A KINETIC STUDY OF THE ELECTRON EXCHANGE REACTION BETWEEN THALLIUM(I) AND THALLIUM(III) IN AQUEOUS SULFURIC ACID SOLUTIONS

By

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A THESIS

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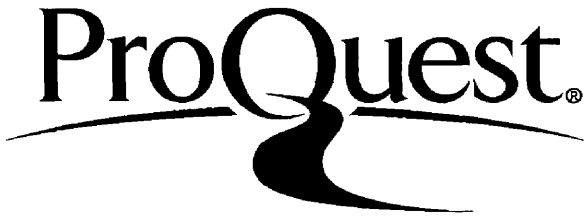

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ABSTRACT

Six separate kinetic studies of the electron exchange reaction between thallium(I) and thallium(III) were carried out in aqueous acid solution.

The work included studies designed to determine the effect of variations in the concentrations of thallium(I), thallium(III), sulfate ion, hydrogen ion, and chloride ion and the effect of changes in ionic strength and temperature on the rate of exchange.

It was found that the reaction is first order with respect to thallium(I) and thallium(III) and that the rate is 200 times as fast in sulfuric acid solutions as in perchloric acid solutions of the same ionic strength and hydrogen ion concentration. The effect of hydrogen ion and sulfate ion on the exchange rate is predicted by any one of three empirical rate equations. The equations and some possible mechanisms which lead to each have been discussed.

The addition of chloride to reaction mixtures in 2.19 M sulfuric acid decreases the rate of exchange to a minimum value of 1/300 that in sulfuric acid solution alone. The minimum is found at a $[Cl^-]/[Tl(III)]$ ratio of 2.5. The rate increases again at higher ratios of $[Cl^-]/[Tl(III)]$. The relationship between the stability of the chloride complexes of thallium(I) and thallium(III) and the effect of chloride on the rate of the exchange have been discussed.

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I. INTRODUCTION

In order to predict the course of a reaction in aqueous solution, the chemist must know what solute species are present and what role each will have in a given chemical environment. Quite often this information is not available, especially if the reaction is to be carried out at high ionic strengths. There are a number of methods by which the solvent species may be identified, but reaction rate (i.e., kinetic) studies are the only means by which their behavior may be quantitatively predicted.

Our lack of understanding of aqueous solutions is strikingly exemplified in the case of oxidation-reduction reactions. Many are fast and reach equilibrium in time of mixing. Several proceed so slowly that their rates are not detectable. None of the theories proposed to explain these differences in rate has proved to be generally applicable.

Shaffer (1) proposed what is called the equi-valence exchange theory. He stated that a slow rate of reaction would be expected where the valence change of the oxidizing agent is different than that of the reducing agent. For instance, the reaction between cerium(IV) and thallium(I) was cited. Although this reaction is very rapid in hydrochloric acid it is very slow in the presence of sulfuric acid. One would expect either a stepwise oxidation of thallium(I) ion by two cerium(IV) ions or a simultaneous reaction between two cerium(IV) ions and one thallium(I) ion. The latter process, requiring three body

collisions should be slower than one requiring two body collisions. If the reaction took place by the stepwise process, third order kinetics would not occur. Weiss (2) suggested coulombic effects could be the cause of the slow rates observed. The objection to the stepwise process was that it involved, as a transient intermediate, thallium(II), until recently an unknown oxidation state for this element. The work of Johnson (3) and of Ashurst and Higginson (4) shows that thallium(II) is an intermediate in the reaction between iron(II) and thallium(III) in sulfuric acid.

It was felt that a kinetic study of the cerium(IV)-thallium(I) reaction in sulfuric acid might shed more light on the mechanism of reactions of this type. However, preliminary laboratory studies indicated that this reaction is too slow for a thorough kinetic study to be practical. It is interesting to note that Duke and Borchers (5) found no reaction between the same ions in perchloric acid solution.

Study of the reaction between thallium(III) and titanium(III) was also considered. It is very similar to the reaction between iron(II) and thallium(III) in that both are very slow in hydrochloric acid. The thallium(III)-titanium(III) system was not considered further when it was found that the rate of the reaction was too rapid to allow the collection of reliable kinetic data.

In view of the somewhat contradictory evidence concerning the effect of sulfuric acid on the reaction rate between thallium ions and other redox reagents, it was decided to study the kinetics of the electron exchange between thallium(I) and thallium(III) in this medium.

Studies of electron exchange between forms of the same element have the additional advantage that the number of ionic species present is reduced, thus facilitating correlation of the data. This same exchange reaction has been thoroughly studied in perchloric acid (6,7,8,9). It was hoped that a comparison of the reaction mechanism in both acids would explain the unusual effects in sulfuric acid solution.

II. HISTORICAL

A. Thallium Chemistry

Thallium differs from other members of the boron group (IIIb) in that it forms monovalent compounds which are more stable than its trivalent compounds. Thallium(I) hydroxide which is formed slowly by the action of aerated water on the metal, or by hydration of the oxide, is comparable to sodium hydroxide in basicity and is even more basic towards the weak acids such as phenol. Thallium(I) ion resembles the alkali metal ions and is often found with them in natural ores. Its similarity to silver lies in the slight solubility of salts such as chromate, sulfide and halides. The oxidation of thallium(I) ions to give insoluble thallium(III) oxide can be effected in basic solution with hydrogen peroxide, potassium hexacyanoferrate(III) sodium hypochlorite or potassium permanganate. Cerium(IV) sulfate and potassium bromate can be used in the presence of hydrochloric acid to oxidize thallium(I) to thallium(III). Thallium(III) oxide is formed by heating the metal in air below a red heat or by hydrolysis of neutral or basic solutions of thallium(III) ions. Iodide ion, sulfur dioxide or hydrogen peroxide in acid solution will reduce thallium(III) ion to the lower valence state and zinc will reduce either ion to give the metal.

