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A Study of the Kinetics of the Oxidation of Uranium(IV) by Cerium(IV)

Floyd Beatty Baker

OXIDATION OF URANIUM (IV) - BAKER

DATE DUE

A STUDY OF THE KINETICS OF THE OXIDATION OF URANIUM(IV) BY CERIUM(IV)

By

Floyd Beatty Baker

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CHAPTER I

INTRODUCTION

The kinetics of a number of oxidation-reduction reactions and exchange reactions involving cations of the transition and inner transition elements have been extensively reviewed by T. W. Newton and S. W. Rabideau.[1] These workers represent the formation of the activated complex by an equation which includes only the principal species in solution as reactants.

This equation for the net activation process is the sum of the equation for the formation of the activated complex in the actual rate-determining step and the equations for any equilibrium reactions which occur prior to the rate-determining step. Newton and Rabideau show, for example, that if the mechanism is

$$A + B \rightleftharpoons C + D, \text{ rapid equilibrium, equilibrium far to the left,}$$

$$C + E \xrightarrow{k} \text{products, rate determining,}$$

the rate law would be

$$\text{Rate} = k[C][E] = kK\frac{[A][B][E]}{[D]}$$

where

$$K = \frac{[C][D]}{[A][B]}$$

and the net activation process would be

$$A + B + E = [\text{Activated Complex}] + D.$$

All the oxidation-reduction reactions reported to date involving the oxidation of a metal ion in the plus four oxidation state are expressed below by equations for the net activation process.

			Ref.	
$U^{+4} + Fe^{+3} + H_2O$	=	$[\text{Activated Complex}]^{+6} + H^+$	2	(I-1)
$U^{+4} + Fe^{+3} + H_2O$	=	$[\text{Activated Complex}]^{+5} + 2H^+$	2	(I-2)
$Np^{+4} + Fe^{+3} + 2H_2O$	=	$[\text{Activated Complex}]^{+4} + 3H^+$	3	(I-3)
$U^{+4} + Pu^{+4} + H_2O$	=	$[\text{Activated Complex}]^{+6} + 2H^+$	4	(I-4)
$Pu^{+4} + Pu^{+4} + 2H_2O$	=	$[\text{Activated Complex}]^{+5} + 3H^+$	5	(I-5)
$Np^{+4} + NpO_2^{+2} + H_2O$	=	$[\text{Activated Complex}]^{+4} + 2H^+$	6	(I-6)
$U^{+4} + PuO_2^{+2} + H_2O$	=	$[\text{Activated Complex}]^{+5} + H^+$	7	(I-7)
$U^{+4} + PuO_2^{+2} + H_2O$	=	$[\text{Activated Complex}]^{+4} + 2H^+$	7	(I-8)

It is of interest to note that for sets of reactions which are formally identical, for example, reactions I-1, I-2, I-3, and I-4, I-5, and I-6, I-7,

I-8, the hydrogen ion dependence differs within each set. Newton and Rabideau have attempted to correlate the entropy of the activated complex with the charge which in turn is related to the hydrogen ion dependence.

Because the reaction of uranium(IV) and cerium(IV) is similar to those summarized on page 2, it was thought worthwhile to investigate the kinetics of the oxidation of uranium(IV) by cerium(IV) in order to gather more information regarding the thermodynamic quantities of activation and the hydrogen ion concentration dependence of such reactions.

The rate of reaction between uranium(IV) and cerium(IV) was studied spectrophotometrically in perchloric acid-sodium perchlorate solutions at ionic strength two, over the perchloric acid concentration range from 0.800 to 2.00 M and the temperature range of 2.4 to 15.6 ^{o}C; the initial cerium(IV) concentration was varied from 4 to 8 X 10^{-5} M, and the initial uranium(IV) concentration from 2 to 9 X 10^{-5} M. The rate of reaction for the main path was found to be first order with respect to both $CeOH^{+3}$ and U^{+4}, and inversely proportional

to the perchloric acid concentration. The hydrolysis of cerium(IV) was studied potentiometrically in the aforementioned media; the cerium(IV) was found to exist primarily as the specie $CeOH^{+3}$ over the perchloric acid concentration range from 0.300 to 2.00 M.

From the above observations the reaction can be represented in terms of the net activation process by the equation

$$CeOH^{+3} + U^{+4} + H_2O = [\text{Activated Complex}]^{+6} + H^+.$$

The thermodynamic quantities of activation at 2.4°C were found to be $\Delta F^{\neq} = 12.2 \pm 0.2$ kcal/mole, $\Delta H^{\neq} = 13.9 \pm 0.7$ kcal/mole, $\Delta S^{\neq} = 6.2 \pm 2.5$ e.u..

CHAPTER II

REAGENTS

Cerium Perchlorate.- Cerium perchlorate stock solutions were prepared in the following way. G. Fredrick Smith reagent grade ceric ammonium nitrate was reduced with hydrogen peroxide. Cerous oxalate was precipitated, washed and subsequently treated with fuming perchloric acid to give cerium(III) perchlorate. Portions of the cerium(III) solution were diluted to about 6 M perchloric acid and oxidized electrolytically;[8] about 80 per cent of the cerium(III) was oxidized to cerium(IV). The cerium(IV) concentration was determined by titration with a standard ferrous sulfate solution; the total cerium concentration was determined spectrophotometrically.[9] The acid concentration was determined by titration with standard base after reducing the cerium(IV) with hydrogen peroxide and removing the cerium as cerous oxalate. The titrations were corrected for the hydrogen ion produced during the reduction.

Uranium Perchlorate.- Uranyl perchlorate was

prepared by dissolving pure uranium oxide (U_3O_8) in fuming perchloric acid. The resulting solution was diluted to about 2 M perchloric acid and the uranyl perchlorate reduced electrolytically with a mercury cathode to uranium(IV); about 90 per cent of the uranium(VI) was reduced. The uranium(IV) concentration was determined by titration with standard ceric sulfate solution. The total uranium concentration was determined by reduction with zinc amalgam and subsequent titration with standard ceric sulfate solution. The acid concentration was determined by adsorbing the uranium on a cation exchange column (Amberlite IR-120) in the acid form and titrating the eluant with standard base. The titrations were corrected for the hydrogen ion equivalent of the uranium ions adsorbed.

Perchloric Acid. - Mallinckrodt 70 per cent perchloric acid was filtered through a fine sintered-glass frit. The filtered acid was boiled at atmospheric pressure to oxidize any organic material, and then boiled at a pressure of about five millimeters of mercury to remove oxides of chlorine.

Sodium Perchlorate. - Sodium perchlorate was prepared by neutralizing reagent grade Mallinckrodt perchloric acid with Mallinckrodt reagent grade sodium carbonate. Solid sodium carbonate was added, with stirring, until the solution became basic. The resulting solution was filtered through a fine sintered-glass frit to remove heavy metal hydroxides. The filtrate was then neutralized with perchloric acid and boiled to remove the carbon dioxide. The sodium perchlorate was then crystallized by the following procedure. Excess water was removed by boiling until the temperature of the solution reached 132°C (boiling point of water is about 92°C at the Los Alamos Scientific Laboratory). The solution was then stirred as it cooled allowing the sodium perchlorate to crystallize. The crystals were filtered off at about 65°C using a coarse sintered-glass frit. It was found that if the filtration was carried out at a lower temperature a thick slurry formed and the salt could not be separated from the mother liquor. The salt was then recrystallized and made up into about a 5 M sodium perchlorate stock solution. The sodium perchlorate concentration was determin-

ed gravimetrically by drying aliquots to constant weight at 150°C. Rate constants obtained from runs using sodium perchlorate which had been crystallized three times were the same within experimental error as those in which the twice-crystallized salt was used.

Water. - Distilled water was further purified by distillation from alkaline permanganate in a pyrex still.

Hydrogen Gas. - Linde Products electrolytic grade hydrogen gas was passed over uranium metal turnings at about 600°C in order to remove oxygen.

Analytical Reagents. - A 0.1 M ceric sulfate stock solution was prepared by dissolving G. Fredrick Smith reagent grade ceric ammonium nitrate in 1 M sulfuric acid. The resulting solution was standardized using arsenious oxide as the primary standard and orthophenanthroline ferrous complex as the oxidation-reduction indicator.

Saturated zinc amalgam was prepared by dissolving Mallinckrodt analytical reagent grade zinc metal in distilled mercury.

Solutions of hydrogen peroxide were prepared from 30 per cent Baker's reagent grade hydrogen peroxide and standardized by titration with potassium permanganate.

CHAPTER III

EXPERIMENTAL

Electromotive Force Measurements.- In all measurements where constant ionic strength was desirable sodium perchlorate was used as the neutral electrolyte. In order to determine the extent of hydrolysis of cerium(IV), the effect of hydrogen ion concentration on the potential of the cerium(III)-cerium(IV) couple was studied.

Apparatus.- The cell consisted of a hydrogen half-cell and a cerium half-cell. The two half-cells were connected by means of a suitable bridge containing a solution of the same composition as that in the hydrogen half-cell. Each half-cell contained two electrodes. The electrodes used were Beckmann number 1282 hydrogen electrodes in the hydrogen half cell and bright platinum electrodes made from 50 mill wire in the cerium half-cell. The bright platinum electrodes were cleaned with hot aqua regia and washed. The electrodes were then treated as an anode in a 1 M perchloric acid solution for about twenty-four hours

using a current of one ampere. After this treatment they came to equilibrium quickly when placed in the cerium half-cell. The electrodes were connected by shielded leads to the potentiometer by means of a switching arrangement, which afforded a check on the equilibrium attained in the cell since a total of four different pairs could be used in taking readings. The half-cells were thermostated to within ±0.05°C by passing water from a conventional thermostat through a water jacket. The hydrogen gas was presaturated with water vapor by passing it through a solution of the same composition and temperature as that in the hydrogen half-cell. The half-cells were stirred with teflon covered magnetic stirring bars actuated by magnetic stirrers. The hydrogen half-cell was provided with a trap to prevent air from diffusing into the cell. The experimental setup is shown in Figure III-1. The measurements were taken with a Leeds and Northrup type K potentiometer which had a sensistivity of 0.01 millivolts. An Eppley standard cell with a potential of 1.01906 volts at 25°C was used as the potential standard. The potentials to be measured were above 1.6 volts,

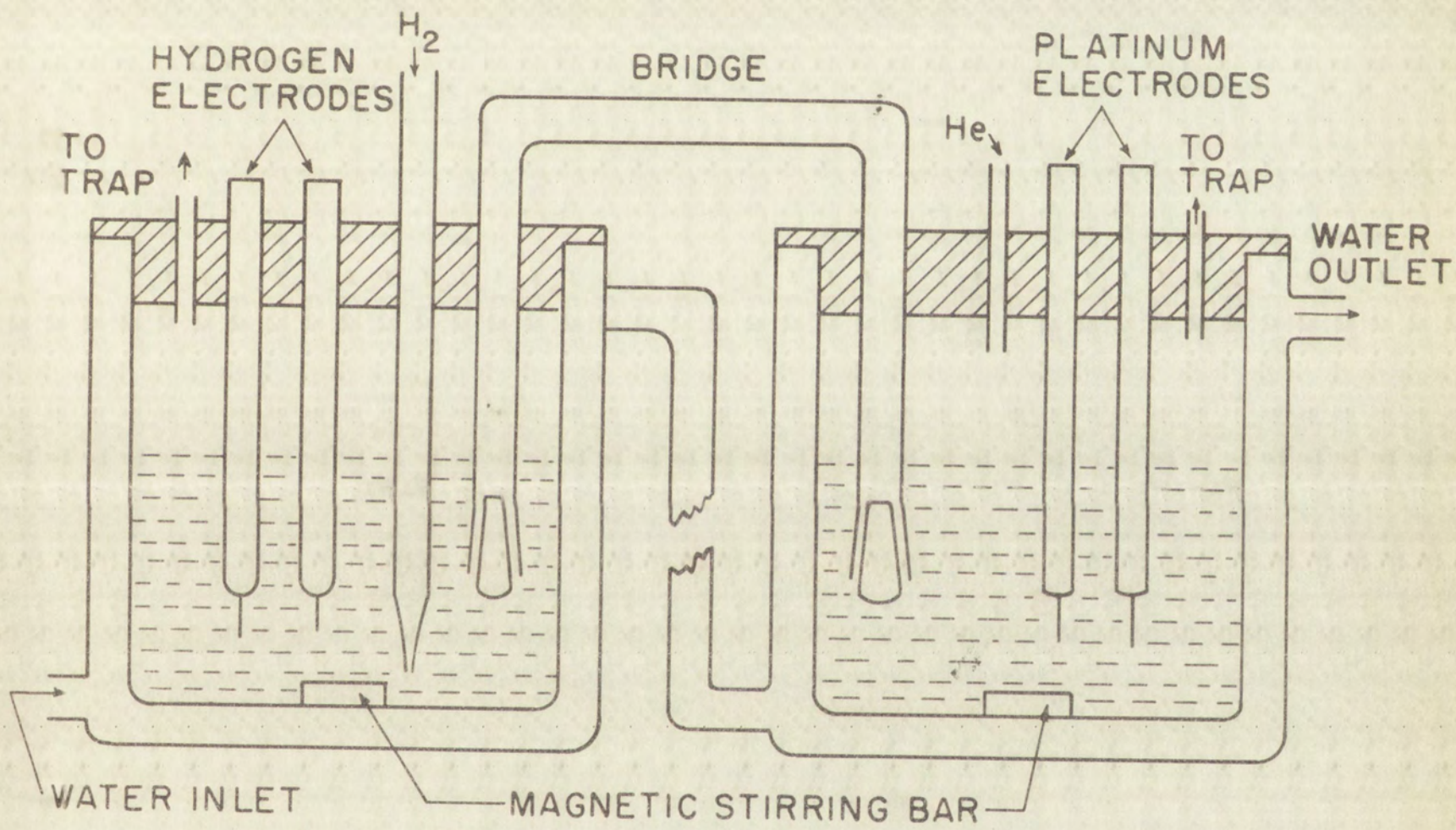


FIG. III-1 EMF CELL

which was the range of the potentiometer; therefore, a second standard cell with a potential of 1.01911 volts was used in opposition to the cell being measured. The potentials of the above cells were determined on November 15, 1957 in terms of standards maintained by the Los Alamos Scientific Laboratory. The experiments using these cells were carried out during the months of December 1957 and January 1958.

