of radioactive atoms to total cerium atoms as defined. However, since ratios of specific activities are always used in these calculations, this substitution was justified provided the counting efficiencies and compositions of all the samples from a given run were the same. The agreement of the data with the predicted exchange law was a good indication that this procedure was justified.

The following subsections will contain the experimental results only, while specific discussion of these results will be found in the subsequent section.

Heterogeneous Catalysis

A series of experiments were devised to study the possibility of heterogeneous catalysis of the exchange. Exchange reactions were run with the reaction solution 2.23 mf. $\text{Ce}(\text{ClO}_4)_3$, 3.83 mf. $\text{Ce}(\text{ClO}_4)_4$ and 6 f. HClO_4 . An experiment was carried out with the reaction vessel packed with soft glass beads. The beads were carefully cleaned with boiling nitric acid and it was calculated that they increased the surface exposed to the solution by a factor of at least three. Similar experiments were also run in the presence of a 24 inch length of 24 gauge, 0.02 inch diameter, platinum wire and in the presence of a circular piece, 5 inch diameter, of platinum foil. The half-times for the exchange reactions were in the presence of glass beads 26.7 minutes, in the presence of platinum wire 26.7 minutes, and in the presence of platinum foil 30.5 minutes. These values may be compared with the half-time of 26.2 minutes obtained under the same conditions in the absence of solid catalysts.

An exchange reaction, the reaction solution 2.05 mf. $\text{Ce}(\text{ClO}_4)_3$, 1.79 mf. $\text{Ce}(\text{ClO}_4)_4$ and 6 f. HClO_4 , was run in the presence of a 1 inch by 0.5 inch piece of platinized platinum. The half-time of the exchange in the presence

of the platinum black was 17.7 minutes compared with a half-time of 18.9 minutes obtained under identical conditions in the absence of platinum black.

Effect of Surface Material, Light and Molecular Oxygen

An exchange reaction, the reaction solution 2.23 mf. $\text{Ce}(\text{ClO}_4)_3$, 3.83 mf. $\text{Ce}(\text{ClO}_4)_4$ and 6 f. HClO_4 , was run using a one pint polyethylene bottle as the reaction vessel instead of the usual 500 ml. erlenmeyer flask. A half-time of 26.5 minutes was obtained using the polyethylene reaction vessel compared to a half-time of 26.2 minutes obtained under the same conditions using the usual reaction vessel.

The effect of daylight on the exchange was briefly studied. Exchange reactions, the reaction mixture 1.72 mf. $\text{Ce}(\text{ClO}_4)_3$, 1.83 mf. $\text{Ce}(\text{ClO}_4)_4$ and 6 f. HClO_4 , were run using as reaction vessels, a 500 ml. erlenmeyer flask made of clear glass and one made of low actinic glass. Half-times of 9.3 and 8.2 minutes were obtained when the clear glass reaction vessel was used compared to half-times of 7.5 and 8.1 minutes when the low actinic glass reaction vessel was used.

No effect was observed on the exchange rate when half of the separatory funnels used in an exchange reaction

run were made of low actinic glass and the other half were made of clear glass.

A series of experiments was performed to ascertain whether or not molecular oxygen was a factor in the exchange. Two experiments, reaction mixture 1.19 mf. $\text{Ce}(\text{ClO}_4)_3$, 1.74 mf. $\text{Ce}(\text{ClO}_4)_4$ and 6 f. HClO_4 , were carried out with nitrogen bubbling through the reaction mixture. All reagents, except the tagged cerium(III), were added to the reaction vessel and nitrogen was bubbled through the solution for approximately ten hours prior to starting the experimental run. Half-times of 44.0 and 46.8 minutes were obtained compared to a half-time of 49.5 minutes for the control run made under identical conditions, except for the absence of bubbling nitrogen.

Dependence of the Exchange Rate on Cerium(III) and Cerium(IV) Concentrations

A series of experiments was performed to determine the dependence of the rate of exchange on the concentrations of cerium(III) and cerium(IV). The usual method in chemical kinetic studies, namely, varying one concentration while holding all other concentrations constant, was applied to determine the dependence of the exchange rate on the various reactants.

In this particular case, the rate law is described by the following equation:

$$R = k' [\text{Ce(III)}]^m [\text{Ce(IV)}]^n \quad (14)$$

where k' is the specific rate constant at a given temperature and hydrogen ion concentration. In theory the concentration of cerium(III) may be independently varied and m evaluated from the slope of a plot of $\log R$ against $\log [\text{Ce(III)}]$. In the same manner, n may be evaluated from the slope of a plot of $\log R$ against $\log [\text{Ce(IV)}]$, when the cerium(IV) concentration is independently varied.