It can be seen that the oxidation of thallium(I) or the reduction of thallium(III) ions in solution can be carried out by means of a number of readily available reagents; however, in some cases the nature

of the medium in which the reaction is carried out has a pronounced effect on its rate. One of the classic examples of this is the reaction between thallium(I) and cerium(IV). In hydrochloric acid solution the reaction is rapid and complete, while in sulfuric acid solutions or in hydrochloric acid solution containing as little as 0.5M sulfuric acid the reaction is extremely slow. Shaffer (1) estimated that the half life of the reaction in sulfuric acid solution is of the order of 1000 hours. Duke and Borchers (5) report that there is no evidence for reaction between these ions in perchloric acid. It is interesting to note that the presence of sulfate slows the oxidation of thallium(I) ions while the reduction of thallium(III) is accelerated. An opposite effect is found in the case of the chloride ion. The reduction of thallium(III) with titanium(III) has been reported (10) to be slow in hydrochloric acid. The reaction between thallium(III) and iron(II) is slow in the presence of chloride ion and accelerated by sulfuric acid and one might expect the thallium(III)-titanium(III) couple to be similarly effected. The kinetics of the reduction of thallium(III) with iron(II) has been studied by Johnson(3) and others (4). The rate of the second-order reaction in perchloric acid solution is increased by the addition of sulfuric acid and decreased by hydrochloric acid. In order to explain the second-order kinetics and the nonequivalence of electron exchange Johnson proposed a stepwise mechanism for this reaction. In the work, he found no evidence for a retarding effect due to iron(III) which, in view of the role it had in the rate determining

step, left some doubt as to the validity of his mechanism. Later work by Ashurst and Higginson (4) showed that iron(III) did retard the rate.

Two possible mechanisms proposed by Johnson are:

(1)

$$Tl(III) + H_2O \xrightarrow{K_1} TlOH^{++} + H^+ \quad \text{(Rapid, reversible)}$$

$$Fe(II) + TlOH^{++} \xrightarrow{k_1} Fe(III) + TlOH^+ \quad \text{(Rate determining)}$$

$$Fe(II) + Tl(II) \longrightarrow Fe(III) + Tl(I) \quad \text{(Rapid)}$$

or

$$Tl(II) + Tl(II) \longrightarrow Tl(III) + Tl(I) \quad \text{(Rapid)}$$

(2)

$$TlOH^{++} + H_2O \quad K_2 \quad TlO^+ + H^+ \quad \text{(Rapid, reversible)}$$

$$Fe(II) + TlO^+ \xrightarrow{k_2} FeO^+ + Tl(II) \quad \text{(Rate determining)}$$

$$Fe(II) + Tl(II) \longrightarrow Fe(III) + Tl(I) \quad \text{(Rapid)}$$

or

$$Tl(II) + Tl(II) \longrightarrow Tl(III) + Tl(I) \quad \text{(Rapid)}$$

The following rate law agrees (within one percent) with his experimental data.

$$-dFe/dt = k_1 \frac{K_1}{[K_1+(H^+)]}[Tl(III)][Fe(II)] + \frac{k_2K_2}{(H^+)[K_1+(H^+)]}[Tl(III)]$$

$$[Fe(II)][K_1+(H^+)]$$

The K's are hydrolysis constants defined by the equations above and the k's are specific rate constants. Values of the first hydrolysis constant were obtained from the data of Prestwood and Wahl (6) and that of Barbottle and Dodson(7). It is of interest to note that in a polarographic study (11) of the reduction of thallium(III), no evidence for the presence of thallium(II) was discovered.

B. Electron Exchange Studies

The term "electron exchange reaction" can be used with reference to any oxidation-reduction reaction. It has come to mean those reactions involving the simultaneous oxidation-reduction of two kinds of ions of one element wherein there is no change in the concentration of either ion.

Although it was generally accepted that a dynamic equilibrium existed in a solution containing two ions in different oxidation states, proof of this fact awaited the development of radiotracer techniques. Early studies in this field were often handicapped by a lack of convenient isotopes. For example, Zirkler (12) and, later, Majors (13) studied the exchange between thallium(I) and thallium(III) using thorium C'' [an isotope of thallium (Tl^{208})] as a tracer. The short half-life of the isotope (3.1 minutes) made the study difficult and inconclusive. Recently Prestwood and Wahl (6) and others (8,9,14) have made a thorough study of this exchange in perchloric acid making use of the four year Tl^{204}. Amphlett (15), in a review of isotopic exchange reactions points out that with the exception of hydrogen nuclides and organic exchange reactions relatively little exchange work has been done.