Experimental Procedure. - Before making a run the cells were washed and dried thoroughly. The acid solution of the desired concentration was put in the hydrogen half-cell to cover about two-thirds of the electrodes and to make contact with the salt bridge. A solution of the same composition was placed in the presaturater (see Figure III-1) and the bridge. A solution of the same acid concentration with 3.51×10^{-3} M total cerium was placed in the cerium half-cell. The hydrogen was connected to the cell and the stirrers and thermostating water started. The hydrogen flow rate was maintained at about one bubble per second from a 0.5 mm capillary. When the four pairs of electrodes gave the same reading to within 0.1 millivolt or less

the cell was assumed to be in equilibrium. The readings of the four pairs of electrodes were then taken and a sample of the cerium solution removed by pipet for analysis. The readings were then immediately repeated. The readings before and after the sample was removed were found to be the same within 0.1 millivolt or less. Using the same solutions the temperature was changed and the readings taken at the new temperature after allowing sufficient time for the system to come to equilibrium. The ratio of the cerium(III) to cerium(IV) concentration was varied by adding about 0.05 milliliter of a hydrogen peroxide solution of a suitable concentration. The barometric pressure was read at the beginning and end of each run.

Analysis. - The cerium was pipetted into a volumetric flask containing enough 5 M sulfuric acid to yield a 0.5 M sulfuric acid solution when diluted to mark. This solution was then analyzed spectrophotometrically at 3200 Å where the absorptivity of cerium(IV) in 0.5 M sulfuric acid is 5580 M^{-1} cm^{-1}.[9] The absorptivity of cerium(III) is negligible at this wave length.

Rate Measurements. - The rate of reaction was followed by determining the cerium(IV) concentration as a function of time, using a spectrophotometric technique. Because the rate of reaction was rapid, a special procedure was adopted. Cerium and uranium solutions were rapidly mixed in a special cell and then allowed to flow directly into an absorption cell positioned in the spectrophotometer.

Apparatus. - The mixing cell was mounted above the absorption cell as shown in Figure III-2. The mixing compartment was provided with a teflon stopper which was removed after the two solutions were completely mixed; thus, allowing the solution to flow into the absorption cell. Mixing was accomplished by means of a motor-driven glass stirrer. The mixing cell was thermostated by means of a water-bath containing copper coils through which water at constant temperature was passed. The absorption cell was thermostated in a similar manner except that the water was passed through channels in the metal cell holder. With this arrangement it was possible to maintain temperatures to within $\pm 0.1^{\circ}C$. Dry helium was

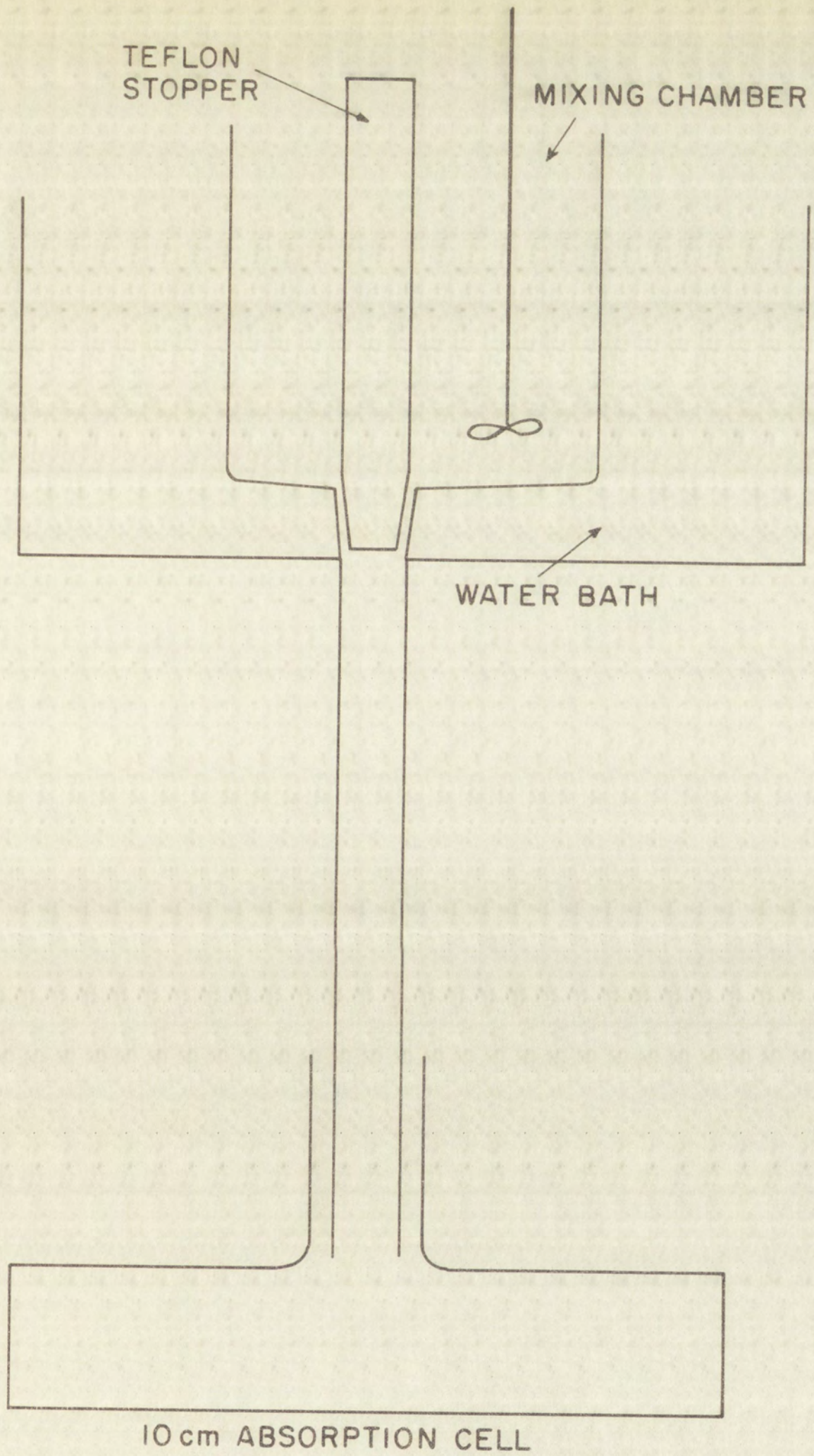


FIG. III-2 MIXING APPARATUS

passed over the windows of the absorption cell holder in order to prevent condensation because the rate measurements were carried out below the dew point of the surrounding air. A Cary Recording Spectrophotometer Model 14 was used for all of the rate measurements. The recorder chart was started at the time of mixing (which was taken as zero time); hence, the absorbance of cerium(IV) as a function of time could be read directly from the recorder chart. A chart speed of eight inches per minute was used. The chart could be read to within ±0.003 absorbance unit and ±0.1 second.

Experimental Procedure.- About 30 milliliters of dilute perchloric acid solution of known concentration was pipetted into the mixing cell. The stirrer was started and when the solution reached the desired temperature, uranium(IV) at a known concentration was added with a 0.20-milliliter micro pipet. The uranium solution was added after the equilibrium temperature had been reached in order to prevent air oxidation. A 5-milliliter hypodermic syringe provided with a glass needle was used to add the cerium(IV) to the uranium(IV)

solution. The syringe was filled to a known volume with cerium(IV) solution of the same acid concentration as that in the mixing cell. Care was taken to remove air bubbles from the syringe. The entire volume of solution (except for the amount left in the needle) was then injected into the mixing cell. The recorder chart was started immediately after the cerium(IV) was injected. After about four seconds, which was found to be sufficient time for complete mixing, the stopper was pulled allowing the solution to drain into the absorption cell. Using the foregoing procedure it was possible to take the first reading within ten seconds of zero time. The cerium(IV) concentration at zero time was determined spectrophotometrically as described under electromotive force measurements (see page 13). The spectrophotometric sample was prepared by injecting the given volume of cerium(IV) solution into a volumetric flask containing sulfuric acid. The volume of solution delivered from the hypodermic syringe could be reproduced to within ±0.2 per cent. The concentration of the uranium stock solution was determined before each run by analyzing the

solution spectrophotometrically using the wave length of 6478 Å where the molar absorptivity of uranium(IV) in 1.00 M perchloric acid is 58.9 M^{-1} cm^{-1}.

All rate measurements were taken at 2900 Å where the absorption of cerium(IV) is a maximum. Blank runs were made to determine the molar absorptivity of cerium(IV) over the hydrogen ion concentration range studied. The molar absorptivities of cerium(III), uranium(IV), and uranium(VI) under these conditions were also determined.

In order to determine if the mixing was satisfactory, 30 milliliters of a solution containing 0.30 milliequivalents of sodium hydroxide with one drop phenolphthalein was substituted for the uranium(IV) solution in the mixing cell, and 5 milliliters of 0.60 N HCl was substituted for the cerium(IV). The colored form of the phenolphthalein was not detectible spectrophotometrically when the solutions were mixed according to the foregoing procedure, which indicated that the mixing was adequate.

Stoichiometry. - The stoichiometry of the reaction

$$2Ce(IV) + U(IV) = 2Ce(III) + U(VI)$$

was checked by adding excess cerium(IV) to uranium(IV) under experimental conditions similar to those used in the kinetic experiments. The calculated final cerium(IV) concentration predicted by the stoichiometry of the above equation was then compared with that determined spectrophotometrically at "infinite" time.

The experimental procedure was as follows. An aliquot of cerium(IV) was added to a 50-milliliter volumetric flask containing 25.0 milliliters of perchloric acid at the desired concentration and about 3×10^{-3} milliequivalents of uranium(IV). After sufficient time had lapsed for the reaction to go to completion, sulfuric acid was added and the cerium(IV) concentration determined as described under electromotive force measurements (see page 13). The initial cerium(IV) concentration was determined from a blank in which uranium(VI) was substituted for the uranium(IV).

CHAPTER IV

EXPERIMENTAL RESULTS

Electromotive Force Measurements. - The measured potentials for the cerium(III)-cerium(IV) couple in aqueous perchloric acid (ionic strength = 2) are given in Table IV-1. The potentials were measured at 25°C and 1.6°C. The concentration ratios of cerium(III) to cerium(IV) were determined from the difference between the total cerium concentration and the cerium(IV) concentration.

Molar Absorptivities. - In order to determine the concentration of cerium(IV) in the rate runs, the molar absorptivities of the various ions in the reaction solution were determined. The molar absorbtivities of cerium(IV) at 2900 Å in aqueous perchloric acid (ionic strength = 2) are given in Table IV-2 for the temperatures at which the rate runs were made. Because the molar absorptivities of cerium(III), uranium(IV) and uranium(VI) at 2900 Å were found to be negligible compared with cerium(IV), they were determined only at a perchloric acid concentration of 1.00 M; the values

were 15, 6, 92, $M^{-1}cm^{-1}$ respectively.

Rate Runs. - The data for runs at 2.4°C in which the perchloric acid concentration was varied from 0.800 M to 2.00 M are given in Tables IV-3 through IV-27. The data for 8°C and 15.6°C are given in Tables IV-28 through IV-33 for 2.00 M perchloric acid. Some data were obtained at the higher temperatures with perchloric acid concentrations less than 2.00 M. These data are given in Tables IV-34 and IV-35, but are not to be considered reliable due to the high reaction rates. The cerium(IV) concentrations at any time t were calculated from the absorbance, (corrected for uranium(VI) absorbance) read from the Recorder chart according to Beer's Law using the proper molar absorptivities given in Table IV-2. Cerium(IV) was found to follow Beer's Law in the concentration range used in the kinetic studies. The concentrations of uranium(IV) at any time t were calculated from the initial uranium(IV) concentration and the cerium(IV) concentration at the time t assuming that cerium(IV) reacted with uranium(IV) according to the equation; U(IV) + 2Ce(IV) = 2Ce(III) + U(VI). The ratio of uranium(IV)

to cerium(IV) is given by the expression

$$\frac{[U(IV)]}{[Ce(IV)]} = \left[\frac{([U(IV)]_o - [Ce(IV)]_o)\ (\ \ l)}{D}\right] + 1/2$$

where D = the absorbance corrected for uranium(VI)

Σ = the molar absorptivity $M^{-1}\ cm^{-1}$

l = the cell length cm

$[U(IV)]_o$ = the initial uranium(IV) concentration

$[Ce(IV)]_o$ = the initial cerium(IV) concentration.

