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DISSERTATION

KINETICS OF THE CERIUM (IV)-VANADIUM (IV) REACTION IN AQUEOUS PERCHLORIC ACID SOLUTION

Submitted by

Robert Leighton Taylor

In partial fulfillment of the requirements

for the Degree of Doctor of Philosophy

Colorado State University

Fort Collins, Colorado

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COLORADO STATE UNIVERSITY

August, 1970

WE HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER OUR SUPERVISION BY ROBERT LEIGHTON TAYLOR ENTITLED KINETICS OF THE CERIUM(IV)-VANADIUM(IV) REACTION IN AQUEOUS PERCHLORIC ACID SOLUTION BE ACCEPTED AS FULFILLING IN PART REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY.

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ABSTRACT OF DISSERTATION

KINETICS OF THE CERIUM (IV)-VANADIUM (IV) REACTION

IN AQUEOUS PERCHLORIC ACID SOLUTION

The kinetics of the cerium (IV)-vanadium (IV) reaction were studied using the spectrophotometric method. Absorbance decreases of the absorbing species of cerium were timed and these data were used to determine metal ion dependence, acid dependence, effect of changing ionic strength and the thermodynamic parameters.

The metal ion dependence of the cerium (IV)-vanadium (IV) reaction was studied in both excess cerium (IV) perchlorate and excess oxovanadium (IV) perchlorate. The acid dependence was studied in excess V(IV) over the range 0.0615 to 4.00 M in perchloric acid. The apparent second order rate constant was found to decrease with increasing acidity. Ionic strength was varied from 0.100 M to 2.50 M at a constant acid strength of 0.100 M. The increase in ionic strength by adding lithium perchlorate resulted in a linear increase in the apparent second order rate constant.

The rate law consistent with all of the experimental data is:

$$\text{Rate} = k_2' [CeOH^{3+}] [VO^{2+}] \quad .$$

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The value of k_2' in excess V(IV) at 20° C, 1.00 M H^+ and 2.00 M μ was found to be 41 M^{-1} sec^{-1}. The value of k_2' under the same conditions in excess Ce(IV) was about 15% lower.

The apparent second order rate constant, k_2', when corrected for the hydrolysis of $CeOH^{3+}$ gives k'. k' can be represented equally well by the two following relations:

$$k' = (k_o + \frac{k_{-1}}{[H^+]} + \frac{k_{-2}}{[H^+]^2}) \qquad (1)$$

$$k' = (\frac{k_{-1}}{[H^+]} + \frac{k_{-2}}{[H^+]^2}) e^{\beta [H^+]} \qquad (2)$$

The major term in both equations is inverse first order in hydrogen ion concentration. The activation parameters for the inverse first order terms are $\Delta H^* = 16.8 \pm 0.3$ kcal mol^{-1} and $\Delta S^* = 5.82 \pm 0.28$ e.u. for both equations. ΔH^* and ΔS^* for the $k_{-2}[H^+]^{-2}$ term in Equation (1) are 19.7 ± 0.8 kcal mol^{-1} and 20.2 ± 2.7 e.u. respectively and 19.1 ± 0.8 kcal mol^{-1} and 8.12 ± 2.59 e.u. respectively for Equation (2).

The rate law is consistent with the formation of two or three activated complexes depending upon the equation used and these are: $(CeOHVO)^{5+}*$, $(Ce(OH)_2VO)^{4+}*$, and $(Ce(OH)_3VO)^{3+}*$. Following formation of these complexes the loss of H^+ ion(s) and transfer of an oxygen from the $CeOH^{3+}$ to VO^{2+} is the suggested

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mechanistic sequence. The inverse hydrogen ion dependence is opposite to that reported by a previous investigator.

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CHAPTER I

INTRODUCTION

Background

Chemical kinetics may be described as the study of the rate at which a chemical reaction occurs and the manner in which it occurs. Kinetics delves into the dynamic aspects of a reaction and consequently involves a variety of considerations. Some of these are the energy of initiation or activation, the formation and lifetime of intermediate species, the rates of all reactions or steps involved and the thermodynamic parameters such as enthalpy of activation (ΔH^*) and entropy of activation (ΔS^*). In view of all of these the study of kinetics demands a diversity of skills and an intuition which at the very best may result in only a fractional and empirical glimpse at the complete reaction picture.

The problems involved in these studies become apparent when one attempts to separate the salient kinetic features of two or more reactions occurring simultaneously or consecutively, or both simultaneously and consecutively, in the same space over the same period of time. The reactants may be well-defined chemical species and the products easily identifiable, however, the routes and energetic gyrations of the reactants during their transition to

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products can be deceptively involved and the rates elusively fast. If the products also react during some phase of the reaction then the problems increase drastically. The main feature in the study of kinetics is the rate at which reactants disappear, or the rate at which products appear. These rates may differ which in themselves provide a clue to a potential complexity and a possible mechanism for explaining these differences.

The experimentally derived rate law is a tool for postulating the routes and the various species which may occur during the reaction. However, as simple as the law may appear it does not always demonstrate the true nature of the reaction. As an example, consider the reaction: $H_2 + I_2 \rightleftharpoons 2HI$. From this equation, supported by experimental evidence, the rate law is given as:

$$\frac{d[HI]}{dt} = k_2 [H_2] [I_2] \quad .$$

This states that the formation of the product, HI, is directly proportional to the concentration of the reactants, H_2 and I_2, where k_2 is the proportionality constant or the specific rate constant and has the units, $\underline{M}^{1-n} - sec^{-1}$, where n is the overall reaction order. Since this reaction as indicated involves a bimolecular collision of single molecules of H_2 and I_2 the value of n is 2. This simplicity is true for only a few reactions and

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recently it has been shown that even the H_2 - I_2 reaction is more involved than indicated by the simple rate expression.[1] It has now been shown that the reaction has two possible routes. One involves a rapid step resulting in the formation of iodine atoms which then react with the hydrogen molecule. The other has a pre-equilibrium step, ($M + I + H_2 \rightleftharpoons IH_2 + M$; where M is essentially a catalyst) followed by the rate determining step, $IH_2 + I \longrightarrow 2HI$. The rate expressions for the two mechanisms are:

$$(1) \quad \frac{d[HI]}{dt} = K'[H_2][I]^2$$

$$(2) \quad \frac{d[HI]}{dt} = k'K^2 [I_2][H_2] = k_2[H_2][I_2]$$

where K's are equilibrium constants and k's are rate constants. The rate law in the earlier explanation of this reaction has the same essential form as the newer proposal but the reaction upon more definitive examination reveals an entirely different mechanism than was originally believed. For this reaction the coefficients for the reactants in the balanced reaction equation are identical to the order of the reactants in the rate law. In some reactions the orders are less than the coefficients which indicates that the reaction pathway involves an intermediate step. More complex reactions can have more than one intermediate and several simultaneous and consecutive steps. For a more comprehensive treatment of these

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types the reader is referred to the text, Kinetics and Mechanisms by A. A. Frost and R. G. Pearson.[2]

Intermediates which occur in the reaction sequences are transient molecular configurations and are indicated by minima in a reaction-coordinate diagram. Experimentally, the best evidence for an intermediate, besides the differences in orders and coefficients, is evidence of a transient physical property. For example, an intermediate may possess a color which is unrelated to any of the reacting species or products. This is not the usual fortunate circumstance so that the presence of an intermediate must be postulated from kinetic considerations. Rate laws which contain non-integral orders, inverse orders or orders larger than three for one of the reactants are indications that an intermediate is involved in the reaction scheme. Intermediates can be classed as reactant species in the sense they possess a finite lifetime and are capable of reacting with other substances.

In a reaction the reactants may assemble in an indefinite configuration of apparently loose and temporary bonding. This ensemble has an energetic choice of returning to the individual reactant species in an equilibrium situation or proceeding onto an intermediate or the products. These configurations are called "activated complexes" and are represented energetically by maxima on a reaction-coordinate diagram. These complexes are

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formed upon their acquisition of sufficient energy to place them in a state for transition. This is the basis of the Transition State Theory which permits calculation of the thermodynamic parameters of the reaction from the equation:

$$k_r = \left(\frac{k_B T}{h}\right) e^{\frac{\Delta S^*}{R}} e^{\frac{-\Delta H^*}{RT}}$$

where k_r = specific rate constants, k_B = Boltzman's constant, T = temperature (^oK), h = Planck's constant, R = General Gas Law constant, ΔS^* = entropy of activation and ΔH^* = enthalpy of activation. The calculation of these parameters is possible from specific rate constants for the reaction obtained at several different temperatures.

Delving deeper into mechanistic considerations one is confronted with explaining the exact manner in which atoms, molecules, radicals, ions, or intermediates as individually responsive entities in the reaction phase are involved in the reaction steps. In oxidation-reduction reactions there is an apparent exchange of electrons; one reactant loses electron(s) and the other gains electron(s). This "loss and gain" of electron(s) is a statement after the fact but does not reveal how the loss and gain transpired.

In gas phase reactions the direct transfer of an electron from one particle to another has been demonstrated.[3] The state

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of matter is simple and one would expect the mechanism for electron transfer to be direct and simple. In solutions the metal ions undergoing reaction are solvated or have ligands other than the solvent particles in their coordination spheres. It is this more complex particle moving in a matrix of other charged and uncharged particles which can complicate simple and direct electron transfer.

The change in oxidation number of a reactant in solution could occur by the simple expedient of direct electron transfer through a solvated electron. Some evidence exists for the involvement of the solvated electron but the evidence is not conclusive.[4] Another mechanism by which oxidation and reduction may occur in aqueous solution is atom or group transfer. The transfer of a positive group or atom from the coordination sphere of one central atom to a substrate is equivalent to the transfer of electron(s) to that central atom, and the transfer of a negative atom or group is equivalent to reduction. The transition state which exists when the transfer of electrons takes place is classed in two general types, the "inner-sphere activated complexes" and the "outer-sphere activated complexes". In the first type there is a ligand which is common to the coordination sphere of both central atoms and forms a bridge between them. For the outer-sphere activated complex the coordination sphere of the reacting central atoms remain intact with no ligand apparently common to their

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respective coordination spheres. In both of these activated states, atom or electron transfer can occur and which process takes place is dependent upon the reacting species and the solvent.

The mechanistic explanation of many redox reactions is explicitly dependent upon the momentary existence of an activated complex of either inner or outer sphere types to explain the process by which one central atom is reduced and the other is oxidized. In a situation where both reacting species are inert to substitution of ligands the exchange of electrons will involve a mechanism related to electron tunneling. Taube[5] denotes the activated complex in this situation as "outer sphere". The reacting species undergo momentary "pairing" to permit electron transfer yet the coordination spheres apparently remain uninvolved and intact throughout the step. It is considered that the reactant groups acquire an energy-rich intermediate configuration which is conducive to easy electron transfer. The energy requirements for the reorganization of coordination spheres have been calculated and found to be sufficiently low to give credence to this explanation.[6] This must be a sequential occurence, i.e., reorganization of the coordination spheres followed by electron transfer, since simultaneous occurrence of both is forbidden on the basis of the Franck-Condon Principle.[7]

In contrast to the outer sphere mechanism is the other mechanism where a ligand of one central atom forms a bridge, or

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acts as a "middle-man". The activated complex then has a ligand which is commonly shared by both central atoms and the resultant "inner-sphere complex" can achieve electron transfer through this common ligand. The fate of this common ligand, i.e., whether it remains with its original central atom, is transferred to the other, or leaves the coordination sphere of both central atoms, is dependent upon the nature of the ligand and the reacting species.

Quantum mechanical considerations indicate it is more probable that two electrons will transfer one at a time rather than simultaneously. Although two electron transfers may occur the transfer of more than two is likely to take place by a series of simpler steps, each involving the transfer of a single electron. When reactant stoichiometry is one to one the transfer of two electrons in a single step is the probable mechanism. Evidence of this is provided by the oxidation reaction of chromium (II) in aqueous solution. The product should be chromium (III) but in some instances the dimeric product, $(Cr^{3+} - O - Cr^{3+})^{4+}$ appears.[8] This dimer is suggested to be the consequence of the two-electron step, $Cr^{2+} \rightleftharpoons Cr^{4+} + 2\ e$, with the subsequent combination of another Cr^{2+} with the Cr^{4+}. Chromium (IV) is a highly reactive species and chromium (III) is substitution inert, therefore, the only plausible explanation for the formation of the dimer is to include a two-electron transfer mechanism in the reaction scheme. Evidence

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for a single step two-electron change is not always so apparent. For non-complementary reactions species with uncommon oxidation states are often postulated to explain the rate law. For example, there is the situation for the two-electron oxidation of tin (II) where tin (III) or a binuclear species of tin (III) is believed to be the metastable intermediate.[9] The evidence for this intermediate oxidation state of tin is based on experimental findings using the green potassium trisoxalatocobalt (III) complex. This complex was added to the reaction between tin (II) and a hydroxodioxalato complex of cobalt (III). The consumption of the trisoxalato complex was negligible in the presence of tin (II) alone but in the reacting mixture it was consumed which suggested that a reactive species of tin was present. The possibility that tin (III) might be detectable in the tin (II)-vanadium (V) reaction was investigated using this trisoxalato complex.[10] The complex was found to aquate slowly and react slowly with tin (II) but it was not consumed in the reaction mixture to any extent to verify the presence of the intermediate tin (III). It was suggested that the tin (III) could be present but the cobalt complex could not compete with vanadium (V) for this intermediate. The highly reactive character of intermediate species offers difficulty in directly establishing their presence in the reaction sequence. By using a third reactant such as the trisoxalatocobalt (III) complex in the tin reaction in so-called

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induction experiments, one may acquire indirect evidence in support of an intermediate species in the reaction scheme.