In their studies of the exchange reactions between thallium(I) and thallium(III) Prestwood and Wahl found that nitrate ion and platinum black accelerated the reaction while an increase in hydrogen ion concentration brought about a decrease in rate. They used sodium perchlorate to maintain a constant ionic strength of 3.68. Harbottle and Dodson (7)

carried out a similar study at an ionic strength of 6.0 and investigated the effect of chloride ion on the rate. Later Dodson (9) extended the study to cover the range from 0.5 M to 6.0 M hydrogen ion and an ionic strength of 0.5 to 6.0. Comparison of the results shows excellent agreement but their interpretations of the role of hydrogen ion in the reaction are somewhat different. Rossotti (16), using recently reported values of the hydrolysis constant showed that Prestwood and Wahl's (6) interpretation was probably the better of the two. Rossotti also pointed out that, although recent work has shown that a fifty percent replacement of sodium ion by hydrogen ion in 3 M sodium perchlorate has a negligible effect on the activity coefficients of the cationic reactants, replacements of up to 95 percent used in the exchange experiments might very well have an effect of a magnitude comparable to the observed variations of the specific rate constants and that for this reason the results should be viewed with caution.

Fronhers and Lih (17) Benoit (18) and others (19,20) have studied the complexes formed by thallium ions in the presence of chloride ions. Harbottle and Dodson (7) were able to interpret their data qualitatively in light of this work and correlate it with the reactive species in solution.

The potential studies of Noyes and Garner (21) et al., (22,23) indicate that there are no complexes formed between sulfate ion and either of the thallium species. This can be compared with the observation of Johnson (3), that sulfuric acid accelerates the reaction between thallium(III) and iron(II) in perchloric acid. Willard and

Young (24) reported that 5 ml. of 1.5 specific gravity sulfuric acid or 70 percent perchloric acid would slow the reaction between cerium(IV) sulfate solutions and thallium(I) ion solutions containing 1 M hydrochloric acid.

Recently Challenger and Masters (25) in preliminary experiments on the x-ray induced exchange between thallium(I) and thallium(III) studied the thermal exchange and found that the reaction was much faster than in perchloric acid.

III. THEORETICAL

It has been shown that, in an exchange reaction where the concentrations of the reactants remain the same throughout, where the exchanging atoms are of the same element, a first order rate law for the transfer of activity from ions of one oxidation state to the other will apply no matter what form each species has in the solution. The derivation of the exponential rate law for this exchange process has been fully described (26,27) and only its logarithmic form is shown here.

$$(1) \qquad -\ln(1-F) = R\,\frac{[Tl(I) + Tl(III)]\,t}{[Tl(I)][Tl(III)]}$$

In the equation Tl(I) and Tl(III) refer to total concentration of each valence state and F, the fraction of exchange, is the ratio of specific activity at any time to the specific activity of the fraction at equilibrium, when the precipitated portion is the initially inactive species. The rate R is defined by the equation:

$$(2) \qquad R = k\,[Tl(I)]^{\alpha}\,[Tl(III)]^{\beta}$$

where k is the specific rate constant and α and β are constants which are one for a second order reaction.

It can be seen from equation (1) that a semilog plot of (1-F) versus t will give a straight line passing through 1.0 at zero time if the specific activity at time t for each sample is representative of

the extent of homogeneous exchange at time of separation. Experimentally this is seldom the case.

Early workers in the field of electron exchange reactions failed to recognise that a chemical method used to separate the fractions may induce some exchange because, during the formation of the precipitate, several intermediate species may be involved, which may exchange much faster than any of the species present during the undisturbed homogeneous exchange. In addition to the induced exchange, heterogeneous exchange between the solution species and the precipitate may occur to an appreciable extent and separation may be incomplete.

Amphlett (15) points out that in cases where the exchange is reported to be complete in time of mixing and separation, the work should be viewed with caution due to the possibility that rapid induced exchange may occur during the separation. Haissinsky (28) has suggested that precipitation of the higher valence species might be expected to produce more induced exchange because of the formation of a greater number of transient intermediates in the formation of a precipitate. In support of Haissinsky's proposal, Prestwood and Wahl (6) found 65% induced exchange when thallium(III) was precipitated as the oxide. Only 5-10% occurred when thallium(I) was precipitated. They studied the precipitation of thallium(I) as the chromate, bromide, and hexachloroplatinate. Thallium(I) chromate precipitation was found to give only about 5% induced exchange. The extent of the heterogeneous exchange can be determined by separate experiments but there is no direct method for determining the extent of induced exchange.

Prestwood and Wahl (6) have shown that if the extent of induced exchange is reproducible the following relation applies.

$$(3) \qquad F = \frac{[F' - F_o']}{[1 - F_o']}$$

In the equation F' refers to the observed fraction of exchange at time t and F_o', to the fraction of exchange at zero time. However, it can be shown by substitution for F in equation (1) that the semilog plot of $(1 - F')$ versus t will have the same slope as that of $(1 - F)$ versus t. The intercept will not be unity. Values of the half life and the specific rate constant can be obtained from the slope of the graph. The half-life is related to the specific rate constant k by the following equation.

$$(4) \qquad t_{\frac{1}{2}} = x \frac{.693}{[T1(I) + T1(III)]}$$

The Arrhenius equation satisfactorily explains the temperature dependency of the specific rate constant for a large number of reactions. Deviations from the law are taken to mean that the reaction in question is complex and that different types of reactions are in effect at different temperatures. The derivation of the equation can be found in any standard text book on kinetics (29,30) and only the result will be shown here.

$$(5) \qquad \ln k = -E_a/RT + C$$

It can be seen that a semilog plot of the specific rate constant against the reciprocal of the absolute temperature will give a straight line

and E_a can be determined from the slope. In the equation, k is the specific rate constant, E_a, the energy of activation, R, the gas constant, and T is the absolute temperature.