Table IV-1

Measured Potentials for the Cerium(III)-Cerium(IV) Couple

Total Cerium, 3.51×10^{-3} M, u = 2.00

$[H^+]$, M	$[Ce(IV)] \times 10^3$, M	P_{H_2}, mm. Hg	E.M.F., volts[a] 25°C	E.M.F., volts[a] 1.6°C
2.00	2.05	584.4	1.71599	1.70977
2.00	1.06	584.4	1.68686	1.68308
1.00	1.94	585.7	1.70946	1.70640
1.00	0.90	585.7	1.67885	1.67856
0.500	2.06	588.5	1.70839	1.70706
0.500	0.95	588.5	1.67705	1.67909
0.300	2.01	585.1	1.70268	1.70264
0.300	0.94	585.1	1.67270	1.67625

a. Calculated from the observed E.M.F. values at the indicated hydrogen pressure for a hydrogen pressure of one atmosphere.

Table IV-2

Molar Absorptivities of Cerium(IV) in Aqueous Perchloric Acid Solutions for 2900 Å, a Cerium(IV) range of 4-5 X 10^{-5} M, and u = 2.00

$[H^+]$,	Molar Absorptivity, $M^{-1}cm^{-1}$			
M	2.4°C	8.0°C	15.6°C	25.0°C
2.00	2370±10	2280±10	2130±10	1930±5
1.50	2240	---	---	1840
1.25	2150	---	---	1780
1.00	2060	1960	---	1720
0.800	1990	---	---	1670
0.500	1850	---	---	1520
0.200	1560	---	---	1250

Table IV-3

Experimental Data for Rate Run 1

$[Ce(IV)]_o = 5.05 \times 10^{-5}$ moles/liter Temperature = 2.4°C

$[U(IV)]_o = 6.06 \times 10^{-5}$ moles/liter $[HClO_4] = 2.00$ moles/liter

Time, sec.	Absorbance	[U(IV)]/[Ce(IV)]
0	---	1.20
10.0	0.743	1.63
12.5	0.665	1.76
15.0	0.595	1.91
17.5	0.534	2.07
20.0	0.478	2.26
25.0	0.387	2.67
30.0	0.317	3.15
35.0	0.260	3.73
40.0	0.216	4.38
45.0	0.179	5.19
50.0	0.147	5.71

Table IV-4

Experimental Data for Rate Run 2

$[Ce(IV)]_o = 4.25 \times 10^{-5}$ moles/liter Temperature = 2.4°C

$[U(IV)]_o = 3.50 \times 10^{-5}$ moles/liter $[HClO_4] = 2.00$ moles/liter

Time, sec.	Absorbance	[U(IV)]/[Ce(IV)]
0	---	0.82
10.0	0.752	0.94
15.0	0.658	1.00
20.0	0.582	1.06
25.0	0.519	1.13
30.0	0.466	1.20
35.0	0.419	1.28
40.0	0.377	1.37
45.0	0.343	1.46
50.0	0.310	1.56

Table IV-5

Experimental Data for Rate Run 3

$[Ce(IV)]_o = 4.28 \times 10^{-5}$ moles/liter Temperature = 2.4°C

$[U(IV)]_o = 7.08 \times 10^{-5}$ moles/liter $[HClO_4] = 2.00$ moles/liter

Time, sec.	Absorbance	[U(IV)]/[Ce(IV)]
0	---	1.66
10	0.576	2.54
12.5	0.501	2.84
15.0	0.431	3.22
17.5	0.378	3.60
20.5	0.329	4.06
22.5	0.290	4.54
25.0	0.254	5.11
30.0	0.195	6.50
35.0	0.158	7.91

Table IV-6

Experimental Data for Rate Run 4

$[Ce(IV)]_o = 4.27 \times 10^{-5}$ moles/liter Temperature = 2.4°C

$[U(IV)]_o = 8.83 \times 10^{-5}$ moles/liter $[HClO_4] = 2.00$ moles/liter

Time, sec.	Absorbance	[U(IV)]/[Ce(IV)]
0	---	2.07
10.0	0.482	3.79
12.5	0.406	4.41
15.0	0.342	5.14
17.5	0.292	5.94
20.0	0.248	6.90
22.5	0.211	8.02
25	0.181	9.26

Table IV-7

Experimental Data for Rate Run 5

$[Ce(IV)]_o = 6.01 \times 10^{-5}$ moles/liter Temperature = 2.4°C

$[U(IV)]_o = 8.02 \times 10^{-5}$ moles/liter $[HClO_4] = 2.00$ moles/liter

Time, sec.	Absorbance	[U(IV)]/[Ce(IV)]
0	---	1.33
5.0	1.125	1.56
7.5	0.901	1.82
10.0	0.752	2.08
12.5	0.643	2.35
15.0	0.556	2.64
17.5	0.478	2.88
20.0	0.413	3.38
22.5	0.360	3.80
25.0	0.312	4.31
30.0	0.237	5.51

Table IV-8

Experimental Data for Rate Run 6

$[Ce(IV)]_o = 8.22 \times 10^{-5}$ moles/liter Temperature = 2.4°C

$[U(IV)]_o = 5.55 \times 10^{-5}$ moles/liter $[HClO_4] = 1.25$ moles/liter

Time, sec.	Absorbance	[U(IV)]/[Ce(IV)]
0	---	0.68
10.0	0.908	0.84
12.5	0.800	0.89
15.0	0.706	0.94
20.0	0.563	1.06
25.0	0.457	1.18

Table IV-9

Experimental Data for Rate Run 7

$[Ce(IV)]_o = 8.63 \times 10^{-5}$ moles/liter Temperature = 2.4°C

$[U(IV)]_o = 6.32 \times 10^{-5}$ moles/liter $[HClO_4] = 1.25$ moles/liter

Time, sec.	Absorbance	[U(IV)]/[Ce(IV)]
0	---	0.74
10.0	0.866	1.00
12.5	0.746	1.08
15.0	0.644	1.18
17.5	0.560	1.28
20.0	0.495	1.38
25.0	0.388	1.62
30.0	0.320	1.86
35.0	0.252	2.22
40.0	0.207	2.60
45.0	0.169	3.07

Table IV-10

Experimental Data for Rate Run 8

$[Ce(IV)]_o = 7.57 \times 10^{-5}$ moles/liter Temperature = 2.4°C

$[U(IV)]_o = 5.39 \times 10^{-5}$ moles/liter $[HClO_4] = 1.25$ moles/liter

Time, sec.	Absorbance	[U(IV)]/[Ce(IV)]
0	---	0.71
10	0.847	0.91
12.5	0.739	0.97
15.0	0.651	1.03
17.5	0.576	1.10
20.0	0.512	1.18
25.0	0.413	1.34
30.0	0.339	1.52
35.0	0.282	1.73
40.0	0.236	1.96
45.0	0.198	2.25

Table IV-11

Experimental Data for Rate Run 9

$[Ce(IV)]_o = 5.56 \times 10^{-5}$ moles/liter Temperature = 2.4°C

$[U(IV)]_o = 3.42 \times 10^{-5}$ moles/liter $[HClO_4] = 1.25$ moles/liter

Time, sec.	Absorbance	[U(IV)]/[Ce(IV)]
0	---	0.61
10.0	0.848	0.66
15.0	0.669	0.71
20.0	0.560	0.75
30.0	0.412	0.84
40.0	0.322	0.93
50.0	0.260	1.04

Table IV-12

Experimental Data for Rate Run 10

$[Ce(IV)]_o = 5.56 \times 10^{-5}$ moles/liter Temperature = 2.4°C

$[U(IV)]_o = 3.42 \times 10^{-5}$ moles/liter $[HClO_4] = 1.25$ moles/liter

Time, sec.	Absorbance	[U(IV)]/[Ce(IV)]
0	---	0.61
10.0	0.818	0.67
15.0	0.667	0.71
20.0	0.563	0.74
25.0	0.481	0.79
30.0	0.417	0.88
40.0	0.327	0.92
50.0	0.264	1.02

Table IV-13

Experimental Data for Rate Run 11

$[Ce(IV)]_o = 5.37 \times 10^{-5}$ moles/liter Temperature = 2.4°C

$[U(IV)]_o = 4.54 \times 10^{-5}$ moles/liter $[HClO_4] = 1.25$ moles/liter

Time, sec.	Absorbance	[U(IV)]/[Ce(IV)]
0	---	0.84
10.0	0.669	1.10
15.0	0.515	1.28
20.0	0.406	1.49
25.0	0.323	1.79
30.0	0.262	2.03
40.0	0.177	2.77

Table IV-14

Experimental Data for Rate Run 12

$[Ce(IV)]_o = 5.37 \times 10^{-5}$ moles/liter Temperature = 2.4°C

$[U(IV)]_o = 4.54 \times 10^{-5}$ moles/liter $[HClO_4] = 1.25$ moles/liter

Time, sec.	Absorbance	[U(IV)]/[Ce(IV)]
0	---	0.84
10.0	0.630	1.14
15.0	0.490	1.32
20.0	0.388	1.54
25.0	0.315	1.78
30.0	0.258	2.06
40.0	0.177	2.77

Table IV-15

Experimental Data for Rate Run 13

$[Ce(IV)]_o = 3.01 \times 10^{-5}$ moles/liter Temperature = 2.4°C

$[U(IV)]_o = 1.76 \times 10^{-5}$ moles/liter $[HClO_4] = 1.00$ moles/liter

Time, sec.	Absorbance	[U(IV)]/[Ce(IV)]
0	---	0.584
10.0	0.454	0.610
15.0	0.397	0.632
20.0	0.353	0.648
25.0	0.317	0.666
30.0	0.288	0.682
35.0	0.260	0.702
40.0	0.240	0.718
45.0	0.222	0.736
50.0	0.204	0.758

Table IV-16

Experimental Data for Rate Run 14

$[Ce(IV)]_o = 7.63 \times 10^{-5}$ moles/liter Temperature = 2.4°C

$[U(IV)]_o = 3.31 \times 10^{-5}$ moles/liter $[HClO_4] = 1.00$ moles/liter

Time, sec.	Absorbance	[Ce(IV)]/[U(IV)]
0	---	2.31
10.0	0.950	2.56
15.0	0.812	2.71
20.0	0.710	2.85
25.0	0.634	3.00
30.0	0.575	3.17
40.0	0.485	3.55
50.0	0.427	3.97

Table IV-17

Experimental Data for Rate Run 15

$[Ce(IV)]_o = 5.91 \times 10^{-5}$ moles/liter Temperature = 2.4°C

$[U(IV)]_o = 3.19 \times 10^{-5}$ moles/liter $[HClO_4] = 1.00$ moles/liter

Time, sec.	Absorbance	[U(IV)]/[Ce(IV)]
0	---	0.540
10.0	0.743	0.566
15.0	0.613	0.576
20.0	0.522	0.593
25.0	0.452	0.608
30.0	0.397	0.622
35.0	0.351	0.638
40.0	0.317	0.653
45.0	0.275	0.676
50.0	0.259	0.688

Table IV-18

Experimental Data for Rate Run 16

$[Ce(IV)]_o = 8.39 \times 10^{-5}$ moles/liter Temperature = 2.4°C

$[U(IV)]_o = 4.30 \times 10^{-5}$ moles/liter $[HClO_4] = 1.00$ moles/liter

Time, sec.	Absorbance	$[Ce(IV)] \times 10^5$, M
0	---	8.39
10.0	0.948	4.58
15.0	0.762	3.68
20.0	0.634	3.06
25.0	0.544	2.63
30.0	0.478	2.31
35.0	0.423	2.04
40.0	0.378	1.83

Table IV-19

Experimental Data for Rate Run 17

$[Ce(IV)]_o = 8.39 \times 10^{-5}$ moles/liter Temperature = 2.4°C

$[U(IV)]_o = 4.30 \times 10^{-5}$ moles/liter $[HClO_4] = 1.00$ moles/liter

Time, sec.	Absorbance	$[Ce(IV)] \times 10^5$ M
0	---	8.39
10.0	0.914	4.42
15.0	0.735	3.55
20.0	0.612	2.96
25.0	0.524	2.53
30.0	0.457	2.21
35.0	0.404	1.95
40.0	0.362	1.75

Table IV-20

Experimental Data for Rate Run 18

$[Ce(IV)]_o = 4.51 \times 10^{-5}$ moles/liter Temperature = 2.4°C

$[U(IV)]_o = 2.31 \times 10^{-5}$ moles/liter $[HClO_4] = 1.25$ moles/liter

Time, sec.	Absorbance	$[Ce(IV)] \times 10^5$ M
0	---	4.65
10.0	0.731	3.38
15.0	0.638	2.95
20.0	0.570	2.64
25.0	0.513	2.38
30.0	0.468	2.17
35.0	0.430	1.99
40.0	0.393	1.82

Table IV-21

Experimental Data for Rate Run 19

$[Ce(IV)]_o = 5.06 \times 10^{-5}$ moles/liter Temperature = 2.4°C

$[U(IV)]_o = 2.62 \times 10^{-5}$ moles/liter $[HClO_4] = 2.00$ moles/liter

Time, sec.	Absorbance	$[Ce(IV)] \times 10^5$ M
0	---	5.06
10.0	0.975	4.11
20.0	0.818	3.45
30.0	0.698	2.94
40.0	0.612	2.58
50.0	0.542	2.29
60.0	0.485	2.05

Table IV-22

Experimental Data for Rate Run 20

$[Ce(IV)]_o = 5.06 \times 10^{-5}$ moles/liter Temperature = 2.4°C

$[U(IV)]_o = 2.62 \times 10^{-5}$ moles/liter $[HClO_4] = 2.00$ moles/liter

Time, sec.	Absorbance	$[Ce(IV)] \times 10^5$ M
0	---	5.06
10.0	0.979	4.13
20.0	0.819	3.46
30.0	0.700	2.95
40.0	0.614	2.59
50.0	0.545	2.30
60.0	0.489	2.06