Intermediates offer an excellent means to relate experimental evidence to a logical reaction mechanism. At present no method exists to predict the formation of an intermediate from considerations of the reactants. In a theoretical discussion of the reaction pathways, Richard Wolfgang[11] considered that energies and complexities of the reacting species were criteria which one could use to predict whether intermediates were formed or whether direct reaction occurred. If the active vibrational modes of the activated complex between which energy could be exchanged were large then intermediate formation would be favored. Intermediates are also favored if the energy of the complex formation is large in comparison to the products. The author further predicted that the life - time of the complex will be shorter and the system will tend toward direct reaction if translational and vibrational energies are large. He stated that the processes involved in reactions are becoming more apparent and in the future predictions of reaction mechanisms will be possible from a knowledge of the structure and energy of the reacting species.

Advances in kinetics have led to surprising discoveries regarding the devious routes reactants will take. These complexities are more clearly resolved when viewed in the absence

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of interfering equilibria and complex formation. Cerium (IV) is an excellent one-electron oxidant for use in elucidating mechanisms but is notorious for its complexing ability in certain acids, e.g., sulfuric and hydrochloric. In perchloric acid the cerium complexes formed are few and simple in an acid range above ca. 0.1 M. These complexes are discussed in more detail in the following Section 1 on Cerium. Understanding the basically simple reaction between cerium (IV) and vanadium (IV) in perchloric acid permits easier entrance into studies of more complex reactions in the same media without interfering involvements due to equilibria and complexes to overlap the primary reaction. In spite of relatively high solution acidities the lanthanide series ion, Ce(IV), is extensively hydrolyzed in perchloric acid. From the stoichiometry of the reaction with V(IV) and the activated complex one expects zero or inverse first order hydrogen dependence.[12] Using the best available reported hydrolysis constants this investigation attempts to describe the acid dependence in greater detail.

Reactants

1. Cerium -- A discussion of the primary reactants, Ce(IV) and V(IV), is considered of value since both are common reagents, especially Ce(IV) which because of its one-electron oxidizing ability has been used extensively in oxidation-reduction reactions and to elucidate reaction mechanisms.

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The oxidizing power of Ce(IV) is apparent from the formal oxidation potentials of the cerous-ceric perchlorate couple. In aqueous perchloric acid with 0.2 to 2.4 weight formal Ce(IV) the potentials increased from 1.6490 to 1.7310 volts respectively.[13] The potential is practically independent of the perchlorate ion concentration but continued to increase steadily from 1.70 volts in 1.00 M perchloric acid to 1.87 volts in 8 M acid. The Ce(IV) was considered to hydrolyze to form $Ce(OH)^{3+}$ and $Ce(OH)_2^{2+}$ to satisfy the equilibrium conditions of the reaction:

$$Ce(OH)^{3+} + H_2O \rightleftharpoons Ce(OH)_2^{2+} + H^+$$

with a reported estimate for the equilibrium constant of 0.6. The molal oxidation potentials for the electrode reactions of $Ce(OH)^{3+}$ and $Ce(OH)_2^{2+}$ are respectively 1.7134 and 1.7265 for the reactions:

$$Ce(OH)^{3+} + H^+ + e \rightleftharpoons Ce^{3+} + H_2O$$

$$Ce(OH)_2^{2+} + 2H^+ + e \rightleftharpoons Ce^{3+} + 2H_2O \quad .$$

These investigators discounted previous declarations that perchlorate complexes were formed to a large extent.[14] They declared that Ce(III) was not hydrolyzed and did not suggest the presence of any Ce(III) perchlorate complexes.

A considerable number of investigations have been conducted and evidence given for different numbers and types of complexes

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formed by cerium (IV) in various media. In addition to the complexes $Ce(OH)^{3+}$ and $Ce(OH)_2^{2+}$ in perchloric acid other investigators have suggested that $(HOCe - O - CeOH)^{4+}$, $(Ce - O - Ce)^{6+}$ and $(Ce - O - CeOH)^{5+}$ also exist.[15, 16] The existence of dimers in perchloric acid was supported by e.m.f. measurements. Extinction coefficient measurements in the 254 nm region were not sufficient to provide the needed evidence.[13] The concentration of interest on the complexes Ce(IV) is capable of forming in perchloric acid has left the studies of Ce(III) somewhat neglected. However, from optical studies in the 279 nm region evidence was obtained for the presence of the $CeClO_4^{2+}$ complex in the perchloric acid range from $0.0057 < [H^+] < 0.42$. This is apparently the sole species of Ce(III) existing in this media.[17]

In a study of the reaction Mn(II)-Ce(IV) in sulfuric acid the major reacting species was given as $Ce(SO_4)_2$ rather than the hydrolytic species which form in perchloric acid.[18] Other kinetic and complexation studies and interpretations suggest that the undissociated Ce^{4+} ion exists in sulfuric acid in addition to such complexes as $CeSO_4^{2+}$, $Ce(SO_4)_3^{2-}$ and even higher species with increasing sulfate ion concentration.[19, 20]

Cerium (IV) perchlorate in aqueous perchloric acid is thermally stable at 25° C, however, slow reduction by water of the Ce(IV) does occur.[21] These solutions were found to evolve

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O_2 if exposed to ultraviolet light in the region 254 nm.[15] The reduction of Ce(IV) decreased gradually as the Ce(III) accumulated. The Ce(III) was believed to undergo photochemical oxidation to account for the decreased reduction of Ce(IV).

Cerium (IV) perchlorate follows Beer's Law when concentrations are below ca. 10^{-2} molar.[20] These investigations were conducted at 1.00 and 3.00 M $HClO_4$. Later investigations extended the acid range from 2.00 M down to 0.800 M at a Ce(IV) concentration of ca. $5X10^{-5}$ M and further substantiated obedience of Ce(IV) to Beer's Law.[22]

2. Vanadium -- Under ordinary conditions the oxidation state of 4+ is considered as the most stable for vanadium. Other than a few compounds such as VCl_4, vanadium (IV) chemistry is predominantly that of the oxovanadium (vanadyl) compounds.

VO^{2+} is considered as the entity which retains its character throughout chemical reaction and is the central "atom" which coordinates with many ligands. The bond between the vanadium and oxygen of the VO unit is essentially a double bond with considerable π bonding thus accounting for the stability.[23]

Work in spectrophotometric and potentiometric measurement within a perchloric acid range of $3\,M > [H^+] > 0.002\,M$ indicate that vanadium (IV) exists in solution as VO^{2+} or $VO(OH)_2^{2+}$.[24] Later work gave a general formula for the oxovanadium ion as

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$[VO(H_2O)_5]^{2+}$ which is supported by electronic[23], e.s.r.[25] and vibrational spectra.[26] The structure VO^{2+} is further supported by the influence of the hydrogen ion concentration on the formal redox potential of the V(IV)-V(V) system.[27, 28]

Absorptiometric and potentiometric studies by Rossotti and Rossotti[29] considered the sole species of vanadium (V) ion to be VO_2^+ in the perchloric acid range $0.048\ \underline{M} < [H^+] < 2.89\ \underline{M}$. Hydrolysis at lower acid concentrations results in formation of polynuclear species of the general form $(VO_2)_q (OH)_p^{(q-p)+}$. The species in higher acid concentrations were not discussed but most probably VO_2^+ prevails in acid solutions higher than $2.00\ \underline{M}$. This is the upper limit of the acidity used in this Ce(IV)-V(IV) investigation. An alternate structure, $V(OH)_4^+$, has been suggested but on the basis of entropy considerations deemed less probable than VO_2^+.[30]

Ce(IV) and V(IV) Reactions and Kinetics

The Ce(IV)-V(IV) reaction in sulfate solution was first studied by Furman[31] whose report on the sluggishness of the reaction in potentiometric titrations near the end point prompted further investigation. To overcome this sluggishness temperatures of 50-60° C were advocated when reaction was conducted in sulfuric, hydrochloric and perchloric acid media.[32] Still later work described the beneficial effects of adding orthophosphoric acid[33]

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and acetic acid[34] during titration with various redox indicators. These measures successfully produced more rapid attainment of the end point at room temperature but no reason for the problem was advanced.

The Ce(IV)-V(IV) reaction has been used in studies of several types where the kinetics were of secondary consideration. These studies were conducted in sulfuric acid where the numerous complexes which were previously discussed can offer difficulties in arriving at an unequivocal resolution of the kinetics. The reaction has also been studied in perchloric acid media,[35] however, the acid dependence was reported to be the opposite expected based on the overall reaction stoichiometry.

The discussion to follow is a chronology of kinetic studies of both Ce(IV) and V(IV) reactions with various other reagents and each other. The reactions in sulfuric acid and perchloric acid will be discussed as they fall in this chronology.

1. Ce(IV)-Tl(I) -- In a study of the kinetics of the Ce(IV)-Tl(I) reaction in the presence of the chloride ion it was found that the chloride is oxidized directly to chlorine.[36] However, at low concentrations of the chloride ion higher oxidation states of chlorine appeared which complicated this study. Since Tl(I) as $TlClO_4$ was not attacked by any substance in the reaction mixture it was used to maintain a constant chloride concentration by the

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ability of Tl(I) to complex with chloride and establish an equilibrium condition. It was declared in this study that the hydrolyzed form of $Ce(OH)^{3+}$ did not appear to react with the chloride ion. Complexes of the type $CeCl_n^{-(n+4)}$ were considered responsible for complicating the rate law. The rate expression was found to be first order in total Ce(IV) concentration and this total was the sum of the many complexes formed from the general type as indicated.

2. Ce(IV)-Sn(II) -- The kinetics of the reaction between Ce(IV) and Sn(II) in aqueous sulfuric acid involved the reacting species $SnSO_4$ and $Ce(SO_4)_3^{2-}$.[37] The reaction in hydrochloric acid has been found to be very fast and the presumed catalytic effect of other contaminating rare earths was eliminated as a reason by Remick in his brief analysis.[38] This reaction was found experimentally to obey the rate law:

$$\frac{-d[Ce(SO_4)_3^{2-}]}{dt} = 2k_1 [SnSO_4] [Ce(SO_4)_3^{2-}] \quad .$$

Most of the experiments were conducted at 0°C with a range of Ce(IV) to Sn(II) ratios of 6.72 to 1.34. This gave an average value for the rate constant, k_1, of 19.8 $\underline{M}^{-1}$ sec^{-1}. In the presence of Ce(III) added initially the rate constant was 18.3 $\underline{M}^{-1}$ sec^{-1}. Upon adding Sn(IV) at the start of the reaction the value of k_1 dropped to a value of 17.8 $\underline{M}^{-1}$ sec^{-1}. Further investigations with adding Sn(IV) by either aging the Sn(II) solutions or air-oxidizing them to

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Sn(IV) gave increases in the rate constant which could not be related quantitatively to the concentration of Sn(IV) considered to exist in the solution. Regardless of this second order behavior was retained throughout the reaction in each case. The manner in which the Sn(IV) was treated and added ruled out the possibility of wall catalysis as a cause for the rate constant increase. The "normal" second order rates were independent of the ionic strength of hydrogen, sulfate and hydrogen sulfate ions. The rates were believed to have a complex dependency on the age, history, and concentration of the tin solutions used due to slowness of the hydrolytic equilibria. Thermodynamic parameters were not calculated although rate runs were made at temperatures from 0°C to 25°C and showed an increase in the rate constant from $19.8 \pm 2.4\ \underline{M}^{-1}\ sec^{-1}$ to $62.9 \pm 10.7\ \underline{M}^{-1}\ sec^{-1}$. Experimental evidence suggested that the intermediate tin (III) may have been present but the possibility that a complex such as $SnCe(SO_4)_x^{6-2x}$ or possibly one containing either Sn(III) and Ce(III) or Sn(II) and Ce(IV) was not discounted.