IV. EXPERIMENTAL PROCEDURE

A. Raw Materials

Thallium(I) nitrate was obtained from E. H. Sargent and Company. Lithium sulfate, lithium carbonate and sodium dichromate were purchased from Merck and Company, and sodium cyanide, from Mallinckrodt Chemical Works. All acids used in these experiments (except perchloric acid) were obtained from E. I. du Pont de Nemours and Company. Perchloric acid came from J. T. Baker Chemical Company. The radioactive tracer used to follow the exchange was prepared by Oak Ridge National Laboratories by irradiation of Tl^{203} with neutrons [$Tl^{203}(n, \ )Tl^{204}$]. Ten millicuries of Tl^{204} were shipped in ten milliliters of 3 M nitric acid. The ammonium hydroxide and sodium hydroxide were Baker's "Analyzed" reagent grade chemicals.

B. Preparation of Reagents

Thallium(I) sulfate was prepared from recrystallized thallium(I) nitrate by treating the latter with an excess of sulfuric acid and evaporating the solution on a hot plate to fumes of sulfur trioxide. Some of the thallium(I) salt is converted to the trivalent state by this process and in order to insure that all of the thallium was in the monovalent state the solution was treated with sulfur dioxide and evaporated to fumes of sulfur trioxide a second time to remove the excess sulfur dioxide. The salt was recrystallized from distilled water until free

of acid. Thallium(I) sulfate stock solutions were prepared with weighed amounts of this salt.

Thallium(III) sulfate solutions were prepared by treating thallium (III) oxide with concentrated sulfuric acid. The oxide was prepared by oxidation of thallium(I) sulfate solutions with potassium hexacyanoferrate(III) in 0.1 M sodium hydroxide solution. The oxide was washed free of hexacyanoferrate(II) and (III) ions by repeated treatment with hot water. The water was removed by decanting after the oxide had settled. After several washings, the oxide was separated by filtration. The thallium(III) sulfate solutions were analysed to determine the concentration of excess acid and both thallium(I) and thallium(III) ions. Total thallium was found by reduction of all the trivalent species to thallium(I) and precipitation as the chromate by methods described in standard analytical texts (31). The concentrations of thallium(III) and hydrogen ions were obtained in the following manner. Excess standard sodium hydroxide was added to the solution and the insoluble oxide separated by centrifuging. The oxide was washed several times and the washings were combined with the supernate from the precipitation and the excess base was titrated with standard acid. The hydrogen ion concentration in the original solution was found by a calculation which included a correction for the hydrogen ion formed in precipitating the oxide. The oxide precipitate was dried at 195°C for one hour and weighed. The thallium(I) ion concentration was found by the difference in the two analyses. The hydrogen ion concentration was also found in

a separate titration by treating a portion of the original solution with sulfur dioxide to reduce the thallium(III) to the monovalent state. The solution was then evaporated overnight on a steam bath to insure the removal of excess sulfur dioxide, and titrated with sodium hydroxide to a phenolphthalein end point. A correction was made for the hydrogen ion formed in the reduction of the thallium(III).

Lithium perchlorate was prepared from lithium carbonate by the addition of a slight excess of perchloric acid to lithium carbonate and evaporating the solution of a steam bath for over twelve hours. After cooling, the salt was separated by filtration and recrystallized from distilled water until free of acid and dried over a portion of the salt which had been dried in an oven at 110 to 115°C for 48 hours. In this manner, $LiClO_4 \cdot 3H_2O$ was obtained. A portion of the salt was dried for 60 hours at 200°C and weighed. The amount of water lost corresponded to that calculated for the trihydrate.

Lithium sulfate was recrystallized from distilled water and dried at 200°C. Sodium dichromate and sodium cyanide were used without further purification.

Standard sodium hydroxide solutions were prepared carbonate free and standardized against potassium acid phthallate. The sulfuric, perchloric and hydrochloric acid solutions were standardized by comparison with the sodium hydroxide.

The radioactive thallium nitrate solution was converted to thallium (I) sulfate and a small amount of iron(III) ion was added. The solution

was then made basic with ammonium hydroxide and filtered. The iron(III) hydroxide precipitate will carry down radioactive impurities which might be present in trace amounts. The solution was treated with potassium hexacyanoferrate(III) and sodium hydroxide solutions and allowed to settle. The oxide was washed several times by decantation, separated by filtration, dried at 195°C and weighed. The oxide (.0649 gm.) obtained in this manner was treated with 10 ml. of 9.28 M sulfuric acid and diluted to 250 ml. in a volumetric flask.

Twenty milliliters of this solution was added to a solution containing inactive thallium(I) carrier and was treated with sulfur dioxide. A thallium(III) sulfate solution was then prepared in a manner described previously. Analysis showed that the solution contained 0.08 M thallium(III) ion and 0.65 M hydrogen ion. One milliliter of this solution added to make 100 ml. total volume of a solution 0.01 M in each thallium(I) and thallium(III) ion which had an equilibrium specific activity of 12 counts per second per milligram. An aluminum absorption curve prepared from thallium(I) chromate precipitated from the above solution gave an initial half-thickness of 30 mg per cm^2 which is in good agreement with that found by Fajans and Voight (32).

