A STUDY OF THE REACTION KINETICS OF TIN (II) AND CERIUM (IV) IN AQUEOUS SULFATE MEDIA

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Anita Jeanne Court

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A THESIS

Submitted to the School of Advanced Graduate Studies of Michigan
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ABSTRACT

The kinetics of the oxidation of tin (II) by cerium (IV) in aqueous sulfate media was studied in the temperature range 0°C. to 25°C. Three reaction paths were found corresponding to 1) low sulfate and tin (IV) ion concentrations 2) high sulfate and tin (IV) ion concentrations and 3) colloidal tin (IV) present in solution. The first is independent of ionic strength and obeys second-order kinetics with an activation energy of 7.59 k.cal. and an activation entropy of -12.9 e.u. The reacting species of tin (II) was postulated to be the complex, $SnSO_4$. The second is dependent upon the ionic strength and obeys second-order kinetics. The reacting species of tin (II) was postulated to be $Sn(SO_4)_2^{=}$ and/or $[SnSn(SO_4)_4]^{=}$. The third, catalysed by colloidal tin (IV), obeys first-order kinetics and could not be correlated with the experimental variables. For both second-order rates, the mechanism of oxidation of tin (II) to tin (IV) occurs in a stepwise manner. The identity of the intermediate can not be established by the kinetic data and might be tin (III) in the form of a sulfate or sulfatocerate (III) complex or tin (II) in the form of a tin (II) sulfato-cerate (IV) complex. For the first-order rate a similar intermediate probably does not exist.

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INTRODUCTION

Chemical reactions occurring in solution are perhaps the largest class of reaction with which a chemist is concerned; elucidation of the mechanisms involved is one of the biggest problems. In this work, a study of the reaction

$$1)\quad Sn(II) + 2\,Ce(IV) = Sn(IV) + 2\,Ce(III)$$

in sulfuric acid medium was made. Of special interest was the mechanism whereby tin (II) was oxidized to tin (IV). Kinetics, the study of reaction rates, is one of the tools available for discerning mechanisms. There are drawbacks, certainly, for when the rate of a reaction is followed by measuring changes in physical or chemical properties of the solution as a reactant disappears or as a product appears, a gross effect is obtained. Similarly, when the properties of the solution are varied with temperature, added salts, or changes in the concentration of the major solute, the gross effect upon the reaction is measured. In many instances these over-all effects reveal a great deal about the species present in aqueous solutions of ionic substances, particularly in solutions of high ionic strength. An equation describing the rate process may be treated mathematically and the results interpreted on the basis of existing theories of rate processes and of properties of ionic species occurring in solution. Thus this kinetics study was undertaken to discern something of the properties of various tin species present in aqueous sulfate media.

THEORETICAL AND HISTORICAL CONSIDERATIONS

Theoretical

The rate of disappearance, $-\frac{dA}{dt}$, of a particular species, A, in a chemical reaction may be said to be zero, first or second order in A depending upon whether the rate is independent of the concentration of A, proportional to (A) or proportional to $(A)^2$. The second-order case could result from a bimolecular reaction between two molecules of A, for which the rate would be

$$2) \qquad -\frac{dA}{dt} = k_1(A)^2.$$

The term "second-order" is also applied to bimolecular reactions between the species A and B obeying the rate expression

$$3) \qquad -\frac{dA}{dt} = k\,(A)(B).$$

Expression 3) is said to be first order in A, first order in B and second order over-all (the over-all order is the sum of the individual orders). k_1 and k are second-order specific-rate constants. On the basis of transition state theory (1), the assumption is made that A and B form and are in equilibrium with an interaction complex which possesses a minimum of stability, with respect to reactants and products. If this critical configuration or activated complex, $C^{\ddagger}$, must be attained before products can be formed, and the activated complex can be considered to be at the top of an energy barrier, the rate of the reaction should be equal to the product of the concentration of $C^{\ddagger}$ and the frequency with which $C^{\ddagger}$ crosses the energy barrier and falls into the energy well of products. These considerations lead to

$$4) \quad -\frac{dA}{dt} = K\,(C^{\ddagger})\left(\frac{k_B T}{h}\right)$$

where K, the transmission coefficient, allows for the possibility that $C^{\ddagger}$ may decompose into the original reactants. k_B is the Boltzmann constant, T, the absolute temperature and h is Planck's constant.

Equating 3) and 4) and solving for the specific rate constant,

$$5) \qquad k = K\left(\frac{k_B T}{h}\right)\frac{(C^{\ddagger})}{(A)(B)}$$

which may be equated to

$$6) \quad k = K\left(\frac{k_B T}{h}\right) K^{\ddagger}$$

where $K^{\ddagger}$ is the equilibrium constant for the equilibrium

$$7) \quad A + B \rightleftharpoons C^{\ddagger}.$$

The implications of 5) and 6) are manyfold. If $K^{\ddagger}$ may be considered analogous to a thermodynamic equilibrium constant, quantities may be defined that are analogous to the functions used in connection with ordinary equilibrium constants. Thus, by definition,

$$8) \quad \Delta F^{\ddagger} = -RT \ln K^{\ddagger}$$

$$9) \quad \Delta H^{\ddagger} = RT^2 \frac{d \ln K^{\ddagger}}{dT}$$

and

$$10)\quad \Delta S^{\ddagger} = \frac{\Delta H^{\ddagger} - \Delta F^{\ddagger}}{T}$$

where $\Delta F^{\ddagger}$ is the free energy of activation, $\Delta H^{\ddagger}$ the enthalpy of activation, $\Delta S^{\ddagger}$ the entropy of activation and R the gas constant. Substituting 6) into 9), it is found, for reactions in solution, that

$$11)\quad \Delta H^{\ddagger} = RT^{2}\left[\frac{d \ln k}{dT}\right] - RT .$$

The first term on the right is designated as the Arrhenius, or empirical, activation energy, Ea. If units of k are arbitrarily selected as cc./mole sec., $\Delta F^{\ddagger}$, $\Delta H^{\ddagger}$ and thus $\Delta S^{\ddagger}$ may be evaluated from the experimental data and compared with standard values. $\Delta S^{\ddagger}$ is viewed as an indication of the probability of activated complex formation. If it is positive, the transition state is easily reached and the reaction proceeds faster than normal; if negative, the species involved may require a special orientation or a particular rotational-vibrational energy relationship and, thus, formation of the activated complex is less probable.

Returning to equation 5), it will be noticed that in fairly concentrated solutions, the value for k will not be a constant for a given temperature value because it is dependent upon the concentrations of A, B and $C^{\ddagger}$ and not the activities of these species. By activity of a substance is meant its effective concentration in the solution, that is, at concentration, c, it does not affect the properties of the solution (for example, the vapor pressure) to the extent of concentration *c* but rather to the extent of *a* where a, the activity, is equal to cf, or the product of the true volume formality and the formal activity coefficient. Rearranging 5) then,

$$12)\qquad k = K\frac{k_B T}{h}\,\frac{a_C^{\ddagger}}{a_A \cdot a_B}\cdot\frac{f_A\; f_B}{f_C}$$

making a change in standard state such that $a^{\circ} = \beta a$,[*] and taking logarithms,

$$13)\quad \ln k = \ln\left[K\frac{k_B T}{h}\;\frac{a^{\circ\,\ddagger}_C}{a^{\circ}_A\, a^{\circ}_B}\right] + \ln\left[\frac{\beta_A \cdot \beta_B}{\beta_C^{\ddagger}}\right] + \ln\left[\frac{f_A \cdot f_B}{f_C^{\ddagger}}\right].$$

For a given temperature, the first term, designated $\ln k_o$, will be constant. Changes in ln k with variations in dielectric constant of the medium will be reflected by changes in $\ln\left[\frac{\beta_A \cdot \beta_B}{\beta_C^{\ddagger}}\right]$; changes in ln k with variations in ionic strength[**] will be reflected by changes in $\ln\frac{f_A \cdot f_B}{f_C^{\ddagger}}$. Therefore the rigor with which the data can be analyzed depends upon existing theories of activity coefficients and dielectric effects of the medium (2).

Tin (II) is slowly oxidised by various oxidising agents in aqueous acid media whose dielectric constants are unknown. Activity coefficients of the species involved can be approximated only after estimation of the nature of these species. Because of the limitations of the tin (II)-cerium (IV)-sulfuric acid system, only a qualitative summary of the

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[*] For a solute, based upon the usual standard state, $\lim_{c \to 0} \frac{a}{c} \cong 1$; however, in order that reaction rates may be independent of solvent effects, another standard state is chosen such that $a\beta = a^{\circ}$, the concentration of solute vapor above the solution, where $\frac{a^{\circ}}{\text{pressure of solute}} \cong 1$.

[**] $u = 1/2 \sum_{\text{all}}^{i} m_i v_i$, where m_i is the weight formality of the ionic substance, i, with charge, v_i.

effect of alteration of dielectric constant or ionic strength upon the activity coefficients as predicted by extended Debye-Huckel theory is presented in Table I.

TABLE I

VARIATION IN ln k* WITH CHANGING DIELECTRIC CONSTANT AND IONIC STRENGTH IN FAIRLY CONCENTRATED SOLUTIONS (1)

	Effect of Increasing	
Species	Dielectric Constant	Ionic Strength
Two dipolar molecules forming a polar product	increase	an increase, dependent upon the 1st power of the ionic strength
Two ions:		
a. same sign	increase	increase dependent upon root and/or first power of ionic strength
b. opposite sign	decrease	may decrease, have no effect or increase depending upon ion charges and electrostatic effects
Ion and neutral molecule	may increase, have no effect or decrease depending upon whether the ion is highly charged or the molecule is highly polar	an increase dependent upon the 1st power of the ionic strength.

* Theoretical expressions for ln $(\beta f)_i$ are found in Table IV.

Historical

Few studies have been made of the properties of tin (II) and tin (IV) in aqueous sulfuric acid. In general, experimental work on tin (II) in this medium has been performed to shed light on one of the commercial applications of tin, electroplating, in which it is desirable to stabilize the species as tin (II) with various organic complexing agents and to adjust the properties of the plating baths to obtain high-quality tin plate (3). The potential of the Sn^0-Sn^{++} electrode has been measured as a function of the concentrations of tin (II) and sulfuric acid at 18°C. (4) and physical properties of the aqueous tin (II)-sulfuric acid system have been measured (5,6,7,8). Measurement of the Sn^{+2}-Sn^{+4} potential has not been possible (9). Phase studies of the SnO-SO_3-H_2O system were made at 25°C. and 50°C. by Denham and King (10); the solid phases isolated corresponded to $SnSO_4 \cdot 2SnO \cdot 4H_2O$, $SnSO_4 \cdot SnO$ and $SnSO_4$. Recently, complexing of tin (IV) in sulfuric acid has been examined (11), and hydrolysis of the species involved has been studied (12). The data indicate that the total solubility of the tin (IV) species is 9.08×10^{-4} wt. f. at 30°C. and 7.72×10^{-4} wt. f. at 18°C. in 0.9605 wt. f. sulfuric acid, and that the following equilibrium exists:

$$14)\quad SnO_2\,(aq) + 2H_2SO_4 \rightleftharpoons SnSO_4^{++} + SO_4^{=} + 2H_2O$$

for which the thermodynamic constants are $K_{30^\circ C.} = 5.0 \times 10^{-2}$ and $K_{18^\circ C.} = 2.8 \times 10^{-2}$. Further complexing of tin (IV) appears to occur in solutions with higher acid concentrations.

Far more experimental work has been done in the aqueous tin (II)-tin (IV)-hydrochloric acid system. Not only have the potentials of the electrode $Sn^{0}-Sn^{+4}$ and the system $Sn^{+2}-Sn^{+4}$ been studied (4,13), but the kinetics of exchange reactions and oxidation-reduction reactions have been examined. In the study of the radioactive exchange of tin (II) and tin (IV) (14), an interaction complex corresponding to $Sn_2Cl_{10}^{-4}$ was detected spectrophotometrically, and a mechanism formulated assuming electron transfer to occur in the complex. Although the rate increased with increasing hydrochloric acid concentration, the exact dependence was not determined. In absolute alcohol, and in the absence of hydrochloric acid, exchange took place between the neutral salts, $SnCl_2$ and $SnCl_4$ (16). No spectral data were reported.

Interactions between tin (II) and the platinum metals in hydrochloric acid have not been fully determined but are of interest. Platinum (II), palladium (II) and rhodium (II) apparently react with tin (II) to give highly colored products (16). Data obtained in the Pt (II)-Sn(II) system (other systems have not been studied quantitatively) indicate that the products are $[PtSn_4Cl_4]^{+4}$* and Sn(IV). Kinetics of the reduction of uranium (VI) by tin (II) has been studied (17). A small concentration of an interaction complex in which the ratio, U (VI) : Sn (II), is 1:1 was observed spectrophotometrically. The reaction rate is proportional to the first powers of U (VI) and Sn (II), increasing with increasing hydrochloric acid concentration, but is essentially constant as $[H^{+}]$ is varied at constant $[Cl^{-}]$, and vice versa.

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*Pt (0), Sn (II).

No mechanism has been proposed. Chlorate ion has been found to oxidize tin (II) at a measurable rate, proportional to the first powers of chlorate and tin (II); above 20°C. in the presence of hydrochloric acid, chlorate apparently oxidizes chloride ion (18).

The reaction between iron (III) and tin (II) has been examined by several authors. Data obtained by Noyes (19) indicate that the reaction does not obey second or third-order kinetics except in the presence of excess reaction products in which case third-order kinetics are obeyed. In all instances, the rate is a function of the hydrochloric acid concentration. One treatment of these and subsequent data (20) has been offered by Weiss (21). Assuming the following reactions are involved, and disregarding for the moment possible complexing of the various iron and tin species by chloride, then

$$15)\quad Fe^{+3} + Sn^{+2} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Fe^{+2} + Sn^{+3}$$

$$16)\quad Fe^{+3} + Sn^{+3} \xrightarrow{k_2} Fe^{+2} + Sn^{+4}$$

and assuming the steady state approximation, $\frac{dSn^{3}}{dt} = 0$, then the rate becomes

$$17)\quad \frac{-d(Fe^{+3})}{dt} = \frac{2k_1k_2(Fe^{+3})^2(Sn^{+2})}{k_{-1}(Fe^{+2}) + k_2(Fe^{+3})} .$$

On the basis of the hydrolytic tendencies of Fe^{+3}, Weiss assumed 1) in acid solutions, $k_2(Fe^{+3}) > k_{-1}(Fe^{+2})$, thus a second-order rate constant, k_1, would be expected and 2) in neutral salt solutions, or in the presence of excess Fe^{+2}, $k_{-1}(Fe^{+2}) > k_2(Fe^{+3})$, thus a third-order rate constant, k_B, would be expected. In general, it has been found that reaction rates increase in the presence of activated complexes containing hydroxyl ions (22). In the above reaction, however, the rate in the presence of hydrochloric acid is much faster than the rate in neutral salt solutions. In spite of the validity of these assumptions, k_A and k_B, if divided by the square of the total chloride concentration, do not vary appreciably. More recent work in which complexing of iron and tin is considered (23) indicates that in acid concentrations from 0.04 to 0.48 M, k_A appears to be proportional to at least the cube of the actual chloride concentration. Thus the activated complex seems to require at least three more chloride ions than are contributed by the complexed iron (III) and tin (II). Available data on the complexity constants for tin (II) and iron (III) (23,24) indicate that there probably is considerable competition for chloride by reactants, intermediates and products. The over-all mechanism is still a matter of interpretation (23,25,26).

In perchloric acid solutions where, theoretically, complexing of tin (II) and iron (III) would be at a minimum, the reaction proceeds much more slowly (25). Hydrolysis becomes a major problem (21,27). The rate appears to be proportional to the first powers of tin (II) and iron (III).

PREPARATION AND ANALYSIS OF MATERIALS

In the study of the reaction of cerium (IV) and tin (II), fairly strongly acid media were used to attain a minimum of complications brought about by hydrolysis of the species involved. Throughout this experimental work, the sulfuric acid used was DuPont C.P. reagent grade and the 70% perchloric acid was Mallinkrodt analytical reagent grade. Aqueous solutions of these acids were standardized with carbonate-free solutions of Merck reagent sodium hydroxide which, in turn, had been standardized with Merck primary standard potassium acid phthallate. For these determinations, phenolphthalein served as indicator. (See Appendix I for analytical results.)

Preparation of tin (II) solutions in sulfuric acid was similar to that of Noyes and Toabe (28) in which the displacement reaction

$$18\text{-a)}\quad Cu^{++} + Sn^{0} = Cu^{0} + Sn^{++}$$

was utilized. It was found that in sulfuric acid concentrations of 2 v. f. to 6 v. f. and in the presence of excess metallic tin, the above reaction was favored. If the mixture were kept just below the boiling point for one to two hours, the reaction proceeded to completion without complication. Hydrolysis occurred as the mixture was heated if the sulfuric acid concentration was less than 2 v. f.; on the other hand, hydrogen was rapidly displaced from the acid by metallic tin as the mixture was heated if the sulfuric acid concentration was greater than

6 v. f. The latter situation made regulation of not only the acidity but also the tin (II) content of the solution rather difficult. Dilute tin (II) solutions are easily decomposed by oxygen, therefore, all preparations were carried out in an atmosphere of nitrogen. A schematic diagram of the system in which the quantity of dissolved oxygen was minimized in the reagents, tin (II) solutions were prepared, purified and stored is given in Figure I. Commercial, water-pumped nitrogen was bubbled through a pyrogallol tower, F, in order to reduce further the oxygen content of the gas. To prepare the pyrogallol solution, 15 gms. of pyrogallic acid, Merck N.F. were added to 250 ml. of water made alkaline by the addition of sodium hydroxide pellets; in general, a freshly prepared pyrogallol solution was used for every tin (II) solution prepared. A second tower, G, contained either distilled water which was used for dilution purposes or 5 v. f. sulfuric acid which was used to maintain a particular vapor pressure of water in the nitrogen bubbling through the reaction mixture. The latter procedure was followed when it was necessary to minimize the net loss or gain of water in the reaction mixture over the course of the preparation of tin (II). In the reaction vessel, A, were placed calculated volumes of a solution of Mallinkrodt reagent grade copper sulfate and a solution of about 5 v. f. sulfuric acid. (For specific details concerning various tin (II) sulfate solutions prepared see Appendix I, Table XIX). Nitrogen was bubbled through the solution for about six hours, after which an excess of C.P. Bakers' Analysed 30-mesh tin was added through glass tubing inserted into the condenser, H. The reaction mixture was heated and kept just below the boiling point until flecks of finely

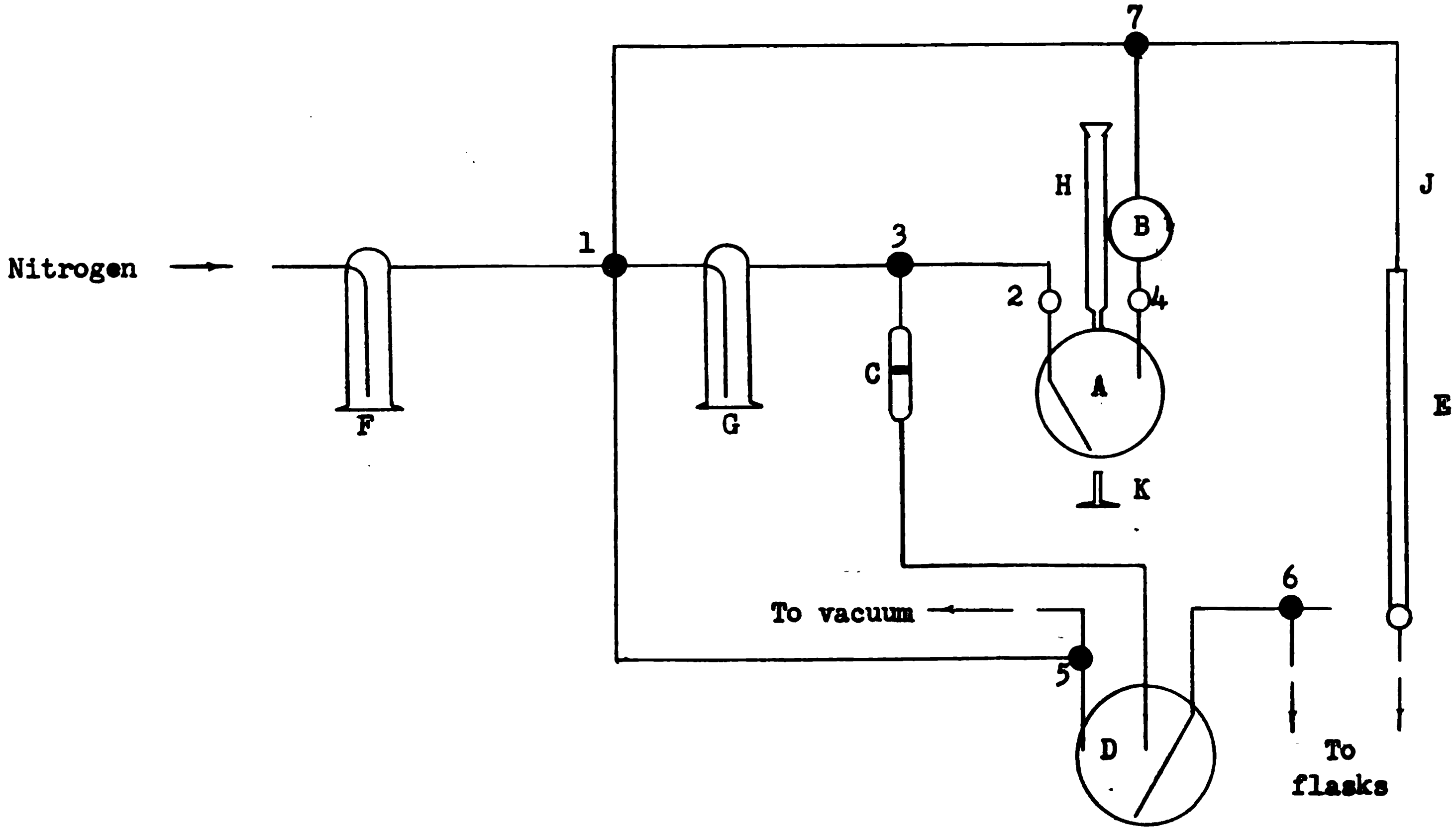

Figure I. Glass apparatus for preparation of tin(II) solutions: A, reaction vessel; B, reservoir; C, sintered-glass disc; D, storage vessel; E, burette; F, pyrogallol tower; H, condenser; J, nitrogen tube for burette; ●, three-way stopcocks; ○, two-way stopcocks and K, microburner.

divided copper, floating on the surface of the solution, were noted. An ice bath was used to reduce the temperature of the mixture before an appropriate dilution. For this purpose, distilled water through which nitrogen had been bubbled was available either in the tower, G, or the reservoir, B. For some experiments, an aqueous solution of lithium sulfate through which nitrogen had been bubbled was available in the reservoir, B. Excess nitrogen pressure was utilized in transferring the various solutions from B or G to the reaction vessel, A, and in subsequent mixing. Transfer of the tin (II) solution from the reaction vessel, A, to the storage vessel, D, was accomplished by sealing the condenser, E, evacuating D and adjusting stopcocks 2 through 6 in the proper manner. As the solution passed through the sintered glass disc (medium), C, the solids, copper and tin, were retained. Usually after complete transfer of the tin (II) solution into storage vessel, D, the pressure in D was less than atmospheric pressure. Atmospheric pressure was attained by bubbling nitrogen into D. In addition, excess nitrogen pressure was used to force the solution into ground-glass-stoppered flasks which could be placed into various thermostatic baths for equilibration. For some experiments, exact dilutions of the tin (II) solution were necessary. These were effected in the following manner: burette, Z, was flushed with nitrogen for one-half hour; a tube from vessel, D, was connected to the tip; a steady flow of nitrogen was maintained in the burette by tube J, inserted in the top, and the nitrogen pressure in D was raised to force the tin(II) solution into the burette. Once sufficient solution had been forced into the burette, the tube from D was disconnected and the solution transferred from burette to nitrogen-filled flasks in a standard manner.