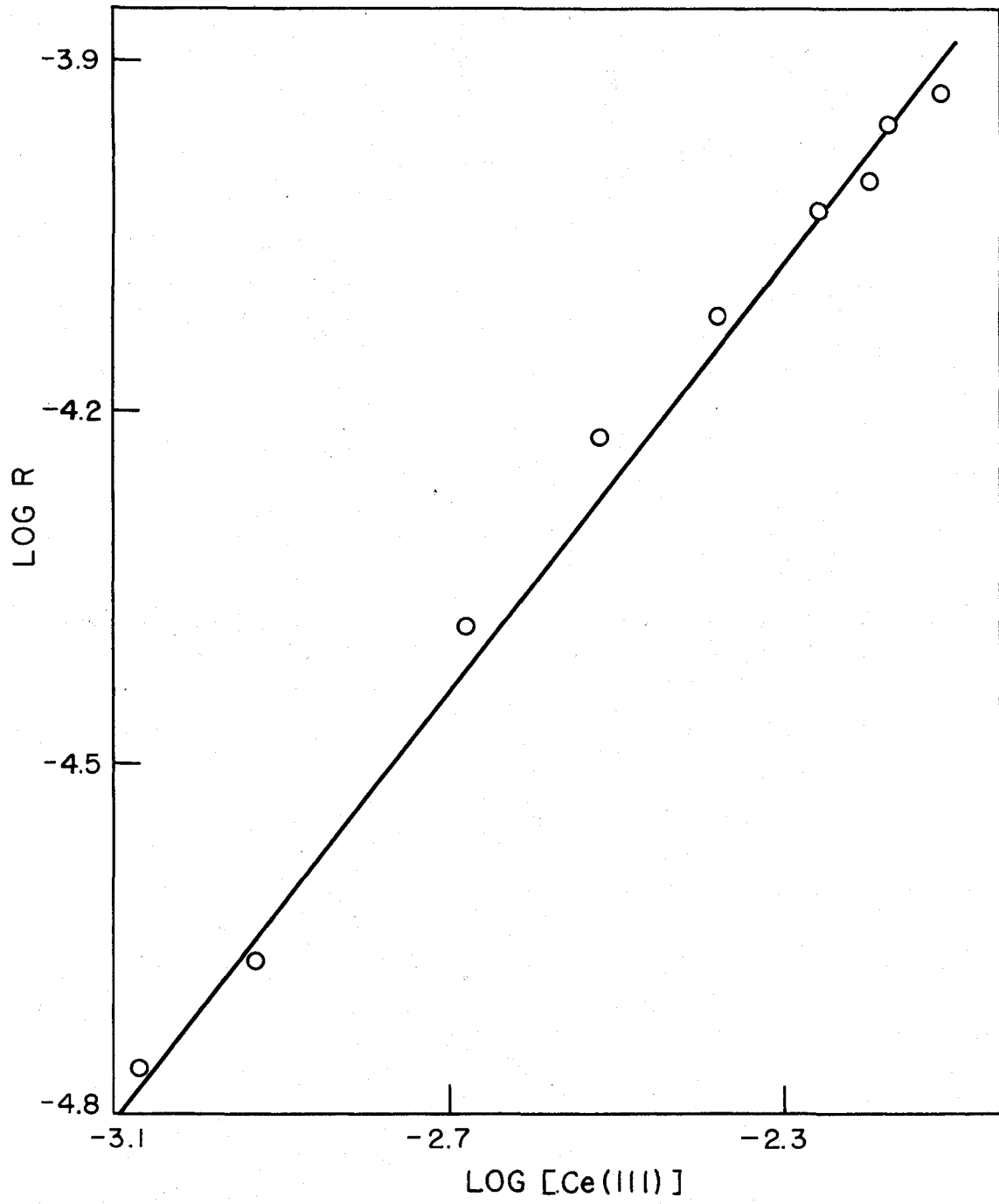
The results of a series of experiments carried out to determine the dependence on cerium(III) at 0°C are given in Table 1, and the data are plotted as $\log R$ against $\log [\text{Ce(III)}]$ in Figure 2. The slope of the line in Figure 2 indicates that the order of the reaction with respect to cerium(III) is 0.90. The fact that the determined value of the order is approximately unity will be discussed subsequently.

In the experiments to determine the dependence of the reaction rate on cerium(IV) concentration the cerium(III) concentration was never held strictly constant because cerium(III) is almost always present to some extent in

Table 1. Dependence of the rate of exchange on cerium(III)
 $[\text{HClO}_4] = 6.0 \text{ f.}$ 0.1° C

$T_{\text{Ce(IV)}}$	$[\text{Ce(III)}]$	$t_{\frac{1}{2}}$	R
f. x 10^3	f. x 10^3	min.	f. min^{-1} x 10^5
3.76	0.865	28.1	1.73
3.92	1.18	29.2	2.14
3.91	2.09	23.0	4.10
3.80	3.05	19.8	5.92
3.82	4.47	18.7	7.65
3.88	5.52	16.9	9.35
3.86	6.26	16.7	9.91
3.82	6.74	15.2	11.1
3.79	7.75	15.1	11.7

Figure 2. Effect of cerium(III) concentration of the rate of exchange, 6.0 f. HClO_4 , 0.1°C



cerium(IV) perchlorate solutions. Consequently, it is not possible to determine the dependence of the rate on cerium(IV) in the same manner as employed for determining the dependence of the rate on the cerium(III) concentration.

Since the dependence of the rate of exchange on cerium(III) concentration was determined to be first order, the rate equation may be expressed as:

$$R = k' [\text{Ce(III)}] f[\text{Ce(IV)}] \quad (15)$$

and hence, $f[\text{Ce(IV)}]$ may be determined by plotting $R/[\text{Ce(III)}]$ against $[\text{Ce(IV)}]$. A representative list of the results of a series of more than seventy-five experiments, carried out to determine the dependence of the rate on cerium(IV) concentration at 0° C, is given in Table 2, and the data are plotted in Figure 3.

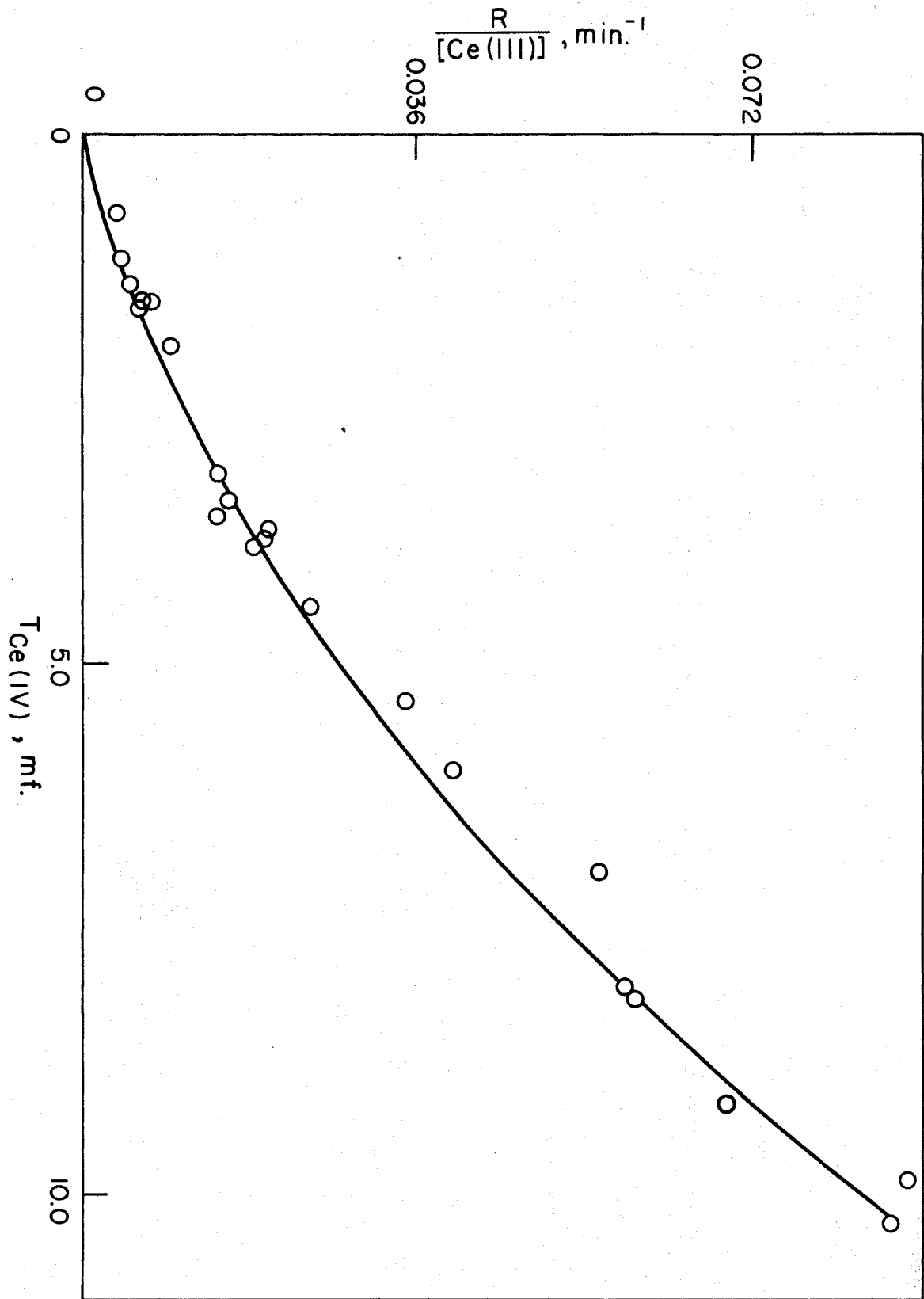
One of the most significant characteristics of the curve in Figure 3 is that the ordinate value approaches zero, when the concentration of cerium(IV) vanishes. It must be concluded from this that there are no exchange reactions, under the experimental conditions, independent of the cerium(IV) concentration. The fact that the curve in Figure 3 is a straight line at low cerium(IV) concentration suggests a first order dependency on cerium(IV)