3. Ce(IV)-Cr(III) -- In the classic study of Ce(IV) with chromium (III) in aqueous sulfuric acid the rate law was determined to be:[39]

$$\frac{d\,[Cr(VI)]}{dt} = \frac{k\,[Ce(IV)]^2\,[Cr(III)]}{[Ce(III)]}$$

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This reaction is a step-wise oxidation of the chromium where the transition state for the reaction has one Ce(IV) and one Cr(III) with an average of 4^+ for the oxidation state of the complex. These factors suggested a mechanism of the following type:

$$(1)\quad Ce(IV) + Cr(III) \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Ce(III) + Cr(IV) \qquad \text{(fast equilibrium)}$$

$$(2)\quad Ce(IV) + Cr(IV) \underset{k_4}{\overset{k_3}{\rightleftharpoons}} Ce(III) + Cr(V) \qquad \text{(slow)}$$

$$(3)\quad Ce(IV) + Cr(V) \underset{k_6}{\overset{k_5}{\rightleftharpoons}} Ce(III) + Cr(VI). \qquad \text{(fast)}$$

The observed rate law is consistent with the proposed mechanism. The concentration of the unstable intermediate, Cr(IV), the reactant in the rate determining step, is fixed by the equilibrium shown in step (1).

4. Ce(IV)-U(IV) -- The rate for the principal reaction in the Ce(IV)-U(IV) system was found to be proportional to both $Ce(OH)^{3+}$ and U^{4+} concentrations.[22] This reaction was studied in 0.80 to 2.00 M perchloric acid with an ionic strength of 2.00 M maintained by using sodium perchlorate. The thermodynamic parameters in 2.00 M perchloric acid at 2.4°C were $\Delta H^* = 14.0 \pm 0.7$ kcal mol^{-1}, $\Delta S^* = 6.2 \pm 2.5$ e.u. and $\Delta F^* = 12.2 \pm 0.2$ kcal mol^{-1}. $Ce(OH)^{3+}$ was declared to be the predominant reacting species of Ce(IV) in the acid range 0.300 to 2.00 M. The

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proposed rate law was given as:

$$\frac{-d\,[Ce(IV)]}{dt} = 2k_1 \frac{[U^{4+}]\,[Ce(OH)^{3+}]}{[H^+]}$$

which shows the formation of an activated complex which can be represented by the net process: $Ce(OH)^{3+} + U^{4+} + H_2O \rightleftharpoons [Complex]^{6+*} + H^+$. The rate determining reaction is: $U(IV) + Ce(IV) \rightarrow U(V) + Ce(III)$ followed by the rapid reaction: $U(V) + Ce(IV) \rightarrow U(VI) + Ce(III)$.

5. Ce(IV)-As(III) -- In a study of the catalytic effect of osmium on the reaction of Ce(IV) with As(III) in sulfuric acid it was found that the As(III) concentration affected its dependency in the rate law.[40] The dependency on Ce(IV) was stated to be more complex. When the ratio As(III)/Ce(IV) was increased, the As(III) dependency tended toward zero order. There are two cycles in which the osmium could operate which involved three equations in each cycle with oxidation states for osmium going from +4 to +8. The authors admitted to the problems which $Ce(SO_4)_x^{+4-2x}$ complexes and the sulfate and hydrogen sulfate concentrations could offer when the ratios of reactants were varied.

6. Ce(IV)-$C_2O_4^{2-}$ -- In addition to other studies on the Ce(IV)-oxalate system,[19, 41] more recent spectrophotometric studies of this standardization reaction in acid sulfate media yielded evidence for a mechanism involving a transient intermediate.[42]

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The experimental rate expression was found to be:

$$\frac{-d\,[Ce(SO_4)_3^{2-}]}{dt} = K_c K_D K_C k_3 \frac{[Ce(SO_4)_3^{2-}][H_2C_2O_4]}{[H^+]\,[HSO_4^-]} \quad .$$

The constants are related to the following reactions:

$$K_c : H_2C_2O_4 \rightleftharpoons H^+ + HC_2O_4^-$$

$$K_D = k_1/k_{-1} : Ce(SO_4)_3^{2-} + H^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Ce(SO_4)_2 + HSO_4^-$$

$$K_C = k_2/k_{-2} : Ce(SO_4)_2 + HC_2O_4^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Ce(SO_4)_2(C_2O_4)^{2-} + H^+$$

$$k_3 : Ce(SO_4)_2(C_2O_4)^{2-} \xrightarrow{k_3} Ce(SO_4) + C_2O_4^{2-} \quad .$$

The sulfate and hydrogen sulfate ions retarded the rate by repressing the formation of a reactive intermediate by competing with the oxalate for the Ce(IV) available. In perchloric acid the reaction was too fast to follow by conventional spectrophotometric means. The phosphate ion has shown a similar retardation effect in Ce(IV) reactions since it will also complex with Ce(IV).

The Ce(IV)-oxalate reaction was also studied by Russian investigators.[43] They suggested the reaction takes place in three steps. First, the formation of an inner-sphere complex between the reagents; second, the decomposition of the complex with the formation of a singly charged oxalate radical; and third, the reduction of the Ce(IV) not bound in the complex by the oxalate

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radical. In small concentrations of $H_2C_2O_4$ the rate determining step was the second and in large excesses of acid the slowest step was the third.

7. V(IV)-Cr(VI) -- In a communication reporting preliminary work on the V(IV)-Cr(VI) reaction in perchloric acid solution the product, VO_2^+, was found to retard the reaction.[44] The rate law to describe this was:

$$\frac{-d\,[HCrO_4^-]}{dt} = \frac{k[VO^{2+}]^2\,[HCrO_4^-]}{[VO_2^+]} .$$

The rate constant had a value of $0.62 \pm 0.06\ \underline{M}^{-1}\ sec^{-1}$ at 25°C in 5.00×10^{-3} F $HClO_4$ at an ionic strength of 2.00 F using $LiClO_4$. The equation fitted experimental data over ca. 6-fold V(V), ca. 20-fold V(IV), and ca. 8-fold Cr(VI) at constant hydrogen concentration. The short communication gave an apparent mechanism as:

$$(1)\quad V(IV) + Cr(VI) \underset{k_2}{\overset{k_1}{\rightleftharpoons}} V(V) + Cr(V)$$

$$(2)\quad V(IV) + Cr(V) \underset{k_4}{\overset{k_3}{\rightleftharpoons}} V(V) + Cr(IV)$$

$$(3)\quad V(IV) + Cr(IV) \xrightarrow{k_5} V(V) + Cr(III) \quad .$$

A comparison with the rate laws of other chromium systems in which the product of the other reactant retarded the rate were offered to support this law and mechanism.

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J. H. Espenson[45] followed his communication on the V(IV)-Cr(VI) reaction[44] with a more complete study which also included the induced oxidation of the iodide ion. The stoichiometry of the reaction as carried out in aqueous perchlorate media was given by:

$$3\ VO^{2+} + HCrO_4^- + H^+ \rightleftharpoons 3\ VO_2^+ + Cr^{3+} + H_2O \quad .$$

Intermediate oxidation states of chromium are involved in the mechanism since the oxidation state of chromium changes by three oxidation numbers in the overall reaction. Two rate expressions were offered to explain the experimental results and these are:

$$(1)\quad \frac{-d[Cr(VI)]}{dt} = \left(\frac{[VO^{2+}]}{[VO_2^+]}\right)^2 k[HCrO_4^-] + k'\{[H^+][HCrO_4^-]^2\}$$

$$(2)\quad \frac{-d[Cr(VI)]}{dt} =$$

$$\left(\frac{[VO^{2+}]}{[VO_2^+]}\right)^2 \{k[HCrO_4^-] + k'\, Q_D^{-1}\, [H^+]\, [Cr_2O_7^{2-}]\}$$

where Q_D^{-1} is the concentration equilibrium quotient for the reaction, $2\ HCrO_4^- \rightleftharpoons Cr_2O_7^{2-} + H_2O$ and has a value of 98. Acid concentrations for this reaction were relatively low, ranging from 0.005 to 0.10 M in perchloric acid. Mechanisms which are

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consistent with the term $\left(\frac{[VO^{2+}]}{[VO_2^+]}\right)^2 k[HCrO_4^-]$ in the rate laws involve a transition state suggested to be $(HCrO_4^- V^{2+} \pm nH_2O)^{+*}$. The path with the second order dependence upon $HCrO_4^-$ presumably has $Cr_2O_7^{2-}$ as the reactant. The transition state suggested in this instance is $(HCr_2O_7 - V^{2+} \pm mH_2O)^{+*}$. From the two above rate laws two mechanisms were proposed, each possible but indistinguishable on the basis of experimental considerations alone. These were given as:

(A) $2\ V(IV) \rightleftharpoons V(V) + V(III)$ (fast)

$V(III) + Cr(VI) \longrightarrow V(V) + Cr(IV)$ (slow)

$V(IV) + Cr(IV) \rightleftharpoons V(V) + Cr(III)$ (fast)

(B) $V(IV) + Cr(VI) \rightleftharpoons V(V) + Cr(V)$ (fast-unfavorable)

$V(IV) + Cr(V) \longrightarrow V(V) + Cr(IV)$ (slow)

$V(IV) + Cr(IV) \rightleftharpoons V(V) + Cr(III)$ (fast) .

The induced oxidation of the iodide ion in the reaction by the Cr(V) intermediate was discussed and ample evidence offered to support mechanism (B) and the existence of the Cr(V) intermediate.

8. Ce(IV)-Mn(II) -- The kinetic study of the Ce(IV)-Mn(II) system offers a different model in that the rates of both the forward

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and reverse reactions were determined.[18] The rate expression for the forward path was given as:

$$\frac{-d[Ce(IV)]}{dt} = k'_a K_{e1} \frac{[Ce(IV)]\,[Mn(II)]}{[HSO_4^-]}\,[H^+] \quad .$$

The main backward path was described by the equation:

$$\frac{-d[Ce(IV)]}{dt} = k_{2b} K_{e3} \frac{[Mn(III)]\,[Ce(III)]}{[H^+]\,[SO_4^{2-}]} \cdot K_{HSO_4^-} \quad .$$

The apparent second order rate constants for the forward and reverse paths are respectively, 0.43 $\underline{M}^{-1}$ sec^{-1} and 5.9 $\underline{M}^{-1}$ sec^{-1} at 25°C in 3 $\underline{M}$ sulfuric acid. The principal reactant species, $Ce(SO_4)^{2+}$ and $Mn(OH)^{2+}$, were suggested for the forward and backward reactions. The thermodynamic parameters as calculated were $\Delta S^* = 17$ e.u., and 13.0 kcal mol^{-1} for ΔH^*. It was suggested that the reaction could be explained on the basis of an outer-sphere mechanism.

9. Ce(IV)-V(IV) -- A kinetic study of the Ce(IV)-V(IV) titration reaction was conducted in an effort to account for the sluggishness of the reaction.[46] In this study the apparent rate constant was found to be $\simeq$ 1350 $\underline{M}^{-1}$ sec^{-1} at 25°C in 1 $\underline{M}$ sulfuric acid. The thermodynamic parameters under these conditions were $\Delta H^* = 12.4 \pm 1$ kcal, $\Delta S^* = +2$ e.u. and the activation energy, $E_a = 13.0 \pm$ kcal mol^{-1}.

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The primary reaction of Ce(IV)-V(IV) was shown to be rapid when the reaction was followed spectrophotometrically in the 400 to 430 nm wavelength region. The sluggishness of the reaction during potentiometric titrations was attributed to the slow attainment of the equilibrium for the V(V)-V(IV) couple at the indicator electrode. In concentration ranges of the order of 10^{-4} to 10^{-5} M for either reactant in 1 M sulfuric acid there were no effects noted from products to vary the form of the rate law or the value of the constant. The rate law was first order in each reactant, Ce(IV) and V(IV). The second order rate constant was found to increase slightly with the addition of sodium perchlorate and decrease with increasing sulfuric acid concentration. The primary objective of this study was to resolve the problem of the reaction sluggishness during potentiometric titrations and to show that it was not a consequence of the primary reaction.

10. Ce(IV)-NH_2OH -- The reaction between Ce(IV) and hydroxylamine, (NH_2OH), was investigated potentiometrically in aqueous sulfuric acid media.[47] In 0.25 M H_2SO_4 the stoichiometric mole ratio of Ce(IV) to NH_2OH was found to be 2 to 1 and increased to 4 to 1 in 1 M to 5 M H_2SO_4. As the acid concentration was increased, the reaction slowed and in 8 to 10 M acid it was found to be too slow to follow. The hydroxylamine in 0.25 M acid was oxidized according to the following equation:

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$$8\ Ce(SO_4)_2 + 2\ NH_2OH + H_2O \longrightarrow N_2O_3 + 4\ Ce_2(SO_4)_3 + H_2SO_4$$

$$N_2O_3 + H_2O \longrightarrow 2HNO_2 \quad .$$

The same reaction was declared to occur in hydrochloric and perchloric acid media. The rate law and constant derived from this study of the reaction were:

$$\frac{-d[Ce^{4+}]}{dt} = \frac{k[NH_2OH]\ [Ce(SO_4)_2]}{[H_2SO_4]^{2.5}}$$

and $k = 5.5\ \underline{M}^{-1}\ sec^{-1}$ at 23°C.