The molar ionic strength and concentrations of the solutions used were calculated from data of Smith (33) by a method described earlier by Young and Blats (34). The solutions were made up from stock solutions shown in Table I.

TABLE I

LIST OF STOCK SOLUTIONS

Solutions	Concentration (M)
H_2SO_4	9.28
H_2SO_4	10.67
$HClO_4$	6.466
$HClO_4$	5.658
Tl_2SO_4	0.04424
Tl_2SO_4	0.0631
$Tl_2(SO_4)_3$	0.0564[a]
$Tl_2(SO_4)_3$	0.0002[b]
$Tl(ClO_4)_3$	0.0851[c]
$Tl_2(SO_4)_3$	0.0809[d]

[a] Tl(I) = 0.007
[b] Radioactive tracer solution
[c] Tl(I) = 0.003
[d] Tl(I) = 0.005

Thallium(I) perchlorate was prepared by the addition of perchloric acid to thallium(I) hydroxide. Thallium(I) hydroxide was prepared from thallium(I) sulfate by titration with standard barium hydroxide, evaporation until crystallization began, collecting the salt and recrystallising it twice from distilled water. Thallium(III) perchlorate solutions were prepared and analysed in the same manner as thallium(III) sulfate solutions with the exception that the acid used in the formulation was perchloric acid.

C. Details of Kinetic Studies

The exchange was carried out in solutions with molar ionic strengths of 3.68 except for the series used to study the variation of rate with

ionic strength. The concentrations of all solutions were 0.0100 M in thallium(I) ion and 0.0108 M in thallium(III) ion except for the series in which the dependence of the rate on thallium concentration was studied. All reactions were carried out in 100 ml. volumetric flasks.

The exchange was studied in the following manner. The desired concentrations of the species in each run were obtained and the volumes or weights of each substance determined and the correct volume of the major acid was added to each flask of a series. If the volume of added reagent was constant for a series of solutions the burette was marked with a red crayon at that volume to minimize the possibility of volume reading errors. The correct volume of thallium(III) and the thallium(I) solutions, the minor acid and lithium salt (if present) were added in that order. The distilled water was added last and the flask filled to a volume approximately one milliliter less than 100 ml. and the flask immersed in a water bath set at 24.94 ± 0.01°C. The flasks were allowed at least three hours to reach equilibrium temperature before the active thallium(III) sulfate was added.

Previous to starting a run a number of Whatman 540 (2.7 cm. dia.) filter papers were dried for one hour at 110°C and weighed. The weight of a dry filter paper was 30 ± 5 mg. A solution prepared as described by Harbottle and Dodson (7) was used to separate the thallium fractions. This was used within twenty-four hours after its preparation. The solution was filtered just prior to use and kept in an ice bath.

The active thallium(III) portion was added (1 ml in all cases), the volume adjusted, and the first shaking of the solution made in

15 seconds. The zero time was taken as the time of the first shaking. Stirring continued for one minute during which time the flask was tipped and shaken and brought upright 12 times. The first precipitation was made two or three minutes after the active thallium(III) had been added. The precipitation was carried out by withdrawing an aliquot from the flask with a pipette and adding it to twice its volume of precipitating solution. The size of the aliquot was 5 ml. for all runs in which the thallium(I) ion concentration was 0.0100 M. Ten ml. samples were taken when the thallium(I) species concentration was 0.0050 M. In more dilute solutions 5 ml. samples were taken, added to the precipitating solution and an aliquot of inactive thallium(I) sulfate solution added immediately of sufficient size to give a total of 13.1 mg. (theoretical) of thallium(I) chromate. In any case the weight of sample was maintained at 12 ± 2 mg. In order to keep the induced exchange as constant as possible the pipette drain time was controlled and was ten seconds in all cases.

The solution was swirled in an ice bath during the addition of the sample to counteract the heat of neutralization. Since thallium(I) chromate is difficult to filter unless the precipitate is aged, the solution was allowed to stand for five minutes before filtration was started. The filtration was carried out in a steel funnel with a removable chimney. At the point of contact with the filter paper the chimney was 19 mm inside diameter. The filter paper was placed on the support and the chimney placed on top. The rate of filtration could be controlled by means of an aspirator and a variable air leak. In all cases

the precipitate was in contact with the supernatant liquid for less than thirty minutes. Prestwood and Wahl have shown that the heterogeneous exchange between the complexed thallium(III) species and the thallium(I) chromate precipitate is very slow and would be negligible under these conditions. After filtration the sample was washed with four 0.5 ml portions of precipitating solution followed by four 0.5 ml portions of cold water. The chimney was removed in order to facilitate the washing procedure. After drying with suction the sample was placed on a plate and a metal cylinder placed on top of it to prevent curling. It was then dried for one hour at 110°C and weighed, mounted on cards previously marked for centering of the sample and counted. Self absorption is negligible in samples of this thickness. The washing procedure was tested and was sufficient to give paper which had background count and zero weight of sample when only active thallium(III) was present in the solution filtered.