Table 2. Dependence of the rate of exchange on cerium(IV)

$$[\text{HClO}_4] = 6.0 \text{ f.} \quad 0.1^\circ \text{ C}$$

$T_{\text{Ce(IV)}}$	$[\text{Ce(III)}]$	$t_{\frac{1}{2}}$	$R/[\text{Ce(III)}]$	$R/[\text{Ce(III)}]T_{\text{Ce(IV)}}$
f. x 10 ³	f. x 10 ³	min.	min. ⁻¹ x 10 ²	f. ⁻¹ min. ⁻¹
0.870	5.03	34.1	0.300	3.45
1.17	5.25	29.9	0.421	3.61
1.43	5.15	26.2	0.523	3.68
1.62	4.33	28.2	0.670	4.12
1.63	3.11	36.1	0.659	4.05
1.63	5.17	26.2	0.623	3.89
2.01	5.01	21.2	0.930	4.65
3.22	3.08	23.9	1.48	4.60
3.48	1.77	30.4	1.51	4.33
3.60	0.810	35.0	1.61	4.49
3.76	0.865	35.0	2.00	5.34
3.80	3.05	19.8	1.96	5.04
3.91	2.09	23.0	1.83	4.66
4.45	3.48	15.1	2.57	5.80
5.36	1.05	17.4	3.49	6.22
6.01	1.09	14.7	4.00	6.65
6.96	1.33	10.5	5.55	7.96
8.06	1.46	10.0	5.86	7.28
8.17	2.68	8.70	5.99	7.35
9.14	1.56	8.60	6.88	7.53
9.86	1.75	6.65	8.85	8.97
10.2	2.37	6.50	8.65	8.48

Figure 3. Effect of total cerium(IV) concentration on the rate of exchange, 6.0 f. HClO_4 , 0.1°C



concentration. Also, the fact that the entire curve is not a straight line indicates that the dependence of the exchange rate on the cerium(IV) concentration is not simple first order but instead it appears to include also a dependency of higher order.

When a second order term is included along with the first order term in the rate expression, equation 14 becomes:

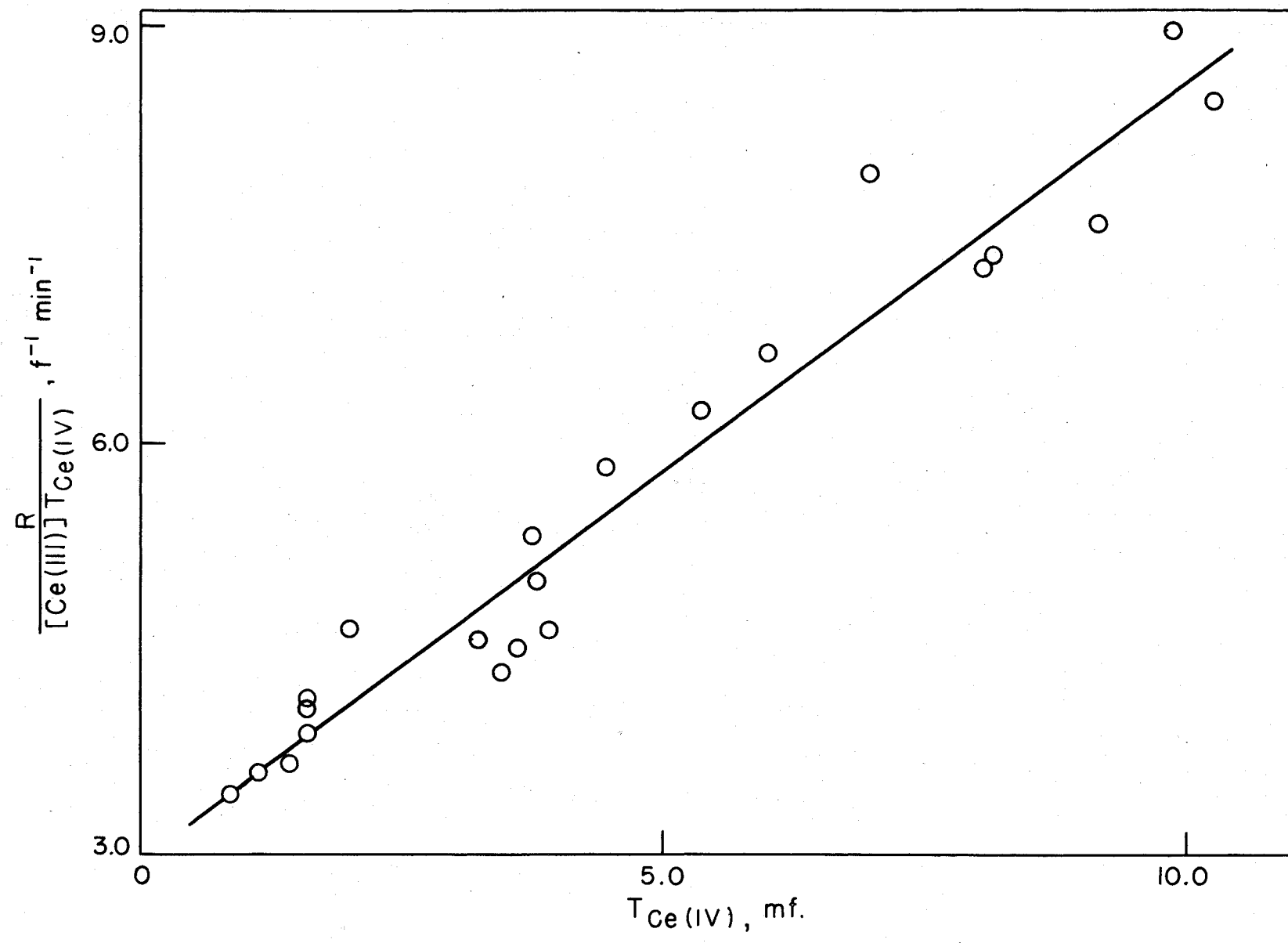
$$R = k' [\text{Ce(III)}] [\text{Ce(IV)}] + k'' [\text{Ce(III)}] [\text{Ce(IV)}]^2 \quad (16)$$