Any analyses of the acid content of the tin (II) solutions must necessarily consider the amount of tin (II) or tin (IV) hydroxide that would be formed during the neutralization of the acid with a solution of standard base. However, concentrations of tin as prepared for this kinetics study were $10^{-3} - 10^{-4}$ v. f., thus it was found that the acid titer of a freshly prepared tin (II) solution was essentially equal to that of a solution through which air had been passed for one hour to assure complete oxidation of tin (II) to tin (IV). (For acidities of tin (II) solutions see Appendix I, Table XX.)

Total tin concentrations were evaluated by measuring the absorption of a dispersion of tin (II) toluene 3-4 dithiolate at 540 mμ (29). Thioglycollic acid, Eastman Organic Chemicals' practical grade, was used to reduce the tin species in solution to tin (II); a small quantity of Santomerse 30X, a Monsanto Chemical Company surfactant, was the dispersing agent; toluene 3-4 dithiol, a product of Eastern Chemical Company, was the specific reagent with which tin forms a strawberry-colored compound. (For details of this procedure and for analyses of tin (II) solutions see Appendix I.)

For a few experiments it was desirable to obtain tin (IV) sulfate and tin (IV) oxide. These were prepared by reaction of tin metal (30 mesh) with concentrated sulfuric acid at 190°C. (30). Subsequent fuming of the solution almost to dryness served to coagulate any colloidal sulfides that appeared and these were not dissolved (as tin (IV) sulfate was) on further addition of hot, concentrated sulfuric acid and hence separated from the tin (IV) sulfate by filtration through sintered glass. Fuming almost to dryness and re-solution were repeated twice to obtain tin (IV) sulfate as a white, hygroscopic solid with no reducing power as indicated by lack of reaction with a solution of potassium permanganate. To obtain a sample of tin (IV) oxide, a small amount of tin (IV) sulfate in a Vycor* crucible was placed in a muffle furnace at 500°C. for twelve hours. After cooling, the oxide was white, insoluble in dilute acid and not hygroscopic.

Lithium sulfate was utilized to maintain constant ionic strength of sulfuric acid-tin solutions while the concentrations of H^+, HSO_4^- and $SO_4^=$ were changed. Mallinkrodt analytical reagent lithium sulfate monohydrate was dissolved in distilled water, the solution filtered and evaporated to recover the monohydrate. Subsequently the salt was dried at 110°C. for two hours and then at 175°C. for 48 hours in order to prepare it in the soft, white anhydrous form.

It has been found that the quality of cerium (IV) sulfate as an oxidizing agent and the stability of its solutions depend greatly upon the purity of the reagents used in its preparation. DuPont sulfuric acid has been found to be fairly satisfactory in this respect (31,32). As for any particular sample of cerium salt, if the salt is thorium-free, one of the better methods of further purification is the preparation and recrystallization of ammonium hexanitrato cerate (IV) (32). Since the reagent grade salt was readily available from the G. Fredrick Smith Chemical Company, a sample of this was dissolved in

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*Trademark, Corning Glass Works.

distilled water, filtered and to the resulting solution were added 1) DuPont reagent nitric acid such that the final ratio of acid to water was 1:1 and 2) Bakers' Analyzed ammonium nitrate such that the reagent was 15% in excess of that required by the cerium in solution. Evaporation until the solution was a deep red and subsequent cooling produced the orange ammonium hexanitrato cerate (IV) which was filtered, then dried at 83°C. for eight hours. Subjecting this recrystallized salt to tests for impurities, it was found that 1) 5.6 gms. contained 1.8 - 2.0 mgs. of iron or that a solution of 10^{-4} v. f. Ce(IV) would contain about 2×10^{-7} v.f . Fe(II) and 2) essentially no thorium was indicated, which was satisfactory for the purposes of this kinetics study. (See Appendix I for tests performed.) To the recrystallized ammonium hexanitrato cerate (IV) was added as little distilled water as possible in order to dissolve it and then this solution was poured into a 1:1 aqueous ammonium hydroxide solution. The light yellow precipitate of hydrated cerium (IV) hydroxide settled, was filtered, washed with distilled water to remove ammonium nitrate and dried for 30 hours at 85°C. Under these conditions, $Ce(OH)_4 \cdot 4H_2O$ was formed.

In order to prepare a standard cerium (IV) sulfate solution, to 20.4878 gms. of the hydrated oxide were added 65 ml. of concentrated sulfuric acid and, after solution was complete, distilled water was added until the total volume of the solution was one liter. All cerium (IV) sulfate solutions used in the kinetics study were obtained by suitable dilutions of this standard solution which was fairly stable over a period of two years. (See Appendix I for data pertaining to standard cerium solutions, i.e., acidity, total cerium and cerium (IV).)

Cerium (III) sulfate solutions were obtained by bubbling sulfur dioxide through an appropriate cerium (IV) sulfate solution. Reduction of cerium (IV) occurred within 10 to 20 minutes but it was necessary to bubble nitrogen through the solution for one to two hours before the odor of sulfur dioxide was no longer detectable.

The reddish, yellow color of cerium (IV) solutions and the concentration of cerium in the standard solution (~ 0.06 v. f.) were sufficient to make the determination of the sulfuric acid concentration somewhat difficult by obscuring the color of the phenolphthalein end point and consuming hydroxide by precipitation of the metal hydroxide. To obviate this difficulty, before titration with sodium hydroxide solution, excess Merck reagent, sodium oxalate was added to the solutions of cerium in order to reduce cerium (IV) to cerium (III) and precipitate the rather insoluble cerium (III) oxalate (33).

Several methods of analysis of cerium (IV) in the standard solutions were attempted and found somewhat unsatisfactory before the following method was selected (34). In the presence of a phosphoric acid-sulfuric acid buffer solution, cerium (IV) may be titrated with iron (II) using sodium diphenylamine sulfonate as indicator. Iron (II) solutions in turn must be standardized with a primary standard, potassium dichromate, in the presence of the same buffer solution and with the same indicator as is used in the Fe(II)-Ce(IV) titration. Merck reagent ferrous ammonium sulfate hexahydrate was used for the solutions of iron (II); Mallinkrodt analytical reagent potassium dichromate and a solution of sodium diphenylamine sulfonate obtained from Dr. E. Leininger were used.

Analyses for total cerium in the standard solutions gave some difficulty. The method of Willard and Young (35,36), in which ammonium persulfate in the presence of catalytic quantities of silver ion is used to oxidize cerium (III) to cerium (IV), gave erratic results. It was found that oxidation with sodium bismuthate was most successful and the results indicated that the cerium (III) content of the standard solutions was fairly small (34).

EXPERIMENTAL PROCEDURES

In general, chemical reactions may be divided into two categories: fast reactions, for which rates must be measured in a matter of micro- or milliseconds, and moderate reactions which permit rate measurements over a period of minutes, hours or even days. In sulfuric or sulfuric-perchloric acid media, the reaction of cerium (IV) and tin (II) is somewhat between the two extremes in that it does not occur in a matter of milliseconds or hours, but in a matter of minutes. Even though a reaction occurring in minutes would not require as elaborate equipment as one occurring in milliseconds, special techniques were nevertheless required to follow the course of the reaction. It was found that the response of the Beckman Model DU Spectrophotometer was fast enough to permit rapid measurements of the absorbancy of a tin (II)-cerium (IV) solution. (Absorbancy = log I/I_o, where I_o is the light intensity entering the solution and I, the intensity after it has traversed the solution. It is assumed that the effect of a silica cell and the solvent present can be cancelled by setting the absorbancy of a matched reference cell plus solvent to be zero.) It was found that the absorbancy of one constituent was measurable with little interference from either reactants or products in solution. Furthermore it was possible to regulate the temperature of the cell housing in which the absorption cells, containing cerium (IV) tin (II) solutions, were placed for absorbancy measurements.

In sulfuric and perchloric acid solutions, an absorption peak of cerium (IV) occurs at 315 mμ, (36,37). The molar extinction coefficient, ϵ_4, of the cerium (IV) is 5.58×10^3 (cf. 36), that is, in a one-cm. silica cell, in 0.05 v. f. to 3 v. f. sulfuric acid, the absorbancy of a 1×10^{-4} v. f. cerium (IV) solution is 0.558. ϵ_4 is not affected by a mixture of sulfuric and perchloric acids in which the ratio $HClO_4$: H_2SO_4 is 2:1; it decreases, however, to 1.27×10^3 in a 2 v. f. perchloric acid solution in which $(H_2SO_4)/(Ce(IV) = 9.489$. Cerium (III) sulfate is also found to absorb in this region (Figure II) but the molar extinction coefficient, ϵ_3, is about 2.7×10^2 so that the contribution of cerium (III) to the absorbancy of the solution is negligible in most instances. (For details of corrections applied, see Section V.) Tin (II), tin (IV) and mixtures of tin (II) and tin (IV) do not absorb in this region, see Figure IV. Since ϵ_4 is essentially insensitive to variations in concentration of sulfuric acid, one standardization was made in 1 v. f. sulfuric acid at 25°C. (Figure V) and used throughout the course of this work. At some cerium (IV) concentrations, ϵ_4 is not constant; the dotted line in Figure V indicates the absorbancy that would be observed if ϵ_4 were constant at all cerium (IV) concentrations. It was assumed that ϵ_4 did not change with temperature so that the values obtained from the standardization were used over a temperature range of 0°C. to 25°C. (Calibration data are available in Appendix I, Table XVII.)

Solutions were equilibrated in two separate thermostatic baths, one of which was maintained at 0°C., 5°C., 10°C., or 15°C. ± 0.1°C.

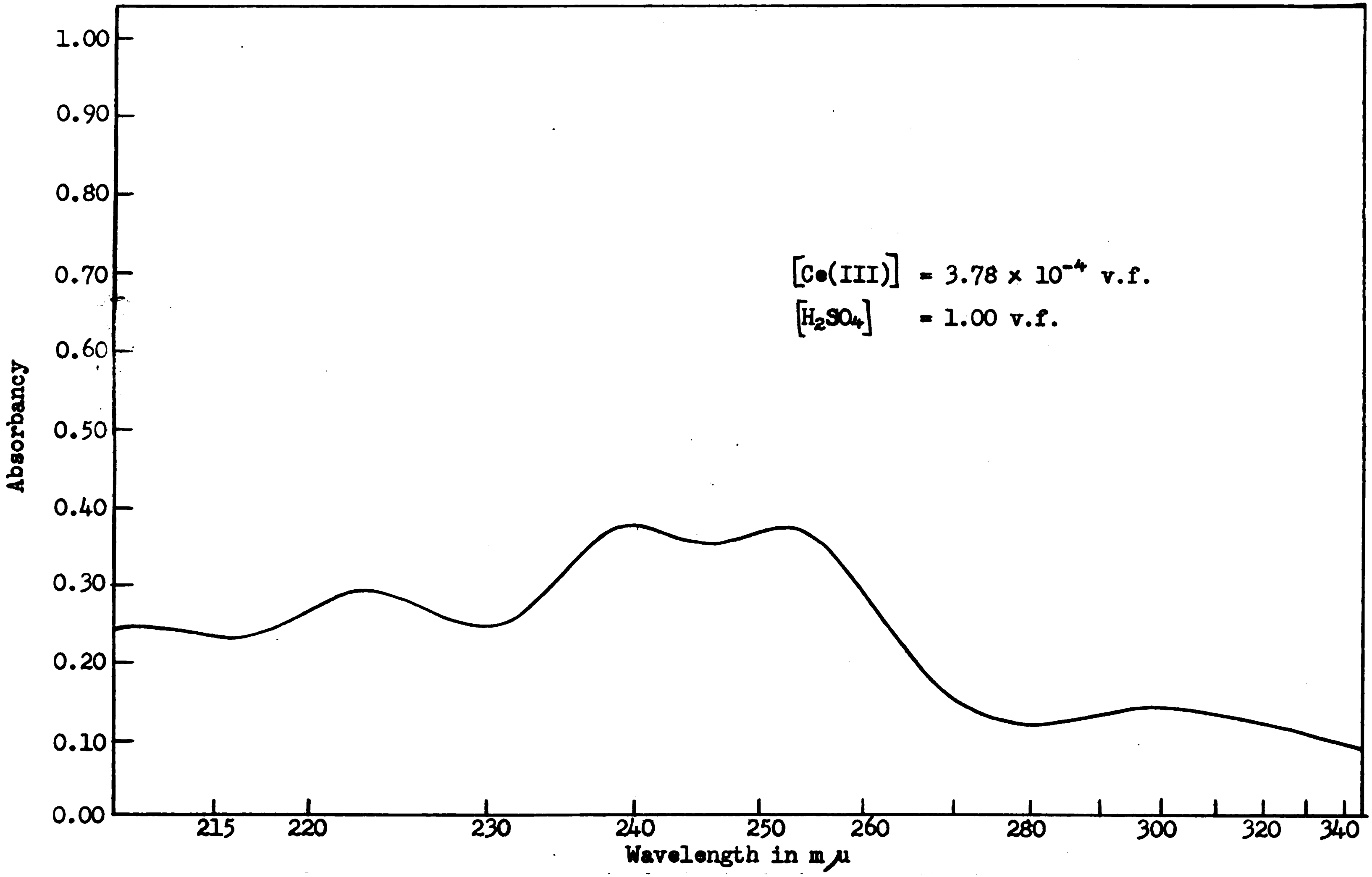

Figure II. Ultra-violet spectrum of cerium(III) sulfate.

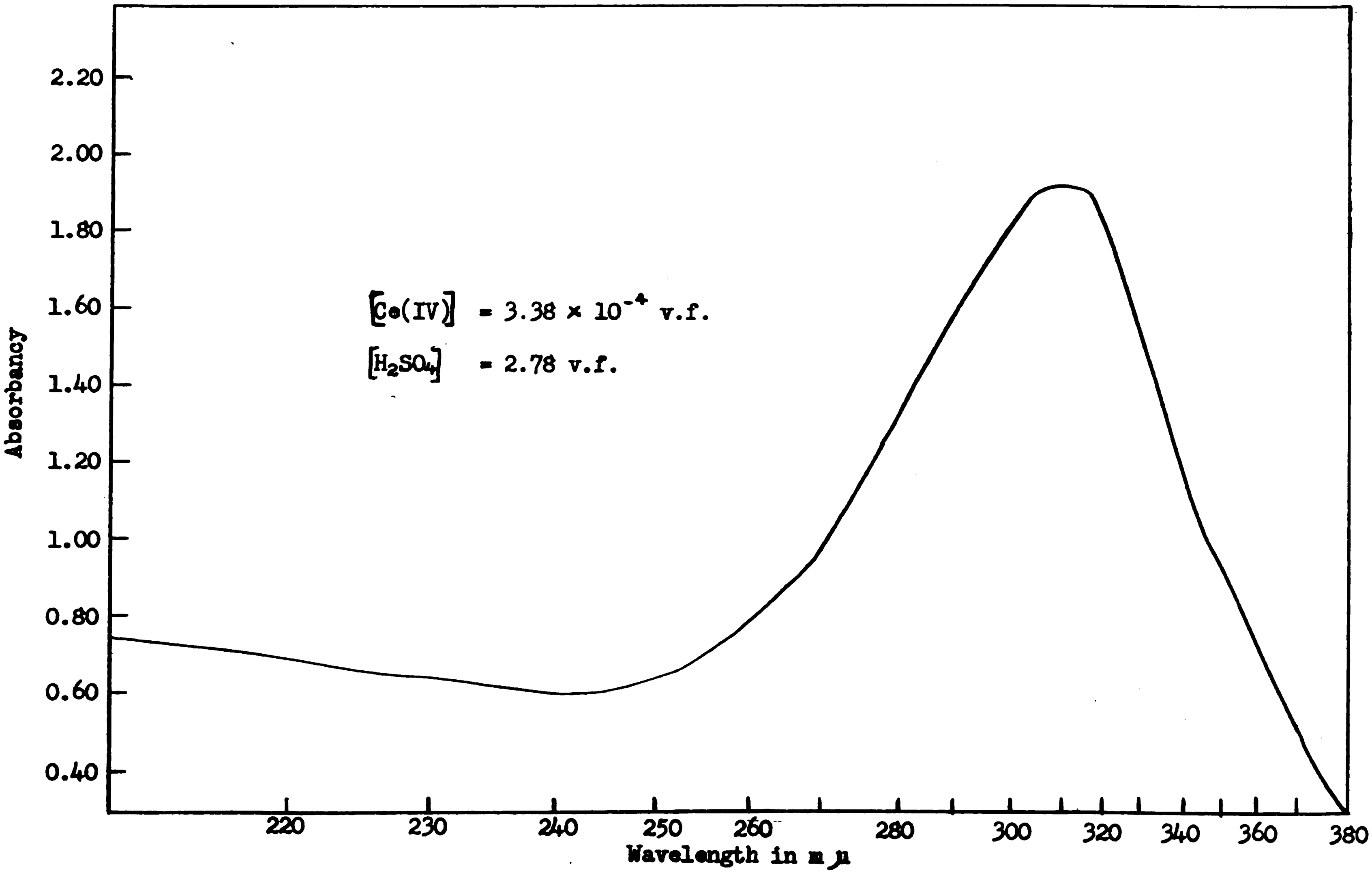

Figure III. Ultra-violet spectrum of cerium(IV) sulfate.

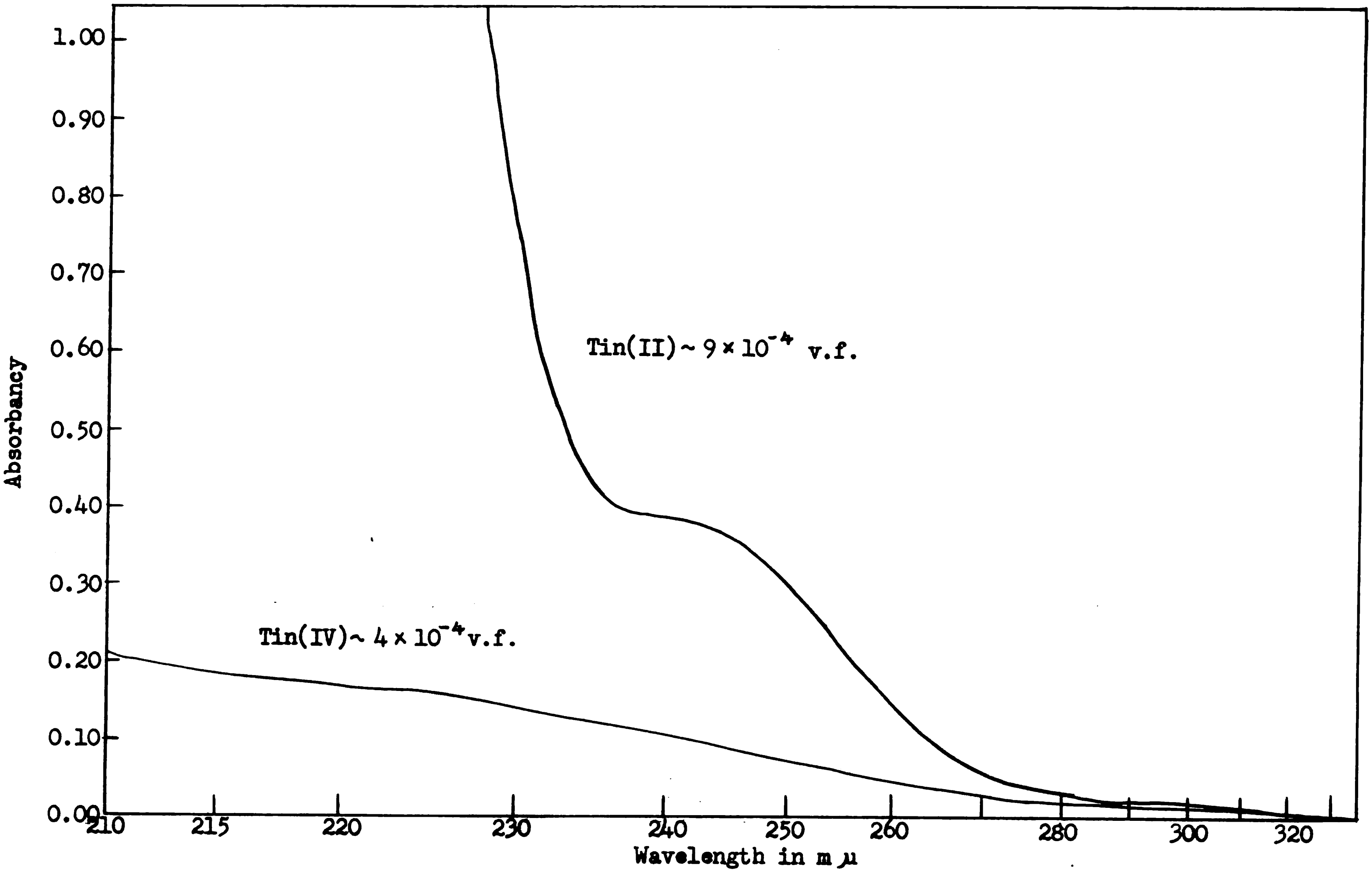

Figure IV. Ultra-violet spectra of tin(II) and tin(IV) sulfate, in 1 v.f. sulfuric acid.