Table IV-23

Experimental Data for Rate Run 21

$[Ce(IV)]_o = 5.32 \times 10^{-5}$ moles/liter Temperature = 2.4°C

$[U(IV)]_o = 2.66 \times 10^{-5}$ moles/liter $[HClO_4] = 0.800$ moles/liter

Time, sec.	Absorbance	$[Ce(IV)] \times 10^5$ M
0	---	5.32
10.0	0.636	3.21
12.5	0.571	2.88
15.0	0.518	2.62
17.5	0.477	2.41
20.0	0.441	2.23
25.0	0.385	1.94

Table IV-24

Experimental Data for Rate Run 22

$[Ce(IV)]_o = 4.10 \times 10^{-5}$ moles/liter Temperature = 2.4°C

$[U(IV)]_o = 2.12 \times 10^{-5}$ moles/liter $[HClO_4] = 0.800$ moles/liter

Time, sec.	Absorbance	$[Ce(IV)] \times 10^5$ M
0	---	4.10
10.0	0.563	2.84
12.5	0.511	2.58
15.0	0.466	2.35
17.5	0.430	2.17
20.0	0.400	2.02
25.0	0.351	1.77

Table IV-25

Experimental Data for Rate Run 23

$[Ce(IV)]_o = 3.97 \times 10^{-5}$ moles/liter Temperature = 2.4°C

$[U(IV)]_o = 2.02 \times 10^{-5}$ moles/liter $[HClO_4] = 0.800$ moles/liter

Time, sec.	Absorbance	$[Ce(IV)] \times 10^5$, M
0	---	3.97
10.0	0.552	2.79
12.5	0.496	2.50
15.0	0.454	2.29
17.5	0.416	2.10
20.0	0.389	1.96
25.0	0.342	1.73

Table IV-26

Experimental Data for Rate Run 24

$[Ce(IV)]_o = 8.38 \times 10^{-5}$ moles/liter Temperature = 2.4°C

$[U(IV)]_o = 4.36 \times 10^{-5}$ moles/liter $[HClO_4] = 0.800$ moles/liter

Time, sec.	Absorbance	$[Ce(IV)] \times 10^5$, M
0	---	8.38
10	0.763	3.85
12.5	0.665	3.36
15.0	0.591	2.98
17.5	0.532	2.69
20.0	0.482	2.43
25.0	0.405	2.04

Table IV-27

Experimental Data for Rate Run 25

$[Ce(IV)]_o = 8.48 \times 10^{-5}$ moles/liter Temperature = 2.4°C

$[U(IV)]_o = 4.41 \times 10^{-5}$ moles/liter $[HClO_4] = 0.800$ moles/liter

Time, sec.	Absorbance	$[Ce(IV)] \times 10^5$, M
0	---	8.48
10.0	0.871	4.40
12.5	0.738	3.73
15.0	0.649	3.28
17.5	0.579	2.92
20.0	0.523	2.64
22.5	0.477	2.41
25.0	0.434	2.19

Table IV-28

Experimental Data for Rate Run 26

$[Ce(IV)]_o = 6.74 \times 10^{-5}$ moles/liter Temperature = 8.0°C

$[U(IV)]_o = 3.68 \times 10^{-5}$ moles/liter $[HClO_4] = 2.00$ moles/liter

Time, sec.	Absorbance	[U(IV)]/[Ce(IV)]
0	---	0.546
10.0	0.970	0.573
15.0	0.811	0.588
20.0	0.687	0.603
25.0	0.595	0.619
30.0	0.525	0.635
40.0	0.423	0.668
50.0	0.349	0.703
60.0	0.295	0.740
70.0	0.254	0.779

Table IV-29

Experimental Data for Rate Run 27

$[Ce(IV)]_o = 5.99 \times 10^{-5}$ moles/liter Temperature = 8.0°C

$[U(IV)]_o = 3.97 \times 10^{-5}$ moles/liter $[HClO_4] = 2.00$ moles/liter

Time, sec.	Absorbance	[U(IV)]/[Ce(IV)]
0	---	0.663
10	0.829	0.768
12.5	0.745	0.798
15.0	0.668	0.833
17.5	0.612	0.863
20.0	0.563	0.895
25.0	0.472	0.971

Table IV-30

Experimental Data for Rate Run 28

$[Ce(IV)]_o = 4.44 \times 10^{-5}$ moles/liter Temperature = 15.6°C

$[U(IV)]_o = 2.23 \times 10^{-5}$ moles/liter $[HClO_4] = 2.00$ moles/liter

Time, sec.	Absorbance	$[Ce(IV)] \times 10^5$, M
0	---	4.44
10.0	0.562	2.64
12.5	0.507	2.39
15.0	0.462	2.17
20.0	0.392	1.84
25.0	0.341	1.60
30.0	0.303	1.43

Table IV-31

Experimental Data for Rate Run 29

$[Ce(IV)]_o = 4.41 \times 10^{-5}$ moles/liter Temperature = 15.6°C

$[U(IV)]_o = 2.21 \times 10^{-5}$ moles/liter $[HClO_4] = 2.00$ moles/liter

Time, sec.	Absorbance	$[Ce(IV)] \times 10^5$, M
0	---	4.41
10.0	0.552	2.60
12.5	0.497	2.34
15.0	0.451	2.12
20.0	0.380	1.79
25.0	0.328	1.54
30.0	0.287	1.35

Table IV-32

Experimental Data for Rate Run 30

$[Ce(IV)]_o = 4.25 \times 10^{-5}$ moles/liter Temperature = 15.6°C

$[U(IV)]_o = 2.18 \times 10^{-5}$ moles/liter $[HClO_4] = 2.00$ moles/liter

Time, sec.	Absorbance	$[Ce(IV)] \times 10^5$, M
0	---	4.25
10.0	0.532	2.50
12.5	0.480	2.26
15.0	0.426	2.00
20.0	0.369	1.74
25.0	0.319	1.50
30.0	0.282	1.33

Table IV-33

Experimental Data for Rate Run 31

$[Ce(IV)]_o = 4.08 \times 10^{-5}$ moles/liter Temperature = 15.6°C

$[U(IV)]_o = 2.10 \times 10^{-5}$ moles/liter $[HClO_4] = 2.00$ moles/liter

Time, sec.	Absorbance	$[Ce(IV)] \times 10^5$, M
0	---	4.08
10.0	0.519	2.44
12.5	0.468	2.20
15.0	0.426	2.00
20.0	0.360	1.69
25.0	0.315	1.48
30.0	0.276	1.30

Table IV-34

Experimental Data for Rate Run 32

$[Ce(IV)]_o = 6.49 \times 10^{-5}$ moles/liter Temperature = 8.0°C

$[U(IV)]_o = 3.21 \times 10^{-5}$ moles/liter $[HClO_4] = 1.00$ moles/liter

Time, sec.	Absorbance	$[Ce(IV)] \times 10^5$, M
0	---	6.49
10.0	0.599	2.81
12.5	0.521	2.45
15.0	0.466	2.19
17.5	0.416	1.95
20.0	0.378	1.77
25.0	0.317	1.49
30.0	0.274	1.29
35.0	0.240	1.13
40.0	0.213	1.00

Table IV-35

Experimental Data for Rate Run 33

$[Ce(IV)]_o = 4.94 \times 10^{-5}$ moles/liter Temperature = 8.0°C

$[U(IV)]_o = 2.44 \times 10^{-5}$ moles/liter $[HClO_4] = 1.00$ moles/liter

Time, sec.	Absorbance	$[Ce(IV)] \times 10^5$ M
0	---	4.94
10	0.508	2.38
12.5	0.452	2.12
15.0	0.415	1.95
17.5	0.379	1.78
20.0	0.348	1.63
25.0	0.297	1.39
30.0	0.262	1.23
35.0	0.232	1.09
40.0	0.211	0.99

Table IV-36

Check of the Stoichiometry of the Reaction 2Ce(IV) + U(IV) = 2Ce(III) + U(VI) in Perchloric Acid Solutions, $\mu = 2.00$

Run	U(IV) X 10^3, meq.	Ce(IV) X 10^3, meq.	Ce(IV) X 10^3, at t = "infinity", meq. Calc.	Found
1[a]	2.99	5.40	2.41	2.33
2	2.99	5.54	2.55	2.52
3	2.99	4.49	1.50	1.42
4	2.97	4.64	1.67	1.61
5	2.97	4.56	1.59	1.50
6[b]	2.96	6.97	4.01	3.96
7	2.96	3.45	0.49	0.46
8	2.96	5.66	2.70	2.64

a. Runs 1 through 5 were made in 25.0 milliliters of 1.00 M perchloric acid and $\mu = 2.00$.

b. Runs 6 through 8 were made in 25.0 milliliters of 2.00 M perchloric acid.

CHAPTER V

DISCUSSION

Effect of hydrolysis on the rate of reaction. - Highly charged metal ions generally undergo hydrolysis in aqueous solution; therefore, the concentration of the metal ion as a function of the hydrogen ion concentration must be taken into consideration in the determination of the specific rate constants. For example, in a second order reaction between the metal ion M_1^{+n} and $M_2^{+n'}$, the rate of reaction R would be given by the expression

$$R = k[M_1^{+n}]\,[M_2^{+n'}] \qquad (V-1)$$

where k = the specific rate constant and $[M_1^{+n}]$ and $[M_2^{+n'}]$ = the concentrations of the metal ions. If the metal ion hydrolyzses according to the equation

$$M^{+n} + qH_2O = M(OH)_q^{+(n-q)} + qH^+$$

then

$$\frac{[M(OH)_q^{+(n-q)}]\,[H^+]^q}{[M^{+n}]} = K \qquad (V-2)$$

where K is the hydrolysis quotient and the

quantities in brackets are the concentrations of the respective ions. By adding unity to both sides of equation (V-2) and rearranging terms, the concentration of M^{+n} is given by

$$[M^{+n}] = \frac{[M^o]\,[H^+]^q}{K + [H^+]^q} \qquad (V-3)$$

where $[M^o]$ is the total concentration of the metal ion M in the +n oxidation state. The rate of reaction given by equation (V-1) can now be expressed in terms of the total concentration of the metal ion $[M^o]$ by the equation

$$R = k \left(\frac{[M_1^o]\,[H^+]^{q1}}{K_1 + [H^+]^{q1}} \right) \left(\frac{[M_2^o]\,[H^+]^{q2}}{K_2 + [H^+]^{q2}} \right). \qquad (V-4)$$

It is easily seen that when K is small with respect to $[H^+]^q$ equation (V-4) reduces to $R = k\,[M_1^o]\,[M_2^o]$. It is also apparent from equation(V-4) that if the hydrolysis can not be neglected, the hydrolysis quotients must be known in order to calculate the specific rate constant k.

In the present study the hydrolysis of cerium(IV) was studied potentiometrically in perchloric acid-sodium perchlorate solutions at ionic strength two, over the perchloric acid concentration range of 0.300 to 2.00 M.

Electromotive Force Measurements. - The hydrolysis of cerium(IV) was determined from the experimental data given in Table IV-1 and the following considerations.

The hydrolysis steps may be represented by equations

$$Ce^{+4} + H_2O = CeOH^{+3} + H^+ \quad K_1 = \frac{[CeOH^{+3}][H^+]}{[Ce^{+4}]} \qquad (V-5)$$

and

$$CeOH^{+3} + H_2O = Ce(OH)_2^{+2} + H^+ \quad K_2 = \frac{[Ce(OH)_2^{+2}][H^+]}{[CeOH^{+3}]} . \qquad (V-6)$$

Where K_1 and K_2 are the hydrolysis quotients for the first and second steps, respectively, and brackets indicate molar concentrations.

By rearrangement and multiplication of equations (V-5) and (V-6)

$$\frac{[Ce(OH)_2^{+2}]}{[Ce^{+4}]} = \frac{K_1K_2}{[H^+]^2} . \qquad (V-7)$$

Now, adding equations (V-5) and (V-7) and unity to each side

$$\frac{[Ce^{+4}]}{[Ce^{+4}]} + \frac{[Ce(OH)^{+3}]}{[Ce^{+4}]} + \frac{[Ce(OH)_2^{+2}]}{[Ce^{+4}]} = 1 + \frac{K_1K_2}{[H^+]^2} + \frac{K_1}{[H^+]}$$

From (V-8) and (V-10)

$$E = E^{o'} - \frac{RT}{F} \ln \frac{[Ce^{+3}][H^+]}{[Ce(IV)]} \left[1 + \frac{K_1}{[H^+]} + \frac{K_1 K_2}{[H^+]^2} \right]. \qquad (V-12)$$

The hydrolysis quotient[12] of Ce^{+3} is the order of 10^{-9}; thus, the total cerous concentration, [Ce(III)], equals $[Ce^{+3}]$.

Equation (V-12) may now be rewritten as

$$E = E^{o'} - \frac{RT}{F} \ln \frac{[Ce(III)][H^+]}{[Ce(IV)]} - \frac{RT}{F} \ln \left[1 + \frac{K_1}{[H^+]} + \frac{K_1 K_2}{[H^+]^2} \right]. \qquad (V-13)$$

If the quantity E_f, the formal potential, is defined as

$$E_f = E + \frac{RT}{F} \ln \frac{[Ce(III)][H^+]}{[Ce(IV)]} \qquad (V-14)$$

where all the quantities on the right hand side of the equation are experimentally determinable, it then follows from equation (V-13) that

$$E_f = E^{o'} - \frac{RT}{F} \ln \left[1 + \frac{K_1}{[H^+]} + \frac{K_1 K_2}{[H^+]^2} \right]. \qquad (V-15)$$

When $K_1 >> [H^+]$, equation (V-15) becomes

$$E_f = E^{o'} - \frac{RT}{F} \ln K_1 - \frac{RT}{F} \ln \left(\frac{[H^+] + K_2}{[H^+]^2} \right). \qquad (V-16)$$

From the calculated values of E_f at various hydrogen ion concentrations and cerium(III) cerium(IV) ratios, K_1, K_2 and $E^{o'}$ can be evaluated using equation (V-15).