11. Ce(IV)-V(IV) -- In another investigation of the Ce(IV)-V(V) reaction it was used to check the method of applying potential-time curves to the study of kinetics.[48] In this study the reaction was conducted in 2N sulfuric acid and the potential-time (E-t) curves data were checked against those obtained by an independent flow method. At 20°C the second order rate constant from the E-t method had a value of $833 \pm 50\ \underline{M}^{-1}\ sec^{-1}$ and by the independent flow method a value of $815 \pm 9\ \underline{M}^{-1}\ sec^{-1}$. An activation energy of 8.29 ± 0.1 kcal mol^{-1} was determined from the time dependence of the rate constants.

12. V(IV)-BrO_3^- -- An investigation of the V(IV)-BrO_3^- reaction was reported to give a rate law as follows:[49]

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$$\frac{-d\,[V(IV)]}{dt} = k_o K_1 \frac{[V(IV)]\,[BrO_3^-]}{1 + K_1\,[BrO_3^-]} \quad .$$

A value of k_o equal to 7.50 min^{-1} was obtained at 20°C in an ionic strength of 0.10 M. K_1 had a value of 88.8 M^{-1} and the activation energy was calculated to be 19 kcal mol^{-1}.

The reaction path was believed to involve an intermediate in the first step with the rate determining step as the decomposition of this intermediate as shown:

$$(1)\quad BrO_3^- + VO^{2+} \underset{-1}{\overset{K_1}{\rightleftharpoons}} [BrO_3^- - VO^{2+}] \quad \text{(fast)}$$

$$(2)\quad [BrO_3^- - VO^{2+}] \xrightarrow{k_o} VO_2^+ + BrO_2\bullet \quad \text{(slow)}$$

$$(3)\quad BrO_2\bullet + VO^{2+} \xrightarrow[k_2]{} \text{Products} \quad \text{(fast)} \quad .$$

With the BrO_3^- in considerable excess and the fact that the total VO^{2+} concentration was represented by the following:

$$[VO^{2+}]_T = [VO^{2+}] + [BrO_3^- - VO^{2+}]$$

then incorporation of this with the equilibrium step (1) resulted in the described rate law. Three structures were offered for the intermediate and argued on the basis of bonding and structural considerations.

13. Ce(IV)-V(IV) -- A study of the Ce(IV)-V(IV) reaction in perchloric acid was made by G. N. Rao.[35] The second order rate

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constant was found to be $62.0 \pm 5.0\ \underline{M}^{-1}\ sec^{-1}$ at 25°C in 1M acid. From the data presented the rate constant in excess V(IV) was shown to be slightly higher than the value in excess Ce(IV). It was declared in this study that an increase in the rate occurred with an increase in the acid concentration but no quantitative indication of the magnitude was given. The activation energy was calculated as 12.0 ± 1.0 kcal. The acidity range in the study was from 0.5 to 2.00 M $HClO_4$ with an ionic strength maintained at 2.00 M using sodium perchlorate.

14. Ce(IV)-Sb(III) -- The oxidation of antimony (III) by cerium (IV) was studied in perchloric acid media.[50] The reaction was found to follow the rate law:

$$\frac{-d\,[Ce(IV)]}{dt} = \frac{2\,[Ce(IV)]\,[Sb(III)]\,(k_2\,[H^+] + k_3K_2)}{[H^+] + K_2}$$

where k_2 and k_3 were determined to be 35 and $300\ \underline{M}^{-1}\ sec^{-1}$ respectively. These values were obtained with reacting conditions of 2 M ionic strength and 25°C. K_2 is the second hydrolysis constant of Ce^{4+} and was calculated as 0.197. The active species were assumed to be the hydrolytic species of Ce(IV) and SbO^+. This was based on the effect of the hydrogen ion concentration and spectrophotometric measurements. With an hydrolysis constant of 52 M for the equilibria:

$$H_3SbO_3 \text{ (or } HSbO_2) + H^+ \rightleftharpoons SbO^+ + 2H_2O$$

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the investigators were able to explain a rate maxima which occurred at lower (ca. 0.2 M) acid concentration. The observed rate constants were found to increase with increasing ionic strength. The activation parameters for k_2 were, $\Delta H^* = 19.7$ kcal mol^{-1} and $\Delta S^* = 7.24$ e.u.. For k_3 the values were 9.6 kcal mol^{-1} and - 27.6 e.u.. The rate was over 3000 times faster than the rate for the same reaction in sulfuric acid. This greater rate was explained to be the consequence of an atom transfer mechanism in the perchloric acid media.

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CHAPTER II

EXPERIMENTAL

Reagents

1. Cerium (IV) perchlorate -- G. F. Smith ceric ammonium nitrate ($Ce(NH_4)_2(NO_3)_6$) was recrystallized from ca. 7 M nitric acid and filtered through a medium grade glass frit. The solid was dissolved in distilled water and then placed in an ice bath. Thirty percent H_2O_2 was added dropwise with stirring until the loss of color indicated reduction of the Ce(IV) to Ce(III). Completeness of the reduction was confirmed using ferroin indicator on a small aliquot. The solution was then boiled for 40 minutes to drive off the residual H_2O_2. This solution was cooled and then added to ca. 1.5 M oxalic acid forming cerium (III) oxalate precipitate. The solution containing the precipitate was boiled about 15 minutes and filtered through a medium grade glass frit. The precipitate was then placed in a crucible and heated to 550-650° for 15 hours. In this step the cerium (III) oxalate was both decomposed and oxidized to cerium (IV) oxide. The CeO_2 was then added to a solution of H_2O_2 and perchloric acid. The conversion of CeO_2 to $Ce(ClO_4)_3$ by this method is slow. This solution is then anodically oxidized to the cerium (IV) perchlorate

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used as the stock solution. The stock solution was analyzed for cerium (IV) content by adding an aliquot to about 20 mls of 9 M H_2SO_4 and titrating to the ferroin end point using freshly standardized iron (II) sulfate solution. The hydrogen ion concentration of the stock solution was determined by the method of Sherrill, et al.[13] The stock solutions were about 0.3 M Ce(IV) and 1 M H^+. Stock solutions were stored in the dark to reduce photochemical reaction. An aliquot of the stock solution was diluted to the desired concentration and standardized before each set of runs.

2. Cerium (IV) sulfate -- Fisher Scientific Company cerium (IV) sulfate was dissolved in ca. 0.5 M H_2SO_4 to give about 0.03 M Ce(IV). The solution was allowed to stand for a week then filtered through a fine grade glass frit. The solution was standardized using iron (II) sulfate and titrating to the ferroin end point.

3. Ferroin Indicator -- G. Frederick Smith Chemical Company 1,10 phenanthroline ferrous sulfate solution (ferroin) was diluted ten-fold to a strength of ca. 0.0025 M and used as the indicator in all redox titrations. (Indicator corrections were not made since they were smaller than the declared experimental accuracy.)

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4. Iron (II) sulfate -- 0.03 M stock iron (II) sulfate solutions were prepared by dissolving Baker Reagent iron (II) sulfate in ca. 0.5 M sulfuric acid. These solutions were standardized against standard cerium (IV) sulfate solutions to the ferroin end point. Iron (II) sulfate solutions were restandardized if over two weeks old. Decreases in concentration of 3 parts per 1000 were the usual noted differences during this period.

5. Lithium perchlorate -- Baker Reagent lithium carbonate was added to concentrated filtered Reagent Grade Mallinkrodt perchloric acid until the solution was slightly acid to pHydrion paper. Sulfate ion present as an impurity was removed by precipitation as barium sulfate using barium hydroxide. Carbonate ion was removed both by boiling the slightly acid solution and precipitation as barium carbonate. The lithium perchlorate thus prepared was recrystallized twice using distilled water. The solid was added to distilled water to give solutions of about 3.5 - 4.5 M in Li^+. The Li^+ concentration was determined by passing an aliquot through a Dowex-50 resin column in the acid form and titrating the effluent acid to the phenolphthalein end point with standard sodium hydroxide. The equivalents of acid found are equal to the equivalents of Li^+ in the aliquot.

6. Perchloric acid -- Reagent Grade Mallinkrodt perchloric acid was filtered through a fine grade glass frit prior to further

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use. Stock solutions were made about 4 M. These were standardized by diluting an aliquot and titrating a known volume of the diluted stock to the phenolphthalein end point using standard sodium hydroxide.

7. Vanadium (IV) perchlorate -- Baker Reagent ammonium metavanadate (NH_4VO_3) was heated at 450°C overnight in a crucible. The resultant V_2O_5 was added to about 1 M perchloric acid and cathodically reduced to vanadium (IV) perchlorate to give a stock solution of about 2 M in V(IV). The solution was analyzed for V(IV) by diluting an aliquot of the stock solution ten-fold and reducing it with zinc amalgam. Air oxidation of the V(II) formed was prevented by bubbling argon through the reaction flask. A known volume of the V(II) was added to an excess of standard cerium (IV) sulfate and the excess Ce(IV) titrated to the ferroin end point using iron (II) sulfate. The acidity of the stock solution was determined by passing an aliquot through a Dowex-50 resin column in the acid form to extract the VO^{2+}. The acid effluent was titrated with standard sodium hydroxide to the phenolphthalein end point. The stock solution acidity was calculated by subtracting the two equivalents of acid released from the column by the VO^{2+} from the total acid equivalents found.

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Apparatus

The Cary Model 14 spectophotometer was used to follow and record the absorbance change of cerium (IV) throughout the course of the reaction. A specially designed Pyrex cell facilitated the control of the temperature, the mixing of the reactants, and the constancy in measuring absorbances. This cell was placed in the light beam of the spectrophotometer by mounting it in a Lucite box fitted to the cell compartment of the spectrophotometer. The box had silica windows in the walls in the area where the light beam penetrated. With a silica cell similar in design to the Pyrex cell studies of other reactions in wavelength regions where Pyrex and Lucite are opaque were possible. This was a design feature of the box not required for the wavelength region used in this investigation.

The Lucite box was fitted with mounts that insured exact positioning of the cell for each run. In the bottom of the cell a Teflon coated magnetic stir bar was rotated rapidly to maintain a constant temperature in the cell and to mix the reactants. The box was filled with distilled water which served as the heat transfer fluid and prevented scattering of light from the rounded ends of the cell. Water from an external constant temperature bath was circulated through a coil of copper tubing set in the box beside the cell. Within the coil of tubing a small paddle stirrer circulated the

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distilled water in the box around the coils and the cell. In this manner the temperature in the cell was maintained to within $\pm$ 0.1°C of that desired for the run. At lower temperatures (10°C) argon was blown across the external faces of the box over the silica windows to preclude condensation which would otherwise form and interfere with the light beam. The arrangement of the cell is shown in Figures 1 and 2.