The mounting cards were cut to fit the plastic holder of an R.C.L. steel castle. The sample was mounted in the center of and two centimeters below the 1.1 inch dural end window of a Tracer lab G-M tube. An R.C.L. (Mark 13, Model 1, Serial A-189) scaler was connected to the G-M tube. The tube had a flat plateau of over 200 volts and samples were counted using a voltage one hundred volts above the "knee." All samples were counted over an interval of time sufficiently long to obtain 10,000 counts. Two G-M tubes were used in the work. One used in the early part of the investigation had a "dead time" of 4×10^{-4} while the other had a "dead time" of 2×10^{-4} seconds. Coincidence and

background corrections were applied to each sample. The corrected radio-activity in counts per second was divided by the weight in milligrams to get specific activity. Equilibrium specific activity was found by a precipitation made after ten half-lives or by using a sample of a size such as to give the same weight as those in the run, reducing it with sulfur dioxide, removing the excess reducing agent and precipitating the sample in the normal way.

All samples in any one run could be counted in two hours and since the half life of Tl^{204} is 4.0 years it was unnecessary to correct for radioactive decay.

V. DISCUSSION OF ERRORS

The errors involved in this study are those encountered in mixing solutions, weighing and counting radioactive samples and in determining the extent of exchange.

Most of the samples weighed between ten and twelve milligrams. The weighing error was slightly greater probably than would be indicated by the sensitivity of the balance used due to the absorption of moisture by the filter paper during weighing. This was minimized by doing all weighings in the same manner.

The viscosity of the stock sulfuric acid solutions caused a somewhat greater error in standardizing these solutions and in preparing of reaction mixtures containing this acid than would be expected at lower concentrations. This error was kept at a minimum by standardizing the stock solution and preparing all reaction mixtures with the same burette. Care was taken to be sure that the delivery rate of the burette was constant during standardization and mixing of solutions. When these precautions were observed, the error in concentrations was less than one percent. Duplicate solutions were prepared which agreed within 0.5 percent.

Errors in counting radioactive samples were about one percent. The effect of these errors was minimized when the specific rate constants were obtained by the graphical methods used in this study. The equilibrium radioactivity had a crucial effect on the specific rate constant.

For this reason duplicate samples were taken for determining equilibrium specific activity.

Sampling was the greatest source of error. Variations in the method of delivering the aliquot for separation into the precipitating mixture affects the extent of induced exchange. Great care was taken to insure that the delivery time was always ten seconds. It is felt that this source of error explains the increased scatter of data when the concentration of either thallium fraction varied far from 0.0100 M.

VI. RESULTS AND DISCUSSION

Six separate studies were made during the course of the investigation. The molar ionic strength of the solutions used was maintained at 3.68 except for one series. This value of the ionic strength corresponds to that used by Prestwood and Wahl (6) in their work on the thallium exchange in perchloric acid. In one final series the ionic strength was varied in order to determine what effect this variable might have on the rate of exchange.

A. The Dependence of Exchange Rate on The Concentration of Thallium(I) and Thallium(III)

The rate of a second order reaction can be described in terms of the following equation which is discussed in the "Theoretical" section.

$$R = k\,[Tl(I)]^{\alpha}\,[Tl(III)]^{\beta} \qquad (2)$$

It can be seen that the rate of exchange, R, divided by the product of the total thallium(I) [Tl(I)] and total thallium(III) [Tl(III)] concentrations will be a constant provided that the exchange is actually first-order in each of thallium(I) and thallium(III), i.e., $\alpha = \beta = 1$.

A value for $\alpha = 0.98 \pm 0.06$ was obtained for constant values of thallium(III) from the slope of a log-log plot of R versus thallium(I) (see Figure 1). The data are listed in Table II. Similarly a value of $\beta = 1.00 \pm 0.01$ was obtained for constant values of thallium(I) from Figure 2. It was concluded that the reaction is second order [i.e., first