If this equation is the correct expression for the exchange rate, a plot of $R/[\text{Ce(III)}] [\text{Ce(IV)}]$ against $[\text{Ce(IV)}]$ should yield a straight line. Experimentally determined values of $R/[\text{Ce(III)}] [\text{Ce(IV)}]$ are given in Table 2, and the data are plotted according to equation 16 in Figure 4.

Dependence of the Exchange Rate on Perchloric Acid Concentration

The dependence of the rate of exchange on the perchloric acid concentration is of particular interest. It was hoped that the results of the dependence of the exchange rate on the acid concentration along with the cerium(III)

Figure 4. Analysis of the effect of the total cerium(IV) concentration at 6.0 f. HClO_4 , 0.10 C



and cerium(IV) dependencies might make it possible to determine the ionic species existing in the reaction mixture.

Two different techniques were employed in studying the dependence of the exchange rate on the acid concentration. The techniques along with the results obtained will be presented here but detailed discussion of the results will be reserved until later. The first experimental procedure used was to determine the rate of exchange at various perchloric acid concentrations, holding the cerium(III) and cerium(IV) concentrations constant, and maintaining a constant ionic strength by adding sodium perchlorate.

A series of experiments was performed employing this technique and the results are given in Table 3. It can be seen that the rate increases as the acidity decreases. Based on the previous discussion for determining the effect of a reactant on the exchange rate a plot of $\log R / \frac{[\text{Ce(III)}]}{[\text{Ce(IV)}]}$ against $\log [\text{H}^+]$ was made. The resulting curve was complicated and could not be easily interpreted. However, the results obtained in this series of experiments were used in another aspect which will be presented in the next section.

The second experimental procedure employed was to determine the rate of exchange in a series of experiments

Table 3. Analysis of the rate of exchange on acid concentration

$$\mu = 5.89 \quad 0.1^\circ \text{C}$$

$[\text{HClO}_4]$	$T_{\text{Ce(IV)}}$	$[\text{Ce(III)}]$	$t_{\frac{1}{2}}$	$R/[\text{Ce(III)}] T_{\text{Ce(IV)}}$
f.	f. x 10^3	f. x 10^3	min.	f. ⁻¹ min. ⁻¹
2.04	1.35	0.427	5.79	6.75
3.00	1.38	0.376	9.30	4.24
3.97	1.39	0.333	13.8	2.90
4.98	1.39	0.345	21.5	1.85
5.89	1.40	0.336	33.3	1.20

at various cerium(III) and cerium(IV) concentrations, but maintaining a constant hydrogen ion concentration. Then a second series of experiments was performed to determine the rate of exchange at a different hydrogen ion concentration, with cerium(III) and cerium(IV) concentrations again being varied. The ionic strength was held constant by adding sodium perchlorate. The results of these experiments are given in Table 4. The data for the series of experiments performed with the perchloric acid concentration 5.85 f. are plotted as curve A, Figure 5. The data for the other series of

Table 4. Dependence of the rate of exchange on acid concentration

$$\mu = 5.85 \quad 0.1^\circ \text{C}$$

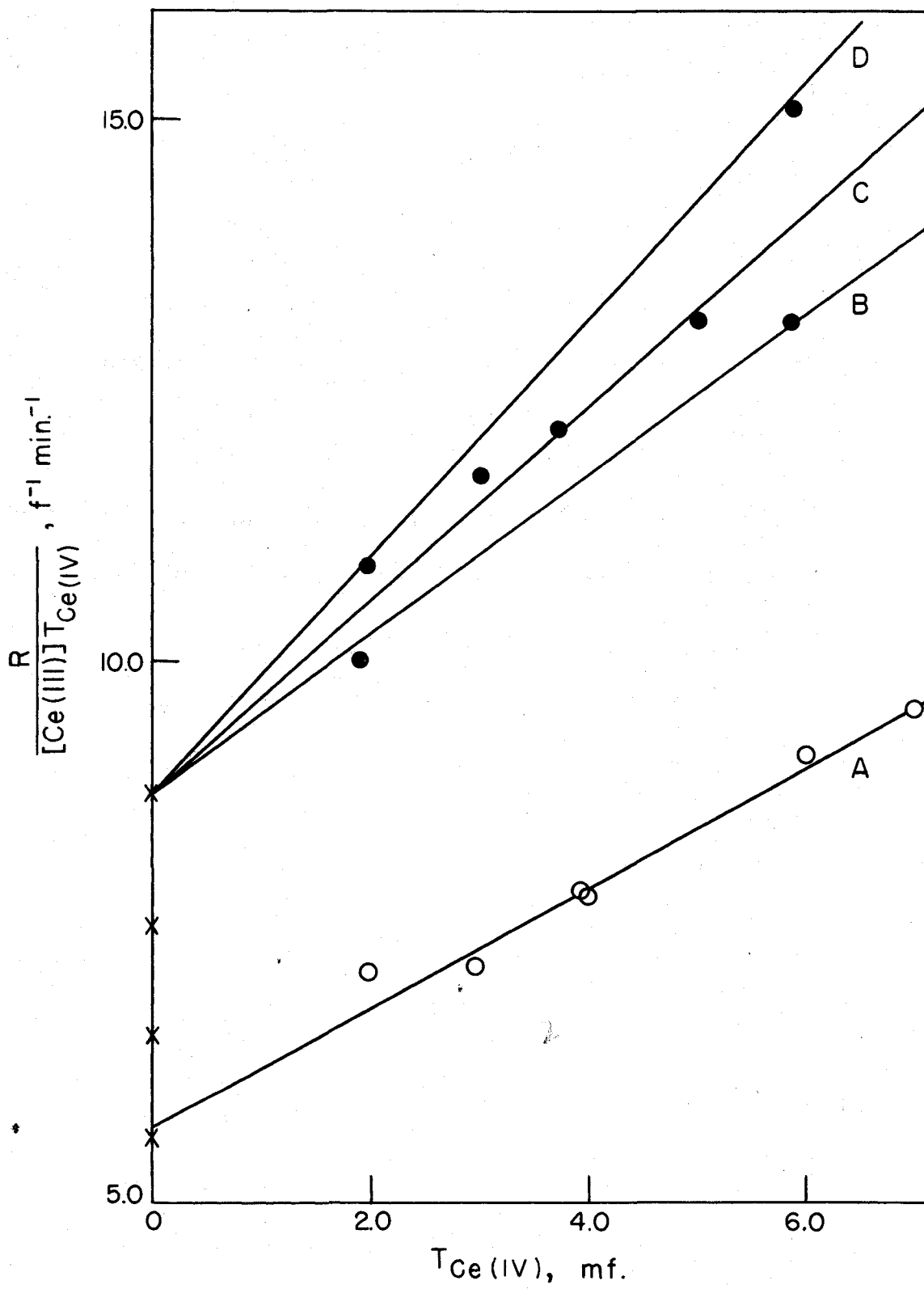
$[\text{HClO}_4]$	$T_{\text{Ce(IV)}}$	$[\text{Ce(III)}]$	$t_{\frac{1}{2}}$	$R/[\text{Ce(III)}] T_{\text{Ce(IV)}}$
f.	f. x 10^3	f. x 10^3	min.	f. ⁻¹ min. ⁻¹
5.85	1.97	0.380	41.3	7.15
	2.95	0.550	27.6	7.20
	3.96	0.705	18.8	7.90
	3.98	0.740	18.8	7.80
	5.95	1.07	10.8	9.15
	6.96	1.23	8.75	9.69
5.04	1.94	0.396	27.0	10.9
	1.98	0.394	28.8	10.1
	2.99	0.608	16.3	11.8
	3.92	0.770	12.1	12.2
	5.00	0.875	8.85	13.3
	5.90	1.06	6.60	13.1
	5.91	1.09	7.44	13.3