Values of E_f, calculated from equation (V-14), are given in Table V-1. It is to be noted that there is a consistent trend in the values of the formal potential which depends on the cerium(IV) concentration. This trend is presumably due to polymerization of the cerium(IV).

King and Pandow[13] investigated the absorption spectra of cerium(IV) in acid perchlorate media and found the existence of an equilibria between monomeric and polymeric species. Using King's data, the per cent of cerium(IV) in the form of a polymer was estimated to be small and at most 10 per cent in the cerium(IV) concentration range covered for the potential measurements.

Because equation (V-11) was derived for the cell reaction

$$Ce^{+4} + 1/2H_2 = Ce^{+3} + H^+,$$

extrapolation of the values for the formal potential to zero cerium(IV) concentration will correct for the effect of polymerization. If cerium(IV) is

Table V-1

Values for the Formal Potential E_f for the Cerium(III)-Cerium(IV) Couple in Perchloric Acid

Total Cerium, 3.51×10^{-3} M. $\mu = 2.00$

$[H^+]$, M	$[Ce(IV)] \times 10^3$, M	E_f, volts 25.0°C	E_f, volts 1.6°C
2.00	1.06	1.7262 ± 0.0005	1.7193 ± 0.0005
2.00	2.06	1.7249	1.7180
1.00	0.90	1.7062	1.7038
1.00	1.94	1.7040	1.7014
0.500	0.95	1.6847	1.6862
0.500	2.06	1.6818	1.6862
0.300	0.94	1.6674	1.6714
0.300	2.01	1.6644	1.6673

assumed to form a dimer, then an expression for the formal potential at zero cerium(IV) concentration can be derived as follows. For the reaction

$$2Ce(IV) = Ce(IV)_2$$

$$\frac{[Ce(IV)_2]}{[Ce(IV)]^2} = K_D \qquad (V-17)$$

where

$[Ce(IV)_2]$ and $[Ce(IV)]$ = the dimer and cerium(IV) concentrations respectively.

K_D = the dimerization quotient.

Let C equal the concentration of cerium(IV) in the form of the dimer. Then equation (V-17) becomes

$$\frac{C}{[Ce(IV)]^2} = 2K_D.$$

By rearranging and adding unity to both sides one obtains

$$\frac{C}{[Ce(IV)]} + \frac{[Ce(IV)]}{[Ce(IV)]} = 1 + 2K_D\,[Ce(IV)]$$

which yields

$$\frac{[Ce(IV)]_o}{[Ce(IV)]} = 1 + 2K_D\,[Ce(IV)]$$

where $[Ce(IV)]_o$ = the total cerium(IV) concentration. Because the amount of dimerization is small

$[Ce(IV)]_o \cong [Ce(IV)]$, and the above equation can be written as

$$\frac{[Ce(IV)]_o}{[Ce(IV)]} = 1 + 2K_D[Ce(IV)]_o \qquad (V - 18)$$

By substitution of the ratio $[Ce(IV)]_o/[Ce(IV)]$ from equation (V - 18) into equation (V - 14) at constant hydrogen ion concentration, the formal potential E_{f_o} for the limit $[Ce(IV)]_o \longrightarrow 0$ is given by the expression

$$E_{f_o} = E_f + A \ln(1 + 2K_D[Ce(IV)]_o), \qquad (V - 19)$$

where the constant A equals RT/F. Equation (V - 19) can be expanded to give

$$E_{f_o} = E_f = 2AK_D[Ce(IV)]_o - 2(AK_D)^2 [Ce(IV)]_o^2 \qquad (V - 20)$$

where higher terms than second power have been neglected. Values of the formal potential E_{f_o} obtained by using equation (V - 20) are given in Table V - 2.

Using the values of E_{f_o} from Table V - 2 and equation (V - 15) or (V - 16) three constants must be evaluated, $E^{o'}$, K_1 and K_2. Values for the hydrolysis quotients K_1 and K_2 which fit the experimental data within the experimental error were found by trial and error. These values were

Table V-2

Formal Potentials of the Cerium(III)-Cerium(IV) Couple in Perchloric Acid (μ = 2.00), Extrapolated to Zero Cerium(IV) Concentration

$[H^+]$, M	E_{f_o}, volts 25.0°C	E_{f_o}, volts 1.6°C
2.00	1.7275 ± 0.0005	1.7207 ± 0.0005
1.00	1.7083	1.7061
0.500	1.6876	1.6899
0.300	1.6706	1.6759

obtained in the following way. From the theory of least squares the best values of the constants $\bar{E}^{o'}$, K_1 and K_2 are those values for which the sum of the squares of the differences between the calculated formal potentials and the experimental formal potentials is a minimum. Trial values of K_1 and K_2 were chosen and the constant $\bar{E}^{o'}$ was then determined by equation (V-15) for the particular pair of K_1, K_2 values from the experimental data for each experimental point. Using the average value $E^{o'}$ so obtained, values of the formal potential were calculated by equation (V-15). For various pairs of K_1, K_2 values, the sum of the squares of the differences are given in Tables V-3 and V-4.

From the probable experimental error in the determination of the formal potentials, any pair of K_1, K_2 values which give a sum of squares less than one would be within the experimental error. Using the data in Table V-3 and Table V-4, the sum of the squares of the differences were ploted in Figures V-1 and V-2 for the corresponding pairs of K_1, K_2 values, giving essentially a topographical map; hence, in Figures V-1 and V-2 any point corresponding to a pair of K_1, K_2 values within

Table V-3

Sum of the Squares of the Differences for Calculated and Experimental Formal Potentials, E_f, for Pairs of K_1, K_2 Values at 25°C.

K_1, M	K_2, M	$\bar{E}^{o'}$, volts	$(\bar{E}^{o'} - \frac{RT}{F} \ln K_1)$, volts	$\Sigma d^2 \times 10^6$, volts^2
$[H^+]$	0.05	---	1.7083	14.4
$[H^+]$	0.10	---	1.7102	2.6
$[H^+]$	0.15	---	1.7119	0.1
$[H^+]$	0.20	---	1.7134	4.5
40	0.10	1.8054	---	5.4
40	0.15	1.8070	---	0.3
40	0.20	1.8086	---	1.25
40	0.25	1.8100	---	6.6
20	0.10	1.7882	---	9.3
20	0.15	1.7898	---	1.6
20	0.20	1.7913	---	0.3
20	0.25	1.7928	---	3.9
10	0.15	1.7730	---	6.9
10	0.20	1.7744	---	1.1
10	0.25	1.7758	---	1.2
10	0.30	1.7772	---	4.5
5	0.20	1.7584	---	13.3
5	0.25	1.7597	---	5.8
5	0.30	1.7610	---	3.3
5	0.35	1.7622	---	3.8
5	0.40	1.7633	---	6.2
2.5	0.30	1.7460	---	23.0

Table V-4

Sum of the Squares of the Differences for Calculated and Experimental Formal Potentials, E_f, for Pairs of K_1, K_2 Values at 1.6°C.

K_1, M	K_2, M	$\bar{E}^{o'}$, volts	$(\bar{E}^{o'} - \frac{RT}{F} \ln K_1)$, volts	$\Sigma d^2 \times 10^6$, volts^2
$[H^+]$	0	---	1.7053	3.4
$[H^+]$	0.01	---	1.7057	3.5
$[H^+]$	0.05	---	1.7072	7.9
$[H^+]$	0.10	---	1.7089	20.7
60	0	1.8026	---	3.1
60	0.01	1.8030	---	2.6
60	0.05	1.8044	---	5.4
60	0.10	1.8062	---	16.2
40	0.01	1.7936	---	2.3
40	0.03	1.794	---	2.6
40	0.05	1.7950	---	4.4
40	0.10	1.7968	---	14.3
20	0.01	1.7774	---	3.1
20	0.03	1.7780	---	1.2
20	0.05	1.7792	---	2.1
20	0.10	1.7808	---	9.5
10	0.01	1.7622	---	5.5
10	0.05	1.7637	---	0.5
10	0.10	1.7653	---	3.0
5	0.05	1.7491	---	6.4
5	0.10	1.7506	---	0.5
5	0.15	1.7521	---	1.8
5	0.20	1.7534	---	7.8
2.5	0-0.1	---	---	5