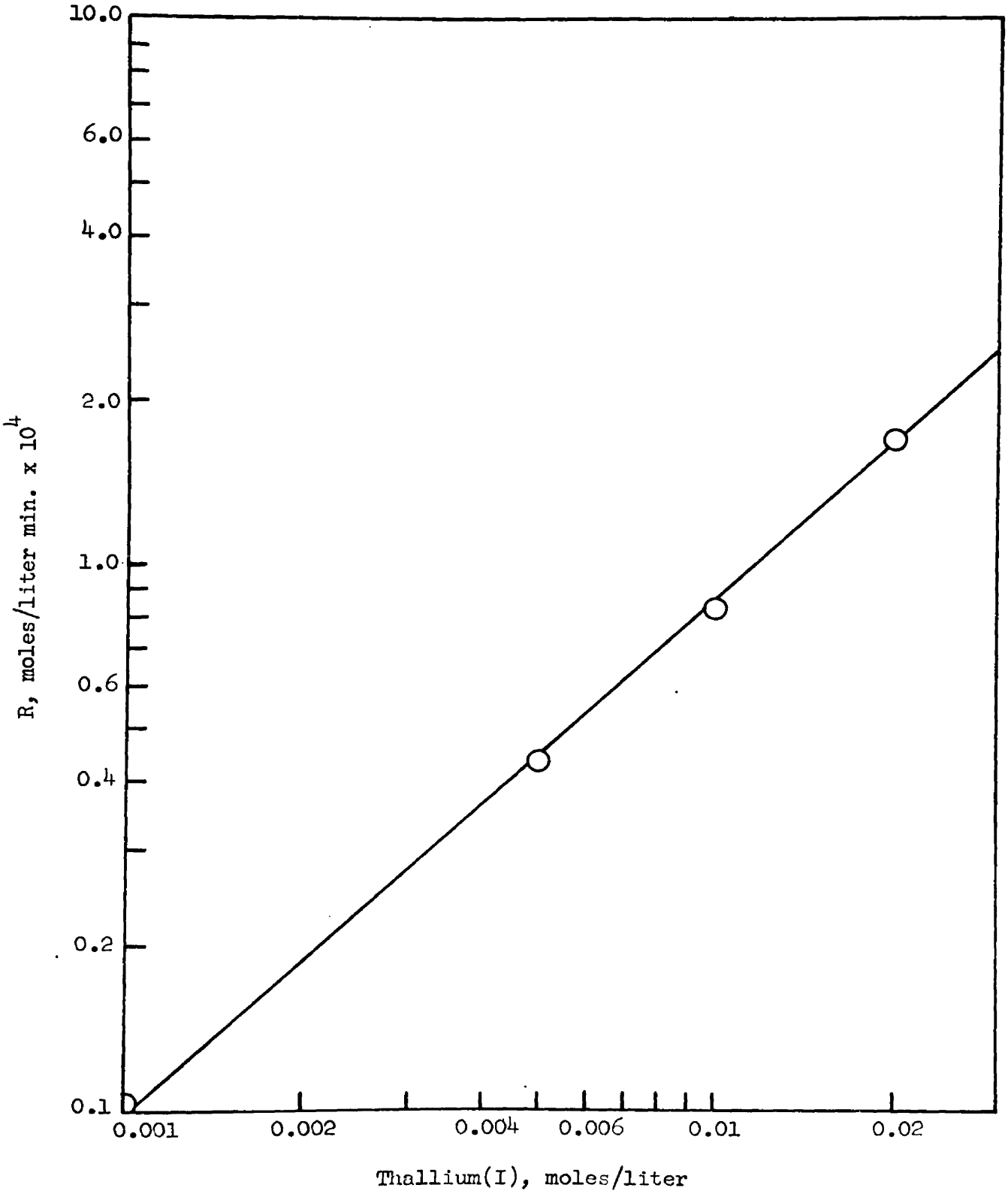

Figure 1. Dependence of Exchange Rate on Concentration of Thallium(I)