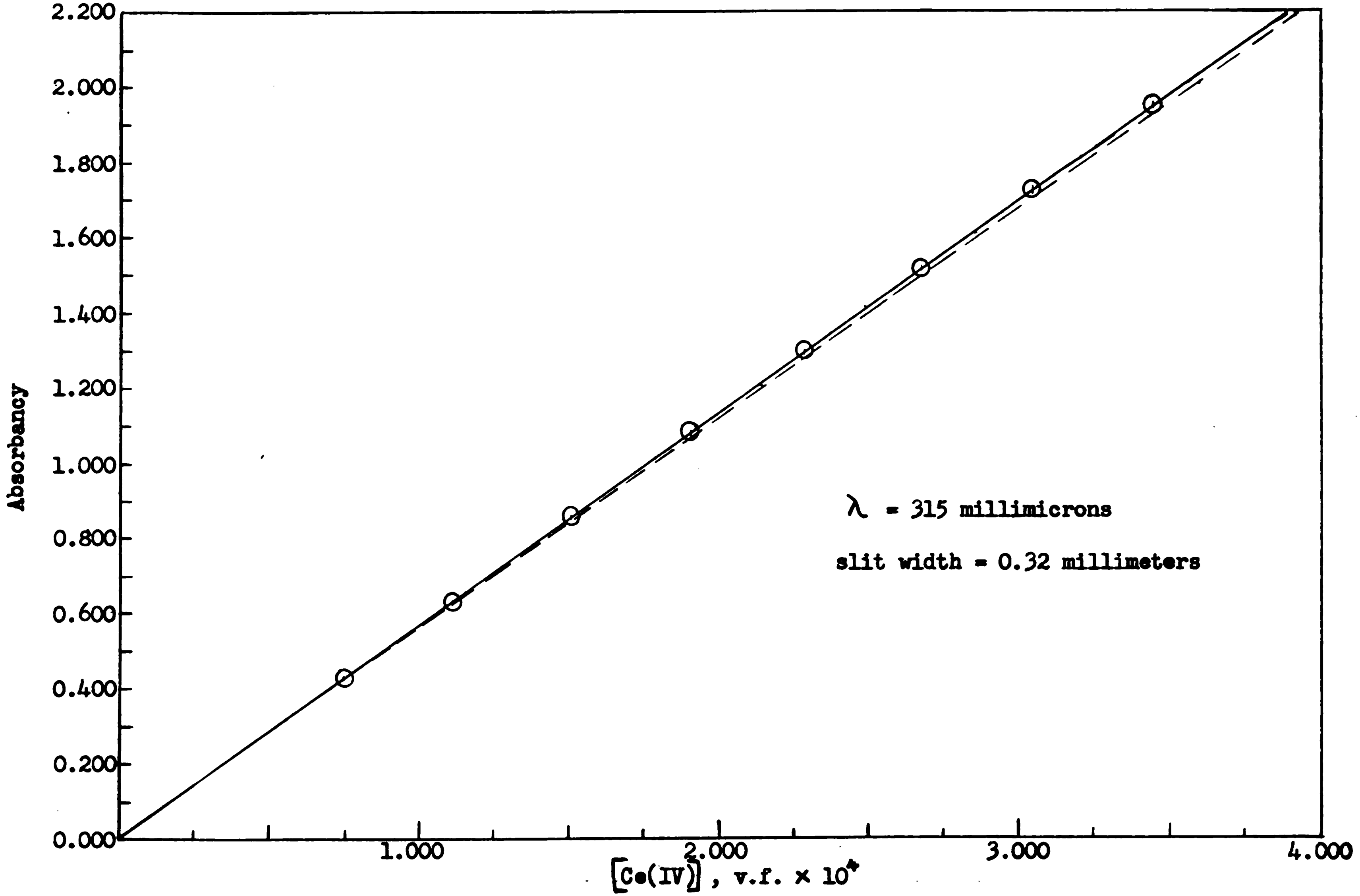

Figure V. Standardization of cerium(IV) sulfate in 1 v.f. sulfuric acid.

All reactions were carried out in the 1 cm. silica cells which have a volume of about four ml. To attain a particular temperature in the Beckman cell compartment, it was possible to circulate through a set of thermospacers[*] a 1:1 glycerin-water mixture from the lower temperature bath or water from the higher temperature bath. Tap water (about 18°C.) was circulated through the housing of the hydrogen lamp (light energy source for cerium (IV) absorption measurements). Under these conditions, the cell compartment was regulated at lower temperatures to within ± 0.2°C. (room temperature 20°C. to 25°C.) and to within ± 0.5°C. (room temperature 25°C. to 37°C.). When controlled by the higher temperature bath, the temperature variation in the cell compartment was ± 0.2°C. over the entire range of room temperatures.

The essentials of the experimental procedure were as follows: into a particular volume of a cerium (IV) solution in a spectrophotometric cell was forced rapidly by means of a pipette, a particular volume of a tin (II) solution. The total volume of the resulting solution was 3 or 4 ml. In the case of 1 v. f. to 1.4 v. f. lithium sulfate and/or 2 v. f. to 3 v. f. sulfuric acid at 0°C., the viscosity of the solution was appreciable and some additional stirring with a glass rod was necessary to assure good mixing. Zero time for the reaction was taken to be the time at which pipetting <u>began</u>. By presetting the transmission dial of the spectrophotometer at various absorbancies and aligning the electric timer[**] with the dial, it was possible to observe the

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[*] Beckman attachment #2021.

[**] Precision Scientific Company, Time-It.

time at which the reacting solution possesses a particular absorbancy to within ± 1 sec. The reaction was followed closely for about 5 minutes; after 50 minutes it was found that the reaction had proceeded to completion and final measurements were made at that time. Thus, when cerium (IV) was stoichiometrically in excess, the final absorbancy was taken to correspond to the excess cerium (IV) value after tin (II) had been completely oxidized to tin (IV). (If cerium (III) concentrations were appreciable, this value was corrected accordingly.) When tin (II) was in excess, weights of the initial cerium (IV) solution and the solution of cerium (IV) plus tin (II) were obtained. To this solution was added enough cerium (IV) such that the original excess tin (II) was oxidized to tin (IV) and an excess of cerium (IV) remained. After 50 minutes, the absorbancy of the solution was measured and the weight recorded. Knowing the absorbancy of the original cerium (IV) solution, and the densities of both the cerium (IV) and tin (II) solutions, in conjunction with the above data, the concentrations of cerium (IV) and tin (II) in the original solution may be obtained. (Sample calculations will be found in the following section.)

ANALYSIS OF DATA

Evaluation of Spectrophotometric Data

The original data (Appendix II) consist of absorbancies of various solutions as a function of time. Plots of these uncorrected values versus time indicated solutions in which there was poor mixing or instances of erratic performance on the part of the spectrophotometer and, on this basis, these data were discarded. The remaining data were corrected for any absorbancies contributed by the absorption cells themselves and then, from these values, concentrations of cerium (IV) were obtained as a function of time. In order to determine the cerium (IV) concentration of a solution containing cerium (III) and (IV) from spectrophotometric data obtained at 315 mμ, it is necessary to make a suitable correction for the amount of cerium (III) present. The measured absorbancy, A, of a solution is equal to $\sum_{\text{all}}^{i} \epsilon_i c_i d$, where ϵ_i is the molar extinction coefficient of the i^{th} absorbing species whose concentration is c_i and d is the length of the path of light going through the solution. Hence, for a solution in which cerium (III) and IV) can be considered the only absorbing species, the absorbancy at a particular time, t, is

$$13)\quad A_t = \epsilon_4 \, [Ce(IV)]_t \, d + \epsilon_3 \, [Ce(III)]_t \, d \ .$$

ϵ_4 and ϵ_3 are the molar extinction coefficients of cerium (IV) and (III) respectively.

In the reaction between tin (II) and cerium (IV) it is possible to determine the initial concentration of cerium (IV) in the following manner: 1) if cerium (III) is absent at the beginning of a reaction, the absorbancy observed in the first 20 to 30 seconds is essentially that of cerium (IV); a good graphical estimate of the initial cerium (IV) concentration, $[Ce(IV)]_o$, is made by plotting log $[Ce(IV)]_t$ versus time and extrapolating to $t = 0$; and 2) if a known amount of cerium (III) is present in the reaction mixture, the corresponding absorbancy is subtracted from the observed absorbancy and the resulting values are treated as in the case of cerium (III) = 0. Cerium (III) and (IV) concentrations at time, t, may be related to the initial concentrations at t = 0 by setting

$$19)\qquad [Ce(IV)]_t = [Ce(IV)]_o - X$$

and

$$20)\qquad [Ce(III)]_t = [Ce(III)]_o + X,$$

where X = f.wts./l. of cerium (IV) that have reacted. Substituting these expressions into 18) and letting d equal 1 cm.,

$$21)\qquad A_t = \epsilon_4 [Ce(IV)]_o + \epsilon_3 [Ce(III)]_o - (\epsilon_4 - \epsilon_3) X$$

and, solving for X,

$$22)\qquad X = \frac{\epsilon_4 [Ce(IV)]_o + \epsilon_3 [Ce(III)]_o - A_t}{\epsilon_4 - \epsilon_3} .$$

Further substitution of this expression into 19) and rearrangement yield

$$23)\quad [Ce(IV)]_t = \frac{A_t - \epsilon_3 \left\{[Ce(IV)]_0 + [Ce(III)]_0\right\}}{\epsilon_4 - \epsilon_3} .$$

If $\epsilon_4 = 5.58 \times 10^3$ l./f.wt.-cm. and $\epsilon_3 = 0.27 \times 10^3$ l./f.wt.-cm.,

then 23) becomes

$$24)\quad [Ce(IV)]_t = (1.883 \times 10^{-4})\, A_t - 0.0508 \left\{[Ce(IV)]_0 + [Ce(III)]_0\right\} .$$

This expression was used in connection with all reactions in which $[Ce(IV)]_0 > 2\,[Sn(II)]_0$. The quantity of tin (II) present under these conditions is determinable if the cerium (IV) concentration at $t = \infty$ is known. From equation 19) at $t = \infty$,

$$25)\quad [Ce(IV)]_{t=\infty} = [Ce(IV)]_0 - X_\infty ,$$

and from the relations

$$26)\quad 2\,[Sn(II)]_t = 2\,[Sn(II)]_0 - X$$

and

$$27)\quad 2\,[Sn(II)]_t = X_\infty + [Ce(IV)]_t - [Ce(IV)]_0 ,$$

the concentration of tin (II) at time, t, is

$$28)\quad [Sn(II)]_t = \frac{[Ce(IV)]_t - [Ce(IV)]_{t=\infty}}{2} .$$

In this work, t_∞ is 50 minutes.

Whenever $2\,[Sn(II)]_0 > [Ce(IV)]_0$, absorbancy measurements at 315 mμ indicate the cerium species present but do not establish the quantity of tin (II) present. Since the absorbancies of tin (II), tin (IV), cerium (III) and cerium (IV) overlap in the region 200 to 260 mμ, additional measurements at these wavelengths were not practical (Figures II, III, and IV). Thus a chemical method was chosen to determine $[\mathrm{Sn(II)}]_t$. Suppose that, originally 2 ml. of cerium (IV) (containing 2×10^{-4} meq. Ce(IV)) was added to 1 ml. of tin (II) (containing 2.7×10^{-4} meq. Sn (II)) to form a reaction mixture of 3 ml. After sufficient reaction, an additional milliliter of cerium (IV) was added and, at $(t_4)_\infty$, the absorbancy of the 4-ml.-volume was measured. Let $[\mathrm{Ce(IV)}]_o$ equal the cerium (IV) present initially in the 3-ml.-volume and let $[\mathrm{Ce(IV)}]_4 = \frac{9}{8}\, [\mathrm{Ce(IV)}]_o$ equal the concentration of cerium species in the 4-ml.-volume. If the initial concentration of cerium (III) is zero, then from equation 22), in the 4-ml.-volume,

$$29) \qquad X_4 = \frac{\epsilon_4\, [\mathrm{Ce(IV)}]_4 - (A_4)}{\epsilon_4 - \epsilon_3} \ .$$

Since X_3 in the 3-ml.-volume is $4/3\ (X_4)$, then

$$30) \qquad X_3 = \frac{3}{2} \left\{ \frac{\epsilon_4}{\epsilon_4 - \epsilon_3}\ [\mathrm{Ce(IV)}]_o \right\} - \frac{4\ (A_4)_\infty}{3\ (\epsilon_4 - \epsilon_3)} \ .$$

If the extinction coefficients are evaluated as before, 30) becomes

$$31) \quad X_3 = 1.5762\ [\mathrm{Ce(IV)}]_o - (2.511 \times 10^{-4})\ (A_4)_\infty \ ,$$

where X_3 is equal to twice the concentration of tin (II) present in the original 3-ml.-volume, $2\,[\mathrm{Sn(II)}]_o$. Using equations 19) and 26), the concentration of tin (II) in the reaction mixture at time, t, is

$$32)\quad [Sn(II)]_t = \frac{2[Sn(II)]_0 - [Ce(IV)]_0 + [Ce(IV)]_t}{2} \quad .$$

If the total tin concentration of the reaction mixture is known, the concentration of tin (IV) may be obtained by difference.

Kinetic Treatment

Once concentrations of cerium (III) and (IV) and tin (II) and (IV) are determined, kinetic treatment of the data is fairly straight forward. It was found that, depending upon the experimental conditions, the reaction obeys either a second-order rate law or a rate law first order in tin (II) but independent of the concentration of cerium (IV). In the event that a second-order rate is observed, if the initial concentrations of cerium (IV) and tin (II) are <u>a</u> and <u>b</u> respectively and, at time t, the concentrations are (a-x) and $(b-\frac{x}{2})$, then the decrease in cerium (IV) with time, $\frac{dx}{dt}$, is found to be (38)

$$33)\quad \frac{dx}{dt} = k'\,(a-x)\left(\frac{2b-x}{2}\right) = k\,(a-x)\,(2b-x).$$

The second-order rate constant is k in units of l./mole sec. When a $\neq$ 2 b, integration of 33) and evaluation of the integration constant at t = 0, yield the rate equation

$$34)\quad kt = \frac{\ln}{(a-2b)}\left[\frac{2b\,(a-x)}{a\,(2b-x)}\right] \quad .$$

If the rate first-order in tin (II) is observed, i.e. the rate no longer depends upon the cerium (IV) concentration, then the decrease in cerium (IV) with time is found to be

$$35)\quad \frac{dx}{dt} = k_1' \frac{(2b-x)}{2} = k_1 (2b - x) ,$$

where k_1 is the first-order rate constant with units of sec.$^{-1}$. The integrated rate equation is

$$36)\quad \ln \left[\frac{2b}{2b - x}\right] = k_1 t.$$

Values of k were graphically determined by plotting $\log \left[\frac{a - x}{2b - x}\right] = \log \left[\frac{Ce(IV)}{2Sn(II)}\right]_t$ versus time. However, a better pictorial representation of the data is obtained if $\frac{1}{[Ce(IV)]_o - 2[Sn(II)]_o} \left\{ \log \left[\frac{Ce(IV)}{2\,Sn(II)}\right]_t \right\}$ is shown as a function of time as is done in Figures VI to VII; the slope is equal to $\frac{k}{2.303}$. Where the first-order rate applies, $\log [Sn(II)]_t$ is plotted versus time (Figure IX); the slope is equal to k_1.

Results

At 0°C. the majority of experiments were performed under experimental conditions such that the oxidation of tin (II) by cerium (IV) obeyed a second-order rate law. Over a range of $[Ce(IV)]_o/[Sn(II)]_o$ from 6.72 to 1.34, the average value of k was found to be 19.8 l./mole sec. Initial cerium (IV) concentrations were 4.09×10^{-4} v. f. to 3.07×10^{-4} v. f. and the stoichiometric sulfuric acid concentration was 1 v. f. (Table II). In the presence of 5.8×10^{-4} v. f. cerium (III) = $[Ce(III)]_o$, k was slightly smaller, 18.3 l./mole. sec. (Table III). When tin (IV) sulfate was present to the extent that a

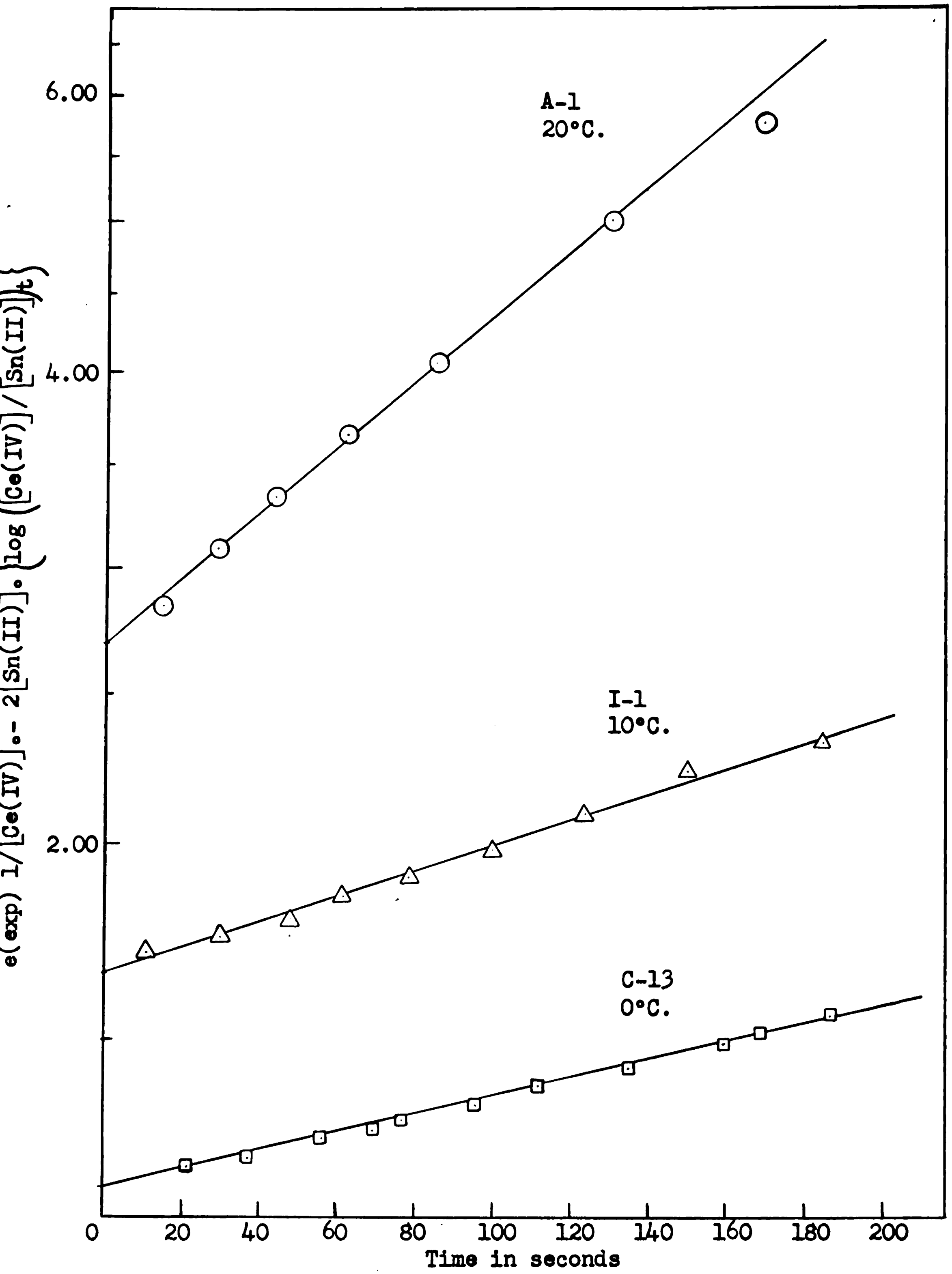

Figure VI. Kinetic treatment of second-order rates at 0°C., 10°C. and 20°C.

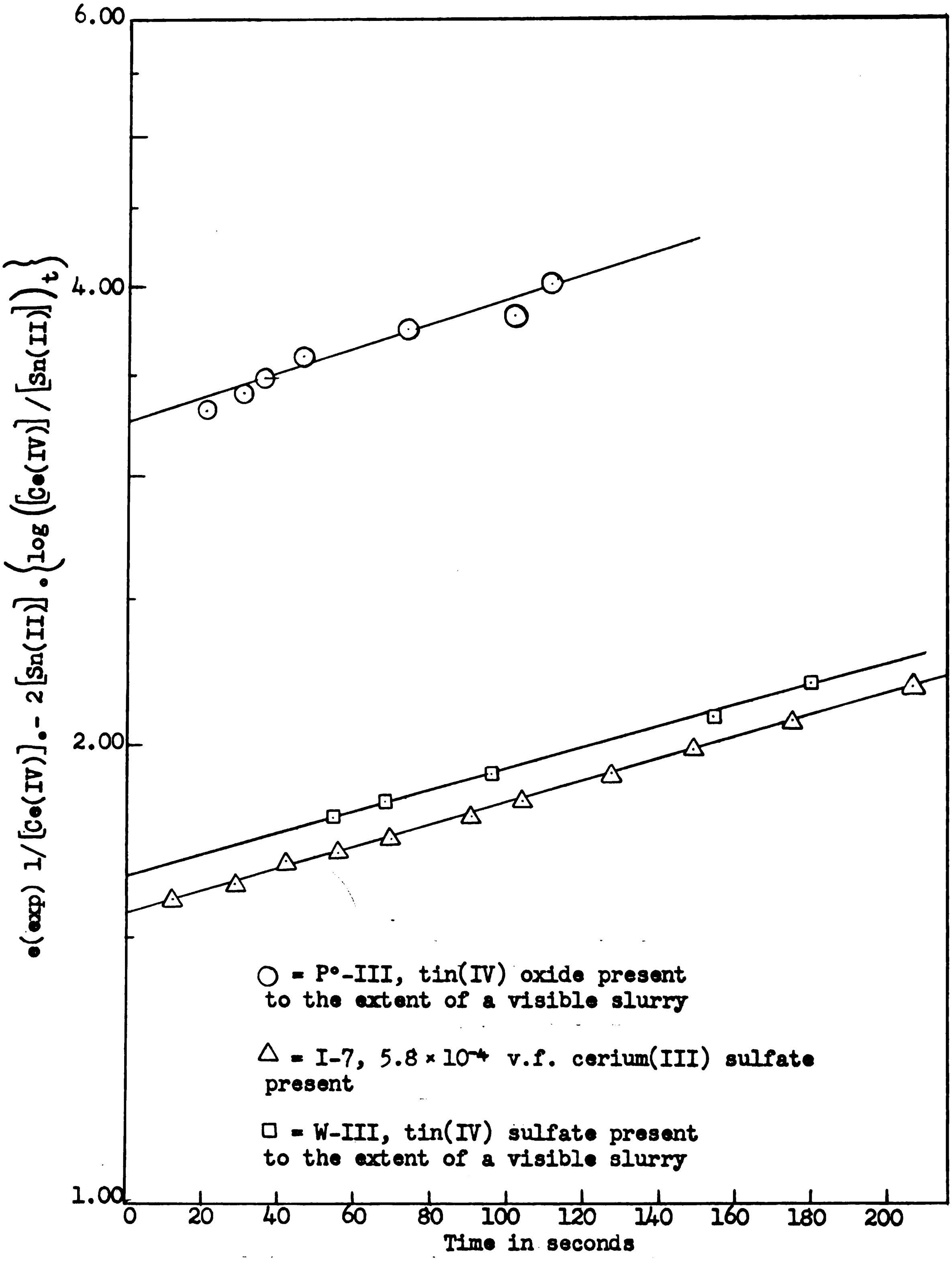

Figure VII. Kinetic treatment of second-order rates in the presence of cerium(III), tin(IV) sulfate and tin(IV) oxide.