Procedure

Appropriate volumes of distilled water, perchloric acid, and lithium perchlorate solutions were pipetted into the reaction cell. The cell was placed in the box and allowed to reach thermal equilibrium. The absorbance base line was set as zero using the "balance" control of the spectrophotometer. The desired amount of cerium (IV) perchlorate solution was pipetted in and the maximum absorbance was noted as D_o (initial absorbance). The desired volume of vanadium (IV) perchlorate solution was then injected using a 5 ml calibrated glass syringe fitted with a Teflon needle. The needle was carefully manipulated to reach into the solution yet not obstruct the light beam within the cell. The vanadium (IV) solution was injected rapidly at the same time the chart drive was turned on. The chart speed was preset to a given value and served to time the loss of absorbance during the course of the reaction. Absorbance values versus the elapsed reaction (or chart)

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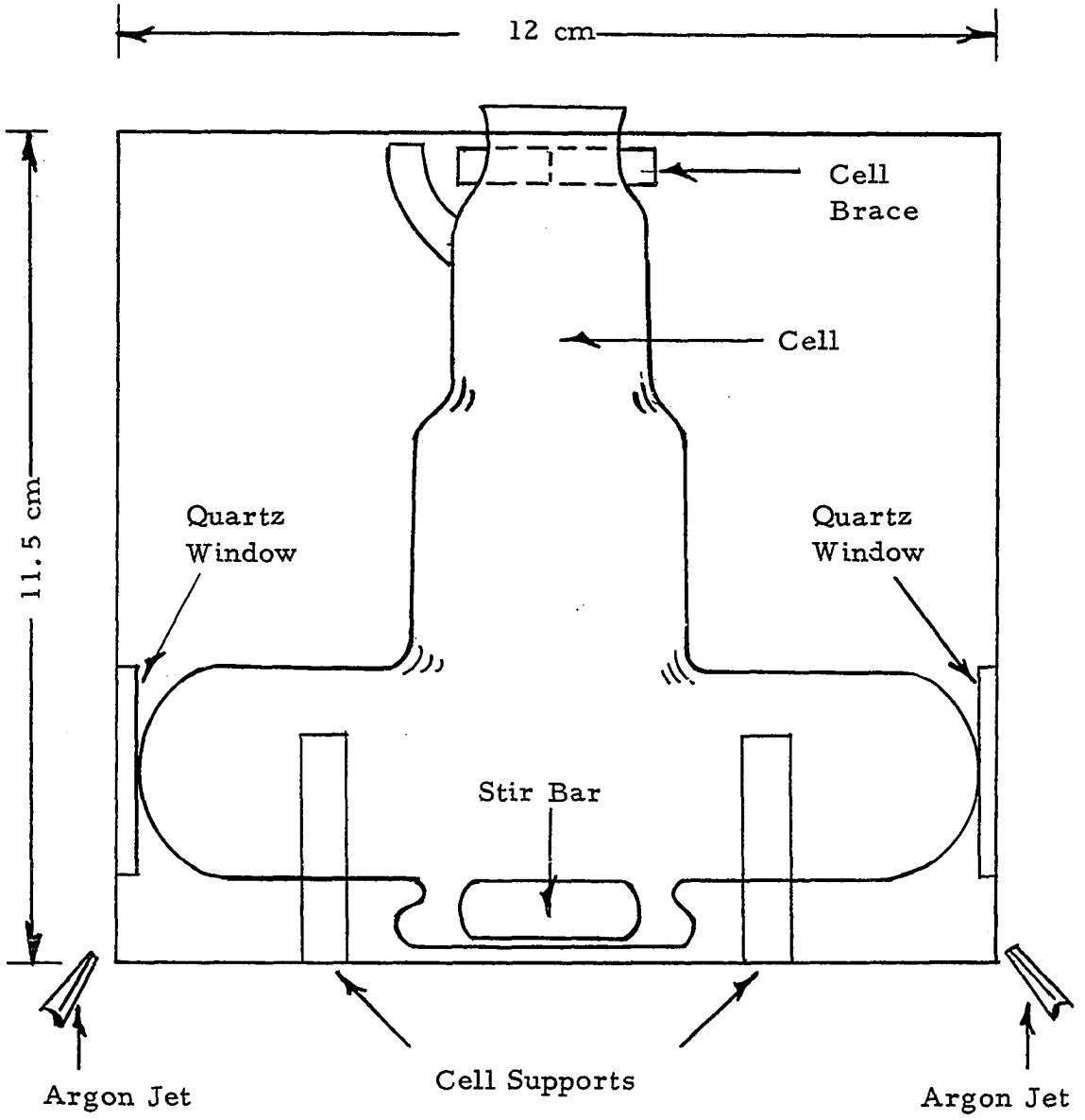

Figure 1. Cell Mounted in Lucite Box (Side View - Cooling Coils Not Included).

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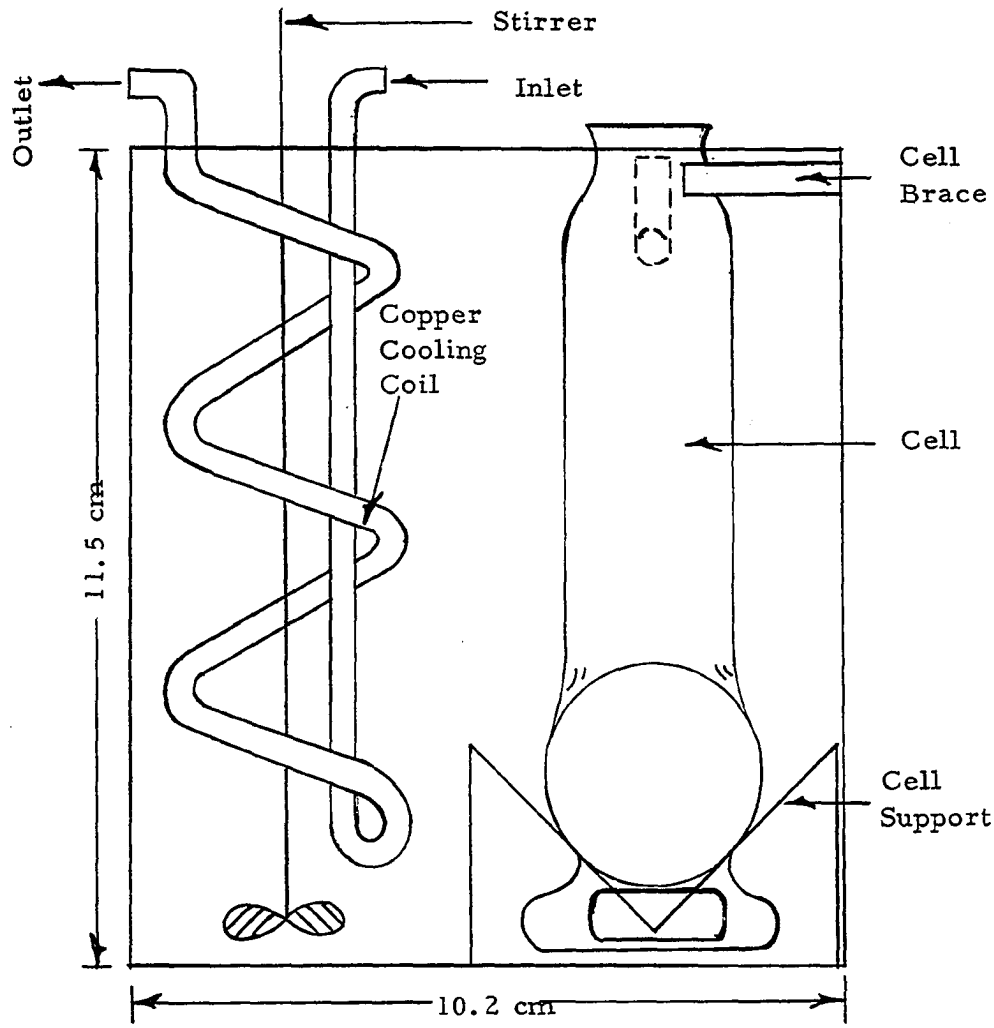

Figure 2. Cell Mounted in Lucite Box (End View).

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time were taken from the chart and used to calculate the various reaction rate constants.

Calculations

The logarithm ratios of [V(IV)] / [Ce(IV)] at a time equal "t" were plotted versus time to verify that the reaction was overall second order in the perchloric acid medium. Estimates of the apparent second order rate constant were obtained from the slope of the curve. From these estimates final calculations were made using the Los Alamos Non-Linear Least Squares Program[51] which was adapted for use in the CDC 6400 computer. This program enabled calculation of the rate constants and the thermodynamic parameters which gave the best fit to the experimental data.

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CHAPTER III

RESULTS

Stoichiometry

No stoichiometry studies were conducted since the Ce(IV)-V(IV) reaction is known to proceed as follows:[31, 32, 33, 34, 35, 46, 48]

$$Ce(IV) + V(IV) \longrightarrow Ce(III) + V(V) \quad .$$

The equilibrium constant, K_{eq}, for this reaction at 25°C has a value of 10^{12}.

Metal Ion Dependence

Metal ion dependence would be expected to follow the simplicity of the stoichiometry and result in a complementary reaction. The reaction was found to be first order in each of the reactants, Ce(IV) and V(IV), and second order overall. The apparent second order rate constants from metal ion dependence were determined at 20°C with the hydrogen ion concentration at 1.00 M in perchloric acid using lithium perchlorate to maintain an ionic strength of 2.00 M. Table I gives those data in excess of Ce(IV) and Table II gives those data in excess V(IV).

Initial absorbances (D_o) were calculated rather than measured for three reasons. First, the human element in manually

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Table I

Metal Ion Dependence in Excess Ce(IV)

Conditions: λ = 370 nm T = 20.0 ± 0.2° C

$[H^+]$ = 1.00 ± 0.01 M μ = 2.00 ± 0.02 M ($LiClO_4$)

$[Ce(IV)]_o$ M X 10^4	$[V(IV)]_o$ M X 10^4	Number of Data Points	k_2' M^{-1} sec^{-1}
9.37	3.82	1	38.2 [a]
4.81	4.77	1	42.8
4.81	1.91	1	37.2
4.81	1.53	1	37.6
4.81	0.763	1	37.6
4.79	4.77	1	42.8
4.79	1.91	1	37.0
4.79	1.53	1	36.6
4.79	0.763	1	35.6
4.69	3.82	1	40.5 [a]
3.85	0.763	1	37.4
3.83	0.763	1	40.4
2.88	0.763	1	36.2
2.87	0.763	1	37.0
1.92	0.763	1	38.7
1.89	0.763	1	37.8
0.961	0.763	1	39.7
0.958	0.763	1	38.4
0.958	0.244	1	34.8 [b]
0.958	0.244	1	31.4 [b]
			Average 37.9 ± 2.5

[a] λ = 400 nm

[b] λ = 320 nm

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Table II

Metal Ion Dependence in Excess V(IV)

Conditions: λ = 370 nm T = 20.0 ± 0.2° C

$[H^+]$ = 1.00 ± 0.01 M μ = 2.00 ± 0.02 M ($LiClO_4$)

$[V(IV)]_o$ M X 10^4	$[Ce(IV)]_o$ M X 10^4	Number of Data Points	k_2' M^{-1} sec^{-1}
14.3	0.910	2	43.9
11.5	1.87	1	47.8 [a]
11.5	1.92	1	41.5
11.5	1.92	1	44.8
9.54	0.958	1	44.0 [b]
9.54	0.958	1	44.3
9.54	0.575	1	44.8 [b]
9.54	0.455	2	44.3 [b]
7.63	4.79	2	44.0
7.63	4.69	1	43.3 [a]
7.63	3.83	2	44.2
7.63	2.39	1	43.5
7.63	1.92	1	43.2
7.63	0.958	1	45.3
4.58	1.92	2	44.0
3.82	1.92	1	42.7
3.05	1.92	1	43.9
			Average 44.1 ± 1.1

[a] 400 nm

[b] 320 nm

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extrapolating to zero time was thus eliminated; second, the absorbance of Ce(IV) is acid dependent[22]; and lastly, the absorbance of Ce(IV) was found to decrease slowly before the reaction could be initiated. The reagents were in 1.00 M perchloric acid and for runs where the acidity during reaction was < 1.00 M the absorbance would increase perceptibly when the V(IV) was added to the Ce(IV) solution in the reaction cell. The jump in absorbance upon injecting the V(IV) was due to the slight increase in solution acidity which caused an increase in the Ce(IV) absorbance. This resulted in a chart trace which was erratic for ca. 1 - 3% of the initial stages of the reaction. At solution acidities > 1.00 M this jump did not occur so a check was conducted to verify agreement between extrapolated and calculated D_o. In no instance was this difference greater than 1 part in 100.

When Ce(IV) was added to the solution in the reaction cell the absorbance decreased slowly regardless of solution acidity or wavelength. No quantitative study was conducted to determine if the rate of decrease were acid dependent. From calculated initial absorbances (D_o), final absorbance (D_∞) and reactant concentrations it was found that within experimental error the total Ce(IV) available for reaction had not changed. The decreasing absorbance may have been due to the slow formation of a dimeric species of Ce(IV) which has a lower extinction coefficient than the

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predominant species at the wavelengths considered in this investigation.[52]

D_∞ values were also calculated since many of the reactions would have required at least an hour to reach completion, however, the rate was followed in each case to at least 70% completion. The absorbance of V(V) at 400, 370, and 320 nm for the concentrations used in this study was negligible so no absorbance corrections were necessary.

Acid Dependence

To permit studies of the reaction at low acid concentrations it was necessary to use the lowest concentrations of reagents which gave reaction rates within the measuring capabilities of the spectrophotometric method. Coincidentally, these same reactant concentrations could be easily determined with excellent precision by standard volumetric methods. Therefore, a wavelength region was required which was suitable to the concentrations used and would give relatively large absorbance changes throughout the course of the reaction. 320 nm was found as the best compromise based on these factors.

The temperatures used in this part of the investigation were 10, 20, and 30°C with ionic strength maintained at 2.00 M using lithium perchlorate. The acidity was varied at convenient increments from ca. 0.06 to 2.00 M in perchloric acid. All of these runs

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were conducted in excess V(IV) since the largest absorbance changes were possible under these circumstances. These results are shown in Tables III, IV and V.