Figure 5. Analysis of the effect of the acid concentration

Curve A: 5.85 f. HClO_4 .

Curves B, C. and D are calculated using constants
evaluated from equation 31 and curve A.

Solid dots are experimental results for the
exchange reaction at 5.04 g. HClO_4 and
 $\mu = 5.85$.



experiments performed with the perchloric acid concentration 5.04 f. are also plotted in Figure 5, and an interpretation of these data will be made subsequently.

INTERPRETATION OF EXPERIMENTAL DATA

The experimental results obtained in the studies on heterogeneous catalysis and effects of light, surface material and molecular oxygen on the exchange rate may be easily interpreted. In all these studies, half-times of the exchange reactions are assumed to be identical, within experimental error, to the half-times of their corresponding control exchange reactions.

The series of experiments performed with an increased amount of glass surface, using glass beads, was undertaken to find out if the glass reaction vessel, transfer pipets and separatory funnels had any appreciable effect on the rate of the exchange reaction. It was concluded from the results that no such effect occurred. No effect on the rate of the exchange reaction was observed either by a change in surface material of the reaction vessel, or by the absence of ordinary diffuse light. It was concluded, from the experiments performed with either pure or platinized platinum, that they did not catalyze the exchange reaction.

Weiss (29) suggested, on the basis of theoretical considerations, that the cerium(III)-cerium(IV) exchange reaction might occur via a mechanism involving molecular oxygen. The results obtained from the series of experiments

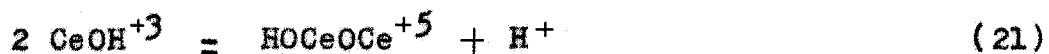
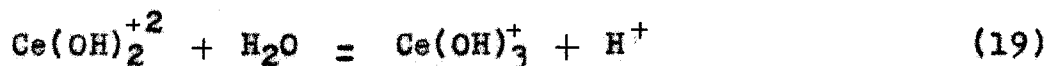
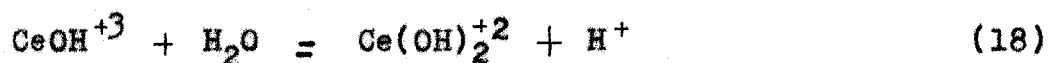
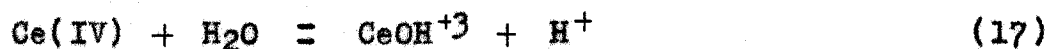
performed with nitrogen bubbling through the reaction mixture indicated that molecular oxygen was not involved in the exchange mechanism, under the experimental conditions employed.

The order of dependence of the exchange rate on the cerium(III) concentration was found to be 0.90. The theoretical considerations for determining the cerium(III) dependence were based on the assumption that the cerium(IV) concentration would be constant throughout the series of experiments performed. As shown in Table 1 the cerium(IV) concentration was not maintained exactly constant. This was due to the instability of the stock solution of cerium(IV) perchlorate as well as possible pipetting errors. It appears that a first order dependence of the exchange rate exists with respect to the cerium(III) concentration. This conforms with the results obtained by previous investigators (5).

Determination of the dependence of the rate of the exchange reaction on the cerium(IV) concentration was found to be more complicated. The dependence on cerium(IV) was found to be a combination of first order and second order components. The fact that a second order reaction appeared to exist indicated that one or more exchange reactions occur involving two cerium(IV) ions individually, or involving a

species containing two cerium(IV) ions. The rate expression, in order to be consistent with these facts, must take a form similar to equation 16.

The analysis of the results on the dependence of the exchange rate with respect to the perchloric acid concentration was found to be complicated. The results in Tables 3 and 4 indicate that the over-all rate constant of the reaction in perchloric acid solution increases as the acidity decreases. Recent evidence (30, 31) suggests that in perchloric acid, cerium(IV) exists as several hydrolyzed species possibly including a polymer. On this basis, the following equilibria exist:



Since these equations represent equilibrium reactions, the following equilibrium constant expressions are obtained:

$$K_1 = \frac{[\text{CeOH}^{+3}][\text{H}^+]}{[\text{Ce(IV)}]} \quad (23)$$

$$K_2 = \frac{[\text{Ce(OH)}_2^{+2}][\text{H}^+]}{[\text{CeOH}^{+3}]} \quad (24)$$

$$K_3 = \frac{[\text{Ce(OH)}_3^+][\text{H}^+]}{[\text{Ce(OH)}_2^{+2}]} \quad (25)$$

$$K_4 = \frac{[\text{CeO}^{+6}]}{[\text{CeOH}^{+3}]^2} \quad (26)$$

$$K_5 = \frac{[\text{HO}^{+5}\text{CeO}^{+5}][\text{H}^+]}{[\text{CeOH}^{+3}]^2} \quad (27)$$

$$K_6 = \frac{[\text{HO}^{+4}\text{CeO}^{+4}\text{CeOH}^{+4}][\text{H}^+]^2}{[\text{CeOH}^{+3}]^2} \quad (28)$$