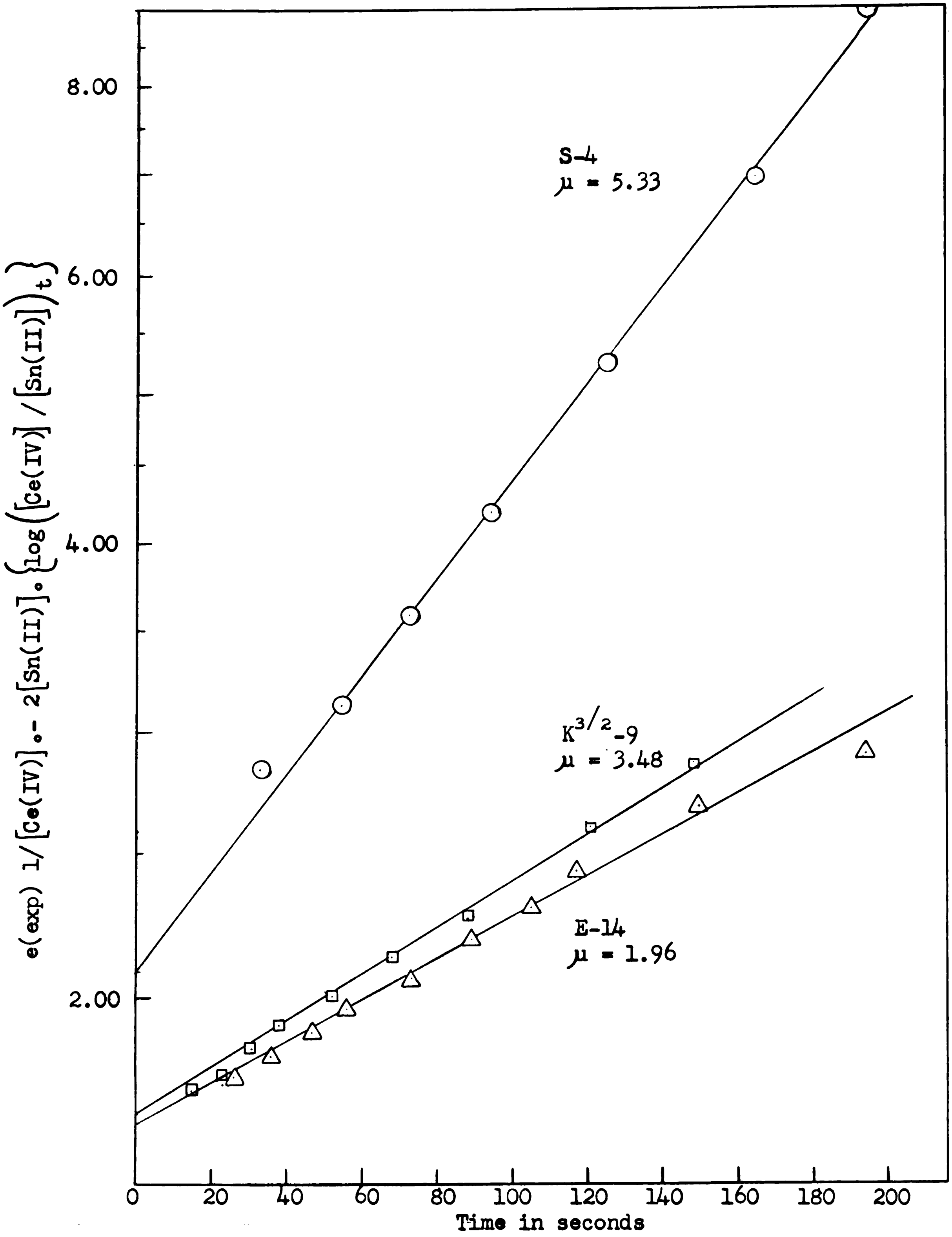

Figure VIII. Kinetic treatment of accelerated second-order rates at different ionic strengths.

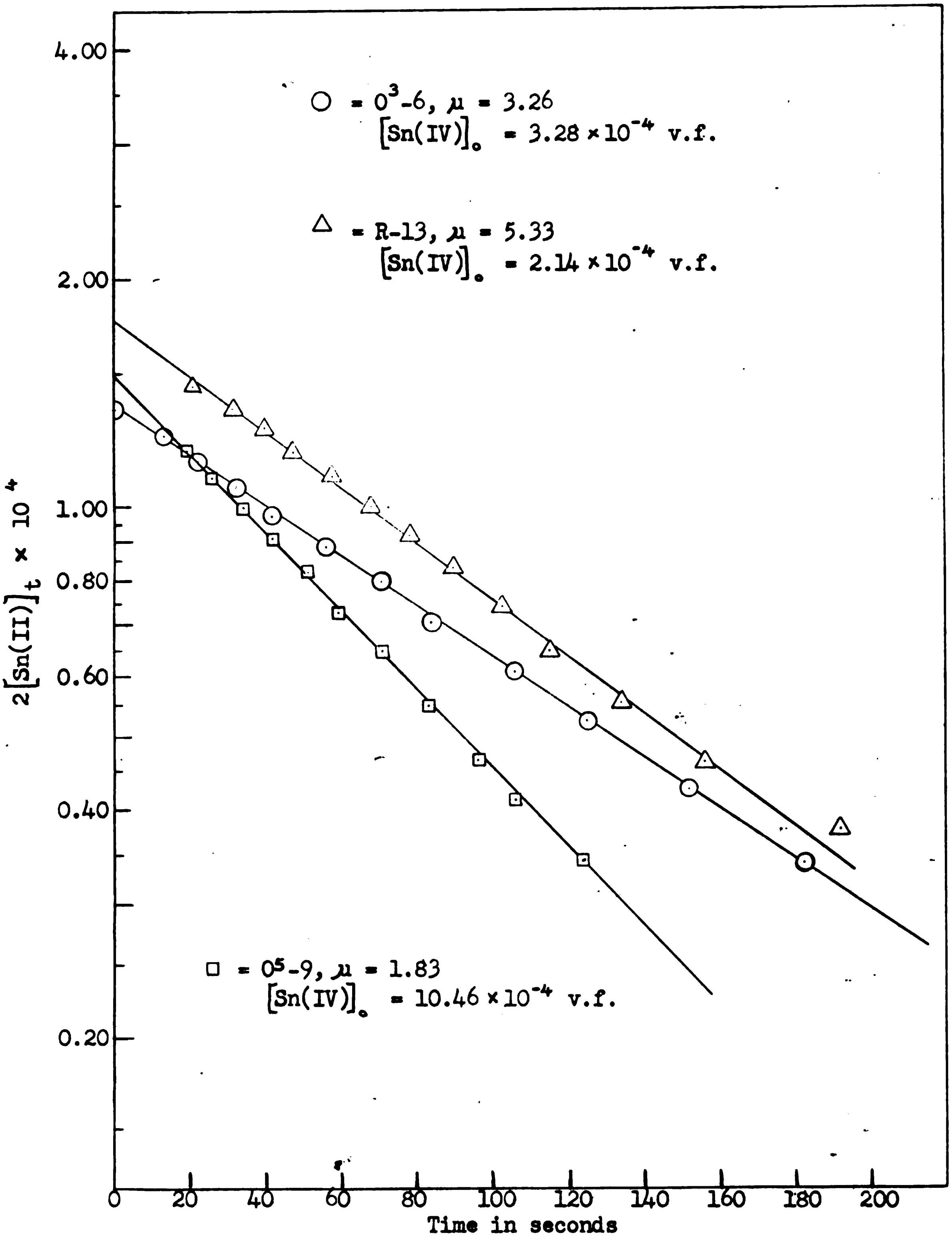

Figure IX. Kinetic treatment of rates first-order in tin(II) at different ionic strengths.

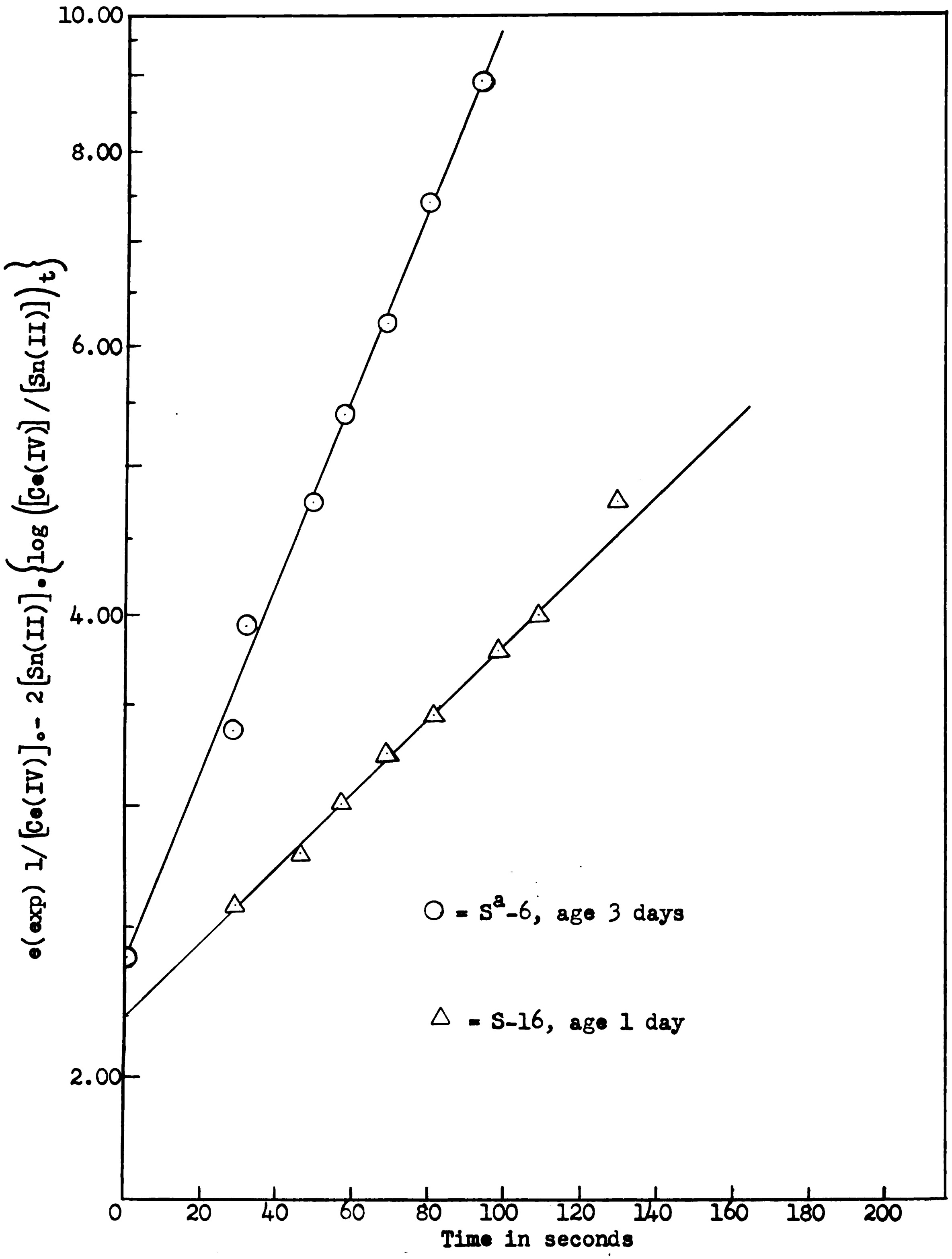

Figure X. Kinetic treatment of second-order rates accelerated by aged tin(II) solutions.

TABLE II

KINETICS OF OXIDATION OF TIN (II) BY CERIUM (IV) AT 0°C.: SECOND-ORDER MECHANISM

Series	$[Ce(IV)]_0$ v.f.x10^4	$2[Sn(II)]_0$ v.f.x10^4	k l./mole sec.	μ	$[H^+]$ v.f.	$[HSO_4^-]$ v. f.	$[SO_4^=]$ v.f.
B-1	3.949	5.473	14.5	2.005	1.488	0.580	0.453
2	3.661	4.908	16.2				
3	4.086	3.833	19.6				
4	3.758	3.454	19.2				
6	3.882	3.568	23.4				
7	3.615	2.968	23.7	Total tin = 3.73 x 10^{-4} v.f.			
8	3.580	2.530	22.1				
10	3.550	2.205	17.6				
11	3.280	.988	18.7				
12	3.758	5.601	13.6				
14	3.694	4.865	18.9				
16	3.596	1.070	14.9				
C-1	3.481	4.980	25.5	1.963	1.454	0.556	0.449
2	3.208	4.249	20.7				
3	3.267	4.366	21.7				
10	3.111	4.575	15.9				
11	3.312	4.049	22.6	Total tin = 3.92 x 10^{-4} v.f.			
12	3.430	4.555	18.3				
13	3.502	4.864	19.9				
16	3.070	4.177	18.0				
L-1	3.253	1.198	17.5	2.008	1.515	0.584	0.465
2	3.262	1.264	22.3				
3	3.192	1.134	21.4	Total tin = 1.813 x 10^{-4} v.f.			
4	3.220	1.158	26.1				
5	3.242	1.212	21.1				
0-10	3.141	3.026	20.4	1.879	1.367	0.599	0.384
11	3.187	2.892	19.4				
13	3.093	2.770	18.6				
14	2.976	2.797	19.3	Total tin = 3.950 x 10^{-4} v.f.			
15	2.930	2.746	17.5				
16	3.031	2.680	21.5				
17	3.145	2.506	20.6				
18	3.025	2.502	23.5				
W-3	3.084	2.434	18.3	2.577	1.915	0.656	0.581
				Total tin = 2.315 x 10^{-4} v.f.			

$k_{av} = 19.8 \pm 2.4$

TABLE III

KINETICS OF OXIDATION OF TIN (II) BY CERIUM (IV) IN THE PRESENCE OF CERIUM (III) AT 0°C.: SECOND-ORDER MECHANISM

Series	$[\mathrm{Ce(IV)}]_0$ v.f.x10^4	$2[\mathrm{Sn(II)}]_0$ v.f.x10^4	k l./mole sec.	μ	$[H^+]$ v.f.	$[HSO_4^-]$ v. f.	$[SO_4^=]$ v. f.	$[\mathrm{Ce(III)}]_0$ v.f.x10^4
I-1	2.539	1.607	14.7	2.024	1.477	0.585	0.454	5.8
2	2.533	1.759	17.1					
3	3.299	1.998	16.0					
5	2.794	1.791	16.0	Total tin = 1.268×10^{-4} v. f.				
7	2.743	1.995	18.3					
8	2.614	1.958	22.8					
9	2.997	1.356	21.9					
10	2.718	1.688	16.0					
11	3.525	1.786	12.8					
12	2.721	1.733	15.8					
E-12*	2.870	1.993	21.3	1.96	1.455	0.562	0.447	5.8
E-13	3.428	2.324	13.0	Total tin = 1.684×10^{-4} v. f.				
			$k_{av} = 18.3 \pm 3.0$					

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* See also Table IX for accelerated second order rates.

TABLE IV

KINETICS OF OXIDATION OF TIN (II) BY CERIUM (IV) IN THE PRESENCE OF TIN (IV) AT 0°C.: SECOND-ORDER MECHANISM

Series	Tin (IV) Species Present	$[Ce(IV)]_0$ v.f.x10^4	$2[Sn(II)]_0$ v.f.x10^4	k l./mole sec.	μ	$[H^+]$ v.f.	$[HSO_4^-]$ v.f.	$[SO_4^=]$ v.f.
W-I	$Sn(SO_4)_2$ slurry*	2.742	1.672	14.0	2.577	1.915	0.656	0.581
II	$Sn(SO_4)_2$ slurry	2.844	2.196	25.8				
III	$Sn(SO_4)_2$ slurry	2.746	1.700	21.6				
P-X	$Sn(SO_4)_2$ slurry	3.044	1.310	9.7	5.34	3.705	1.308	1.167
II°	SnO_2 slurry	2.325	1.618	21.9				
III°	SnO_2 slurry	2.391	1.960	20.5				
W-i	Air oxidized Sn(II) soln.	1.675	.950	38.4	2.577	1.915	0.656	0.581
ii	Sn(II) soln.	1.939	1.447	70.5				
iii	Sn(II) soln.	1.821	1.731	84.8				
P-i	Sn(II) soln.	2.564	2.496	33.9	5.34	3.705	1.308	1.167
ii	Sn(II) soln.	2.246	2.205	21.8				
O^6-1**	Sn(II) soln.	1.808	1.464	79.5	1.831	1.370	0.512	0.419
2	Sn(II) soln.	2.279	1.804	82.7				
3	Sn(II) soln.	1.930	1.544	121.0	Total tin = 11.27 x 10^{-4} v.f.			
4	Sn(II) soln.	1.940	1.651	94.2				
6	Sn(II) soln.	1.984	1.626	72.0				
7	Sn(II) soln.	1.693	1.384	70.6				

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[*] Absorbancy of slurries: W-I, 0.125; W-II, 0.128; W-III, 0.063; P-X, 0.050; $P_{II}°$, 0.034; $P_{III}°$, 0.027.

[**] See also Table XII, for reactions of this series not following second order rate.

TABLE V

KINETICS OF OXIDATION OF TIN (II) BY CERIUM (IV) AT CONSTANT IONIC STRENGTH: SECOND-ORDER MECHANISM AT 0°C.

Series	$[Ce(IV)]_0$ v.f. x 10^4	$2[Sn(II)]_0$ v.f. x 10^4	k 1./mole sec.	$[H^+]$ v.f.	$[HSO_4^-]$ v.f.	$[SO_4^=]$ v.f.	$[Li^+]$ v.f.	k_{av} 1./mole sec.
P-13	3.967	3.585	16.4	3.705	1.308	1.167	0.000	18.7 ± 4.2
14	2.597	2.280	24.2					
15	2.490	1.960	21.7	Total tin = 2.451 x 10^{-4} v.f.				
16	2.756	2.650	12.7	$\mu = 5.33$				
U- 1	2.558	2.462	15.3	1.884	0.774	1.406	1.705	26.0 ± 5.5
4	2.465	1.935	17.5					
5	2.480	2.000	19.2					
6	2.480	1.960	21.1					
8	2.706	2.297	36.1					
11	2.497	1.999	29.4					
12	2.622	2.192	26.4					
13	2.385	1.782	24.4					
14	2.515	1.983	34.5	Total tin = 3.270 x 10^{-4} v.f.				
16	2.443	2.193	32.9	$\mu = 5.33$				
17	2.523	1.909	25.5					
18	2.305	1.805	29.6					
V- 2	1.753	1.657	22.7	2.321	0.917	1.335	1.268	23.5 ± 3.7
3	1.558	1.520	21.9					
11	1.986	1.137	16.0					
12	1.922	1.165	22.3	Total tin = 2.840 x 10^{-4} v.f.				
10	1.894	0.862	30.3	$\mu = 5.33$				
16	1.438	1.257	28.0					

TABLE VII

KINETICS OF OXIDATION OF TIN (II) BY CERIUM (IV) OF VARIOUS IONIC STRENGTHS AND ACIDITIES: SECOND-ORDER MECHANISM AT 0°C.

Series	$[Ce(IV)]_o$ v.f. x10^4	$2[Sn(II)]_o$ v.f. x 10^4	k l./mole sec.	μ	$[H^+]$ v.f.	$(HSO_4^-]$ v.f.	$[SO_4^=]$ v.f.	$[Li^+]$ v.f.
M^A-1	3.311	1.971	22.7	2.305	0.776	0.303	0.631	0.859
3	3.362	2.108	23.6					
4	3.259	2.432	23.0					
5	3.547	2.156	21.2					
6	3.416	2.316	23.4	Total tin = 3.647 x 10^{-4} v.f.				
7	3.407	2.198	21.1					
8	3.499	2.256	23.1	$k_{av} = 23.6 \pm 1.5$				
9	3.572	2.350	23.6					
12	3.462	2.163	27.1					
15	3.566	2.215	26.3					
17	3.303	2.014	27.6					
18	3.344	2.468	20.3					
M^B-2	3.673	1.874	20.3	2.138	1.010	0.463	0.543	0.538
4	3.677	1.747	19.3	Total tin = 3.647 x 10^{-4} v.f.				
5	3.805	1.718	21.7	$k_{av} = 20.2 \pm 1.1$				
9	3.654	1.774	20.7					
10	3.644	1.429	19.4					
12	3.658	1.463	18.9					
13	3.559	1.278	19.7					
16	3.636	1.174	18.9					
18	3.739	1.372	22.4					

TABLE VIII

SUMMARY OF SECOND-ORDER REACTION RATES OBTAINED AT 0°C.