Runs is excess Ce(IV) were made over a limited acid range of 0.0615 to 0.300 M at 20° C. The apparent second order rate constants were consistently lower by a factor of about 15% from those in excess V(IV) at the same acid concentrations. (Reference Tables IV and VI). This difference is also apparent in Metal Ion Dependence studies.

Medium Effect

At 20° C and 0.100 M H^+ in perchloric acid the ionic strength of the reactant solution was varied from 0.100 to 2.50 M. The apparent second order constant increased linearly with increasing ionic strength. The data and results are given in Table VII.

Product and Impurity Effects

A test was conducted to determine if the products, Ce(III) and V(V), affected the rate of the reaction in any manner. The products were prepared by reacting Ce(IV) with a slight excess of V(IV). An aliquot of this solution was added to the reaction cell then Ce(IV) was added and allowed to react with the slight excess of V(IV) in the product sample in the cell. When the reaction was considered complete and thermal equilibrium established the V(IV) was injected.

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Table III

Acid Dependence at 10° C

Conditions: $T = 10.0 \pm 0.1^{\circ}$ C $\quad \lambda = 320$ nm

$\mu = 2.00 \pm 0.02$ M ($LiClO_4$)

$[H^+]$ M	$[V(IV)]_o$ M X 10^5	$[Ce(IV)]_o$ M X 10^5	Number of Data Points	k'_2 $M^{-1}sec^{-1}$
0.0615	10.5	9.58	2	145
0.100	10.5	9.58	2	101
0.200	10.5	9.58	2	54.2
0.300	10.5	9.58	2	40.3
0.400	10.5	9.58	2	31.0
0.600	10.5	9.58	2	23.1
0.800	10.5	9.58	2	18.9
1.00	10.5	9.68	2	14.8
1.50	10.5	9.58	2	11.5
2.00	10.5	9.58	2	9.2

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Table IV

Acid Dependence at 20° C

Conditions: $T = 20.0 \pm 0.2^{\circ}$ C $\lambda = 320$ nm

$\mu = 2.00 \pm 0.02$ M ($LiClO_4$)

$[H^+]$ M	$[V(IV)]_o$ M X 10^5	$[Ce(IV)]_o$ M X 10^5	Number of Data Points	k_2' M^{-1} sec^{-1}
0.0615	10.5	9.59	1	351
0.100	10.5	9.59	4	256
0.200	10.5	9.59	2	151
0.200	10.5	9.59	2	148
0.300	10.5	9.59	2	110
0.400	10.5	9.59	2	85.8
0.400	10.7	9.70	4	85.3
0.600	10.7	9.70	2	63.9
0.800	10.5	9.59	2	48.1
0.800	10.7	9.70	4	48.7
1.00	10.5	9.59	2	40.8
1.00	10.7	9.70	2	40.5
1.20	10.7	9.70	4	36.2
1.60	10.7	9.70	4	29.7
2.00	10.5	9.59	2	25.2
2.00	10.7	9.70	4	26.0

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Table V

Acid Dependence at 30° C

Conditions: T = 30.0 ± 0.3° C λ = 320 nm

μ = 2.00 ± 0.02 M ($LiClO_4$)

$[H^+]$ M	$[V(IV)]_o$ M X 10^5	$[Ce(IV)]_o$ M X 10^5	Number of Data Points	k_2' $M^{-1} sec^{-1}$
0.100	10.5	9.55	2	615
0.200	10.5	9.55	2	374
0.200	10.5	9.53	2	374
0.300	10.5	9.55	2	268
0.300	10.5	9.53	2	272
0.400	10.5	9.55	2	213
0.400	10.5	9.53	2	214
0.500	10.5	9.52	2	184
0.600	10.5	9.55	2	159
0.600	10.5	9.53	2	162
0.700	10.5	9.52	2	136
0.800	10.5	9.55	2	122
0.800	10.5	9.53	2	123
0.900	10.5	9.53	3	111
1.00	10.5	9.68	1	106
1.10	10.5	9.52	2	95.7
1.50	10.5	9.55	2	74.3
2.00	10.5	9.55	2	59.7

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Table VI

Acid Dependence at 20° C (Excess Ce(IV))

Conditions: T = 20.0 ± 0.2° C λ = 320 nm

μ = 2.00 ± 0.02 M ($LiClO_4$)

$[H^+]$ M	$[Ce(IV)]_o$ M X 10^5	$[V(IV)]_o$ M X 10^5	Number of Data Points	k_2' $M^{-1}sec^{-1}$
0.0615	9.70	7.63	2	301
0.100	9.70	7.63	2	221
0.200	9.70	7.63	2	133
0.250	9.70	7.63	2	111
0.300	9.70	7.63	2	99.5
0.350	9.70	7.63	2	83.9

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Table VII

Medium Effect

Conditions: $T = 20.0 \pm 0.2^{\circ}$ C $\lambda = 320$ nm

$[H^+] = 0.100 \pm 0.001$ M

μ M	$[V(IV)]_o$ M X 10^5	$[Ce(IV)]_o$ M X 10^5	Number of Data Points	k_2' $M^{-1} sec^{-1}$
0.100	10.5	9.59	2	97.1
0.500	10.5	9.59	2	150
1.00	10.5	9.59	2	182
1.50	10.5	9.59	2	227
1.80	10.5	9.59	2	253
2.50	10.5	9.59	2	314

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The average for the apparent rate constant, k_2' from Table II is 43.8 $\underline{M}^{-1}$ sec^{-1}. The value of 43.2 M^{-1} sec^{-1} from this test shows favorable experimental agreement and indicates there is no effect on the reaction from the products, Ce(III) or V(V).

Since the rate in excess V(IV) is higher than that in excess Ce(IV) by a factor of ca. 15% a test was conducted to determine if impurities existed in the stock solutions. A new stock solution of $Ce(ClO_4)_4$ was prepared in the same manner as the primary stock solution except that additional recrystallizations were made and longer times were allowed for the various reactant preparation steps. A new stock solution of V(IV) was prepared in a different manner from that used in preparing the primary stock solution. The new stock V(IV) was prepared by adding a slight excess of $Ba(ClO_4)_2$ to a solution of $VOSO_4$ in 1 $\underline{M}$ perchloric acid. The solution was allowed to stand for a day and the clear $VO(ClO_4)_2$ was carefully decanted and filtered through a fine grade glass frit. The solution was tested for excess Ba^{2+} by adding concentrated H_2SO_4 to a sizeable aliquot of the new $VO(ClO_4)_2$ solution. Slight but discernible cloudiness verified that excess Ba^{2+} was present. The V(IV) and H^+ concentrations were determined in the manner described in the Experimental section of this report. The conditions, data and results of this investigation are given in Table VIII. The results tend to suggest that there were more impurities in the

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Table VIII

Product and Impurity Effects

Conditions; λ = 370 nm T = 20.0 ± 0.2° C

$[H^+]$ = 1.00 ± 0.01 M μ = 2.00 ± 0.02 M

$[V(IV)]_o$ M X 10^4	$[Ce(IV)]_o$ M X 10^4	$[Ce(III)]_o$ M X 10^4	$[V(V)]_o$ M X 10^4	Number of Data Points	$M^{-1}sec^{-1}$
0.286	0.203	1.59	1.59	1	43.2
7.63 [a]	49.3 [b]	--	--	2	37.3
114.5 [a]	19.7 [b]	--	--	2	45.2
7.98 [c]	49.3 [b]	--	--	1	32.0
119.7 [c]	19.7 [b]	--	--	1	41.8

a Primary V(IV) stock

b New Ce(IV) stock

c New V(IV) stock

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$VO(ClO_4)_2$ prepared from the $VOSO_4$ than in the electrolytically prepared primary stock used throughout this investigation.

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CHAPTER IV

INTERPRETATION AND DISCUSSION

Reaction and Rate Law

The predominant species of Ce(IV) and V(IV) in the aqueous perchloric acid range of $0.0615 < [H^+] < 2.00\ \underline{M}$ are $CeOH^{3+}$ and VO^{2+}. The predominant Ce(III) and V(V) species in this range are Ce^{3+} and VO_2^+. This investigation supports the following stoichiometric relation:

$$CeOH^{3+} + VO^{2+} \rightarrow Ce^{3+} + VO_2^+ + H^+ \quad .$$

Metal ion dependence studies show the reaction to be first order in each reacting species and second order overall following the rate law:

$$\frac{-d\,[CeOH^{3+}]}{dt} = k_2'\,[CeOH^{3+}]\,[VO^{2+}] \quad .$$

The apparent second-order rate constant, k_2', at 20°C has a value of $44.1 \pm 1.1\ \underline{M}^{-1}\ sec^{-1}$ in excess V(IV) and $37.9 \pm 2.5\ \underline{M}^{-1}\ sec^{-1}$ in excess Ce(IV). The difference in these values is about 15% and considered beyond experimental error. The rate law may be more intricate but limitations in concentrations and absorbances which could be conveniently used prevented a detailed study to resolve this difference.

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There are no measurable effects of products on the rate of the reaction. The rate is also independent of wavelength in the region 320 to 400 nm. At a constant acidity of 0.100 M the apparent second-order rate constant shows a linear increase as ionic strength is increased from 0.100 M to 2.50 M using lithium perchlorate. Previous investigators studying the reaction in sulfuric acid medium reported an increase in the rate with increasing ionic strength using sodium perchlorate but offered no quantitative evidence.[46]

The reaction rate for the Ce(IV)-V(IV) system is considerably slower in perchloric acid than in sulfuric acid. The rate constants have been variously reported as 1350 M^{-1} and 815 $M^{-1}sec^{-1}$ in 1 M H_2SO_4.[46, 48] In this investigation the constant in 2.00 M $HClO_4$ for essentially the same temperature and ionic strength was determined to be 26.0 M^{-1} sec^{-1}.

Acid Dependence

The apparent second-order rate constant decreased with increasing acidity at the three temperatures; 10°, 20°, and 30°C used in this study. Hydrogen ion dependence must be determined to show reaction paths and activated complexes for the reaction. This dependence is obtained at various temperatures to permit calculation of the thermodynamic parameters.

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Ce^{4+} undergoes extensive hydrolysis in perchloric acid solution and this must be taken into account in order to specify the reacting species. In 2 M perchloric acid the following equilibrium is essentially complete.[13, 22]

$$Ce^{4+} + H_2O \rightleftharpoons CeOH^{3+} + H^+ \qquad (A)$$

With lower acidity further hydrolysis occurs according to the equilibrium:

$$CeOH^{3+} + H_2O \rightleftharpoons Ce(OH)_2^{2+} + H^+ \ . \qquad (B)$$

The presence of dimers and polymers have been postulated[13, 15, 16] but in this investigation the major Ce(IV) species considered to be present and kinetically important are $CeOH^{3+}$ and $Ce(OH)_2^{2+}$. To write the rate law in terms of the major species $CeOH^{3+}$, it is necessary to consider the hydrolysis of this species. Therefore, the apparent second order rate constant must be corrected as follows:

$$k' = k_2' \, [\, f(K_h) \,]$$

where $f(K_h) = 1/(1 + K_h [H^+]^{-1})$, k_2' is the apparent second order rate constant, k' is the apparent second order rate constant corrected for hydrolysis and K_h is the hydrolysis constant for reaction (B). This correction translates the rate expression into

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terms of the major reacting species of Ce(IV) which is declared to be $CeOH^{3+}$. The VO^{2+} ion is not hydrolyzed to any extent within the acid range of this investigation.

The rate constant versus the hydrogen ion concentration show that the constant is inversely proportional to the hydrogen ion concentration. However, it is apparent that a relation to express the acid dependence will consist of a term or terms in addition to the inverse term, $k_{-1}[H^+]^{-1}$. A logical function to assume is $k' = k_o + k_{-1}[H^+]^{-1}$. A straight line will result for this relation if $k'[H^+]$ versus $[H^+]$ is plotted. Figure 3 shows a plot of this relation which is linear over a major region of the acid range but bends sharply upward at lower acid. This indicates the increasing importance of another parallel term which was assumed to be inverse second order in hydrogen ion concentration.