In a 6.0 f. perchloric acid solution of cerium(IV) the predominating species are Ce(IV) and CeOH⁺³ ions, in fact, calculations show these two ions constitute more than ninety-nine per cent of the total cerium(IV) concentration. The

total cerium(IV) concentration then may be approximated by:

$$T_{\text{Ce(IV)}} = [\text{Ce(IV)}] + [\text{CeOH}^{+3}] \quad (29)$$

The first order cerium(IV) dependency component of equation 16 may be expressed in terms of the unhydrolyzed cerium(IV) ion alone, a hydrolyzed monomer of cerium(IV), or a combination of the unhydrolyzed ion with one or more hydrolyzed monomers. Similarly, the second order cerium(IV) dependency component of the same equation may be expressed in terms of one or more of the hydrolyzed dimers of cerium(IV). The general rate equation upon inclusion of the unhydrolyzed and the hydrolyzed forms of cerium(IV) becomes:

$$\frac{R}{[\text{Ce(III)}]} = k_1 [\text{Ce(IV)}] + k_2 [\text{CeOH}^{+3}] + k_3 [\text{Ce(OH)}_2^{+2}] +$$

$$k_4 [\text{Ce(OH)}_3^+] + k_5 [\text{CeO}^{+6}] + k_6 [\text{HO}^{+5}\text{CeO}^{+5}] +$$

$$k_7 [\text{HO}^{+4}\text{CeO}^{+4}\text{CeOH}^{+4}] \quad (30)$$

When the various unhydrolyzed and hydrolyzed terms are expressed in terms of the total cerium(IV)

concentration and appropriate equilibrium constants, equation 30 becomes:

$$\begin{aligned}
 \frac{R}{[\text{Ce(III)}]} &= \frac{k_1 [\text{H}^+]^T \text{Ce(IV)}}{[\text{H}^+ + K_1]} + \frac{k_2 K_1^T \text{Ce(IV)}}{[\text{H}^+ + K_1]} \\
 &+ \frac{k_3 K_1 K_2^T \text{Ce(IV)}}{[\text{H}^+] [\text{H}^+ + K_1]} + \frac{k_4 K_1 K_2 K_3^T \text{Ce(IV)}}{[\text{H}^+]^2 [\text{H}^+ + K_1]} \\
 &+ \frac{k_5 K_1^2 K_4^T \text{Ce(IV)}}{[\text{H}^+ + K_1]^2} + \frac{k_6 K_1^2 K_5^T \text{Ce(IV)}}{[\text{H}^+] [\text{H}^+ + K_1]^2} \\
 &+ \frac{k_7 K_1^2 K_6^T \text{Ce(IV)}}{[\text{H}^+]^2 [\text{H}^+ + K_1]^2}
 \end{aligned} \tag{31}$$

Equation 31 was analyzed termwise in order to determine which, if any, of the included unhydrolyzed or hydrolyzed forms of cerium(IV) are involved in the rate determining exchange reactions. The specific rate constant or pseudo-rate constant for each term representing first order dependency with respect to the cerium(IV) concentration was individually evaluated from the intercept of curve A, Figure 5, neglecting all the other first order dependency terms. Similarly, the pseudo-rate constant for each term

representing second order dependency with respect to the cerium(IV) concentration was individually evaluated from the slope of curve A, Figure 5, neglecting all the other second order dependency terms.

The pseudo-rate constants must be evaluated as such because each pseudo-rate constant contains a specific rate constant and equilibrium constants, all of which are unknown. Hardwick and Robertson (31) have determined the equilibrium constant K_1 , of equation 16, to be 0.52.

Using the individually determined values of the specific rate constant or pseudo-rate constants for the first order dependency terms, corresponding values were evaluated for the intercepts with the hydrogen ion concentration equal to 5.04 f. These values are plotted as X's on the ordinate of Figure 5. The value of the intercept increases progressively as the hydrolysis of the monomer increases. The ordinate value of 8.88 corresponds to the hydrolyzed form $Ce(OH)_3^+$ and it was concluded that this ordinate value best agrees with the intercept of a plot of the experimentally determined results, which are also plotted in Figure 5.

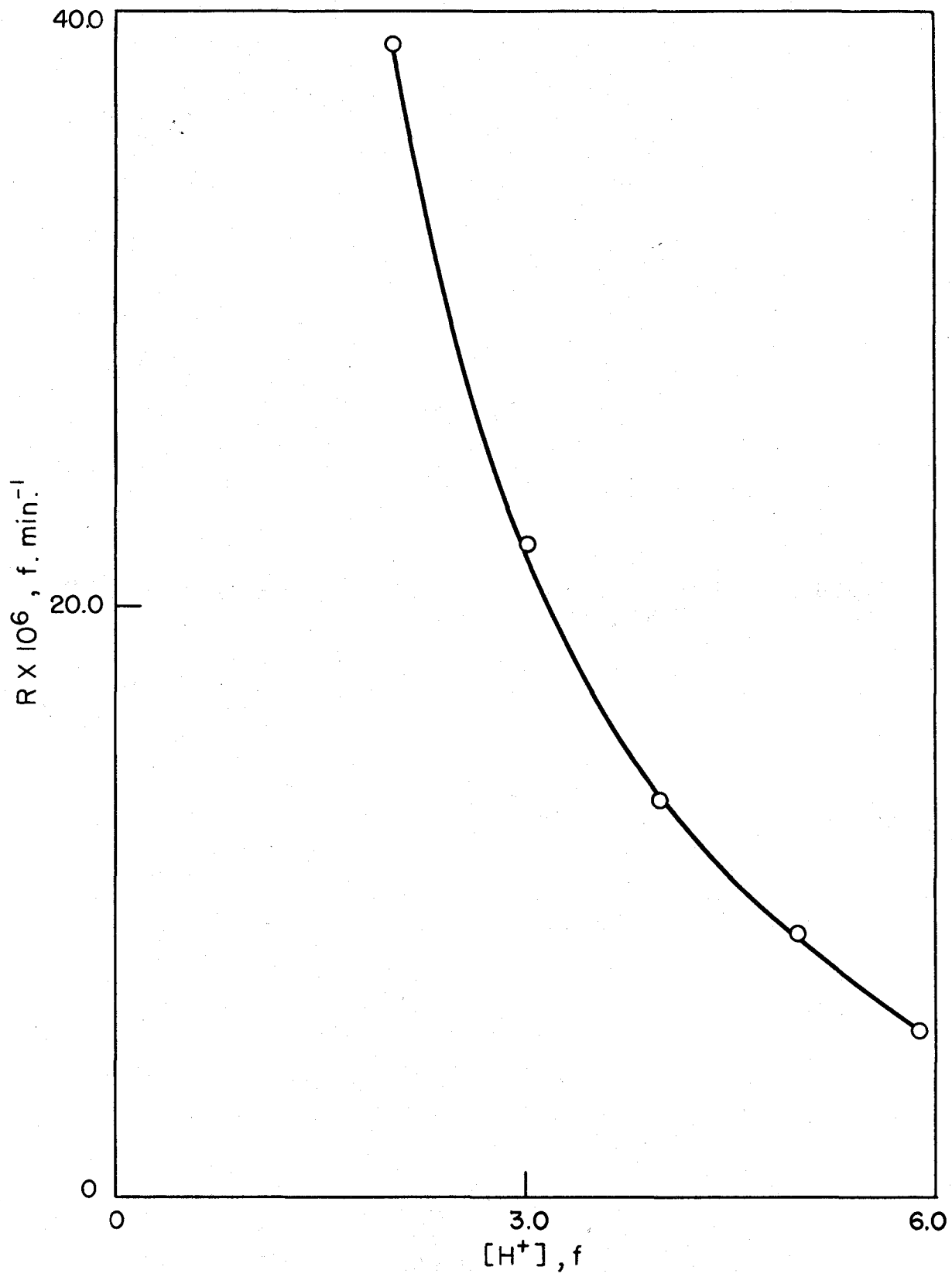
By using the individually determined values of the pseudo-rate constants for the second order dependency terms, corresponding values were calculated for the slopes, with