Symbol	Number of Reactions	μ	$[H^+]$ v.f.	$[HSO_4^-]$ v.f.	$[SO_4^=]$ v.f.	Other ions Present v.f.	k_{av} l./mole sec.
L	5	2.008	1.515	0.584	0.465		19.8 ± 2.4
B	12	2.005	1.488	0.580	0.453		
C	8	1.963	1.454	0.556	0.449		
O	8	1.879	1.367	0.599	0.384		
W	1	2.577	1.915	0.656	0.581		18.3
P	4	5.33	3.705	1.308	1.167		18.7 ± 4.2
V	6	5.33	2.321	0.917	1.335	Li^+, 1.268	23.5 ± 3.7
U	12	5.33	1.884	0.774	1.406	Li^+, 1.705	26.0 ± 5.5
S	14	5.33	0.946	0.420	1.533	Li^+, 2.537	66.5 ± 6.7
O^4	1	4.057	3.516	0.568	0.418	ClO_4^-, 2.112	19.8
O^3	1	3.264	2.752	0.573	0.413	ClO_4^-, 1.353	15.4
L^4	9	2.965	2.444	0.602	0.428	ClO_4^-, 0.986	23.7 ± 4.3
N^D	9	2.573	2.307	0.346	0.223	ClO_4^-, 1.593	20.3 ± 1.4
L^3	16	2.483	1.974	0.600	0.431	ClO_4^-, 0.483	17.1 ± 3.1
M^A	12	2.305	0.776	0.373	0.631	Li^+, 0.859	23.1 ± 1.5
M^B	9	2.138	1.010	0.463	0.543	Li^+, 0.538	20.2 ± 1.1
N^C	13	1.326	1.077	0.342	0.227	ClO_4^-, 0.280	19.6 ± 2.1
I	10	2.024	1.477	0.585	0.454	Ce(III), 5.8 x 10^{-4}	18.3 ± 3.0
E	2	1.960	1.455	0.562	0.447	Ce(III), 5.8 x 10^{-4}	
W^s	3	2.577	1.915	0.656	0.581	$Sn(SO_4)_2$ slurry	20.4 ± 4.6
P^s	1	5.34	3.705	1.308	1.167	$Sn(SO_4)_2$ slurry	17.8
P^o	2	5.34	3.705	1.308		SnO_2 slurry	21.2 ± 0.7
W^i	3					air oxidized tin	no
P^i	2	5.34	3.705	1.308		air oxidized tin	constant
O^s	6	1.831	1.370	0.512		air oxidized tin	value

TABLE IX

KINETICS OF OXIDATION OF TIN (II) BY CERIUM (IV) AT 0°C.: ACCELERATED SECOND-ORDER RATES

Symbol	$[Ce(IV)]_0$ v.f. x 10^4	$2[Sn(II)]_0$ v.f. x 10^4	k l./mole sec.	μ	$[H^+]$ v.f.	$[HSO_4^-]$ v.f.	$[SO_4^=]$ v.f.	Other ions v.f.
A								
P-4*	2.236	1.629	97.2	5.34	3.705	1.308	1.167	. . .
5	1.693	0.813	138					
6	1.734	0.974	140	Total tin = 3.350 x 10^{-4} v.f.				
O^a-5*	1.664	1.447	72.4	3.264	2.752	0.573	0.413	ClO_4^-, 1.353
6	1.570	1.351	66.3					
7	1.567	1.388	48.0	Total tin = 3.950 x 10^{-4} v.f.				
8	1.567	1.388	57.2					
9	1.440	1.262	90.9					
T-5	1.470	1.180	51.9	5.34	2.770	1.061	1.261	Li^+, 0.847
					Sn(IV) = 1.082 x 10^{-4} v.f.			
B-3	2.081	1.445	33.9	1.963	1.455	0.562	0.447	Ce(III), 5.8 x10^{-4}
				Total tin = 2.717 x 10^{-4} v.f.				
11	2.501	2.067	27.0	Total tin = 1.684 x 10^{-4} v.f.				
14	2.324	1.737	34.7					
$K^{3/2}$-2	3.315	1.135	49.3	3.482	1.447	0.621	0.817	Li^+, 1.007
3	3.366	1.315	37.7					
5	3.231	1.078	32.0*					
6	3.013	1.428	56.1*	Total tin = 2.275 x 10^{-4} v.f.				
8	3.059	1.188	53.7					
9	3.344	1.122	43.7					
			k_{av} = 46.1 ± 5.4					
$K^{3/4}$-2	3.404	1.825	41.0	2.705	1.447	0.621	0.666	Li^+, 0.495
3	3.467	1.667	30.3					
6	3.210	1.466	45.1					
8	3.430	1.225	33.0	Total tin = 2.275 x 10^{-4} v.f.				
9	3.435	1.324	46.9					
11	3.391	1.130	35.7					
			k_{av} = 38.7 ± 5.6					

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*Second order rate observed for first 120 seconds of reaction, see also Table III for first order rates

$K^{3/2}$, solution 5 days old; $K^{3/4}$, solution 3 days old. Compare values obtained for K at 15°C., solution 1 day old, and those for M^A and M^B, Table VII.

TABLE X

EFFECT OF AGEING UPON KINETICS OF OXIDATION OF TIN (II) BY CERIUM (IV) AT 0°C.: SECOND-ORDER MECHANISM

Series	$[Ce(IV)]_o$ v.f. x 10^4	$[Sn(II)]_o$ v.f. x 10^4	k l./mole sec.	μ	$[H^+]$ v.f.	$[HSO_4^-]$ v.f.	$[SO_4^=]$ v.f.	$[Li^+]$ v.f.	Age
S - 3	1.438	1.324	73.0	5.33	0.946	0.420	1.533	2.537	1 day
4	1.457	1.083	67.2						
5	1.514	1.167	47.3						
6	1.568	1.148	68.2						
7	1.314	0.914	70.3						
8	1.512	1.139	65.6	Total tin = 0.667 x 10^{-4} v.f.					
9	1.504	1.291	99.9**						
10	1.461	1.051	65.1	$k_{av} = 66.5 \pm 6.7$					
11	1.492	1.007	52.7						
12	1.487	0.840	78.1						
13	1.355	1.109	59.8						
14	1.445	1.262	76.6						
15	1.334	1.107	65.3						
16	1.299	0.952	63.2						
17	1.295	0.914	78.8						
S'* 1	1.067	0.464	100	5.33	0.946	0.420	1.533	2.537	3 days
2	1.128	0.962	135	Total tin = 1.186 x 10^{-4} v.f.					
3	1.175	1.148	176						
6	1.223	1.005	143						

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*Second order rate observed for first 120 seconds of reaction, see also Table XII for first order rates.

TABLE XI

SUMMARY OF ACCELERATED SECOND-ORDER RATES OBTAINED AT 0°C.

Symbol	Number of Reactions	μ	$[H^+]$ v.f.	$[HSO_4^-]$ v.f.	$[SO_4^=]$ v.f.	Other Ions Present v.f.	k_{av} 1./mole sec.	$k_{av}/e^{\sqrt{\mu}}$ 1./mole sec.
$K^{3/2}$	6	3.482	1.447	0.621	0.817	Li^+, 1.007	46.1 ± 5.4	7.11
$K^{3/4}$	6	2.705	1.447	0.621	0.666	Li^+, 0.495	38.7 ± 5.6	7.51
S	14	5.33	0.946	0.420	1.533	Li^+, 2.537	66.5 ± 6.7	6.65
S^1	4	5.33	0.946	0.420	1.533	Li^+, 2.537	138 ± 21	13.8*
P^1	3	5.34	3.705	1.308	1.167	. . . .	116 ± 22	11.6*
O^3	5	3.264	2.752	0.573	0.413	ClO_4^-, 1.353	66.5 ± 10.5	10.9*
T	1	5.34	2.770	1.061	1.261	Li^+, 0.847	51.9	5.19
E	3	1.963	1.455	0.562	0.447	Ce(III), 5.8×10^{-4}	31.5 ± 3.3	7.77

*Second order rates are observed for the first 120 seconds only.

TABLE XII

KINETICS OF OXIDATION OF TIN (II) BY CERIUM (IV): FIRST-ORDER MECHANISM AT 0°C.

Symbol	$[Ce(IV)]_o$ v.f.x10^4	$[Sn(II)]_o$ v.f.x10^4	$[Sn(IV)]_o$ v.f.x10^4	$\frac{K_1}{sec.^{-1}x10^3}$	μ	$[H^+]$ v.f.	$[HSO_4^-]$ v.f.	$[SO_4^=]$ v.f.	Other Ions Present v.f.
S^1-1	1.067	0.232	0.435	0.859	5.33	0.946	0.420	1.533	Li^+, 2.537
2	1.128	0.481	0.166	0.810			age = 3 days		
6	1.223	0.502	0.165	0.868					
R-5	1.851	0.816	2.199	0.951	5.36	1.882	0.774	1.405	Li^+, 0.851
9	2.045	0.893	2.122	1.12					
12	2.385	1.015	2.000	0.916					
13	1.887	0.875	2.140	1.08					
14	1.685	0.678	2.337	0.912			age = 2 days		
17	2.268	0.961	2.054	1.21					
18	1.999	0.715	2.300	1.21					
C-30	2.145	1.117	9.443	0.802	5.33	2.763	1.060	1.279	Li^+, 0.845
48	1.934	0.830	9.730	1.12			age = 10 days		
T-4	1.876	0.861	0.811	0.623	5.34	2.770	1.061 age = 1 day	1.281	Li^+, 0.845
O^5-5	1.778	0.664	10.61	1.21	1.831	1.370	0.512	0.419	. . .
9	1.921	0.810	10.46	1.11			age = 26 days		
O^3-5	1.664	0.723	3.227	0.822	3.264	2.752	0.573	0.413	ClO_4^-, 1.353
6	1.570	0.675	3.275	0.763					
7	1.487	0.611	3.339	0.638					
8	1.567	0.694	3.256	0.560			age = 14 days		
9	1.440	0.631	3.319	0.753					
O^4-2	1.820	1.100	2.850	0.410	4.057	3.516	0.568	0.418	ClO_4^-, 2.112
4	1.560	1.020	2.930	0.403					
6	1.517	0.972	2.978	0.440			age = 14 days		

slurry was visible (concentration greater than ~ 5.9×10^{-4} v.f.), the average value for k was 17.8 l./mole. sec. (Table IV). Similarly, in the presence of a slurry of tin (IV) oxide, the average k observed was 16.4 l./mole. sec. However, if a solution of tin (II) sulfate was aged, or exposed to air (to the extent of bubbling air through the solution for one to three hours) and then added to the reaction mixture, two successive phenomena were observed. At first, accelerated second-order rates were observed; values of k were 30, 70 and even 100 l./mole. sec. (Table IV); these rates did not approach a lower order near the end of the reaction (Figure I). Secondly, as the age of the tin (II) sulfate solution increased, the rate remained first order in tin but became no longer dependent upon the cerium (IV) concentration (Figure II). When a 26-day tin (II) solution was added to a reaction mixture in which the stoichiometric sulfuric acid concentration was 1 v.f., the average first-order rate was 1.16×10^{-3} sec^{-1}. If the small amount of iron (III) present in the reaction mixture ($10^{-3} \times [Ce(IV)]_0$) were responsible for these phenomena, the reaction rate would be noticeably increased as the concentration of iron was increased. It was found that iron concentrations up to 0.1 $[Ce(IV)]_0$ did not bring about an increase in reaction rate. Aged tin solutions were tested for the presence of copper (II) and a possible peroxo-tin (IV) complex. Less than 3×10^{-6} v.f. Cu (II) was found present in a given reaction mixture as indicated by the dithizone test (39). Titanium (III), iron (II) and iodide were used to test for a peroxo-tin complex. Formation of the peroxo-complex of titanium, iron (III) thiocyanide and iodine was determined spectrophotometrically. A titanium complex was not detected; oxidation of iron (II) was negligible; iodine was formed, but not in excess of the amount that appeared from the oxidation of iodide ion by the sulfuric acid present. Thus, it was assumed that neither copper nor a peroxo-tin complex were responsible for acceleration of second-order rates and reaction rates first-order in tin (II). Throughout the course of a particular type of reaction (second-order, accelerated second-order or first-order) the order of the reaction did not change, nor was the rate accelerated with time. There was no direct correlation between the concentration of tin (IV) present initially in the reaction mixture and either the amount of acceleration of the second-order rate or the magnitude of the rate first-order in tin (II). Thus tin (IV) could not be directly related to alteration of the reaction rate. Since the reaction remained second order in the presence of tin (IV) sulfate and tin (IV) oxide slurries it is assumed that ordinary wall-catalysis did not produce these phenomena.

In order to obtain more information about the tin (II)-cerium (IV)-sulfuric acid system, a study was made of the effects of ionic strength, hydrogen, bisulfate and sulfate ion concentrations upon the reaction rates. Sulfuric acid, in its second dissociation, is a weak acid. Thus, determination of the concentration of each species is dependent upon measurement of the degree of dissociation of the bisulfate ion. The thermodynamic dissociation constant of HSO_4^- is defined as

$$37)\quad K = \frac{a_{H^+} \cdot a_{SO_4^=}}{a_{HSO_4^-}} = \frac{c_{H^+} \cdot c_{SO_4^=}}{c_{HSO_4}} \cdot f_R \quad ,$$

where a is the activity of a particular species (see Section II), c is the concentration in f. wts./l. and f_R is the corresponding activity coefficient ratio, $\frac{f_{H^+} \cdot f_{SO_4^=}}{f_{HSO_4^-}}$. Values of f_R, obtained from Raman spectral data by H. M. Smith (40), are available, based upon $K_{25^\circ C} = 0.0104$. If the basis is changed to the Young, Klotz and Singleterry value (41), $K_{25^\circ C.} = 0.0101$, values of f_R' are obtained. Two transformations are then made: 1) volume formalities, c, are converted to weight formalities, m, (42) and $f_{R'}$ becomes γ_R, the weight formality activity coefficient ratio, and 2) for $K_{25^\circ C.}$ is substituted $K_{0^\circ C.} = 0.021$ (41) with the assumption that $\gamma_{R_{25^\circ C.}} = \gamma_{R_{0^\circ C.}}$ Thus,

$$38)\quad 0.021 = \frac{m_{H^+} \cdot m_{SO_4^=}}{m_{HSO_4}} \cdot \gamma_R = K_m \gamma_R \quad .$$

Assuming the effect of 10^{-4} v.f. Ce(IV) and Sn (II) upon a sulfuric acid solution is negligible, concentrations of the sulfuric acid species may be defined as,

$$39)\quad m_{SO_4^=} = x$$

$$40)\quad m_{HSO_4^-} = m_{H_2SO_4} - x$$

$$41)\quad m_{H^+} = m_{H_2SO_4} + x \; .$$

By definition, $\mu = 1/2 \sum_{all}^{i} m_i (Z_i)^2$, where m_i is the weight formality of species i with charge, Z_i. In terms of the previous equations,

$$42)\quad \mu = m_{H_2SO_4} + 2x \quad ,$$

and

$$43)\quad K_m = \frac{(\mu - x)\,(x)}{(m_{H_2SO_4} - x\,)}\quad .$$

If K_m is known as a function of $m_{H_2SO_4}$ (40), then μ and x may be determined from 42) and 43). For convenient evaluation, values of K_m were plotted versus μ, $m_{H_2SO_4}$ and m_{H^+} at 0°C. (cf. Figure XI). When volume formalities, at 0°C., of $SO_4^=$, HSO_4^- and H^+ were desired, each weight formality was multiplied by the ratio, $\left(\frac{C_{H_2SO_4}}{m_{H_2SO_4}}\right)_{0^\circ C.}$, (42).

If the system contained lithium sulfate as well as sulfuric acid, it was assumed that this salt is essentially completely ionized (43) and that the concentrations of the sulfuric acid species are

$$44)\quad m_{SO_4^=} = m_{Li_2SO_4} + x$$

$$40)\quad m_{HSO_4^-} = m_{H_2SO_4} - x$$

and

$$41)\quad m_{H^+} = m_{H_2SO_4} + x.$$

In this instance

$$45)\quad \mu = 3m_{Li_2SO_4} + m_{H_2SO_4} + 2x$$

and

$$46)\quad K_m = \frac{(m_{H_2SO_4} + x)\ \ (m_{Li_2SO_4} + x)}{(m_{H_2SO_4} - x)}\quad .$$

Assuming the addition of lithium sulfate does not alter the correspondence of μ to K_m (Figure XI), concentrations of $SO_4^=$, HSO_4^- and H^+ may

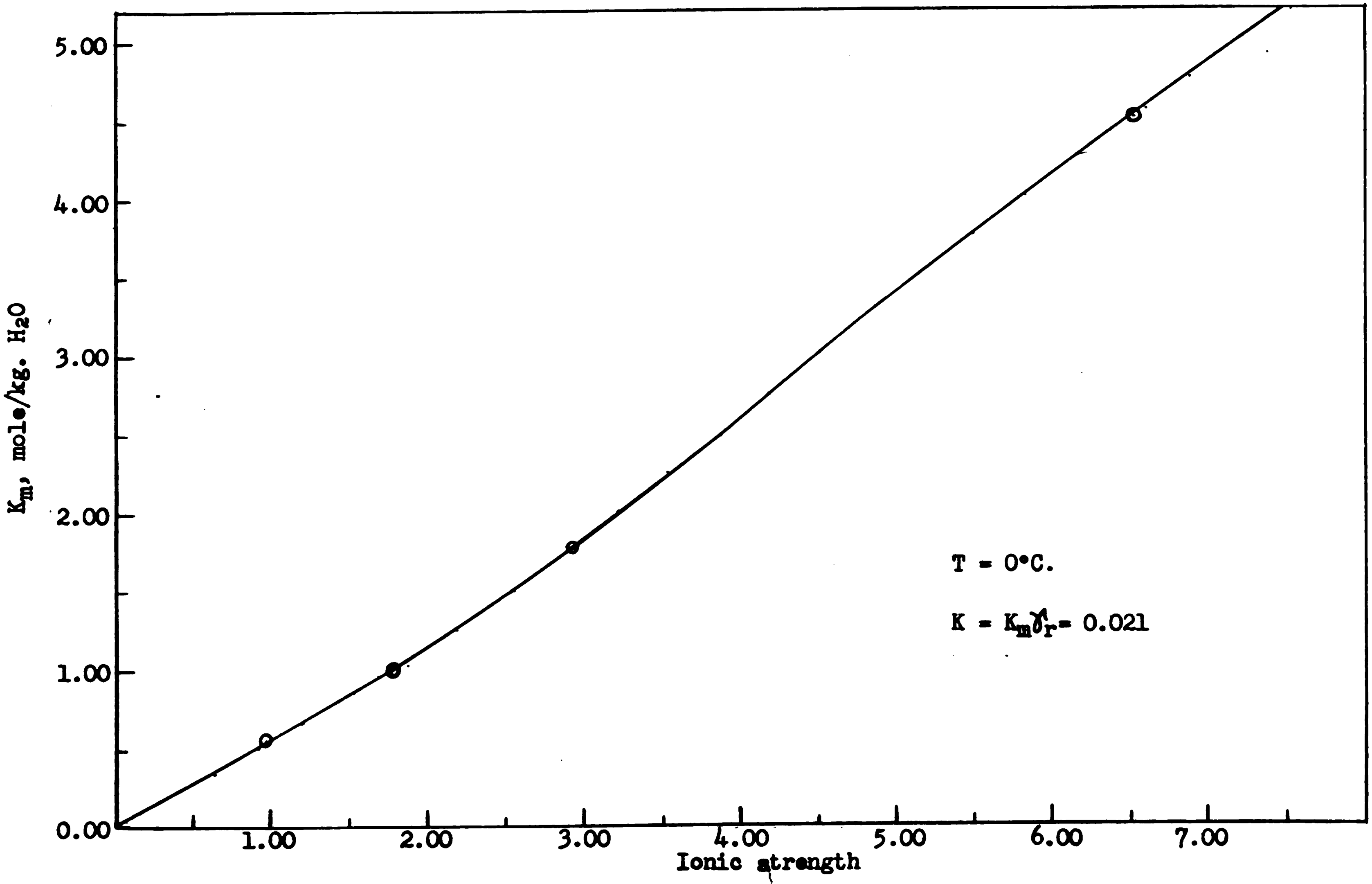

Figure XI. Concentration dissociation constant of the bisulfate ion as a function of ionic strength.

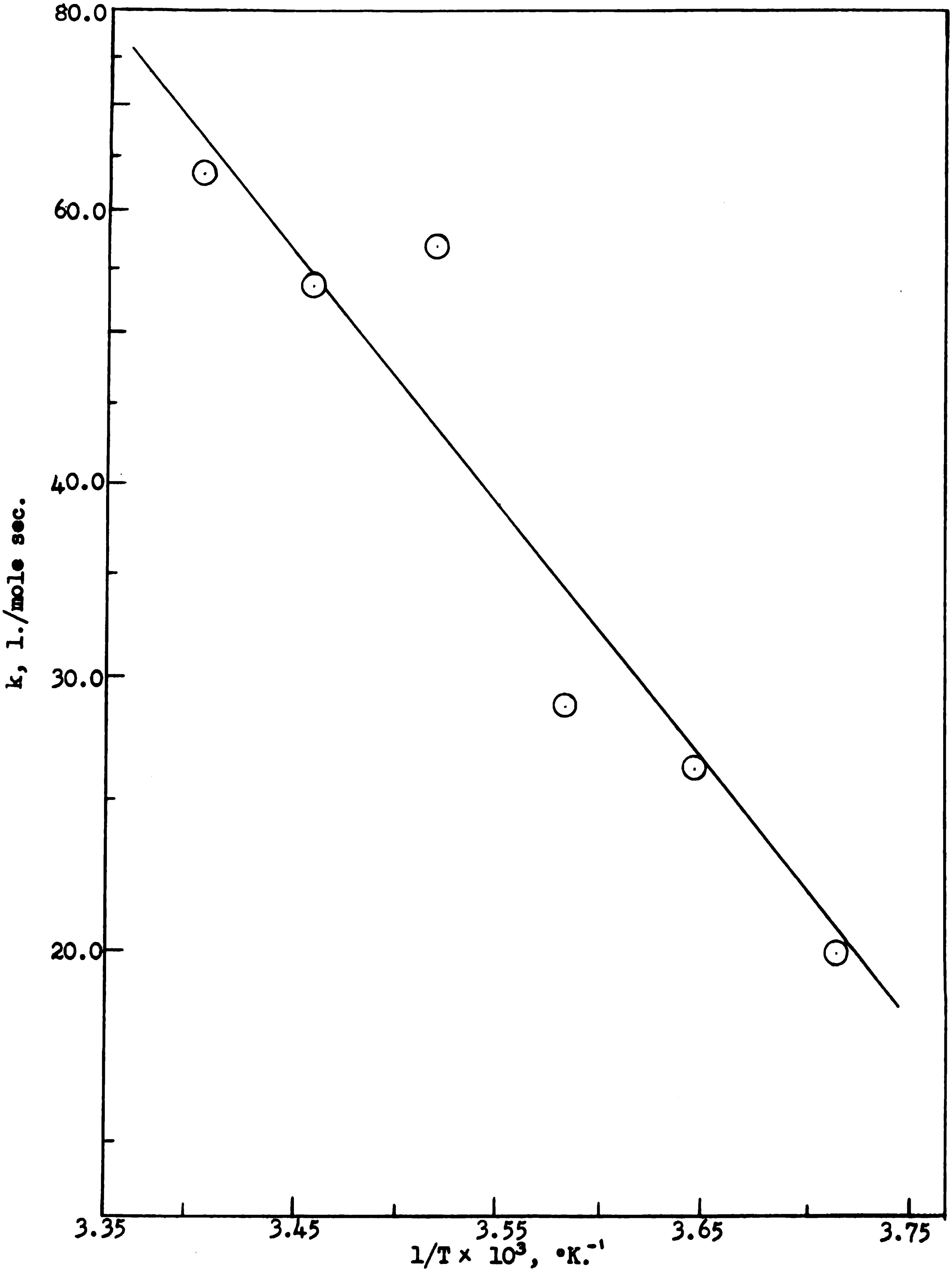

Figure XII. Arrhenius plot for the tin(II)-cerium(IV) reaction: second -order mechanism.

be estimated for particular concentrations of lithium sulfate and sulfuric acid.

Similarly, in perchloric-sulfuric acid solutions, perchloric acid is assumed completely ionized; the concentrations of the sulfuric acid species are

39) $m_{SO_4^{=}} = x,$

40) $m_{HSO_4^{-}} = m_{H_2SO_4} - x,$

and

47) $m_{H^+} = m_{H_2SO_4} + m_{HClO_4} + x$.