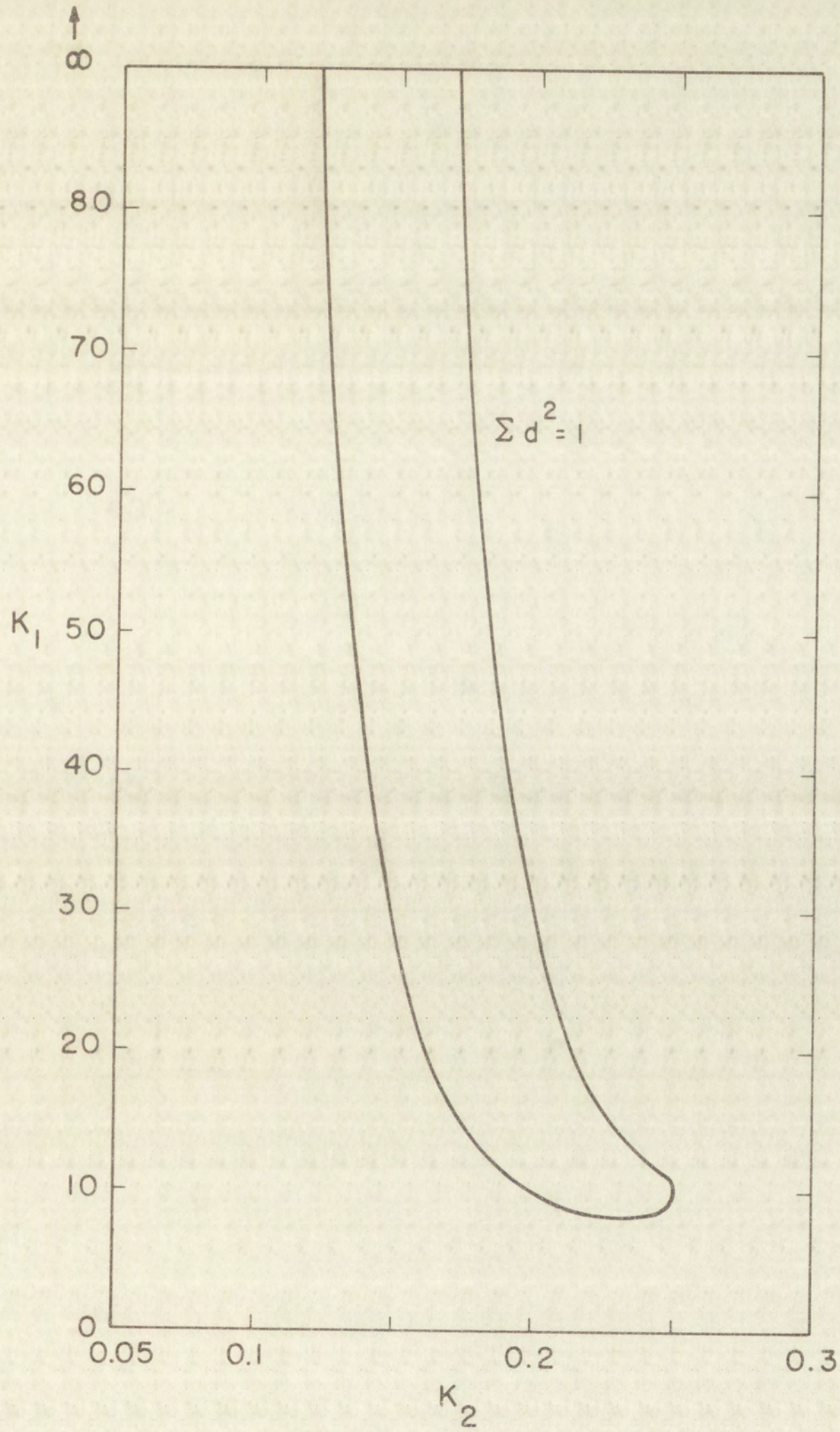


FIG. V-1 Σd^2 FOR K_1, K_2 PAIRS AT 25 °C

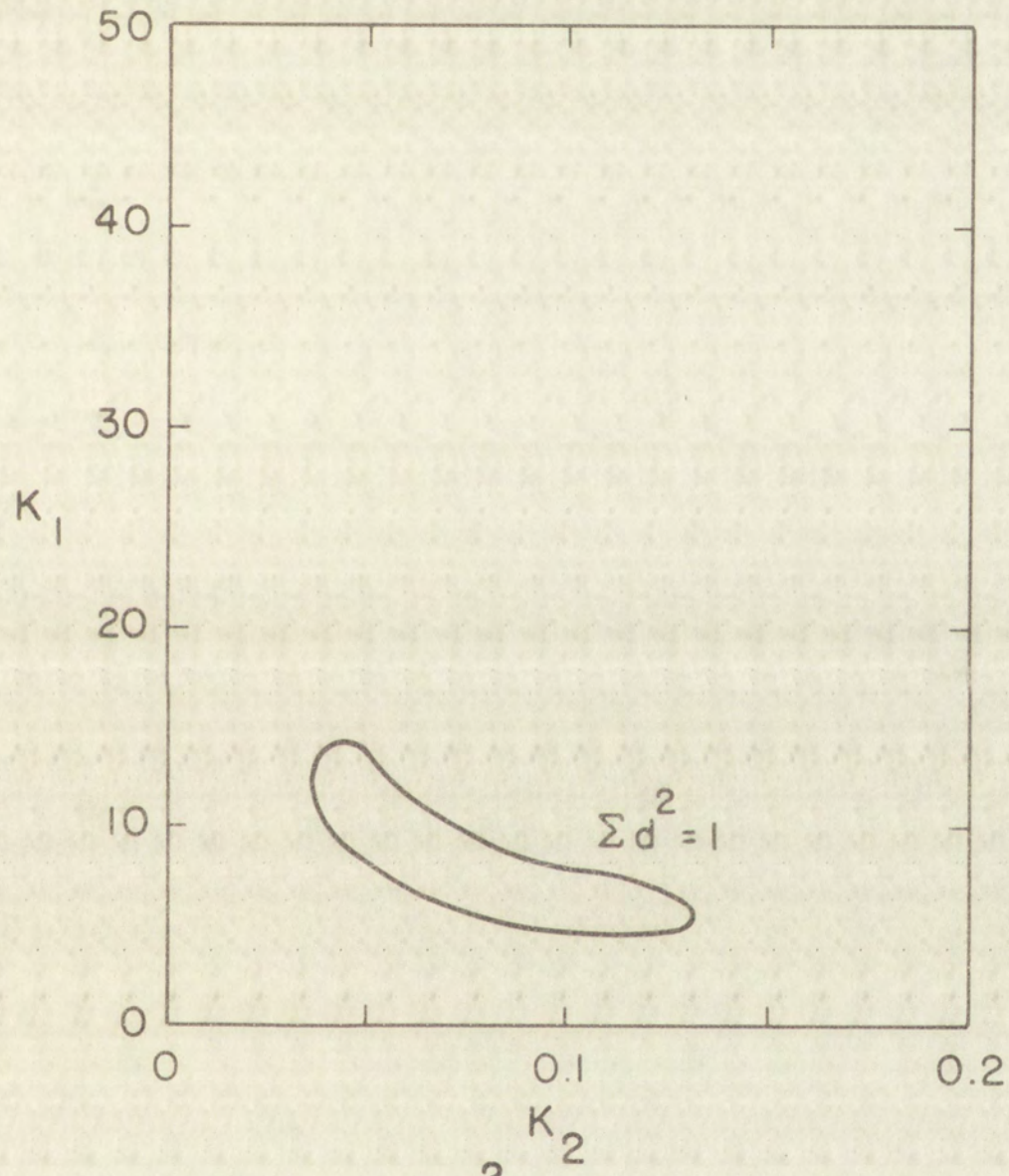


FIG. V-2 Σd^2 FOR K_1, K_2 PAIRS AT 1.6 °C

the contour line $\Sigma d^2 = 1$ will reproduce the formal potentials within the experimental error.

From Figures V-1 and V-2 it can be seen that unique values of the constants cannot be found, but limits can be set. Formal potentials calculated from the limits and best values of K_1 and K_2 are compared with the experimental formal potentials in Table V-5. The data indicate that in 2 M perchloric acid the first hydrolysis step is at least 85 per cent complete at 25°C. While at 1.6°C the first hydrolysis step is at least 70 per cent complete but not more than 90 per cent complete. Thus, one may conclude that the predominant cerium(IV) species in 2 M perchloric acid is $CeOH^{+3}$. This is contrary to the assumption made by Hardwick and Robertson[14] but is in agreement with the conclusion of Sherrill, King, and Spooner.[16] The latter authors, in their study of the cerium(III)-cerium(IV) potential at 25°C found K_1 to be much greater than the hydrogen ion concentration and K_2 to equal 0.6. In the present work K_1 was also found to be much greater than the hydrogen ion concentration at 25°C; however, K_2 ranged from 0.12 to 0.22. It is to be noted that in the work of Sherrill et al. the ionic strength

Table V-5

Experimental Formal Potentials Compared with Calculated Values, for the Limits and Best Values of K_1 and K_2 at 25°C and 1.6°C.

Temperature = 25°C

$[H^+]$, M	Exp. E_f, volts	Calculated E_f, volts: $K_1 >> [H^+]$, K_2 = 0.15, best value	$K_1 >> [H^+]$, K_2 = 0.12, lower limit	K_1 = 10, K_2 = 0.22, upper limit
2.00	1.7275±0.0004	1.7278	1.7271	1.7268
1.00	1.7083	1.7083	1.7079	1.7088
0.500	1.6876	1.6874	1.6875	1.6879
0.300	1.6706	1.6706	1.6713	1.6704
$\Sigma d(\text{volts})^2 \times 10^6$		0.1	1.0	0.9

Temperature = 1.6°C

$[H^+]$, M	Exp. E_f, volts	Calculated E_f, volts: K_1 = 8, K_2 = 0.08, best value	K_1 = 14, K_2 = 0.05, lower limit	K_1 = 5, K_2 = 0.14, upper limit
2.00	1.7207±0.0004	1.7210	1.7214	1.7210
1.00	1.7061	1.7062	1.7059	1.7068
0.500	1.6899	1.6895	1.6892	1.6897
0.300	1.6759	1.6758	1.6761	1.6752
$\Sigma d(\text{volts})^2 \times 10^6$		0.3	1.1	1.1

varied from 0.32 to 2.38.

Even though the uncertainties in the values of K_1 and K_2 are rather large, the values are sufficiently precise for the treatment of the kinetic data. From the best values of K_2 at 25° C and 1.6° C, values at the intermediate temperatures were determined by interpolation on a log K_2 versus 1/T plot. Because K_1 could be evaluated only at 1.6°, an estimate of its temperature coefficient was made. The entropies of hydrolysis for Pu^{+4} and U^{+4} are 30 e.u. and 19 e.u., respectively.[16, 17, 18] It is reasonable to assume that the entropy change in the analogous reaction $Ce^{+4} + H_2O \rightleftharpoons CeOH^{+3} + H^+$ should lie in the range 18 e.u. to 30 e.u. because of the relative ionic radii and is probably 24 e.u. Using the best measured value of K_1 at 1.6° and equations $d\Delta F/dT = -\Delta S$ and $\ln K = -\Delta F/RT$, values for K_1 were estimated at temperatures between 25° and 1.6° C. Values of K_1 and K_2 evaluated from the above considerations for temperatures of the kinetic experiments can be found in Table V-6.

Stoichiometry.- A standard analytical procedure for the determination of uranium(IV) involves the oxidation by cerium(IV) in sulfuric acid as represented by the equation

Table V-6

Cerium(IV) Hydrolysis Constants K_1 and K_2 at Various Temperatures

Temp., °C	K_1, M	K_2, M
1.6	8	0.08
2.4	8	0.08
8.0	11	0.10
15.6	14	0.14
25.0	15	0.15

$$2Ce(IV) + U(IV) = 2Ce(III) + U(VI).$$

The final cerium(IV) concentrations, calculated assuming the stoichiometry for the above equation, are compared in Table IV-36 with those found experimentally. The data indicate that a small amount of cerium(IV) was reduced in excess of that equivalent to the uranium(IV), and was probably the result of the presence of oxidizable impurity in the uranium or perchloric acid-sodium perchlorate stock solution. The concentration of the reducing agent was estimated to be the order of 10^{-7} M. The initial cerium(IV) concentrations were corrected for this small amount of reduction assuming that the reducing agent reacted very rapidly with the cerium(IV).

The Variation of the Rate of Reaction with Uranium(IV) and Cerium(IV) Concentration at Constant Hydrogen Ion Concentration. - It can be seen from the stoichiometry of the reaction that

$$-\frac{d[Ce(IV)]}{dt} = -2\frac{d[U(IV)]}{dt} \qquad (V-21)$$

where $-\frac{d[Ce(IV)]}{dt}$ = the rate of disappearance of cerium(IV) in moles/liter.time,

and $-\frac{d[U(IV)]}{dt}$ = the rate of disappearance of uranium(IV) in moles/liter.time.

If the reaction is first order with respect to both the cerium(IV) and uranium(IV) concentrations then both of the following two differential equations hold

$$-\frac{d[Ce(IV)]}{dt} = k\,[U(IV)]\,[Ce(IV)] \qquad (V-22)$$

and

$$-\frac{d[U(IV)]}{dt} = k'\,[U(IV)]\,[Ce(IV)]. \qquad (V-23)$$

From equations (V-21) and (V-23)

$$-\frac{d[Ce(IV)]}{dt} = 2k'\,[U(IV)]\,[Ce(IV)]. \qquad (V-24)$$

Integration of equation (V-24) between the limits $t = 0$ and t yields

$$\frac{2.3}{(2[U(IV)]_o - [Ce(IV)]_o)} \log \frac{[U(IV)]\,[Ce(IV)]_o}{[Ce(IV)]\,[U(IV)]_o} = k't \qquad (V-25)$$

where $[U(IV)]_o$ and $[Ce(IV)]_o$ = the initial uranium(IV) and cerium(IV) concentrations, respectively, at time zero

and [U(IV)] and [Ce(IV)] = the uranium(IV) and cerium(IV) concentrations, respectively, at time t.

As the quantity $(2[U(IV)]_o - [Ce(IV)]_o)$ approaches zero the ratio $[U(IV)][Ce(IV)]_o / [Ce(IV)][U(IV)]_o$ approaches unity and equation V-25 cannot be used conveniently to determine k'. However, it can be shown[19] that under these conditions equation V-25 can be expanded in a logarithmic series to give

$$\frac{1}{(2[U(IV)] + [Ce(IV)]) / 2} = k't. \qquad (V-26)$$

From the kinetic data in Tables IV-3 through IV-17 plots of log [U(IV)] / [Ce(IV)] versus time yielded straight lines up to a point where the reactions were about eighty per cent complete as can be seen in Figure V-3. Using the data from Tables IV-18 through IV-27 for experiments where $2[U(IV)]_o \cong [Ce(IV)]_o$ straight lines were obtained from plots of the reciprocal of $(2[U(IV)] + [Ce(IV)]) /2$ versus time as shown in Figure V-4. The linearity of the foregoing plots suggests that the reaction is first order with respect to both cerium(IV) and uranium(IV) concentration. The values of the apparent second order rate constant k' calculated