the hydrogen ion concentration equal to 5.04 f. Three curves are obtained using the $\text{Ce}(\text{OH})_3^+$ hydrolyzed monomer and one each of the three hydrolyzed dimer forms. These are plotted as curves B, C, and D of Figure 5 and correspond to the dimers $\text{CeO}^+\text{Ce}^{+6}$, $\text{HO}^+\text{CeO}^+\text{Ce}^{+5}$, and $\text{HO}^+\text{CeO}^+\text{CeOH}^{+4}$ respectively. The experimental results might fit any of the calculated curves, but it was concluded that they best fit curve C, corresponding to dimer $\text{HO}^+\text{CeO}^+\text{Ce}^{+5}$. On this basis, equation 31 may be simplified to:

$$\frac{R}{[\text{Ce}(\text{III})]} = \frac{k_4 K_1 K_2 K_3 T_{\text{Ce}(\text{IV})}}{[\text{H}^+]^2 [\text{H}^+ + K_1]} + \frac{k_6 K_1^2 K_5 T_{\text{Ce}(\text{IV})}^2}{[\text{H}^+] [\text{H}^+ + K_1]^2} \quad (32)$$

Results, obtained from the study of the exchange rate at varying hydrogen ion concentration but at constant cerium(III) and cerium(IV) concentrations, are given in Table 3 and are plotted as $R/[\text{Ce}(\text{III})] T_{\text{Ce}(\text{IV})}$ against hydrogen ion concentration in Figure 6. At a constant total cerium(IV) concentration the total concentration of all the hydrolyzed forms of cerium(IV) increases as the acidity decreases. Qualitatively the curve in Figure 6 indicates that at low acidity the exchange rate is very fast due first to the relatively large total concentration of hydrolyzed species,

Figure 6. Analysis of equation 33 with respect to acid concentration at $\mu = 5.89$



and second, to the possible existence of cerium(IV) forms which are more highly hydrolyzed or more highly polymerized.

As the curve in Figure 6 is extrapolated the rate approaches zero or a value near zero at higher hydrogen ion concentrations. At high acid concentration the total concentration of hydrolyzed species approaches zero. This indicates that the rate of electron transfer between cerium(III) and the unhydrolyzed ion of cerium(IV) is very slow compared to the rate of the reactions involving various hydrolyzed species. This compares favorably with the result that the rate of exchange involving uncomplexed europium(III) is very slow compared to rate of the chloride-catalyzed reactions for the europium(II)-europium(III) exchange reaction in hydrochloric acid (18).

On the basis of the results obtained from the acid dependency studies, the relative reactivity of various hydrolyzed monomer forms of cerium(IV) with respect to electron exchange can be predicted to increase in the following order: $\text{Ce(IV)} < \text{CeOH}^{+3} < \text{Ce(OH)}_2^{+2} < \text{Ce(OH)}_3^+$.

DISCUSSION

The cerium(III)-cerium(IV) exchange reaction was studied. In particular, the effect on the rate of exchange by pure and platinized platinum, glass and polyethylene surfaces, diffuse light and the absence of molecular oxygen has been studied. The dependence of the exchange rate on the concentrations of cerium(III), cerium(IV) and perchloric acid has been determined under the experimental conditions employed. As a result tentative conclusions can be made concerning the reaction mechanisms and the ionic species involved in the exchange reactions, and suggestions for future investigations can be proposed.

It was found that neither platinum, pure or platinized, nor diffuse light catalyzed the exchange reaction. It was also observed that different construction materials for the reaction vessel employed had no effect upon the rate of exchange. The possibility of the existence of an exchange mechanism involving molecular oxygen was eliminated by bubbling nitrogen through the reaction mixture during the experimental runs.

Gryder and Dodson (5) found, in the perchlorate system, first order dependency with respect to the cerium(III) concentration and a combination of zero order and first order

dependencies with respect to the cerium(IV) concentration. In comparison, results of this investigation indicate first order dependency with respect to the cerium(III) concentration and a combination of first order and second order dependencies with respect to the cerium(IV) concentration. It was determined on this basis that a study of the kinetics of the exchange as a function of the concentration of perchloric acid should give an indication of the complexes formed and the reactivity of these complexes from the standpoint of ability to give up or receive electrons. Such an approach was carried out in order to gain a better knowledge of the nature of the ionic species existing in a cerium(IV)-cerium(III)-perchlorate system.

The fact that cerium(IV) complexes with various anions has been known for some time (32). As an indication of this the formal electrode potentials vary from -1.2 to -1.7 volts, depending upon whether the solution contains hydrochloric, sulfuric, nitric, or perchloric acid. Cerium(IV) migrates to the anode in 1 f. sulfuric acid (12) and in 6 f. nitric acid, but it migrates to the cathode in 1.8 f. perchloric acid (31) and in 2 f. nitric acid.