Subsequently,

48) $\mu = m_{HClO_4} + m_{H_2SO_4} + 2x$

and

43) $K_\mu = \dfrac{(\mu - x)(x)}{(m_{H_2SO_4} - x)}$

If the correspondence of μ to K_μ (Figure XI) is unaffected by the presence of perchloric acid, then at various concentrations of the two acids, the concentrations of the sulfuric acid species may be calculated.

As illustrated by Tables II, V, VI, VII and the Summary of Table VIII, the second-order rate constant, k, remains constant, within experimental error, as 1) hydrogen ion is varied at constant ionic strength and 2) the ionic strength is varied as the hydrogen ion is held at a constant value. In almost every case (see Tables IX, X, XI and the group of reactions listed at the end of Table VIII), as the age of the tin (II) solution increases, second-order rates increase and finally in very old (14 days) solutions the reaction rate becomes first order in tin (II) only (Table XIII).

The accelerated second-order rates are summarized in Table XI. Experimental values were obtained for ionic strengths of 1.96 to 5.33. In order to determine the dependence of the rate constant upon ionic strength, values of k are divided by $e^{\sqrt{\mu}}$ for dilute solutions or $e^{\sqrt{\mu}}(i + j\sqrt{\mu})$ for concentrated solutions.* Although the accelerated second-order rates were experimentally determined in fairly concentrated solutions, values of k/e^{μ} differed by factors of 10 to 100. However, values of $k/e^{\sqrt{\mu}}$ were relatively constant and have an average value of 6.85 l./mole.sec. Those reactions obeying second-order kinetics for only about 120 seconds have an average value of $k_{av}/e^{\sqrt{\mu}}$ = 12.1 l./mole. sec. It was not possible to correlate quantitatively the rates first-order in tin only with μ, hydrogen, sulfate or bisulfate ion concentrations, tin (IV) concentrations or age of the solution. (See Table XII for oxidation reactions first-order in tin (II).)

Both second-order rates and rates first-order in tin (II) were studied as a function of temperature. Data obtained for the rate first-order in tin (II) could not be related to the Arrhenius equation (Section on Theoretical and Historical Considerations, page 4) (Table XIV). Thus E_a and $\Delta S^{\ddagger}$ were not calculated for this

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*The relationship between k and μ is derivable from equations, page 5 relating k to the activity coefficients of the various species and equations for activity coefficients as presented in Table IV, with the consideration that in dilute solutions, the electrostatic coefficients, $b_i \doteq 0$.

TABLE XIII

KINETICS OF OXIDATION OF TIN (II) BY CERIUM (IV) AT VARIOUS TEMPERATURES: SECOND-ORDER MECHANISM

Reaction Series	$[Ce(IV)]_o$ v.f. x 10^4	$2[Sn(II)]_o$ v.f. x 10^4	k l./mole.sec.	T °C.	k_{av} l./mole.sec.
0-28	3.034	2.611	24.0	5	26.0 ± 1.5
33	3.011	2.626	25.1		
35	3.038	2.651	26.3		Total tin = 3.950 x 10^{-4} v.f.
36	3.078	2.773	28.7		
0-38	3.245	2.934	30.8	10	28.6 ± 4.2
39	2.902	2.637	33.8		
41	3.197	3.077	36.3		
43	3.219	3.031	36.8		Total tin = 3.950 x 10^{-4} v.f.
45	3.037	2.713	25.5		
I- 1	3.716	2.266	27.6		Total tin = 1.691 x 10^{-4} v.f.
3	3.563	2.255	21.8		
5	3.734	2.063	26.5		
6	3.670	2.109	24.0		
7	3.741	2.089	26.5		
8	3.681	2.204	24.9		
9	3.505	2.068	17.5*		
K- 3	3.326	2.139	58.3	15	56.3 ± 4
5	3.426	2.287	64.2*		
6	3.390	2.338	57.5		Total tin = 2.275 x 10^{-4} v.f.
9	3.259	2.271	51.8		
10	3.385	2.333	62.0		
11	3.403	2.350	51.7		
12	3.422	2.320	52.0		
13	3.065	1.940	46.1*		
14	3.468	2.454	61.0		
15	3.487	2.564	64.9		
L- 1	3.961	3.047	53.3	20	53.3 ± 2.0
2	3.132	0.595	52.2		
3	3.763	3.149	46.2		
8	3.703	2.703	57.1		Total tin = 1.78 x 10^{-4} v.f.
9	3.858	2.717	52.2		
10	3.999	3.076	61.9*		
11	3.654	2.420	55.5		
12	3.697	1.275	34.5*		
15	3.842	1.367	49.6		
0- 7	3.147	2.240	57.2	25	62.9 ± 10.7
8	2.906	1.845	79.1		
9	2.592	1.309	52.6		Total tin = 3.950 x 10^{-4} v.f.

* Excluded from the average on statistical basis.

TABLE XIV

KINETICS OF OXIDATION OF TIN (II) BY CERIUM (IV) AS A FUNCTION OF TEMPERATURE: FIRST-ORDER MECHANISM

Symbol	$[Ce(IV)]_o$ v.f.x10^4	$[Sn(II)]_o$ v.f.x10^4	$[Sn(IV)]_o$ v.f.x10^4	K_1st sec.$^{-1}$ x10^2	T, °C.	Age days	$(K_1)_{Av}$ sec.$^{-1}$x10^2	$\frac{(K_1)_{Av}}{a_{SO_4^=}}$
0- 1	2.740	1.654	2.306	1.52	25	1	1.62±0.18	2.62
2	3.222	1.885	2.075	1.97				
3	3.081	1.940	2.010	1.73				
4	2.493	1.152	2.808	1.36				
6	2.397	1.242	2.718	1.53				
26	2.297	1.067	2.893	1.71	20	2	1.91±0.20	2.79
27	2.782	1.250	2.700	2.11				
46	2.576	0.950	3.000	2.26	15	4	2.05±0.20	2.84
47	2.941	1.210	2.740	1.87				
48	3.196	1.400	2.550	2.62				
49	3.315	1.297	2.663	1.89				
50	2.917	1.295	2.665	1.81				
51	3.154	1.355	2.605	2.20				
52	2.979	1.260	2.690	2.07				
53	2.985	1.300	2.650	1.95				
54	2.922	1.207	2.753	1.83				
40	3.080	1.445	2.515	1.02	10	3	0.923±0.074	1.33
41	3.090	1.485	2.475	0.878				
43	3.028	1.420	2.530	0.973				
44	2.981	1.370	2.580	0.820				
29	3.487	1.570	2.380	0.726	5	2	0.759±0.048	0.895
30	2.960	1.322	2.638	0.683				
31	2.948	1.315	2.645	0.869				
32	3.039	1.365	2.595	0.771				
34	3.020	1.321	2.639	0.747				

reaction rate. Plotting ln k versus 1/T for the second-order case, Ea is found to be 7.59 k.cal./mole and $\Delta S^{\ddagger}$ is -12.9 e.u.(Figure XII). If, according to the method of Ringbom (44), the maximum analysis error per 1% spectrophotometric error is 2.31%, and time is measurable to within ± 1 sec., then for k = 20, t = 500 sec., the error in Ea may be estimated as ± 0.08 k.cal. and the error in $\Delta S^{\ddagger}$ as ± 0.4 e.u.

Discussion

To be consistent with the data obtained for the second-order reaction, the mechanism for the oxidation of tin (II) by cerium (IV) must indicate 1) relative invariance of the system with changing ionic strength, hydrogen, bisulfate and sulfate ion concentrations, 2) a negligible cerium (III) effect and 3) a relation to the quantity of tin (IV) present such that a high concentration of prepared sulfate or oxide produces no effect but an aged tin solution or a high concentration of sulfate ion accelerates the rate and then favors a change in mechanism to that of a reaction first-order in tin (II).

Because of the complexity of the sulfuric acid system for a series of experiments it is not possible to maintain all but one of the variables (μ, H^+, HSO_4^-, $SO_4^=$) constant. Thus, the data summarized in Table VIII indicate that the system, as a whole, is relatively unaffected by these variables. For the effect of a small variation in sulfate ion concentration (the other variables are nearly constant) compare series L^A with W; for decrease of hydrogen ion accompanied by an increase in sulfate ion compare series N^D with N^A; for a decrease in ionic strength and hydrogen ion compare series N^C with N^D and for an increase in ionic strength, bisulfate ion and sulfate ion compare series V with N^D. In every instance, the second-order rate constant is essentially constant within experimental error.

It has been fairly well established by Hardwick and Robertson (45) that cerium (IV), in the acid media used for these experiments, is present as trisulfato cerate (IV) ion, $Ce(SO_4)_3^=$. Assuming that tin(II) is present as an ion-pair or complex, $SnSO_4$, the rate (if dependent upon reaction of a negatively charged complex with the neutral complex) would be moderately slow, as observed. However, the experimental conditions of ionic strengths from 1.8 to 5.4 and sulfuric acid concentrations from 1 to 3 v.f. are such that some dependence upon ionic strength would be predicted for formation of the activated complex by an ion and a neutral "molecule" (cf. Table X). At least two explanations of the relative invariance of the reaction rate with changing ionic strength can be offered. Formation of the activated complex may be represented by the schematic equilibrium,

$$49)\quad A^= + M \rightleftharpoons AM^=$$

As mentioned in the section—Theoretical and Historical Considerations—the expression

$$50)\quad \ln \frac{f_{A^=}\ f_M}{f_{AM^=}} = (b_{A^=} + b_M - b_{AM^=}) \quad ,$$

where

$$51)\quad b_M = \frac{1}{k_B T} \left\{ \frac{\epsilon^2 S}{D} \right\} ,$$

and

$$52)\quad \delta = \frac{D_0 - D}{n_B} ,$$

(see Table IV for definition of terms) should reflect changes in the system with variation in ionic strength.* δ is equal to the <u>difference</u> in dielectric constant of the pure solvent and that of the solvent containing n_B molecules of non-electrolyte per cc. divided by n_B. The concentration of $SnSO_4$ is small ($n_B = 10^{-7}$), however, the dielectric constant of the sulfuric acid solution is probably high and essentially unaffected by the presence of tin (II). Thus if the electrostatic terms ($b_i=$, $b_{im}=$) for $Ce(SO_4)_3^{=}$ and the activated complex are nearly identical and b_B is very small, it is conceivable that the reaction rate would be independent of changes in ionic strength. Another phenomenon that might produce the same effect would be variation in the dielectric constant of the medium upon addition of perchloric acid or lithium sulfate which, by chance, masks any increase or decrease in the reaction rate brought about by variation in ionic strength.

Since it can be assumed that the nature of the cerium (IV) species does not change with time, acceleration of the second-order rate accompanied by dependence of the rate upon the ionic strength of the medium must be brought about by a change in tin (II) species. If $k_{av}/e^{\sqrt{\mu}} = k_o$, then a plot of [ln k_{av} - ln k_o] versus μ 1/2 will give an indication of the sign of the charge on the apparently ionic tin species (Figure XIII). The positive slope obtained indicates a negatively

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*Disregarding for the moment any changes in the dielectric constant of the medium.

TABLE XV

EQUATIONS FOR ln (   ) IN FAIRLY CONCENTRATED SOLUTIONS

Dipolar molecule, A, in a solution containing electrolytes:

$$\ln(\beta f)_A = 1 \frac{1}{k_BT} \frac{\mu^2_A}{r_A^3} \left\{\frac{D_e - 1}{2D_e - 1}\right\} - \frac{1}{k_BT}\left(\frac{\epsilon^2 \delta}{2D}\right) \sum_{all}^{i} \frac{m_i z_i^2}{r_i}$$

μ_A = dipole moment

D_e = dielectric constant of pure solvent

r_A = molecular radius

T = absolute temperature

ϵ = electronic charge

k_B = Boltzmann constant

m_i = concentration of ion of charge, z_i, and radius, r_i.

$\delta = \frac{D_o - D}{n_B}$

D = dielectric constant of solution of solvent and n_B molecules of non-electrolyte per cc.

An ion, of radius, r_A, and charge z_A

$$\ln(\beta f)_A = \frac{\epsilon^2 z_A^2}{2 k_BT r_A}\left(\frac{1}{D} - 1\right) - \frac{\epsilon^2 z_A^2}{2Dk_BT}\left\{\frac{K}{1 + K a_A}\right\} + \frac{\phi_A}{k_BT} + b_A \mu.$$

a_A = mean distance of closest approach of ions.

D = dielectric constant of the medium.

$K = \sqrt{\frac{8N\pi\epsilon^2}{10^3 Dk_BT}\mu}$; N = Avogadro's number.

ϕ_A = non-electrostatic contribution

μ = ionic strength

b_A = electrostatic coefficient for high salt concentrations

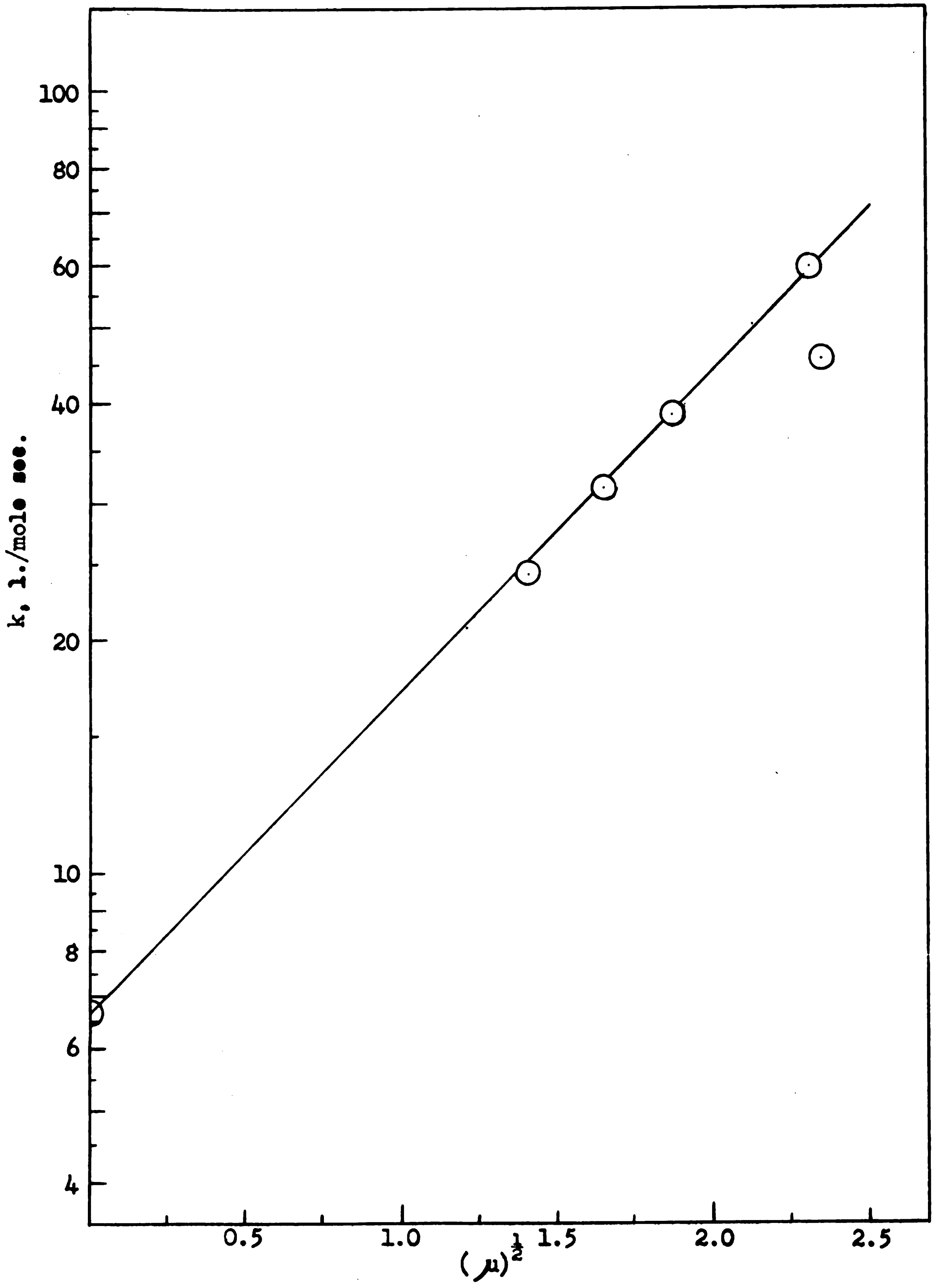

Figure XIII. Dependence of accelerated second-order rates upon the ionic strength.

charged species (cf. Table I). Accelerated second-order rates appear to be enhanced by sulfate ion concentrations greater than 1 v.f. (Series S, T, see also V, U) or the combination of moderate sulfate concentrations (0.4 to 1.0 v.f.) and high concentrations of tin (IV) (1 to 3x $[Sn(II)]_0$. Thus two different ion types may produce the same kinetic effect, $Sn(SO_4)_2^{=}$ or $Sn[Sn(SO_4)_4]^{=}$. The presence of each of these species is probably the result of some of the following equilibria:

53) $SnSO_4 + SO_4^{=} \rightleftharpoons Sn(SO_4)_2^{=}$

54) $SnSO_4^{++} + SO_4^{=} \rightleftharpoons Sn(SO_4)_2$

and

55) $Sn(SO_4)_2^{=} + Sn(SO_4)_2 \rightleftharpoons Sn[Sn(SO_4)_4]^{=}$.

The dependence of the reaction rate constant upon the root of the ionic strength is surprisingly well-defined.* Apparently the electrostatic or dielectric effects are either small or the net effect produced with changing ionic strength is essentially negligible.

The final shift from second-order to first-order reaction brought about by ageing of tin solutions can be explained by postulating the formation of a colloidal tin (IV) species. On the basis of this assumption the reaction rate, which is dependent upon the state of the surface of the colloid, would be a function of the age of the solution, and the temperature of equilibration. The composition of the solid may be variable as well as the charges present over the surface. Under these

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*A function of the form $k \propto e^{\sqrt{\mu}}(1 + j\sqrt{\mu})$ would be expected on the basis of the extended theory of electrolytes.

conditions, little correlation would be expected between the rate first-order in tin (II) and the experimental variables.

Thus, the following mechanism is consistent with the second-order reaction occurring at moderate sulfate ion concentrations:

$$56)\quad SnSO_4 + Ce(SO_4)_3^{=} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Sn\,Ce(SO_4)_2^{++} + 2SO_4^{=}$$

$$57)\quad Sn\,Ce(SO_4)_2^{++} + Ce(SO_4)_3^{=} \xrightarrow{k_2} Sn(SO_4)^{++} + 2\,Ce(SO_4)_3^{\equiv}.$$

If reaction 56) is the rate determining step, and the steady state approximation is made for $Sn\,Ce(SO_4)_2^{++}$, then

$$58)\quad -d\,\frac{[Ce(SO_4)_3^{=}]}{dt} = k_1\,[SnSO_4]\,[Ce(SO_4)_3^{=}]$$

$$-k_{-1}\,[SnCe(SO_4)_2^{++}]\,[SO_4^{=}]^2 + k_2\,[SnCe(SO_4)_2^{++}][Ce(SO_4)_3^{=}]$$

and

$$59)\quad \frac{d\,[SnCe(SO_4)_2^{++}]}{dt} = 0 = k_1\,[SnSO_4]\,[Ce(SO_4)_3^{=}]$$

$$-k_{-1}\,[SnCe(SO_4)_2^{++}]\,[SO_4^{=}]^2 - k_2\,[SnCe(SO_4)_2^{++}]\,[Ce(SO_4)_3^{=}].$$

Rearranging 59),

$$60)\quad [SnCe(SO_4)_2^{++}] = \frac{k_1[SnSO_4]\,[Ce(SO_4)_3^{=}]}{k_{-1}[SO_4^{=}]^2 + k_2[Ce(SO_4)_3^{=}]},$$

and substituting the above expression into 48) and rearranging,

$$61)\quad \frac{-d[Ce(SO_4)_3^{=}]}{dt} = \frac{2k_1k_2\,[SnSO_4]\,[Ce(SO_4)_3^{=}]^2}{k_{-1}\,[SO_4^{=}]^2 + k_2\,[Ce(SO_4)_3^{=}]}.$$

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*Cerium (III) in sulfuric acid solutions used in this study occurs as the bisulfate cerate (III) ion and probably, to some extent, as the trisulfato cerate (III) ion. For studies of cerium (III) complexes in acid solutions, see Fronaeus (47) and Newton and Arcand (46); for a study of the neutral salt solution see Spedding and Jaffe (48).

If $k_2 [Ce(SO_4)_3^{=}] \gg k_{-1}[SO_4^{=}]^2$, then 61) becomes

$$62) \quad -\frac{d[Ce(SO_4)_3^{=}]}{dt} = 2k_1[SnSO_4]\,[Ce(SO_4)_3^{=}] \quad .$$

The experimental data do not clearly establish the nature of the products of reaction 56). Equally probable are $SnSO_4^{+} + Ce(SO_4)_2^{-} + SO_4^{=}$. In either event the intermediate tin species has been postulated as a cation in view of the experimental evidence that k_2 is large and, as such, may be the rate constant for the reaction of highly reactive, oppositely charged species. Postulation of tin (III) itself as an intermediate (i.e. $SnSO_4^{+}$, as opposed to the mixed complex which may or may not contain tin (III)) does not go without precedent (see section Theoretical and Historical Considerations). However, no experimental evidence has been obtained to determine the properties of the tin intermediate other than its high reactivity. The intermediate, $SnSO_4^{+}$, or the intermediate "interaction complex" $[SnCe(SO_4)_2]^{++}$ were not detectable spectrophotometrically. The negligible effect of cerium (III) may mean that the relation $k_2[Ce(SO_4)_3^{=}] \gg k_{-1}[Ce(SO_4)_2^{-}][SO_4^{=}]$ was not being tested (as would be the case if $[SnCe(SO_4)_2]^{++}$ were formed) or that k_{-1} is so very small that extreme "swamping" would be necessary to indicate that cerium (III) (thus, tin (III)) is a product of reaction 56).