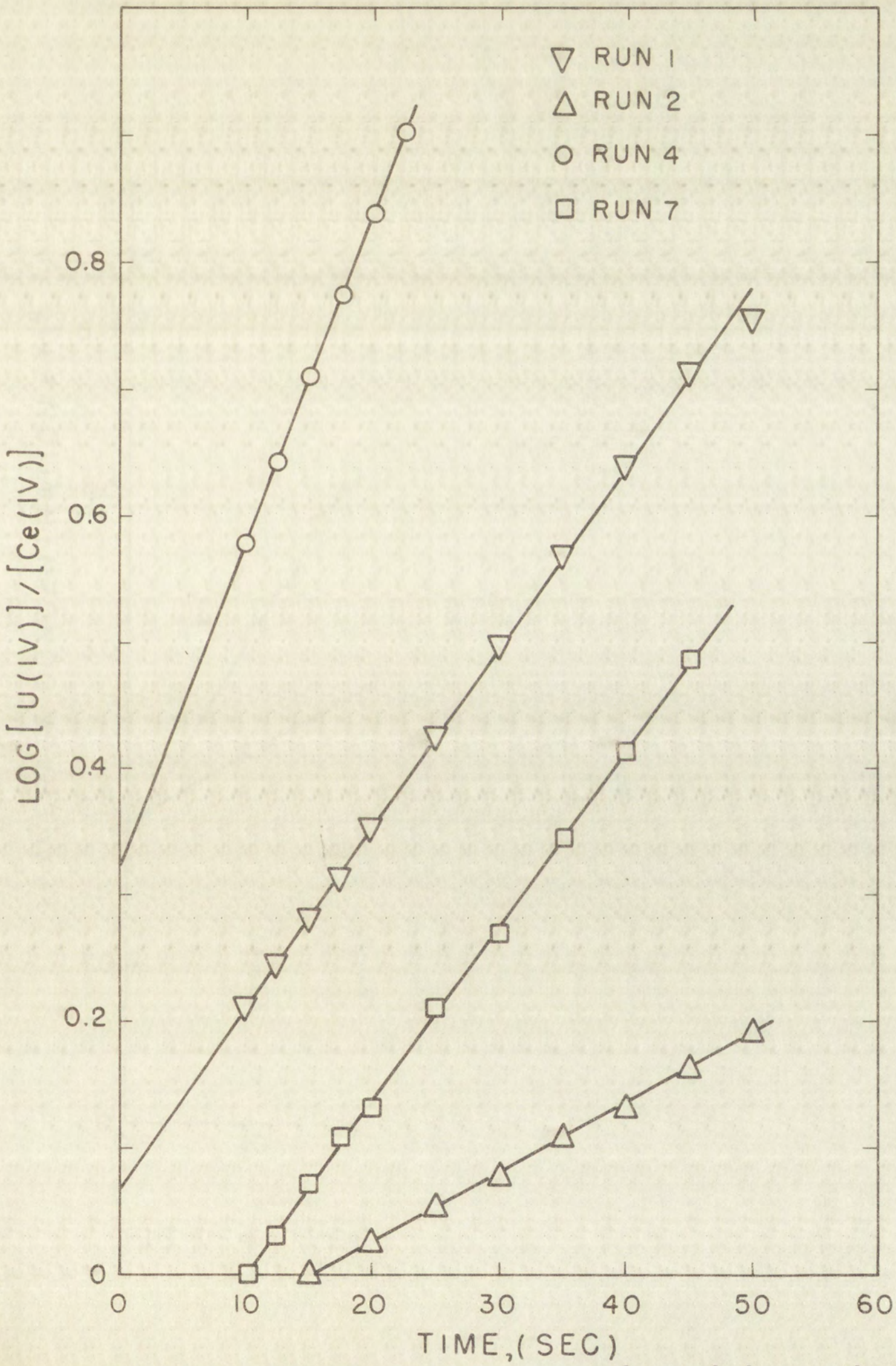


FIG. V-3 TYPICAL PLOTS OF LOG[U(IV)]/[Ce(IV)] VS TIME 2.00 M $HClO_4$ AT 2.4 °C

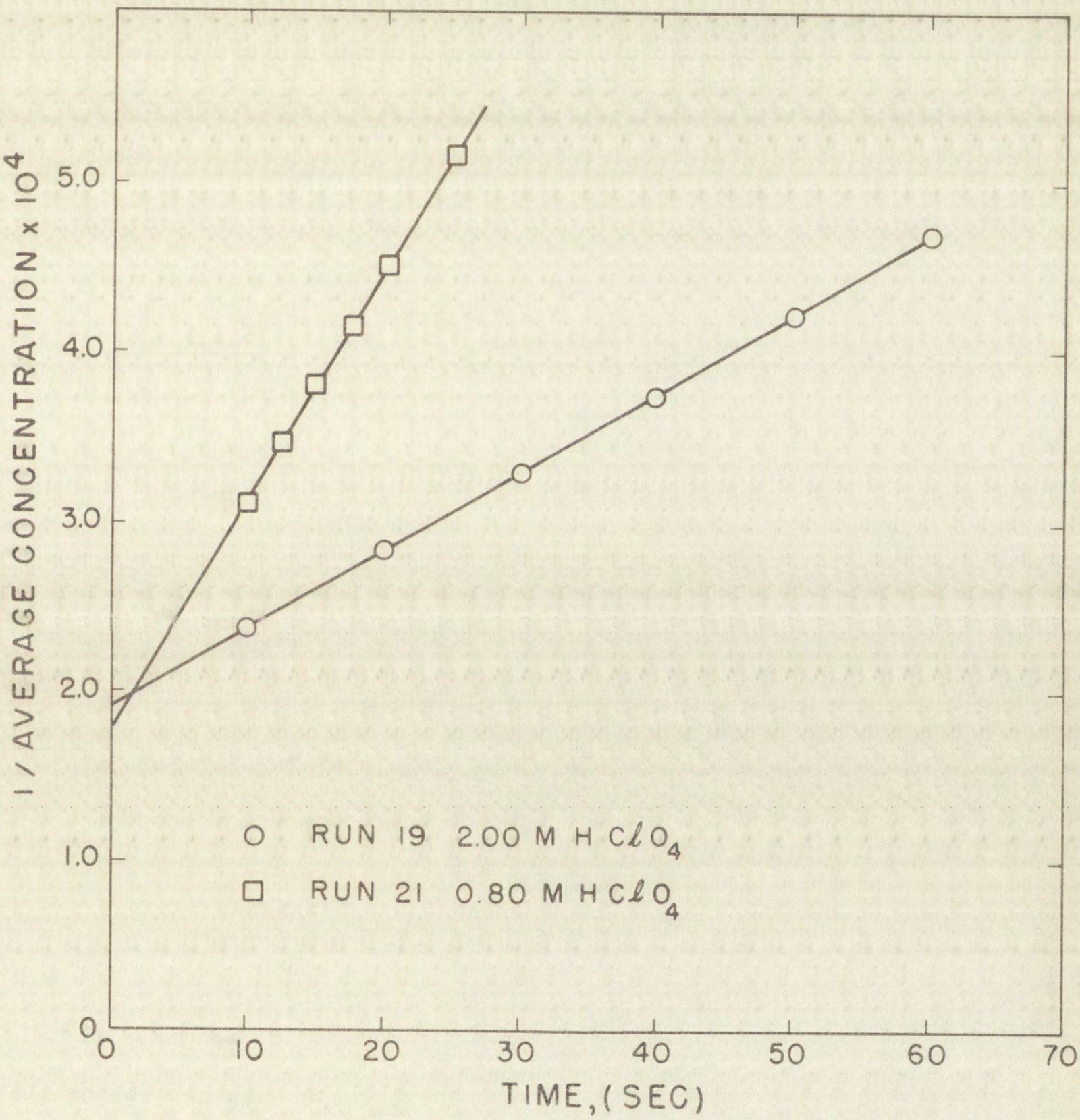


FIG. V-4 TYPICAL PLOTS OF 1/AVERAGE CONCENTRATION VS TIME AT 2.4 °C

from the slopes of the appropriate plots according to equations (V-25) and (V-26) are given in Table V-7.

Hydrogen Ion Dependence. - The results of runs made at different hydrogen ion concentrations are summarized in the second column of Table V-8. The hydrogen ion dependence was studied only at 2.4°. At higher temperatures the rates were too high for accurate measurement at hydrogen ion concentrations less than 2 M.

Rate Law. - In order to be consistent with the data in Tables V-7 and V-8 the rate law must have the form

$$-\frac{d[Ce(IV)]}{dt} = k2\,[U(IV)]\,[Ce(IV)]\,f\,[H^+]. \qquad (V-28)$$

Where $f[H^+]$ = some function of hydrogen ion concentration.

In terms of the predominant ions in solution the following rate law is proposed:

$$-\frac{d[Ce(IV)]}{dt} = 2[U^{+4}]\,[CeOH^{+3}]\left(\frac{k_1}{[H^+]} + \frac{k_2}{[H^+]^2}\right). \qquad (V-29)$$

In the acid concentration range studied, the hydrolysis of U^{+4} is negligible,[17, 18] so that

$$[U^{+4}] = [U(IV)]. \qquad (V-30a)$$

Table V-7

Apparent Second Order Rate Constants in
Perchloric Acid-Sodium Perchlorate Solution at 2.4°C and μ = 2.00

Run	$[H^+]$, M	$[U(IV)]_o \times 10^5$, M	$[Ce(IV)]_o \times 10^5$, M	k', moles/liter-sec.
1	2.00	6.06	5.05	464
2	2.00	3.50	4.25	455
3	2.00	7.08	4.28	472
4	2.00	8.83	4.27	447
5	2.00	8.02	6.01	483
6	1.25	5.55	8.22	779
7	1.25	6.32	8.63	792
8	1.25	5.39	7.57	806
9	1.25	3.42	5.56	844
10	1.25	3.42	5.56	829
11	1.25	4.54	5.37	828
12	1.25	4.54	5.37	798
13	1.00	1.76	3.01	1010
14	1.00	3.31	7.63	1030
15	1.00	3.19	5.91	1050
16	1.00	4.30	8.39	1060
17	1.00	4.30	8.39	995
18	1.25	2.31	4.51	800
19	2.00	2.62	5.06	462
20	2.00	2.62	5.06	458
21	0.800	2.66	5.32	1360
22	0.800	2.12	4.10	1410
23	0.800	2.02	3.97	1410
24	0.800	4.36	8.38	1350
25	0.800	4.41	8.48	1360

Table V-8

Apparent Second Order Rate Constants k' in
Perchloric Acid-Sodium Perchlorate Solution at 2.4°C and μ = 2.00

$[H^+]$, M	Experimental k', moles/liter. sec.	Mean Deviation experimental k', per cent	Calculated k', moles/liter. sec.
2.00	460	2.0	460
1.25	810	2.5	810
1.00	1030	2.0	1050
0.800	1380	2.0	1350

From equations (V - 5) and (V - 6) it can be shown that the concentration of $CeOH^{+3}$ is related to the total cerium(IV) concentration according to the equation

$$[CeOH^{+3}] = \frac{[Ce(IV)]\, K_1[H^+]}{[H^+]^2 + K_1[H^+] + K_1K_2} \qquad (V - 30b)$$

By substitution of equations (V - 30a) and (V - 30b) into equation (V - 29)

$$-\frac{d[Ce(IV)]}{dt} = 2[U(IV)][Ce(IV)]\, \frac{K_1[H^+]}{[H^+]^2 + K_1[H^+] + K_1K_2} \left(\frac{k_1}{[H^+]} + \frac{k_2}{[H^+]^2} \right) \qquad (V - 31)$$

Since k', the apparent second order rate constant, was defined by the equation

$$k' = \frac{\dfrac{-d[Ce(IV)]}{dt}}{2[U(IV)]\,[Ce(IV)]}$$

it can be seen from equation (V - 31) that

$$k' = \frac{K_1[H^+]}{([H^+]^2 + K_1[H^+] + K_1K_2)} \left(\frac{k_1}{[H^+]} + \frac{k_2}{[H^+]^2} \right). \qquad (V - 32)$$

This expression may be rearranged for graphical testing to give

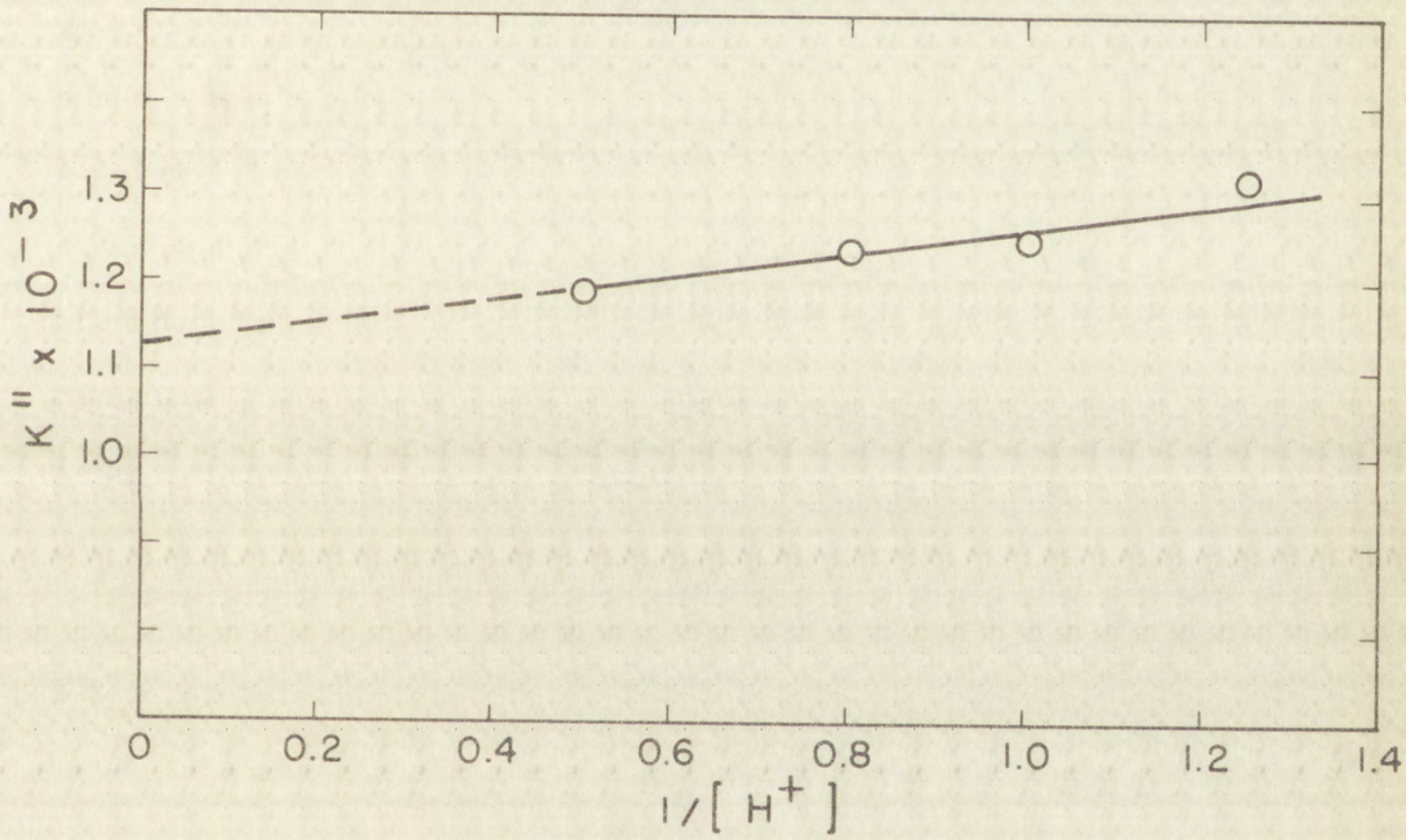
$$k'\left(\frac{[H^+]^2}{K_1} + [H^+] + K_2\right) = k'' = k_1 + \frac{k_2}{[H^+]} . \qquad (V-33)$$

A plot of k'' versus $1/[H^+]$ is shown in Figure V-5 using the data from Table V-8 and the best values of K_1 and K_2 given in Table V-5. The data give a satisfactory straight line; hence, the proposed rate law (equation V-28) describes the kinetics adequately. The best values for k_1 and k_2, calculated from the intercept and slope of the k'' versus $1/[H^+]$ plot, were found to be 1150 sec^{-1} and 140 moles/liter sec. respectively. The calculated values of k' given in Table V-8 were obtained using these values for k_1 and k_2 and agree quite well with the experimental values of k'.