Verification of the presence and dominance of an inverse first-order hydrogen ion term at higher acidity was made experimentally and the results are given in Table IX and plotted in Figure 4. Based on all of these analyses four equations were derived which cursory examination showed were plausible and these were then subjected to more rigorous tests. These equations are:

$$k' = (k_o + \frac{k_{-1}}{[H^+]}) \qquad (1)$$

$$k' = (\frac{k_{-1}}{[H^+]}) \, e^{\beta [H^+]} \qquad (2)$$

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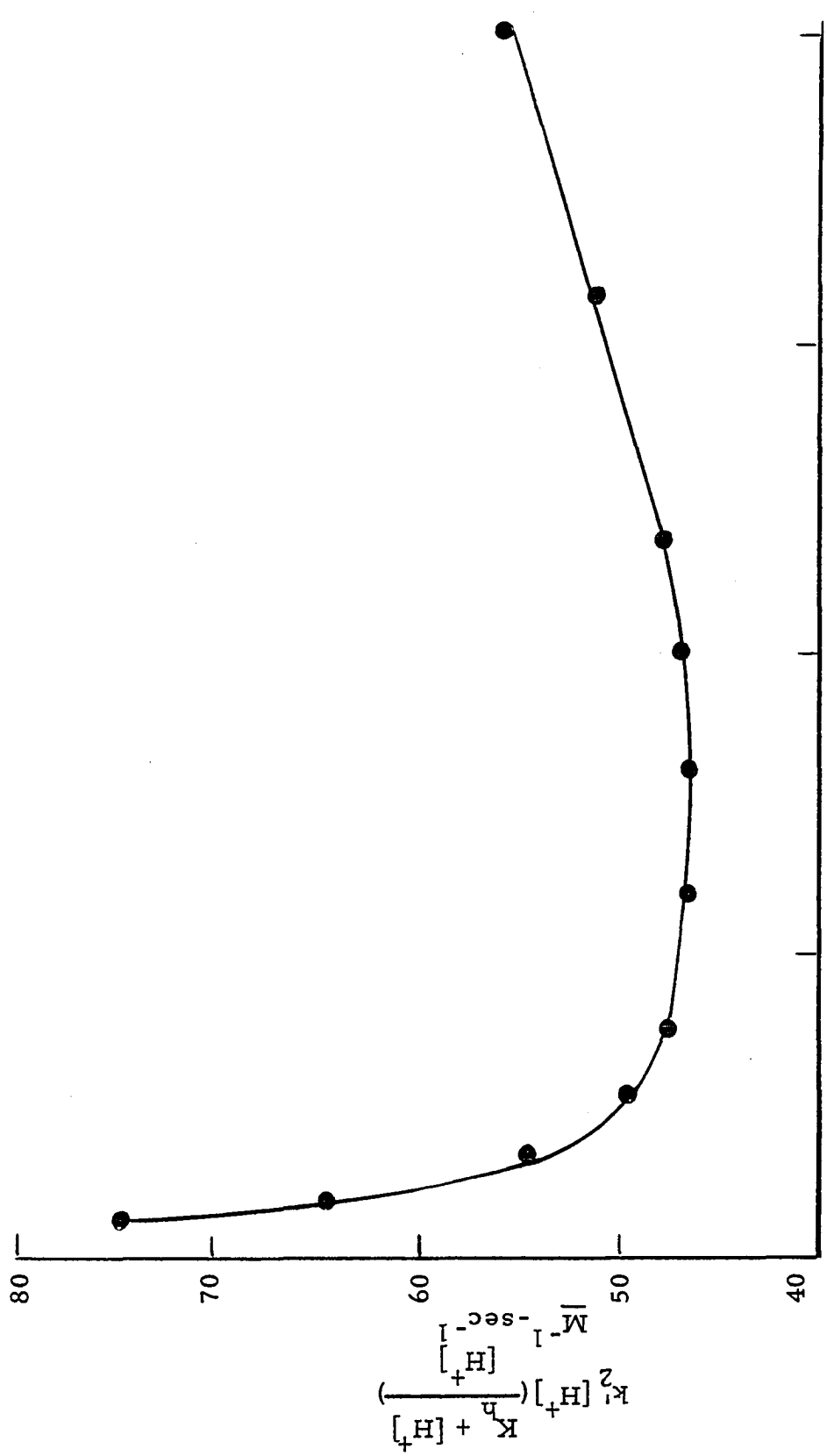

Figure 3. Two Term Parallel Paths

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Table IX

Acid Dependence at Higher Acidity

Conditions: $T = 20.0^{\circ}C \pm 0.2^{\circ}C$ $\lambda = 320$ nm

$\mu = 4.00 \pm 0.04$ M ($LiClO_4$)

$[H^+]$ M	$[V(IV)]_o$ M X 10^5	$[Ce(IV)]_o$ M X 10^5	Number of Data Points	k_2' $M^{-1}sec^{-1}$
1.50	10.5	9.53	2	52.2
2.00	10.5	9.53	2	44.1
2.50	10.5	9.53	2	39.6
3.00	10.5	9.53	2	34.8
3.50	10.5	9.53	2	33.5
4.00	10.5	9.53	2	30.1

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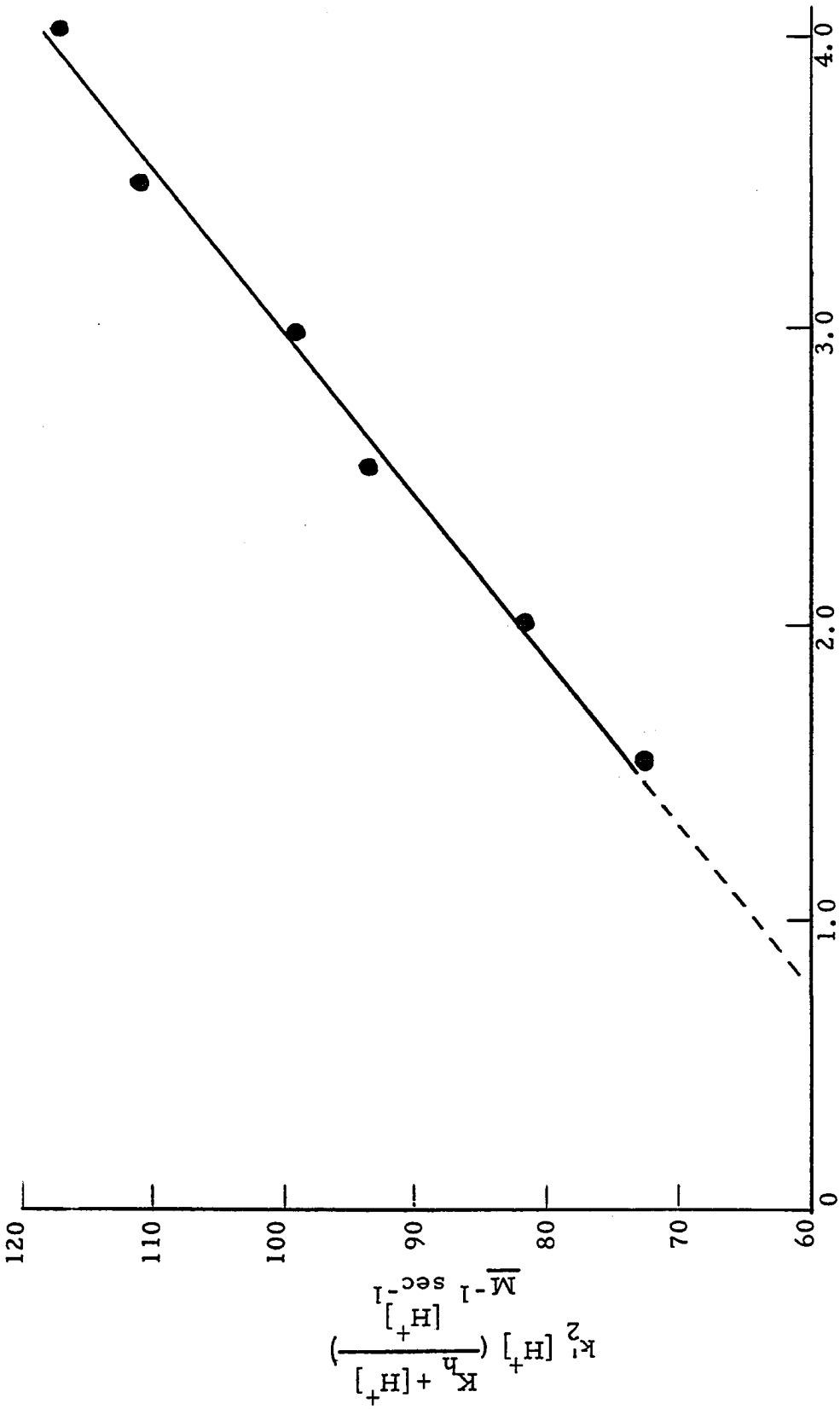

Figure 4. Two Term Parallel Paths (Higher Acidity)

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$$k' = (k_o + \frac{k_{-1}}{[H^+]} + \frac{k_{-2}}{[H^+]^2}) \qquad (3)$$

$$k' = (\frac{k_{-1}}{[H^+]} + \frac{k_{-2}}{[H^+]^2}) e^{\beta[H^+]} \qquad (4)$$

The term $e^{\beta[H^+]}$, which appears in equations (2) and (4) is a Harned term.[53] This term makes a correction for the changing activity coefficient due to changing medium while maintaining a constant ionic strength. A minor term of an empirical rate law may be indistinguishable from the effects due to changing the medium which is apparently the case in this investigation where lithium perchlorate is used to maintain a constant ionic strength while the perchloric acid concentration is varied.

In Tables X, XI, XII, and XIII are shown calculated data compared to experimental for the four equations previously described. It should be noted that equations (1) and (2) do not reproduce experimental data unless a hydrolysis constant correction of ca. 0.035 is used. This value is considerably smaller than the best reported value of 0.15.[22] Equations (3) and (4) give good agreement with the experimental values using $K_h = 0.15$.

Since equations (1) and (2) require too small a value for the hydrolysis constant to reproduce experimental data they are considered unsatisfactory in explaining the acid dependence of the

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Table X

Equation (1) $k' = \left(k_o + \frac{k_{-1}}{[H^+]}\right)$

$[H^+]$ M	k'_2 [a]	k'_2 $K_h = 0.15$	k'_2 $K_h = 0.035$
0.0615	351	237	353
0.100	256	201	255
0.200	150	143	150
0.300	110	112	108
0.400	85.5	91.3	85.5
0.600	63.9	67.0	61.5
0.800	48.5	53.0	49.0
1.00	40.7	43.8	41.3
1.20	36.2	37.3	36.2
1.60	29.7	28.9	29.6
2.00	25.8	23.5	25.6
		1.14×10^{-2} [b]	4.32×10^{-4} [b]

a Average experimental values from Table IV

b Weighted variance

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Table XI

Equation (2) $k' = \left(\frac{k_{-1}}{[H^+]}\right) e^{\beta [H^+]}$

$[H^+]$ M	k'_2 a	k'_2 $K_h = 0.15$	k'_2 $K_h = 0.035$
0.0615	351	237	357
0.100	256	200	258
0.200	150	143	151
0.300	110	111	108
0.400	85.5	91.3	85.4
0.600	63.9	67.0	61.1
0.800	48.5	53.0	48.6
1.00	40.7	43.8	40.9
1.20	36.7	37.3	35.8
1.60	29.7	28.9	29.6
2.00	25.8	23.6	25.9
		1.14×10^{-2} b	4.53×10^{-4} b

a Average experimental values from Table IV

b Weighted variance

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Table XII

Equation (3) $k' = \left(k_o + \frac{k_{-1}}{[H^+]} + \frac{k_{-2}}{[H^+]^2} \right)$

$[H^+]$ M	k'_2 [a]	k'_2 $K_h = 0.15$
0.0615	351	371
0.100	256	253
0.200	150	147
0.300	110	107
0.400	85.5	85.4
0.600	63.9	61.9
0.800	48.5	49.5
1.00	40.7	41.7
1.20	36.2	36.4
1.60	29.7	29.6
2.00	25.8	25.4
		6.53×10^{-4} [b]

a Average experimental values from Table IV

b Weighted variance

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Table XIII

Equation (4) $k' = \left(\frac{k_{-1}}{[H^+]} + \frac{k_{-2}}{[H^+]^2} \right) e^{\beta [H^+]}$

$[H^+]$ M	k'_2 a	k'_2 $K_h = 0.15$
0.0615	351	370
0.100	256	253
0.200	150	148
0.300	110	107
0.400	85.5	85.5
0.600	63.9	61.9
0.800	48.5	49.3
1.00	40.7	41.5
1.20	36.2	36.2
1.60	29.7	29.5
2.00	25.8	25.6
		5.76×10^{-4} b

a Average experimental values from Table IV

b Weighted variance

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Ce(IV)-V(IV) reaction. Equations (3) and (4) agree with experimental data equally well and both are considered to describe the acid dependence for this reaction.