At sulfate ion concentrations 1 v.f. or larger and at moderate sulfate concentration in the presence of aged tin solutions, the previously given mechanism is applicable with modification of the tin (II) species present. Thus for sulfate ion concentrations larger than 1 v.f.

a mechanism in accordance with the experimental results would be,

$$63)\quad Sn(SO_4)_2^{=} + Ce(SO_4)_3^{=} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Sn(SO_4)^{+} + Ce(SO_4)_2^{-} + 2SO_4^{=}$$

$$64)\quad Sn(SO_4)^{+} + Ce(SO_4)_3^{=} \xrightarrow{k_2} Sn(SO_4)_2 + Ce(SO_4)_2^{-} .$$

Similarly,

$$65)\quad \frac{-d[Ce(SO_4)_3^{=}]}{dt} = 2k_1 [Sn(SO_4)_2^{=}] [Ce(SO_4)_3^{=}] .$$

If $Sn[Sn(SO_4)_4]^{=}$ were the predominant tin (II) species, the rate would become

$$66)\quad -d [Ce(SO_4)_3^{=}] = 2k_1 \left\{ Sn[Sn(SO_4)_4]^{=} \right\} [Ce(SO_4)_3^{=}] .$$

A first-order rate may be derived if adsorption of the tin (II) species upon colloidal tin (IV) is assumed to be the determining step. Thus,

$$67)\quad \text{tin (II)} + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{tin (II)} \cdot S ,$$

followed by rapid reaction with cerium (IV) on the colloid surface, S,

$$68)\quad \text{tin (II)} \cdot S + 2\,Ce(IV) \xrightarrow{k_2} \text{tin (IV)} \cdot S + 2\,Ce(III).$$

The rate of disappearance of cerium (IV) is then,

$$69)\quad \frac{-d\,[Ce(IV)]}{dt} = k_2 \;[\text{tin (II)} \cdot S]\,[Ce(IV)]^2 .$$

Assuming the steady state approximation,

$$70)\quad \frac{-d\,[\text{tin(II)} \cdot S]}{dt} = 0 = k_1[\text{tin (II)}]\,[S] - k_2[\text{tin(II)}\cdot S] - k_2[\text{tin(II)}\cdot S]\,[Ce(IV)]^2 ,$$

then

$$71) \quad \frac{-d[Ce(IV)]}{dt} = \frac{k_2 k_1[tin(II)] [S] [Ce(IV)]^2}{k_{-1} + k_2 [Ce(IV)]^2} \quad .$$

If $k_2 [Ce(IV)]^2 \gg k_{-1}$, then

$$72) \quad \frac{-d[Ce(IV)]}{dt} = k_1[tin(II)] [S] \quad ,$$

which corresponds to the experimental results.

Final Considerations

It has been found that the oxidation of tin (II) by cerium (IV) may be described by three different reactions that occur as a result of the properties of the surrounding medium. The first, which may be termed a normal second-order reaction (first-order in tin (II) and in cerium (IV)), is generally observed in solutions in which sulfate ion concentrations are less than 1.0 v.f. If $[SO_4^=]$ is 0.4 v.f. to 1.0 v.f., the initial concentration of tin (IV) must be less than twice the initial concentration of tin (II), otherwise the normal second-order rate is not observed. Constancy of this reaction rate with changing ionic strength of the medium indicates the reacting species of tin (II) is the neutral complex, $SnSO_4$. The second reaction observed proceeds at a faster rate but remains second order. This accelerated reaction occurs in solutions with sulfate ion concentrations from 1.0 v.f. to 1.54 v.f., in the presence of tin (IV) at least equal in concentration to $[Sn(II)]_0$. If the concentration of tin (IV) is equal to 3 or 4 $[Sn(II)]_0$, accelerated second-order rates are observed in solutions with sulfate ion concentrations from 0.4 v.f. to 1.0 v.f. Conditions under which the rate is accelerated plus the dependence of the accelerated rate upon the ionic strength indicate the reacting species of tin (II) is a negative species, such as $Sn(SO_4)_2^=$ or $[SnSn(SO_4)_4]^=$. In the presence of very old (14 day) tin (II) solutions or solutions through which air has been passed, the reaction between tin (II) and cerium (IV) no longer depends upon the cerium (IV) concentration. The rate observed could not be correlated with the reaction variables (temperature, ionic strength, sulfate, bisulfate, hydrogen or tin (IV) ion concentrations). As such, the experimental data would be explained if the reaction is assumed to take place rapidly on the surface of a colloidal tin (IV) species present in solution under these conditions.

For the two different second-order reactions that occur, the reaction rate is never greater than first order in cerium (IV) even in the presence of excess cerium (III). This implies that the rate determining step,

73) $Sn(II) + Ce(IV) \rightleftharpoons$ products,

produces a tin intermediate (such as tin (III), a tin (II)-cerium (IV) complex or even a tin (III)-cerium (III) complex) that reacts rapidly with an additional cerium (IV) complex ion to form tin (IV) but the rate at which products form the original reactants is very slow. Thus these kinetic data establish the presence of an intermediate, but not its identity.

It would be of interest, then, to study the oxidation of tin (II) by an agent such as iron (III) or the reduction of tin (IV) by titanium (III) in aqueous sulfate media. If reaction rates were slow enough to be easily measurable, identification of the tin intermediate might be possible. The tin (II)-cerium (IV) system may be altered sufficiently in another acid medium, such as trifluoroacetic acid, that additional information about the tin intermediate may also be obtained in this system.

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APPENDIX I

ANALYTICAL METHODS

Determination of Purity of $(NH_4)_2\ Ce(NO_3)_6$

A. Solubility in water

In a minimum quantity of distilled water, 0.1885 gms. of the salt were completely soluble.

B. Iron

The solution resulting from A, was reduced with 3% H_2O_2 and then $H_2NOH \cdot HCl$ was added to reduce any iron present to Fe(II). Phenanthroline was added and the resulting color was visually compared with Fe(II) standards. Mg. Fe(II) found = 6-7.

C. Solubility in ethanol

In a minimum quantity of 95% ethanol, the salt was completely soluble.

D. Ignition test

Salt that had been dried at 85°C. was weighed, decomposed with a gas flame, ignited at 950°C. for 6 hours, and reweighed.

Weight before ignition 1.0348 gms.

Weight after ignition 0.3238 gms.; Theoretical = 0.3248.

TABLE XVI

STANDARD CERIUM (IV) SOLUTIONS

Symbol	[Ce(IV)] v.f.x10^3	[Ce(IV)] + [Ce(III)] v.f. x 10^3	Acidity v.f.[H^+]	Remarks
q	0.9499	0.9515	3.569	Used for spectrophotometric calibration and reaction series, A through L.
r	1.229	1.233	2.011	Used for reaction series, M through W
s	58.70	58.73	2.069	Standard solution

TABLE XVII

SPECTROPHOTOMETRIC CALIBRATION OF CERIUM (IV) IN 1 v.f. H_2SO_4 AT λ = 315 mμ

[Ce(IV)] v.f.x10^4	Absorbancy (with cell correction)	Ce(IV) v.f.x10^4	Absorbancy (with cell correction)
4.939	2.628	2.280	1.287
4.560	2.468	1.900	1.065
4.180	2.298	1.520	0.829
3.800	2.138	1.140	0.628
3.420	1.939	0.760	0.422
3.040	1.713	0.380	0.163
2.660	1.500		

Note: The slit width used was 0.32 mm.

TABLE XVIII

PREPARATION OF CERIUM (IV) SOLUTIONS USED IN KINETICS STUDY

Reaction Series	Volume of Ce(IV) Standard Used (ml.)	Additional Reagents H_2SO_4 (ml.)	$HClO_4$ (ml.)	Li_2SO_4
A	30 q**	. . .	. . .	. . .
B	30 q	. . .	. . .	. . .
C	27 q	. . .	. . .	. . .
E	40 q	. . .	. . .	. . .
I	40 q	. . .	. . .	. . .
I (10°)	30 q	. . .	. . .	. . .
K	30 q	. . .	. . .	. . .
$K^{3/4}$	30 q	. . .	. . .	4.1432 gm.
$K^{3/2}$	30 q	. . .	. . .	8.2364 gm.
L^3	30 q	. . .	6.4 g***	. . .
L^4	30 q	. . .	12.5 g	. . .
M^A	18 r	. . .	. . .	32 ml(1.003v.f.)
M^B	20 r	. . .	. . .	20 ml(1.003v.f.)
N^C	18 r	. . .	32 k	. . .
N^D	18 r	. . .	20 k	. . .
O	17 r	33 o	. . .	. . .
P	10 r	18.5m,3.4o	. . .	. . .
Q****	12 r	14.5m,0.3o	. . .	2.3484 gm.
R	16 r	26 e	. . .	4.7510 gm.
S	16 r	9.7 e	. . .	7.2190 gm.
T	12 r	14.5m+0.3e	. . .	2.3494 gm.
U	16 r	26 e	. . .	4.7516 gm.
V	10 r	14.5m+1.3e	. . .	2.3504 gm.
W	12 r	27.6 e	. . .	. . .

*Final volume = 50 ml.

**For notation, see Table XVI.

***o = 1.001 v.f. H_2SO_4; g = 11.461 v.f. $HClO_4$; k = 1.999 v.f. $HClO_4$; m = 5.761 v.f. H_2SO_4; e = 1.973 v.f. H_2SO_4.

****Final volume, Q through V, [50 ml. + volume Li_2SO_4].

TABLE XIX

PREPARATION OF TIN SOLUTIONS USED IN KINETICS STUDY

Symbol	Reagents				Time of			Addition after Reaction
	$CuSO_4$ ml. 0.04988 v.f.	H_2O (ml.)	H_2SO_4 (ml.)	Li_2SO_4 (gms.)	Deoxidation (hrs.)	Preheating (min.)	Reaction (hrs.)	
A	10	100	110 of 1:1	. . .	10	30	10	780 ml. H_2O
B	10	100	109 of 1:1	. . .	10	15	10	781 ml. H_2O
C	10	65.5	54.5 of 1:1	. . .	7	15	7	370 ml. H_2O
E	10	382	108 of 1:1	. . .	1	60	1	. . .
I	7	300	100 of 1:1	. . .	10.8	30	10.3	593 ml. H_2O
K	7	300	100 of 1:1	. . .	3.75	15	3	593 ml. H_2O
L	7	300	100 of 1:1	. . .	11	15	1	593 ml. H_2O
M	8	300	101 of 1:1	. . .	5	60	4	592 ml. H_2O
N	8	300	101 of 1:1	. . .	5.5	16	4	592 ml. H_2O
O	10	300	101 of 1:1	. . .	1	60	5.5	592 ml. H_2O
P	3.0	3	213.7 p*	. . .	15.25	60	3.25	283.4 ml. H_2O
Q	2.2	264.2	133.6 p	18.7988	15.5	15	3.5	None
R	2.2	. . .	93.0 p	. . .	10	15	1.1	300.0 ml. H_2O + 28.0271 gms. Li_2SO_4
S	2.2	9.0	48.8 p	. . .	10.5	15	0.5	340.0 ml. H_2O 57.7564 gms. Li_2SO_4
T	2.2	4.2	133.6 p		11	30	0.5	260.0 ml. H_2O 18.8081 gms. Li_2SO_4
U	2.0	4.8	93.0 p	. . .	11	30	0.5	300.0 ml. H_2O 38.019 gms. Li_2SO_4
V	2.0	4.8	93.0 p	. . .	11	30	1.0	300.0 ml. H_2O 38.023 gms. Li_2SO_4
W	26.55 ml. Tin solution, P, and 23.45 ml. H_2O by burette transfer.							

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* p = 5.798 v.f. H_2SO_4.

Determination of Tin

Preparation of Standards

A. Standard tin solutions: $\alpha = 0.1344$ gms. Sn(0) were dissolved in 25 ml. concentrated HCl and diluted to 250 ml.; $\beta = 5.$ ml. plus 5 ml. concentrated HCl diluted to 100 ml. Solution β is stable no longer than one week.

B. Dithiol reagent: to approximately 0.08 gms. dithiol were added 4 drops of thioglycollic acid and then 25 ml. of 2% NaOH. If kept cold, the solution is stable for one week.

Calibration and Determination Procedure

A known volume of the appropriate solution, 5 ml. of a 3:7 H_2SO_4 and enough water to increase the volume to 25 ml. are added to a 50 ml. beaker. This solution is evaporated, without boiling, to light fumes of SO_3. With mixing after every addition, the following reagents are added: 10 ml. H_2O, 5 drops thioglycollic acid, 2 drops Santomerse X (30%), 1 ml. of dithiol reagent and 8 additional drops of Santomerse X. The resulting mixture is diluted to a volume of 50 ml., mixed and the absorbancy determined at 536 mu. The absorbancy of distilled water, treated as above was taken to be 0.000.

Analytical Results

Results are tabulated in Table XX.

TABLE XX

SPECTROPHOTOMETRIC [Sn(II) + Sn(IV)], AND ACIDITIES OF TIN SOLUTIONS

Tin Solution	Volume Diluted to 50 ml. (ml.)	Absorbancy (corrected)	Sn(II)+Sn(IV) f.wts./l.x10^4	Acidity v.f.$[H^+]$, 20°C.
A	5	0.365	5.344	1.615
B	5	0.765	11.19	1.882
C	5	0.803	11.97	2.139
E	5	0.568	8.152	1.586
I(10°C.)	5	0.349	5.072	1.920
I Ce(III)	5	0.349	5.072	1.920
K	2	0.176*	6.825	1.872
L	2	0.141	5.439	1.884
M	2	0.280	10.94	1.978
N	2	0.150	5.914	1.954
O	2	0.306	11.85	1.848
P^{A}	2	0.274	10.05	2.510
Q	1	0.438	31.67	3.873
R	1	0.165	12.06	2.696
S	2	0.046	1.779	1.414
T	2	0.091	3.345	3.873
U	2	0.142	7.116	1.348
V	2	0.121	6.182	1.348
P	1	0.181	17.435	2.510
W	Prepared by dilution of solution P,		9.259	1.316

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* For this and subsequent solutions, $\alpha = 0.1055$ gms. Sn(0)/250 ml.

APPENDIX II

ORIGINAL KINETIC DATA

Absorbancy versus time*: Series B and V at 0°C.

A(cell) A obs.	B-1 -.004	2 -.002	3 -.006	4 -.002	5 -.006	6 -.006	7 -.002	8 -.006	10 -.002	11 -.006	12 -.006	14 -.002	16 -.006	V-3 +.004
						Reaction Number								
2.100		5												
2.050	11													
2.000	15		18	10		11						6	13	
1.900	22	14		17	16		10	11	12		16	14	44	
1.800	30	21	36	27	28	24	20	24	30	14	25	23	95	
1.700	38	32	46	40	40	35	32	40	48	57	34	31	173	
1.600	47	41	58	54	54	45	45	57	68	108	42	39	328	19
1.500	57	51	72	68	70	58	60	76	92	187	51	49		39
1.400	68	63	88	84	86	72	77	99	121	331	63	60		59
1.300	81	75	106	102	106	89	97	125	156		76	72		74
1.200	94	89	126	122	127	107	119	155	199		90	85		106
1.100	110	105	150	146	154	129	147	193	260		104	99		129
1.000			177	173	182	154	179	243	357		120	115		160
.940		137			204	173	193	283			132	126		180
.900		144		204	218	185		313			139	133		193
.840	167	160			247	210		378			154	146		220
.800	176	170	248	245	266	226	275	436			162	155		240
.750	190	184	274	269	295	253	313				176	168		267
.700	204	198	298	294	306	280	353				190	186		296
.650	219	214	327	324	342	312	403				206	195		332
.600	238	233	368	358	400	354	479				224	212		
	.298	.337	...	...	...	...	...	...	...	...	.119	.384	(1 obs.) in 4 ml-volume after addition of 1 ml. Ce(IV)	
(A obs.), no additions			.244	.260	.357	.347	.440	.656	.811	1.299	...	...	1.445	.432

* Time in seconds.

Absorbancy versus time*: Series C and I at 0°C.

	Reaction Number												
	C-1	2	3	10	11	12	13	16	I-1	2	3	5	7
A(cell)	+.002	+.003	+.004	+.003	+.004	+.002	+.003	+.003	-.008	-.007	-.008	-.007	-.007
A obs.													
1.840									[illegible]	[illegible]	27		[illegible]
1.700		10							[illegible]	[illegible]	66	6	[illegible]
1.650	14	14		14	15	20	19	8	[illegible]	[illegible]	82	17	[illegible]
1.600	17	17	17	15	18	24	24	11	[illegible]	[illegible]	100	32	[illegible]
1.550	20	21	19	19	21	28	29	17	[illegible]	6	122	47	26
1.500	24	24	23	22	25	32	33	21	10	20	144	61	38
1.450	[illegible]	27	26	28	29	36	38	25	28	34	171	78	52
1.400	32	31	31	33	34	41	43	30	43	49	202	96	68
1.350	[illegible]	[illegible]	35	38	39	47	49	36	60	66	[illegible]	115	85
1.300	42	41	40	44	43	52	54	41	78	83	254	139	102
1.250	46	[illegible]	46	49	48	58	59	47	98	103	[illegible]	160	123
1.200	51	51	51	55	54	65	66	53	122	125	[illegible]	187	146
1.150	57	[illegible]	56	61	59	71	72	60	150	151		221	173
1.100	62	63	63	67	65	79	79	67	183	186		263	204
1.000	76	76	75	81	78	95	94	82	266	260			273
.900	90	90	90	97	93	114	111	98					391
.800	110	109	108	116	112	137	132	119					
.700	133	134	129	140	137	165	158	144					
.600	159	157	155	169	165	197	187	173					
.500	192	190	[illegible]	204	200	238	225	209					
	.163	.334	.290	.216	.563	.360	.212	.334	(A obs.) in 4 ml-volume after addition of 1 ml. Ce(IV).				
(A obs.) in 4 ml-volume containing 5.8×10^{-4} v.f. Ce(III) at t = o									.714	.642	.924	.758	.622

*Time in seconds.

Absorbancy versus time*: Series 0 and L at 0°C.

	Reaction Number												
	0-10	11	13	14	15	16	17	18	L-1	2	3	4	5
A(cell)	+.002	+.006	+.002	+.006	+.001	+.002	+.006	+.001	+.004	0.00	+.004	+.004	0.00
A obs.													
1.800									12	8		7	16
1.750									26	23	11	17	20
1.700				8					41	32	27	28	35
1.650		10			7			5	56	42	38	41	46
1.600			15	12			22		73	56	52	57	61
1.550		29	21		12		29		93	72	69	74	78
1.500	26		26	25	20	21	35	21	118	90	89	95	97
1.450		43	34	32	27	27	44	29	148	113	114	120	122
1.400	38	51	42	39	35	36	52	36	186	141	143	152	154
1.350	45	60	50	47	43	44	62	44	234	174	182	191	193
1.300	53	69	58	55	50	52	72	51	301	218	229	244	246
1.250	62	79	67	63	58	60	83	60		283	300	326	332
1.200	71	89	76	72	67	69	95	69					
1.150	81	100	87	81	75	79	109	78					
1.100	92	112	98	92	84	90	124	89					
1.050	103	125	110	102	95	102	135	101					
1.000	110	151	132	132	120	127	176	110					
.940	125	165	145		134	144	198	126					
.900	137	181	158	163	144	154	215	138					
.840	156	202	179	182	162	175	246	160					
.800	169	220	194	195	174	190		176					
.750	190	244	216	215	193	212							
.700	211					234							
.650	234				233								
(A obs.)	.146	.244	.241	.182	.179	.267	.428	.368	1.182	1.147	1.176	1.179	1.165

---

*Time in seconds.

Absorbancy versus time*: Series I, E and O^8 at 0°C.

	Reaction Number												
	I-8	9	10	11	12	E-12	13	O^8-1	2	3	4	6	7
A(cell)	-.006	-.005	-.006	-.007	-.005	-.005	-.003	-.013	-.011	-.016	-.013	-.016	-.013
A obs.													
2.000				34			13						
1.900				74			31						
1.800				105			55						
1.700		37		155		12	81						
1.650		52		186	11	20	96						
1.600		68	19	221	23	30	114						
1.550	15	87	31	263	36	41	132						
1.500	26	108	44	312	50	52	153						
1.450	37	131	60	378	66	65	177						
1.400	48	159	76	456	85	78	203						
1.350	61	190	96		105	93	231						
1.300	75	226	118		128	110	265						
1.250	91	272	144		156	129	304						
1.200	109	325	172		186	149	349						
1.150	129	395	206		223	173	404						
.900	296												
.840								18		11	18	11	16
.800	445							21	33		21	27	20
.750								26	43	18	28	36	36
.700								37	52	30	33	46	46
.650								47	60	37	40	54	56
.600								60	69	46	53	63	69
.550								71	83	55	63	74	86
.500								81	103	67	73	85	102
.450								96	147	83	86	104	120
.400										106	107	134	151
	.570	1.100	.769	1.167	.751	.654	.835	(A obs.) in 4 ml.-volume containing 5.8×10^{-4} v.f. Ce(III) at t = o					
	..	..	..	..	..	..	..	.214	.304	.240	.192	.226	.196 (A obs.)

---

*Time in seconds.

Absorbancy versus time*: Series K^a/a and K^a/s at 0°C.

	Reaction Number											
	K^a/a-2	3	6	8	9	11	K^a/s-2	3	5	6	8	9
A(cell)	-.008	0.00	-.008	-.007	-.008	-.007	-.008	0.00	0.00	-.008	-.008	0.00
A obs.												
1.850		16										
1.800	10	21		20	14	17	8	13	8			13
1.750	15		7	29	20	25	14	20	15			20
1.700	19	34	10	38	27	34	21	27	23			28
1.650	24	42	16	50	34	46	29	35	34		9	37
1.600	29	52	21	66	44	61	39	46	46	7	14	50
1.550	36	63	29	85	54	81	51	59	62	11	20	66
1.500	42	74	37	109	67	106	64	74	80	16	27	86
1.450	49	88	46	144	83	140	81	93	104	22	36	116
1.400	58	104	57	197	104	195	105	118	135	29	47	161
1.350	67	122	70	287	133	293	139	152	180	37	59	247
1.300	77	144	85		176		193	203	256	46	74	
1.250	40	174	105		249		319			58	96	
1.200	104	211	128							72	126	
1.150	122	265	160							90	170	
1.100	146		211							116	279	
1.050	182		305							152		
1.000	251											
.950												
(A obs.)$_\infty$	.930	1.052	1.007	1.271	1.154	1.290	1.245	1.182	1.232	.919	1.074	1.281
	contain 0.247 v.f. Li_2SO_4						contain 0.503 v.f. Li_2SO_4					

*Time in seconds.

Absorbancy versus time*: Series L³ at 0°C.

	Reaction Number												
	1	2	3	4	5	6	7	8	9	10	11	12	13
A(cell)	+.004	+.002	+.004	+.002	+.004	+.002	+.004	+.002	+.004	+.002	+.002	+.004	+.002
A obs.													
1.880									20				
1.840			22		13		7			20			
1.800	26		30		20		12		34	28			
1.750	42		46		32		23	10	49	41	8	7	11
1.700	58		62		43		37	17	66	55	15	13	30
1.650	75		80		58	11	51	25	86	70	24	21	39
1.600	99	15	105	10	76	19	70	34	110	87	34	31	50
1.550	125	22	130	17	95	28	89	45	136	107	46	42	64
1.500	154	30	158	26	116	37	113	55	166	129	59	54	80
1.450	189	39	192	34	142	48	139	67	202	154	74	68	96
1.400	228	49	232	44	171	60	170	81	245	183	93	84	117
1.350	277	60	280	55	205	73	205	97	296	217	112	103	140
1.300	334	72	337	67	245	87	247	113	356	255	136	124	166
1.250		86		81	294	104	298	133		302	163	148	196
1.200		101		96	352	122	358	155		358	195	175	233
1.100		137		133		168		210			281	248	
1.000		179		179		216		282				411	
.940		211		212		260		354					
.900		236		236		291							
.840		285		283		361							
.800		326		341									
(A obs.)	1.049	.658	1.041	.531	.938	.644	.951	.820	1.062	1.065	.850	.804	.908

*Time in seconds.