The uncertainties in the hydrolysis quotient K_1 and K_2 introduce a much larger uncertainty into the determination of k_1 than that introduced by the randomness of the apparent second order rate constants k'. Plots of the data using the limiting values for K_1 and K_2 (given in Table V-5) lead to a value of $k_1 = 1150 \pm 150$ sec^{-1}.

Although the assumption of the second

FIG. V-5
PLOT OF K" VS $1/[H^+]$ AT 2.4 °C



constant k_2 in the rate law satisfactorily fits the data within the experimental error, the trend in the values of k", given in Table V-9, could also be explained with the assumption of only one constant, k_1, and a lack of constancy in the pertinent activity coefficients. Indeed a straight line with zero slope can be drawn through the plots of k" versus $1/[H^+]$ as shown in Figure V-5 giving a slightly higher value of k_1. Therefore, only one constant, k_1, can be determined with any reliability in the hydrogen ion concentration range studied.

Mechanism.- The first order dependance of cerium(IV) and uranium(IV) suggests that the rate determining step, without regard to hydrogen ion, is

$$U(IV) + Ce(IV) \xrightarrow{k_a} U(V) + Ce(III). \qquad (V-34)$$

This reaction is followed by one or both of the fast reactions

$$U(V) + Ce(IV) \xrightarrow{k_b} U(VI) + Ce(III) \qquad (V-35)$$

and

$$U(V) + U(V) \xrightarrow{k_c} U(VI) + U(IV). \qquad (V-36)$$

By applying the steady-state approximation to equations (V-34), (V-35), and (V-36) for $d[U(V)]/dt = -d[U(V)]/dt$, the concentration of uranium(V) is given

Table V-9

Dependence of Apparent Second Order Rate Constant k'
on the Hydrogen Ion Concentration at 2.4°C and μ = 2.00

$HClO_4$, M	No. Determinations	Ave. observed[a] k', M^{-1} sec^{-1}	k'', sec^{-1}[b]	Calculated k', $M^{-1}sec^{-1}$	Calculated k', $M^{-1}sec^{-1}$[c]
2.00	9	460	1190	460	470
1.25	7	810	1240	810	810
1.00	5	1030	1240	1050	1040
0.80	5	1380	1320	1350	1360

a. The mean deviation from the average k' was in the range from 2 to 2.5% and the maximum deviation ranged from 2 to 4.3%.

b. Equation (V-33) defines k''.

c. It is assumed that $k_2 = 0$.

by the expression

$$[U(V)] = \frac{-k_a[Ce(IV)] \pm \left[(k_a[Ce(IV)]^2 + 4k_c k_a[Ce(IV)][U(IV)])\right]^{1/2}}{2k_c} \qquad (V-37)$$

The rate of disappearance of cerium(IV) is

$$-\frac{d[Ce(IV)]}{dt} = k_a[U(IV)][Ce(IV)] + k_b[Ce(IV)][U(V)] \qquad (V-38)$$

Substitution of [U(V)] given by equation (V-37) into equation V-38, yields for the disappearance of cerium(IV)

$$-\frac{d[Ce(IV)]}{dt} = k_a[Ce(IV)][U(IV)] + \frac{k_b^2[Ce(IV)]^2}{2k_c}\left[\left(1 + \frac{4k_c k_a[U(IV)]}{k_b^2[Ce(IV)]}\right)^{1/2} - 1\right] \qquad (V-39)$$

If the ratio $4k_c k_a / k_b^2$ is approximately zero, the whole second term in equation V-39 will drop out yielding the observed second order rate law. The second order rate constants k_a and k_c are the same order of magnitude. (A value for k_c of about 300 liter/mole.sec was estimated from Kern and Orelemann's study of the uranium(V) disproportionation.)[20] Therefore, k_b must be large in comparison to k_a in order that equation V-39 be reduced to the observed rate law. From the

above considerations it is clear that only equations (V-34) and (V-35) are of importance.

The analysis of the inverse hydrogen ion concentration dependance observed in the rate law is more complex. The appearance of the two terms $k_1/[H^+]$ and $k_2/[H^+]^2$ in the rate law indicates that the reaction proceeds by two parallel paths. Because k_2 was found to be much smaller than k_1, ($k_2/k_1 \lesssim 0.1$) the path involving the reciprocal of the square of the hydrogen ion concentration is relatively unimportant as compared to the main path.

The appearance of an inverse hydrogen ion concentration dependance in the rate law can be explained by assuming that hydroxyl groups are present in the activated complex. However, no unique mechanism in terms of hydrolyzed reactant species can be given. Therefore, the reaction will be described in terms of the net reaction for the formation of the activated complex from the principal species in solution.

In the hydrogen ion concentration range studied the principal reactant species are assumed to be U^{+4} and $CeOH^{+3}$ (on the basis of the discussion of the hydrolysis on pages 59 through 74); the

concentrations of these species are essentially constant in the aforementioned hydrogen ion concentration range.

Fromthe above considerations the following mechanism is proposed for the oxidation of uranium(IV) by cerium(IV) in the perchloric acid concentration range from 2.00 to 0.800 molar at an ionic strength of 2.00; the initial cerium(IV) and uranium(IV) concentrations ranged from 6.0 to 4.2×10^{-5} M and 8.8 to 2.6×10^{-5}, respectively. The proposed mechanism is consistent with the experimental rate law and withthe known chemistry of uranium(IV) and cerium(IV).

$$CeOH^{+3} + U^{+4} + H_2O = [\text{Activated Complex}]^{+6} + H^+ \qquad (V-39)$$

and

$$CeOH^{+3} + U^{+4} + 2H_2O = [\text{Activated Complex}]^{+5} + 2H^+. \qquad (V-40)$$

It is to be noted that equations (V-39) and (V-40) are net reactions and are not meant to imply that the hydrogen ions necessarily split off during the formation of the activated complex. The rate determining steps are

$$[\text{Activated Complex}]^{+6} \longrightarrow U(V) + Ce(III)$$

and

$$[\text{Activated Complex}]^{+5} \longrightarrow U(V) + Ce(III)$$

followed by the fast reaction

$$U(V) + Ce(IV) \longrightarrow U(VI) + Ce(III)$$

Thermodynamic Quantities of Activation. - The apparent second order rate constants k' measured at 2.00 M hydrogen ion concentration and three temperatures are given in Table V-10. Using the appropriate values of K_1 and K_2 from Table V-6 values of k'' as defined by equation (V-33) are also given.

It has been mentioned in the previous section that the term $k_2 / [H^+]^2$ in the rate law could be explained as representing an unimportant minor path or an activity effect. From the rate law (equation V-28) and the values of k_1 and k_2 it was found that the term $k_2 / [H^+]^2$ was only about five per cent of $k_1 / [H^+]$ at 2.00 M hydrogen ion concentration. Therefore, as a first approximation the term $k_2/[H^+]$ in equation (V-33) can be neglected and $k'' = k_1$. The activation energy determined from the plot of log k'' versus 1/T was used to calculate the thermodynamic quantities of activation in the usual way.[21] The values obtained were: $E^{\neq} = 14.8$ kcal/mole, $\Delta H^{\neq} = 14.2$ kcal/mole, $\Delta F^{\neq} = 12.2$ kcal/mole, $\Delta S^{\neq} = 7.3$ e.u.

Table V-10

Apparent Second Order Rate Constants At Various Temperatures in Perchloric Acid-Sodium Perchlorate Solution at $\mu = 2.00$

Temp., °C	k', moles/liter. sec. $[H^+] = 2.00$	k', moles/liter. sec. $[H^+] = 1.00$	k_1, sec^{-1}	k'', sec^{-1}
2.4	460	1030	1150	1150
8.0	810	1890	1880[a]	2010
15.6	1670	---	3760[a]	4060

a. Calculated, assuming $E^{\neq}_2 = 19$ kcal.

On the other hand, if the trend in k'' is attributed to the operation of a minor path, the thermodynamic quantities of activation for the predominant path will be slightly different and $k_1 = k'' - k_2/[H^+]$. In order to determine k_1 from the previous equation as a function of temperature, values of k_2 as a function of temperature are needed. The rate constant k_2 was determined only at 2.4^o, hence, values at the other temperatures must be obtained from an estimate of its temperature coefficient. In the reaction between uranium(IV) and iron(III) it was found that paths involving activated complexes with one OH group and with two OH groups are important, and $\Delta S^{\neq}$ value for the two-OH path was 10 ± 3 e.u. more positive than that for the one-OH path.[2] Similarly in the reaction between uranium(IV) and plutonium(VI), one-OH and two-OH paths were found with $\Delta S^{\neq}$ values which differed by 15 ± 3 e.u.[4]

The two reaction paths under consideration here also differ by one OH; so, it is reasonable to assume that since $\Delta S^{\neq}$ for the predominant path is about 7.3 e.u. the value of the minor path lies in the range from 14 to 25 e.u. and is probably about 19 e.u. These estimated entropy values together

with the known value of k_2 at 2.4°C lead to a range of activation energies from 15 to 25 kcal/mole for the minor path.

The lower limit of 15 kcal/mole is consistent with the data at 2.4° and 8.0°C in Table V-10, which indicates that $E^{\neq}_2$ is not less that $E^{\neq}_1$, where $E^{\neq}_1$ and $E^{\neq}_2$ are the activation energies associated with k_1 and k_2. Values of k_2 at 8.0° and 15.6° were estimated using the probable activation energy of 19 kcal. Values for k_1 corrected for the minor path given in the fourth column of Table V-10 were then plotted as log k_1 versus 1/T to give an activation energy of 14.5 kcal/mole. The method of least squares was used to determine the best value for the slope and the uncertainty of the slope. It is seen that this value does not greatly differ from that calculated ignoring the possible additional path. The calculation was repeated using the extreme values of K_1 and of $E^{\neq}_2$ in order to estimate the uncertainty in $E^{\neq}_1$ from these sources. An overall uncertainty of ±0.7 kcal in $E^{\neq}_1$ was estimated by taking the square root of the sum of the squares of the errors due to the uncertainties in K_1, $E^{\neq}_2$, and the log k_1 versus 1/T plot. The calculated thermodynamic

quantities of activation[21] (assuming a minor path) at 2.4°C for the process

$$CeOH^{+3} + U^{+4} + H_2O = [\text{Activated Complex}]^{+6} + H^+$$

are: $\Delta F^{\neq} = 12.2 \pm 0.2$ kcal/mole, $\Delta H^{\neq} = 13.9 \pm 0.7$ kcal/mole, $\Delta S^{\neq} = 6.2 \pm 2.5$ e.u.

From equation (V - 6) and the assumption of 24 e.u. for ΔS (page 76) of the first hydrolysis step, the calculated thermodynamic quantities of activation at 25°C for the process

$$Ce^{+4} + U^{+4} + 2H_2O = [\text{Activated Complex}]^{+6} + 2H^+$$

are: $\Delta F^{\neq} = 10.4$ kcal/mole, $\Delta H^{\neq} = 19.4 \pm 1.8$ kcal/mole, and $\Delta S^{\neq} = 30.2 \pm 6$ e.u. These results are compared with those from other kinetic studies in Table V - 11. Two correlations were observed. First, considering the three reactions involving uranium(IV) it can be seen that the $\Delta F^{\neq}$ values increase smoothly as the ΔF^{o} values become more positive. Second, the apparent ionic entropies of the three activated complexes with a charge of plus six are all about the same. This suggests that the total charge on the complex is an important factor in determining its entropy. These entropies were calculated by adding the standard entropies $\bar{S}^{o}$ of the reactants

Table V-11

Thermodynamic Quantities of Activation at 25°C

Net Activation Process	ΔF° kcal/mole	$\Delta F^{\neq}$ kcal/mole	$\Delta H^{\neq}$ kcal/mole	$\Delta S^{\neq}$ e.u.	$\bar{S}^{\neq}$ e.u.	Ref.
$Ce^{+4} + U^{+4} + H_2O = [\text{Activated Complex}]^{+6} + 2H^+$	-28	10.4	19.4	30.2	-116	this work
$Pu^{+4} + U^{+4} + H_2O = [\text{Activated Complex}]^{+6} + 2H^+$	- 9.3	15.4	24.3	30.1	-118	4
$Pu^{+3} + Pu^{+4} + H_2O = [\text{Activated Complex}]^{+6} + H^+$	0	13	9.5	-13	-120	22
$Fe^{+3} + U^{+4} + H_2O = [\text{Activated Complex}]^{+6} + H^+$	- 3.7	16.8	21.4	15.5	-118	2

to the $\Delta S^{\neq}$ values and are shown in the last column of the Table V-11 where the equations are written with the minimum number of water molecules. The values of $\bar{S}^{o}$ for uranium, neptunium, and plutonium ions are those given in Katz and Seaborg.[23] The values of S^{o} for Ce^{+4} was estimated to be 84 e.u. using the equation of Powell and Latimer,[24] and the radius value given by Pauling.[25]

Effect of Sulfate: Several runs were made at 2.4° and 2 M perchloric acid with added sodium sulfate. The sulfate concentration was varied from 0.0010 to 0.10 M. The rates in this range increased with increasing sulfate concentration and were immeasurably faster than in pure 2 M perchloric acid. However, in 1.1 M sulfuric acid in which the sulfate concentration was estimated to be 0.45 M, the rate was measurable and only 1.3 times as fast as the rate under comparable conditions of 1.5 M perchloric acid at $\mu = 2$.

These results suggest that the effect of sulfate is similar to that found in neptunium(IV)-neptunium(VI) reaction which has been extensively studied.[26]

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