Thermodynamic Parameters

The temperature dependences of the apparent second order rate constant at 10°, 20°, and 30°C were used to calculate the thermodynamic parameters. From Eyring's absolute rate theory one can apply the rate expression:

$$k_i = (k_B/h)\, T([H^+]^i) \exp(\Delta S^*_i / R) \exp(-\Delta H^*_i / RT)$$

to each of the k values in the acid dependence expressions. As an example consider the relation $k' = k_o + k_{-1}[H^+]^{-1}$. Using Eyring's equation and all k' values at all hydrogen ion concentrations and temperatures simultaneously in a non-linear least squares program the best values of the enthalpies and entropies of activation for k_o and k_{-1} may be determined. For k_o these thermodynamic parameters are derived from the relation:

$$k_o = (k_B/h)\, T \exp(\Delta S^*_o/R) \exp(-\Delta H^*_o/RT)$$

and for k_{-1} from the relation:

$$k_{-1} = (k_B/h)\, T([H^+]^{-1}) \exp(\Delta S^*_{-1}/R) \exp(-\Delta H^*_{-1}/RT).$$

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Tables XIV, XV, XVI, and XVII show the calculated thermodynamic parameters for equations (1), (2), (3), and (4). The Harned parameter, β, is linear in temperature in accordance with the relation $\beta = \beta' [1.0 + \alpha (T - 273.16)]$ where β is the temperature corrected term, β' is the uncorrected term, α is the temperature coefficient and T is in degrees Kelvin. Both α and β were calculated for equations (2) and (4). The data in these tables make it further apparent that equations (3) and (4) are best suited to describe the acid dependence.

It should be noted that regardless of the equation, the values of ΔH_h, the values of ΔS^* and ΔH^* for the minor paths or the value of β, the value of ΔH^* for the major inverse H^+ dependent path remains at 16.7 ± 0.3 kcal mol^{-1} with companion ΔS^* values ranging between 4.80 and 6.92 e.u.

The two equations (3) and (4) are equally able to demonstrate the acid dependence of the Ce(IV)-V(IV) reaction. Equation (4) containing a Harned term shows modestly better agreement, however, the major term, $k_{-1}[H^+]^{-1}$ and the term $k_{-2}[H^+]^{-2}$ are both required to permit good agreement with experimental results.

Conclusions

From experimental evidence the empirical rate laws for the reaction Ce(IV)-V(IV) are:

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Table XIV

Thermodynamic Parameters

Equation (1) $k' = \left(k_o + \frac{k_{-1}}{[H^+]}\right)$

K_h		o term		-1 term		
ΔS_h [a]	ΔH_h [a]	ΔS^*	ΔH^*	ΔS^*	ΔH^*	W. V. [b]
e.u.	kcal-mol^{-1}	e.u.	kcal-mol^{-1}	e.u.	kcal-mol^{-1}	X10^3
10.9	4.37	-26.62 ± 66.0	9.35 ± 18.7	4.27 ± 1.0	16.2 ± 3.0	9.72
10.9	2.37	-18.4 [a']	10.8 [a']	15.0 ± 0.4 [c]	18.4 ± 1.3	209
10.9 [d]	4.37 [d]	-18.4 [a']	10.8 [a']	5.50 ± 0.94	16.6 ± 0.3	12.1
10.9	6.37	-18.4 [a']	10.8 [a']	4.88 ± 1.08	16.6 ± 0.3	16.0
4.20 [d]	2.37 [d]	-18.4 [a']	10.8 [a']	4.03 ± 1.00	16.6 ± 0.3	13.7
17.6 [d]	6.37 [d]	-18.4 [a']	10.8 [a']	6.92 ± 0.89	17.0 ± 0.3	10.9

[a] Treated as a fixed parameter

[a'] Fixed to obtain convergence for comparative data

[b] Weighted variance

[c] Uncertainties in values are standard deviations determined by least-squares program

[d] Free energy values equal and based on $K_h = 0.15$.

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Table XV

Thermodynamic Parameters

Equation (2) $k' = \left(\frac{k_{-1}}{[H^+]}\right) e^{\beta [H^+]}$

K_h		-1 term				
ΔS_h [a]	ΔH_h [a]	ΔS^*	ΔH^*	β	α	W. V. [b]
e.u.	kcal-mol^{-1}	e.u.	kcal-mol^{-1}			X 10^3
10.9	2.37	----	----	----	----	---- [e]
10.9 [d]	4.37 [d]	6.10 ± 1.33 [c]	16.7 ± 0.4 [c]	0.906 ± 0.055 [c]	-0.0046 ± 0.009 [c]	4.48
10.9	6.37	3.85 ± 0.92	16.3 ± 0.3	0.359 ± 0.037	-0.0068 ± 0.004	5.31
4.20 [d]	2.37 [d]	3.65 ± 1.40	16.0 ± 0.4	0.0317 ± 0.059	-0.0317 ± 0.043	10.5
17.6 [d]	6.37 [d]	8.45 ± 1.25	17.4 ± 0.4	0.148 ± 0.052	-0.0453 ± 0.005	8.43

[a] Treated as a fixed parameter

[b] Weighted variance

[c] Uncertainties in values are standard deviations determined by the least squares program

[d] Free energy values equal and based on $K_h = 0.15$

[e] No convergence from program.

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Table XVI

Thermodynamic Parameters

Equation (3) $k' = \left(k_o + \frac{k_{-1}}{[H^+]} + \frac{k_{-2}}{[H^+]^2} \right)$

K_h		o term		-1 term		-2 term		
ΔS_h[a]	ΔH_h[a]	ΔS^*	ΔH^*	ΔS^*	ΔH^*	ΔS^*	ΔH^*	W.V.[b]
e.u.	kcal-mol^{-1}	e.u.	kcal-mol^{-1}	e.u.	kcal-mol^{-1}	e.u.	kcal-mol^{-1}	
10.9	2.37	--	--	--	--	--	--	--[e]
10.9[d]	4.37[d]	-11.4 ± 4.1[c]	12.6 ± 1.2[c]	5.54 ± 0.94[c]	16.7 ± 0.3[c]	10.2 ± 2.7[c]	19.7 ± 0.8[c]	1.00
10.9	6.37	--	--	--	--	--	--	--[e]
4.20[d]	2.37[d]	-10.4 ± 4.1	13.0 ± 1.2	4.80 ± 0.94	16.4 ± 0.3	1.23 ± 2.5	17.0 ± 0.7	1.01
17.6[d]	6.37[d]	-12.0 ± 4.1	12.5 ± 1.2	6.13 ± 0.95	16.8 ± 0.3	19.8 ± 2.8	22.6 ± 0.8	1.01

[a] Treated as a fixed parameter

[b] Weighted variance

[c] Uncertainties in values are standard deviations determined by the least squares program

[d] Free energy values equal and based on $K_h = 0.15$

[e] No convergence from program

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Table XVII

Thermodynamic Parameters

Equation (4) $k' = \left(\frac{k_{-1}}{[H^+]} + \frac{k_{-2}}{[H^+]^2} \right) e^{\beta[H^+]}$

K_h		-1 term		-2 term				
ΔS_h[a] e.u.	ΔH_h[a] kcal-mol^{-1}	ΔS^* e.u.	ΔH^* kcal-mol^{-1}	ΔS^* e.u	ΔH^* kcal-mol^{-1}	β	α	W.V.[b] X 10^3
10.9	2.37	--	--	--	--	--	--	--[e]
10.9[d]	4.37[d]	6.40 ± 0.89	16.9 ± 0.3[c]	8.12 ± 2.59[c]	19.1 ± 0.8[c]	0.258 ± 0.002[c]	-0.018 ± 0.002[c]	0.93
10.9	6.37	--	--	--	--	--	--	--[e]
4.20[d]	2.37[d]	5.68 ± 0.87	16.7 ± 0.3	-0.82 ± 2.44	16.4 ± 0.7	0.243 ± 0.024	-0.017 ± 0.003	0.92
17.6[d]	6.37[d]	6.95 ± 0.88	17.1 ± 0.3	17.8 ± 2.7	22.0 ± 0.8	0.265 ± 0.024	-0.019 ± 0.003	0.92

[a] Treated as a fixed parameter

[b] Weighted variance

[c] Uncertainties in values are standard deviations determined by the least squares program

[d] Free energy values equal and based on $K_h = 0.15$

[e] No convergence from program

$$\frac{-d[CeOH^{3+}]}{dt} = \frac{1}{1 + \frac{K_h}{[H^+]}} \left(k_o + \frac{k_{-1}}{[H^+]} + \frac{k_{-2}}{[H^+]^2} \right) [CeOH^{3+}] [VO^{2+}]$$

and/or

$$\frac{-d[CeOH^{3+}]}{dt} = \frac{1}{1 + \frac{K_h}{[H^+]}} \left(\frac{k_{-1}}{[H^+]} + \frac{k_{-2}}{[H^+]^2} \right) e^{\beta[H^+]} [CeOH^{3+}] [VO^{2+}]$$

The major term in either rate law is the $k_{-1}[H^+]^{-1}$ term and the other path(s) in the empirical laws are parallel. The net activation processes for all paths are given in Table XVIII with calculated entropies for the activated complexes (S^* complex). Included in this table are entropy values for +4 charged activated complexes formed in other reactions. Newton and Rabideau[54] have indicated a correlation between $S^*_{complex}$ and the charge on the activated complex. The value of S^* for the +4 complex from this investigation is slightly above the range of -59 to -88 e.u. for the compiled list. Entropy values for activated complexes are calculated using the relation:

$$S^* \text{ complex} = \Delta S^* + \Sigma S^o \text{ (reactants)} - \Sigma S^o \text{ (products other than complex)} .$$

The entropy for $CeOH^{3+}$ (aq) was roughly estimated by considering that the $CeOH^{3+}$ ion has an ionic radii equivalent to Ce^{3+}. From the

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Table XVIII

Entropies of Activated Complexes

Net Activation Processes	$S^*_{complex}$ e.u.	Ref.
$CeOH^{3+} + VO^{2+} \rightleftharpoons [CeOHVO]^{5+}$	-77	This work
$CeOH^{4+} + VO^{2+} + H_2O \rightleftharpoons [Ce(OH)_2VO]^{4+} + H^+$	-42	This work
$CeOH^{3+} + VO^{2+} + 2H_2O \rightleftharpoons [Ce(OH)_3VO]^{3+} + 2H^+$	-20	This work
Net Activation Processes for Other 4+ Complexes		
$V^{3+} + VO^{2+} + H_2O \longrightarrow [*]^{4+} + H^+$	-77	12
$V^{2+} + VO^{2+} \longrightarrow [*]^{4+}$	-65	12
$PuO_2^{2+} + Ti^{3+} + H_2O \longrightarrow [*]^{4+} + H^+$	-88	12
$NpO_2^{2+} + V^{3+} + H_2O \longrightarrow [*]^{4+} + H^+$	-59	12
$PuO_2^{2+} + V^{3+} + H_2O \longrightarrow [*]^{4+} + H^+$	-81	12
$UO_2^{2+} + V^{3+} + H_2O \longrightarrow [*]^{4+} + H^+$	-62	12

entropy values of the aquated La^{3+} and Pr^{3+} ions which are -39 and -41 e.u. respectively[55] the value of $S^*_{Ce^{3+}} \approx S^*_{CeOH^{3+}} \approx -40$ e.u.. The ΔS^* value used was the average from the k_{-1} term for both equations (3) and (4) with $\Delta S_h = 10.9$ e.u. and $\Delta H_h = 4.37$ kcal mol^{-1}. The formulas shown for the activated complexes are not intended to illustrate the structure or bonding. These factors are not known. The zero and inverse first order hydrogen ion dependence of equations (3) and (4) are consistent with the proposition that the gain or release of hydrogen ions in the activation process will lie between zero and the total number gained or released in the overall process. The exception to this rule is the +3 charged activated complex. This illustrates the tendency of activated complexes to hydrolyze to reduce their charge. In addition, the intrinsic tendency of Ce(IV) to hydrolyze or complex readily could be expected to carry over into the activated complex.

It is difficult to visualize the Ce(IV)-V(IV) reaction mechanism as involving any other process than the transfer of a single electron. The dominance of the inverse first order hydrogen term provides strong evidence for an inner sphere reaction. The VO^{2+} ion in being oxidized gains an oxygen to form the VO_2^+ ion. It is reasonable to assume that an inner sphere activated complex forms with an oxygen or hydroxide ion bridge then the loss of the H^+ ion(s) and the transfer of an oxygen from the $CeOH^{3+}$ in the activated complex to VO^{2+} is a logical sequence.

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The kinetic findings in this investigation agree with those of other investigators regarding the reactant and overall orders and the rate in perchloric acid. However, in regard to the acid dependence this investigation shows that the observations of G. N. Rao[35] are not correct. He states that the rate increased when increasing the acidity from 0.5 to 2.0 M using perchloric acid at $\mu = 2.0$, T = 25°C, and 340 nm. With virtually identical experimental conditions the exact opposite was found in this investigation. Although the hydrogen ion dependence cannot be specified simply by one equation nor in unequivocal detail it is quite apparent that there is a single most important path. Regardless of the assumptions made about minor terms in the rate law and the hydrolysis corrections, there is no alteration of the fact that the major term in the law is one which is inverse first order in hydrogen ion.

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