Absorbancy versus time*: Series L^3, L^4 and O^3 at 0°C.

	Reaction Number												
	L^3-14	15	16	L^4-4	5	7	8	9	10	11	12	14	O^3-4
A(cell)	+.002	+.004	+.002	+.005	+.003	+.005	+.003	0.00	+.003	+.005	0.00	+.003	-.008
A obs.													
1.960											11		
1.900											20		
1.840	15										34		
1.800	23				16					15	43	21	
1.750	34	9	6		28					22	61	36	
1.700	47	17	11		43	8				35	82	56	
1.650	62	27	16		62	14		10		50	108	80	
1.600	82	38	22		85	24	12	17		71	148	113	
1.550	103	51	31		112	36	19	25		96	199	154	
1.500	128	64	41	10	147	50	27	34	9	128	267	204	
1.450	159	81	55	17	191	69	38	45	15	167			
1.400	195	100	70	25	245	91	51	58	21	219			
1.350	238	121	88	34		119	66	74	30				
1.300	290	141	107	46		154	84	93	40				
1.250		175	129	60		203	107	119	52				
1.200		209	154	76		263	134	153	67				
1.100		300	218	121			213	280	111				
.700													10
.600													18
.550													23
.500													29
.450													35
.400													42
.350													49
.300													57
.250													67
.200													80
(A obs.)	1.060	.868	.898	.825	1.167	1.089	.875	1.066	.890	1.183	1.432	1.267	0.00

---

*Time in seconds.

Absorbancy versus time*: Series M^A at 0°C.

	Reaction Number											
	M^A-1	3	4	5	6	7	8	9	12	15	17	18
A(cell)	-.004	+.001	+.001	-.004	-.006	+.001	-.004	-.006	-.006	-.006	-.004	-.006
A obs.												
1.900								16	7	10		
1.800		14		28	14	17	18	26	15	20		9
1.750	17	20	13	34	19	23	25	32	21	26		15
1.700	22	26	18	42	24	30	31	38	27	32	17	19
1.650	30	33	23	50	30	37	38	45	34	40	24	26
1.600	38	41	29	60	38	47	47	53	42	47	32	32
1.550	47	50	36	71	46	56	56	62	50	56	39	39
1.500	58	60	42	82	54	66	65	71	59	66		47
1.450	70	70	49	97	65	78	76	82	70	76	57	56
1.400	83	83	58	112	76	90	89	94	82	89	67	66
1.350	99	97	67	128		104	103	107	96	102	79	77
1.300	115	112	78	148	101	120	118	122	110	116	91	90
1.250	134	130	88	170	117	139	135	139	127	134	106	105
1.200	155	150	101	196	133	159	155		147	153	123	121
1.150	178	171	114	225	153	181	177	180	168	176	142	140
1.100	209	199	131	263	175	210	204	207	196	204	167	164
1.050	244	230	148		200	242	235	235	227	238	196	190
(A obs.)	.798	.760	.528	.831	.671	.737	.752	.741	.778	.808	.770	.550

*Time in seconds

Absorbancy versus time*: Series M^B and T at 0°C.

	Reaction Number										
	M^B-5	9	10	12	13	16	18	2	4	T-4	5
A(cell)	+.004	0.00	+.002	0.00	+.002	+.002	0.00	+.004	+.002	0.00	+.001
A obs.											
2.100	23		5	6	7	7	7				
2.000	39	12	7	15	10	20	20				
1.900	59	24	28	34	24	41	38	26			
1.800		42	54	59	47	74	66	43	48		
1.750	73	53	68	75	60	97	84	54	61		
1.700	83	66	86	93	75	121	105	64	73		
1.650	99	79	106	113	96	154	129	76	89		
1.600	116	96	134	167	125	200	163	91	108		
1.550	136	114	165	202	163	255	204	108	130		
1.500	161	135	214	250	217		259	126	154		
1.450	191	161	267					148	218		
1.400	223	191						174	262		
1.350	267	227						205			
1.300								241			
.750										30	
.700										53	29
.650										65	40
.600										80	70
.550										99	92
.500										115	117
.450										133	155
.400										159	212
(A obs.)	1.212	1.094	1.284	1.264	1.303	1.413	1.358	1.058	1.123	.144	.193

---

*Time in seconds.

Absorbancy versus time*: Series N^C at $0^\circ C$.

	Reaction Number												
	1	2	3	7	8	10	11	13	14	15	16	17	18
A(cell)	+.002	+.003	0.00	+.002	+.003	+.002	+.003	+.002	+.003	0.00	+.002	+.003	0.00
A obs.													
1.880											15		
1.800											31		
1.750		7			5		10		12	6	43	5	
1.700		16			13		19	11	20	13	57	16	
1.650	16	24			22		29	19	28	23	71	26	
1.600	24	34	9	8	32	14	40	28	38	33	88	37	8
1.550	33	44	17	16	43	25	53	38	49	45	107	49	18
1.500	42	55	26	23	55	34	67	49	61	57	129	62	27
1.450	52	67	37	32	69	46	85	60	75	71	158	76	36
1.400	64	81	49	41	85	60	107	74	90	87	197	92	47
1.350	77	98	61	52	101	76	131	90	107	104	237	110	58
1.300	91	115	76	64	120	95	160	108	125	124		131	70
1.250	106	138	92	78	143	118	201	131	147	146		154	85
1.200	124	163	109	92	169	145	251	156	172	171		182	100
1.150	143	193	129	110	199	179		188	202	200		213	117
1.100	167	232	154	130	236	226		227	238	236		253	137
1.000	253		218	192									200
(A obs.)	.659	.821	.666	.602	.803	.897	1.006	.818	.779	.763	1.118	.812	.571

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*Time in seconds.

Absorbancy versus time*: Series N^D and E at 0°C.

	Reaction Number											
	N^D-3	6	7	10	11	13	16	17	18	E-3	11	14
A(cell)	-.003	-.003	-.004	-.004	-.003	-.004	-.004	-.003	-.003	-.007	-.006	-.006
A obs.												
1.866								14				
1.800					7			24	13			
1.770				13								
1.750		11		17	21	11		35	23			
1.700		18		28	36	22	7	47	35			
1.650	23	27	11	40	54	33	13	62	48			
1.600	33	37	20	56	76	47	23	80	65			
1.550	43	48	29	75	104	63	35	103	86			
1.500	54	59	39	97	134	81	47	130	110			
1.450	66	72	50	127	175	104	63	165	141		15	
1.400	79	87	62	162	231	130	80	211	182		23	
1.350	94	103	76	207		164	102		233		33	
1.325												19
1.300	110	122	92	267		207	127				43	24
1.250	130	144	110			261	160			14	54	34
1.200	150	169	132				200			19	65	44
1.150	175	199	158				255			25	79	56
1.100	208	237	190							31	94	71
1.050	244		229							39	111	87
1.000										48		105
.940										60	160	
.900										69	180	149
.840										89	224	192
.800										103	254	222
(A obs.)$_\infty$	.668	.782	.758	1.118	1.227	1.084	.969	1.166	1.163	...	...	...
(A obs.)$_0$ in 4 ml.-volume containing 5.8×10^{-4} v.f. Co(III) at t = o										.511	.450	.525

*Time in seconds.

Absorbancy versus time*: Series B and O^B at 0°C.

	Reaction Number											
	B-5	9	12	13	14	17	18	OB-5	6	7	8	9
A(cell)	+.001	+.006	+.006	−.005	+.001	+.001	+.006	−.010	−.010	−.008	−.010	−.020
A obs.												
0.960			32				17					
0.920	16	22	40				26					
0.880					21							
0.840	26	30	51			31	36					
0.800	33	36	58	19	34	36	43	15	10	10	13	
0.750	43	45	68	30	45	44	54	24	19	19	24	
0.700	52	54	78	37	55	51	64	34	30	30	37	10
0.650	61	62	89	46	64	59	75		40	43	53	17
0.600	70	72	102	56	75	69	88	58	54	59	71	26
0.550	80	82	116	66	86	79	103	71	69	77	92	38
0.500	90	93	133	76	99	90	121	86	85	97	115	53
0.450	102	105	154	87	114	106	151	102	103	120	145	70
0.400	116	121	187	100	133	126	218	121	124	149	184	92
0.375			211		144							
0.350	155	141	250	114	159	159		143	149	185	245	117
0.325			316		179							
0.300	197	174		131	207	187		171	181	236		148
0.275					266	242						
0.250	355	262		153				217	231			195
0.225												
0.200				199								
(A obs.)	.165	.197	.259	.116	.223	.245	.360	.149	.147	.174	.226	.122

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*Time in seconds.

Absorbancy versus time*: Series S at 0°C.

	Reaction Number												
	3	4	5	6	7	8	9	10	11	12	13	14	15
A(cell)	+.003	-.001	-.002	+.003	-.001	-.002	+.003	-.001	-.002	+.003	-.002	-.002	+.003
A obs.													
0.750			20	25		17			18				
0.700			25	34		30	18	25	31	31			
0.650		32	39	49	23	43	27	37	45	48		25	23
0.600	33	51	55	64	42	61	38	56	64	70	31	34	39
0.550	48	72	74	85	63	79	51	77	87	102	48	46	54
0.500	64	93	97	112	88	102	69	102	118	149	67	62	71
0.450	82	123	128	150	122	133	91	135	155	254	90	85	96
0.400	103	165	168	244	170	178	118	187	211		117	112	127
0.375	116	194	195	299	204	207	133	213	256		133	129	148
0.350	131	231	231		254	243	149	261	336		153	148	170
0.325	148	282	275		327	293	169	331			175	171	194
0.300	167	360	334				191				202	198	227
0.275	192						238				235	232	267
0.250	224						295				300	276	326
0.225	264											332	
0.200	318												
(A obs.)	.102	.238	.229	.268	.266	.237	.155	.256	.295	.387	.166	.130	.160

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*Time in seconds.

Absorbancy versus time*: Series S, S^A, O^8, O^4 and Q

	Reaction Number												
	S-16	17	S^A-1	2	3	6	O^8-5	9	O^4-2	4	6	Q-30	48
A(cell)	-.001	-.002	-.001	-.002	+.003	+.003	-.011	-.016	-.007	-.007	-.007	-.001	0.00
A obs.													
1.000												28	
.940												37	
.900												41	22
.840							19					50	36
.800							21	17	27			55	46
.750							24	23	41	16	15	62	60
.700							36	31	54	27	25	67	74
.650							46	40	68	39	37	74	88
.600	35						55	49	84	53	50	80	103
.550	56	44					64	59	101	68	65	87	118
.500	79	63	34	17	17	26	74	69	118	84	80	95	133
.450	106	90	71	29	24	33	94	81	138	101	97	103	148
.400	145	126		40	31	47	123	95	159	120	115	115	168
.375	172	151		48	37	57	137	106					178
.350	208	187		57	45	68	151	141	180	141	135	147	191
.325	244	235		68	53	79	179	151					208
.300		305		80	63	92	211	173	202	162	156	190	228
.275				94	73	107		243					263
.250				111	85	124			225	186	180		325
.225				131	98	147							
(A obs.)	.219	.235	.330	...	...	...	.265	.190	...	...	...	.160	.197
(A obs.) in 4 ml.-volume after addition of 1 ml. Ce(IV).	...	...	...	.414	.350	.448	...	...	.265	.162	.194		

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*Time in seconds.

Absorbancy versus time*: Series P and W at 0°C.

	Reaction Number											
	P-13	14	15	16	P-II°	III°	I	II	X	W-I	II	III
A(cell)	+.007	+.007	+.006	+.002	+.006	+.002	+.007	+.006	+.006	+.006	+.007	+.004
A(slurry)					+.034	+.021			+.050	+.125	+.128	+.063
A obs.												
1.700	40								39			
1.650	67								65	16		
1.600	73								90	22	12	
1.550	81								122		19	
1.500	88								165	65	27	19
1.450	97								214	78	35	32
1.400	109			20					314	87	44	42
1.350	122			28						97	53	51
1.300	134	14	17	38						108	63	65
1.250	149		29	49	20	19				118	75	92
1.200	162	42	36	60	33	29		12		129	87	128
1.150	173	54	54	73	51	35		25		142	100	152
1.100	184	65	71	86	70	45	41	37		156	115	175
1.050	195	76	87	101	91	74	52	49		173	131	
1.000	210	89	103	115	104		63	62		225	147	228
.940		104	123	134	138	100	77	76			170	
.900		116	137	143	155	110	85	87			185	
.840		137	163	165	174	127	99	107			219	
.800		150	176	178	189	140	109	120			240	
.750		170	198	196	231	156	119	138			278	
.700		190	219	215	335	172	130	154			320	
(A obs.)	.316	.246	.354	.128	.480	.316	.112	.190	1.056	.770	.549	.694

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*Time in seconds.

Absorbancy versus time*: Series V, P^A and W at 0°C.

	Reaction Number											
	V-2	3	10	11	12	15	P-1	5	6	W-4	II	III
A(cell)	+.005	0.00	0.00	+.005	+.006	0.00	+.007	+.006	+.002	+.006	+.007	+.004
A obs.												
1.000				61	29							
.980			30									
.940			52	104	58						15	
.900	28		67	126	84		29				22	
.840	42		118	187	124		38			32	36	
.800	52	23	138	225	152		44		18	54	44	
.750	74	45	171				54	30	24	86	54	20
.700	106	69	209		271	40	64	42	34	117	63	28
.650	134	90				66	77	57	48	148	76	35
.600	159	119				105	93	87	67	206	98	44
.550	182	148				133	117		89		123	54
.500	204	177				178	190		121		154	64
.450	243	208				221					189	77
.400	294	244				283					226	91
.375		267				308					248	100
.350		296									287	112
.325												126
.300												146
.275												177
.250												230
.225												
(A obs.)	.104	.067	.599	.508	.460	.135	.390	.518	.452	.431	.320	.200

*Time in seconds.

Absorbancy versus time*: Series U and O^4 at 0°C.

	Reaction Number												
	U-1	4	5	6	8	11	12	13	14	16	17	18	O^4-3
A(cell)	+.004	+.004	+.003	-.003	+.003	+.003	-.003	+.004	+.003	+.004	+.003	-.003	+.002
A obs.													
1.300	17		14										
1.250	24	15	25	20	18	20	25				24		
1.200	39	29	38	32		27	34		22		33	21	
1.150	55	47	55	49	29	38	46	18	33	24	47	32	
1.100	67	62	68	61	33	46	55	24	42	32	57	41	
1.050	81	74	83	77	37	56	66	31	52	41	68	51	
1.000	96	92	101	94	42	66	78	40	65	52	82	63	
.950		113		115	50	79	93	51	80	65	100	76	
.900	128	129	136	130	55	88	103	58	89	73	111	86	
.850	153	156	183	157	63	105	121	72	108	90	132	105	
.800	169	175	212	177	68	133	133	81	121	100	148	116	
.750	194	203	241	205	76	150	153	96	140	117	172	135	13
.700	219	233	276	236	85	170	171	113	161	133	197	154	24
.650	247	267	320	270	94	196	193	132	184	152	226	177	35
.600	278	310		317	106	226	229	158	214	174	266	204	49
.550	315				120	265	250	192	251	199	319	238	62
.500					137		286	241	300	226		280	77
.450					161					261			94
.400					196					305			112
.350					269								131
.300													151
.250													174
.200													195
(A obs.)	.120	.295	.322	.340	.292	.236	.294	.389	.354	.201	.397	.326	...
A obs. in 4 ml.-volume after addition of 1 ml. Ce (IV)													.145

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*Time in seconds.

Absorbancy versus time* at various temperatures: Series A and K

	Reaction Number											
	20°-A-1	2	3	8	9	10	11	12	15	15°-K-3	5	6
A(cell)	+.009	+.009	+.009	+.009	+.009	+.009	+.009	+.005	+.009	0.00	0.00	+.004
A obs.												
2.050									9			
2.000								11	15			
1.900				8	11	10		19	26			
1.880	12											
1.850			15									
1.800			19		15	13	12	37	42		6	6
1.700				17	21	17	17	60	70		10	9
1.600	27	20	22	21	27	23	24	95	87	14	15	
1.500	33	25	28	27	34	30	32	165	116	21	21	20
1.400	42	31	36	36	44	38	42			28	28	28
1.300			45	45	55					37	38	38
1.225	60	44					68					
1.200			55	57	70	59	72			49	50	50
1.125	75	54		69								
1.100				73	92	76	97			66	66	66
1.025	95	67	82	89	114	91	122					
1.000				98	125					96	86	86
.940		81		113	149		167			119	104	103
.900	129	88	111	127	171	125	196			136	117	115
.840	157	103	135	157		153	285			181	148	143
.800	180	113	152	184	284	175	387			228	175	167
.750	226			239		230				361	229	214
.700	293		227	333								
.690		155										
(A obs.)	.602	.421	.553	.638	.720	.600	.763	1.387	1.431	.715	.692	.642

*Time in seconds.

Absorbancy versus time*: Series K at 15°C.

	Reaction Number						
	9	10	11	12	13	14	15
A(cell)	+.004	0.00	+.004	-.008	0.00	-.008	+.004
A obs.							
1.800	5	5	4	7	4	6	7
1.700		9	7	13		13	9
1.600	13	14	11	18	8	16	14
1.500	20	20	18	24	17	22	19
1.400	28	29	27	33	25	29	26
1.300	37	40	37	43	36	38	35
1.200	49	53	50	58	50	50	47
1.150	56	61	58	66	58	57	54
1.100	64	71	68	76	68	66	61
1.050	73	81	78	88	80	76	70
1.000	92	98	94	105	99	89	79
.940	107	115	113	124	119	105	94
.900		130	127	139	134	118	104
.840	143	160	157	175	168	146	126
.800	163	187	182	205	198	171	143
.750	199	239	233	269	267	221	177
.700	254		317			283	212
(A obs.)	.603	.645	.643	.670	.678	.636	.573

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*Time in seconds.

Absorbancy versus time* at various temperatures: Series C

A(cell)	Reaction Number											
	15°-7 +.002	8 +.006	9 +.001	5°-26 +.002	33 +.001	35 +.006	36 +.001	10°-38 +.006	39 +.001	41 +.006	43 +.002	45 +.001
A obs.												
1.600				8	9	8	10	9	7	8	7	8
1.550				18								
1.500		10		21	19	13	19	11	10	13	17	13
1.450			7									
1.400	21	12		33	31	33	29	22	18	22	21	23
1.350			19	39								
1.300		19		45	43	16	42	31	28	29	28	31
1.250				52								
1.200	39	29	39	59	57	60	55	40	39	39	37	42
1.150			48	67								
1.100	54	41	60	76	71	78	70	52	50	49	46	53
1.050			75	86			79					
1.000	73	58	116	100	98	115		74	71	74	63	73
.950			154	113	109	129	107	83	80	82	69	82
.900	106	81	187	122		138	119	89	85	87	74	86
.850	140			139	132	155	126	101	96	95	83	99
.800	172	122		151	142	166	141	109	103	101	88	106
.750	244	156		170	157	185	150	122	113		96	117
.700		206		189	172	204	166	135	125	120	104	128
.650				213	190	228	182	149	138	130	114	140
.600				244			201	169	156	143	125	156
.550					213		224	191	175	157	138	173
(A obs.)	.569	.592	.759	.308	.254	.297	.242	.260	.219	.155	.178	.254

*Time in seconds.

Absorbancy versus time* at various temperatures: Series 0

A(cell)	[illegible]										
	5°-29 ±.006	30 ±.001	31 ±.002	32 ±.006	34 ±.002	10°-40 ±.002	44 ±.006	20°-26 ±.006	27 ±.001	15°-53 ±.006	54 ±.001
A obs.											
1.700	9										
1.600	15	11		11	11	10	9				
1.550			9	17							
1.500	22	21			18	16	13			8	12
1.450			18	25							
1.400	33	30	22		28	23	21	9	7	12	
1.350				35							
1.300	45	43	31		39	31	30			16	
1.250				46							
1.200	59	56	42		52	40	39	18	14	21	
1.100	75	71	54		67	52	50	27	19	26	28
1.000	110	93	69	99	92	69	71		25	35	38
.950		105	78	109	104	77	79				
.900			85	117	113	82	84		30	41	45
.850		125	98	131	128	92	94				
.800	156	136	106	142	139	98	101	39	37	48	53
.750	172	150	118	157	156	107	111				
.700	190	165	132	174	174	115	121	47	46	57	65
.650	210	182	145	196	195	125	132			63	72
.600	237	204	163	223	223	137	147	57	58	70	82
.550		228	183			154	163			79	94
.500		258	209			170	181	71	75	88	113
(A obs.)	.277	.252	.256	.331	.292	.190	.213	.169	.227	.296	.340

*Time in seconds.

Absorbancy versus time* at various temperatures: Series 0

	Reaction Number											
A(cell)	25°-1 +.002	2 +.006	3 +.001	4 +.002	6 +.001	15°-46 +.002	47 +.006	48 +.001	49 +.002	50 +.006	51 +.001	52 +.002
A obs.												
1.650	10				6							
1.600		6	6	5								
1.500						6	9	8	9		10	5
1.400					11	13	12	12	11	11	12	11
1.300						17	16	15	17	15	16	14
1.250	16	15	15									
1.200						23	21	19	22	19	22	21
1.150				14								
1.100		19	20		22	27	28	25	27	25	27	27
1.050				23								
1.000		24			29	34	39	34	32	35	39	34
.900	27			38	36	42	45	40	39	40	45	40
.800	32	33	32	47	45	52	54	47	48	48	53	49
.750						59						
.700	39	40	39	59	55	67	66	57	59	53	64	60
.650							74	63	67		72	66
.600	47	47	46	74	69	89	86	70	76	71	81	75
.550						107	103		88	81	94	86
.500	55	55	54	96	88	141	133	92	106	93	113	101
.450				112	101	248	202	113	123	113	149	127
.400	63	64	61	133	119			151	185	151	238	180
.300	72	73	68	214	178							
.200	82	82	76									
	.667	.590	.607	(A obs.)		in 4-ml. volume after addition of 1 ml. Ce(IV)						
(A obs.)	...	...	...	.163	.145	.387	.369	.295	.320	.260	.326	.326

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*Time in seconds.