An obvious marked color change occurs when nitric or sulfuric acid is added to a perchloric acid solution of cerium(IV). Cerium(IV) nitrate is not precipitated when

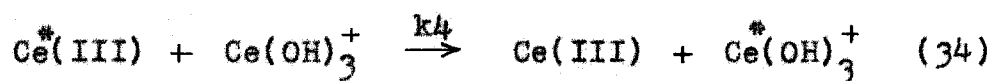
nitric acid is added to a concentrated solution of cerium nitrate, but cerium(IV) ammonium hexanitrate is precipitated when ammonium nitrate is added. All these observations along with stability studies of the various acid solutions of cerium(IV) seem to indicate that chloride and sulfate form rather strong complexes with cerium(IV), while nitrate forms a weaker complex, and, even though perchlorate complexes have been postulated (33), it appears that perchlorate probably does not enter into complex formation with cerium(IV).

The nature of cerium(IV) solutions is undoubtedly very complex, and it appears likely that no single species predominates. On the other hand, complexes of cerium(III) are not well known and in most instances have been assumed not to exist. Yost, Russell, and Garner (32) suggest that in nitric acid hydroxyl ion takes part in the complexing of cerium(IV). Recently (31) considerable evidence has been presented that suggests that in perchloric acid cerium(IV) undergoes considerable hydrolysis and probably exists to some extent as a polymer of the form $CeOCe^{+6}$ or a similar structure.

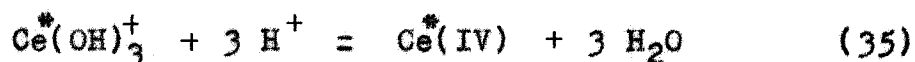
The kinetic data, which are well represented by the rate law given in equation 32, indicate that in 5-6 f. perchloric acid solutions the exchange between cerium(III) and

cerium(IV) proceeds via two independent paths. The following simple mechanism is consistent with the experimental rate law.

In path 1, part of the cerium(IV) is hydrolyzed as a monomer, and an electron is transferred between the hydrolysis product, $\text{Ce}(\text{OH})_3^+$, and the other reactant, $\text{Ce}(\text{III})$:



(rate-determining)



(rapid following reaction)

In path 2, a small fraction of the cerium(IV) is hydrolyzed as a dimer and an electron is transferred between the hydrolysis product, $\text{HOCeO}^+\text{Ce}^{+5}$, and the other reactant, $\text{Ce}(\text{III})$:



(rate-determining)



(rapid follow reaction)

The experimental activation energies for the above rate determining reactions were not determined in this investigation. Even if apparent activation energies had been determined, comparison of the energies and entropies of activation for the rate determining reaction with that predicted from absolute rate theory for reactions between ions of this charge type would not be possible at present as the experimental rate constants and activation energies include unknown association constants and heats of formation for the hydrolyzed species.

This explains to some extent, the rather large apparent activation energies obtained by Gryder and Dodson (5). Presumably, the true activation energies would be appreciably smaller after correction for these factors. Hardwick and Robertson (31) have observed that two of the hydrolyzed species, CeOH^{+3} and $\text{CeO}^+\text{Ce}^{+6}$, have very large temperature coefficients, and on this basis, corrections of 5-6 kcal./mole would bring the activation energies found by Gryder and Dodson into the range of values which have been observed by other workers for one electron transfer systems.

The mechanisms of electron transfer reactions and the relative importance of factors which determine the rates of such reactions are not well understood (34, 35). This investigation of the cerium(III)-cerium(IV) exchange does little to clarify this important subject. Shaffer (36) and Remick (37) have proposed that oxidizing and reducing agents which gain or lose the same number of electrons should react rapidly. The slowness of the cerium(III)-cerium(IV) exchange and many other exchange reactions do not substantiate this particular theory.

Gorin (38), Weiss (29), and Duke (39) have suggested that if the reacting species have like charges, coulombic repulsion should cause the reaction to be slow, or the reaction might take place through neutral, nearly neutral, or oppositely charged intermediates. The slowness of the cerium exchange reaction and the decrease in magnitude of the positive charge in the predicted order of relative reactivity of the various cerium(IV) species in the exchange are consistent with this theory.

Duke (35) has suggested that when the products of the reaction have no effect on the rate of the reaction, the reaction mechanism may involve a bridge type intermediate. Fluorine has been found to catalyze the cerium exchange

reaction (9), and fluorine might in this case substitute for water in the formation of a bridge.

At the present time there is still too little information available concerning the cerium exchange reaction to determine which mechanism or mechanisms of exchange actually are important.

In proposing future work to be done on the cerium(III)-cerium(IV) exchange reaction it must be remembered that the mechanism of exchange may alter as the acidity is varied. Therefore, more of the type of experiments carried out in this investigation, namely, experiments in which the cerium-(III) and cerium(IV) dependencies are determined at various acid concentrations, are needed. However, a new separation technique will be necessary, particularly at low acidities because of the short half-times. Another phase of interest is the effect on the exchange rate of certain complexing agents, such as 1, 10-phenanthroline, ethylenediaminetetraacetate, and others.

SUMMARY AND CONCLUSIONS

1. A technique was employed and found to be very satisfactory for the separation of cerium(IV) from cerium(III) by means of a tri-n-butyl phosphate extraction from nitric acid solution.
2. Neither platinum, pure or platinized, nor diffuse light were observed to catalyze the exchange reaction.
3. It was found that the various construction materials for the reaction vessels employed had no effect upon the rate of exchange.
4. The possibility of the existence of an exchange mechanism involving molecular oxygen was eliminated.
5. The dependence of the exchange rate on the cerium(III) concentration was found to be first order in 5-6 f. perchloric acid solution.
6. The dependence of the exchange rate on the total cerium(IV) concentration was found to be a combination of first order and second order in 5-6 f. perchloric acid solution.
7. The over-all rate of the exchange reaction was observed to increase as the perchloric acid concentration decreased with the ionic strength maintained constant by the addition of sodium perchlorate.

8. From studies of the dependence of the exchange rate on cerium(III) and cerium(IV) concentrations carried out in 5.85 f. and 5.04 f. perchloric acid solutions, the over-all rate of exchange can be explained on the basis of two exchange reactions occurring simultaneously, one involving cerium(III) ion and the hydrolyzed cerium(IV) monomer $\text{Ce}(\text{OH})_3^+$ and the other involving cerium(III) ion and hydrolyzed cerium(IV) dimer $\text{HOCeO}^+\text{Ce}^{+5}$.

9. On the basis of experimental evidence, the relative reactivity of the various hydrolyzed monomer forms of cerium(IV) with respect to electron exchange may be predicted to increase in the following order: $\text{Ce}(\text{IV}) < \text{CeOH}^{+3} < \text{Ce}(\text{OH})_2^{+2} < \text{Ce}(\text{OH})_3^+$.

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