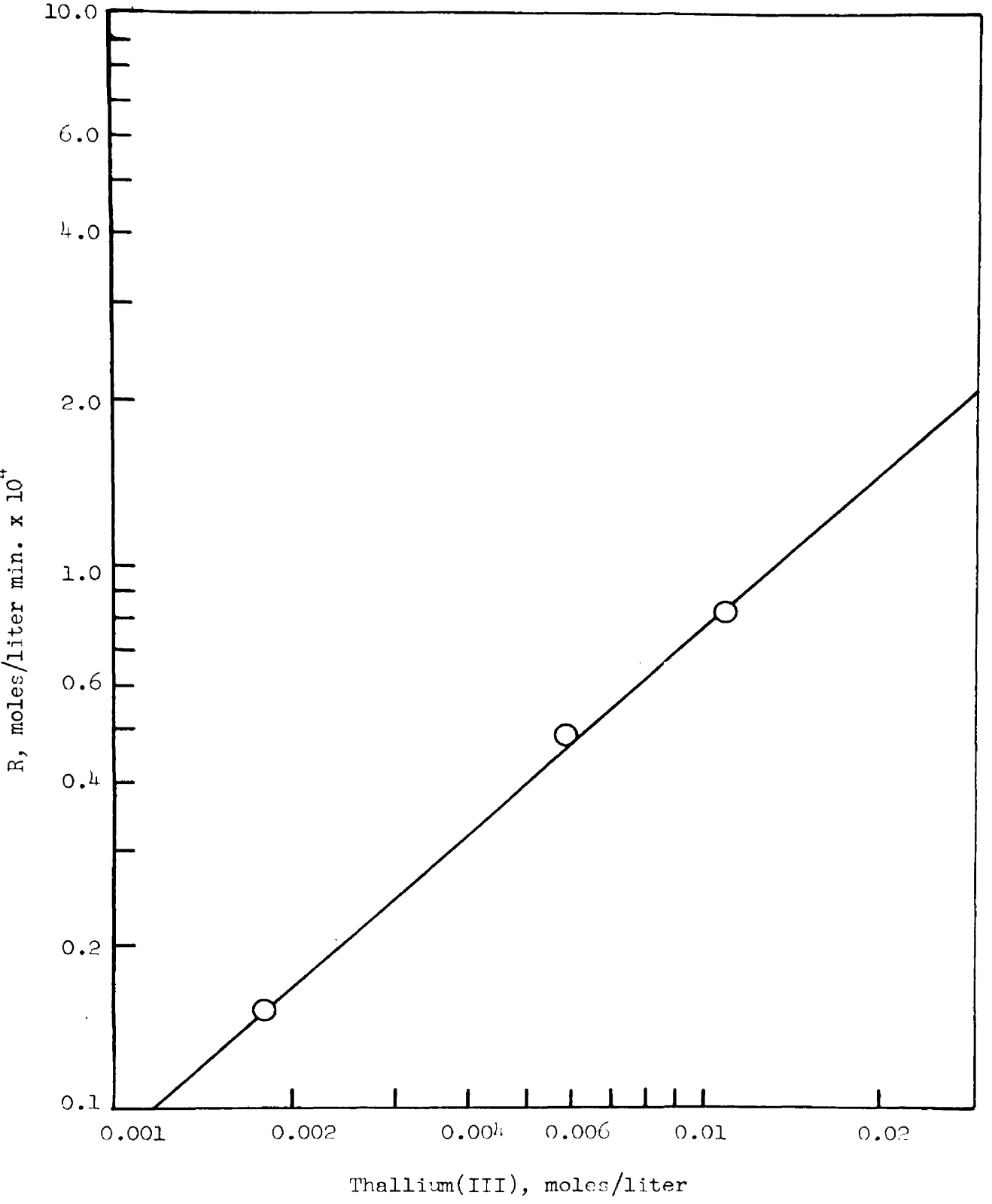

Figure 2. Dependence of Exchange Rate on Concentration of Thallium (III).

order with respect to each of the thallium fractions within the limits of experimental error).

TABLE II

DEPENDENCE OF EXCHANGE RATE ON CONCENTRATION OF Tl(I) AND Tl(III) AT 25°C., μ = 3.68; (H^+) = 2.90; ($SO_4^=$) = 0.70

Number of Runs	Tl(I) Moles/liter	Tl(III) Moles/liter	k Liter/mole-minute
4	0.0100	0.0108	0.77
1	0.0100	0.0058	0.84
1	0.0100	0.0018	0.85
1	0.0050	0.0108	0.81
1	0.0010	0.0108	0.95
1	0.0050	0.0058	0.74
1	0.0200	0.0108	0.79

B. Variation of Exchange Rate with Sulfate Ion Concentration at Constant Ionic Strength and Hydrogen Ion Concentration

The rate of exchange in 2.19 M sulfuric acid is approximately 200 times as high as that in perchloric acid solution at a comparable ionic strength and hydrogen ion concentration. In order to determine what species were responsible for the increase in rate, a series of experiments was conducted in which the proportions of sulfuric acid and perchloric acid were varied while the ionic strength and hydrogen ion concentrations were held constant. The data from these experiments are summarized in Table III. The results show that, as the sulfate ion concentration diminishes to a negligible value, k also becomes very small. The value of k in very nearly pure perchloric acid agrees quite well with that reported by Prestwood and Wahl (6). It was found that k

is proportional to the three halves power of the sulfate ion concentration. This value was obtained from the slope of the log-log plot of k versus sulfate ion concentration shown in Figure 3.

TABLE XII

DEPENDENCE OF EXCHANGE RATE ON SULFATE ION CONCENTRATION WHEN $\mu = 3.68$; $(H^+) = 2.90$; Tl(I) = 0.0100; Tl(III) = 0.0108

Number of Runs	$(HClO_4)$ M	(H_2SO_4) M	$(LiClO_4)$ M	$(SO_4^=)$ M	k Liter/mole-minutes (Exp.)	(Calc.)
4	0.000	2.19	—	0.70	0.77	0.79
1	0.0001	2.19	—	0.70	0.77	0.79
1	0.0010	2.19	—	0.70	0.76	0.79
1	0.0100	2.19	—	0.70	0.73	0.79
1	0.100	2.12	—	0.69	0.71	0.77
1	0.500	1.80	0.130	0.59	0.59	0.60
1	1.00	1.43	0.243	0.47	0.41	0.40
2	1.50	1.06	0.380	0.35	0.25	0.25
1	2.00	0.679	0.490	0.23	0.15	0.14
1	2.50	0.294	0.620	0.10	0.057	0.055
1	2.89	0.000	0.720	0.007	0.0044	0.004
1	3.50*	0.000	0.110	0.007	0.0039	0.004

*$(H^+) = 3.50$

It will be seen after considering further experimental evidence that this dependence of the rate constant on sulfate ion concentration is the result of several equilibria.

C. Variation of Exchange Rate with Hydrogen Ion and Sulfate Ion Concentration at Constant Ionic Strength and a Discussion of the Results

A series of measurements were made on a number of solutions wherein the molar ionic strength was constant (3.68) and the concentrations of both the hydrogen ion and sulfate ion were allowed to vary. The results are summarized in Table IV.

TABLE IV

DEPENDENCE OF EXCHANGE RATE ON HYDROGEN AND SULFATE ION CONCENTRATIONS
$\mu = 3.68$; Tl(I) = 0.0100; Tl(III) = 0.0108

Number of Runs	(H_2SO_4) M	(Li_2SO_4) M	(H^+) M	$(SO_4^=)$ M	k Liter/mole-minutes Exp.	Calc.
4	2.19	0.000	2.90	0.70	0.77	0.79
1	1.94	0.167	2.50	0.77	0.88	0.92
1	1.60	0.386	2.00	0.83	0.96	1.04
2	1.28	0.574	1.56	0.88	1.08	1.13
1	0.852	0.805	1.00	0.99	1.40	1.36
1	0.652	0.944	0.750	1.07	1.75	1.67
1	0.404	1.021	0.450	1.10	1.94	1.91

It has been found that the experimental variables of Tables III and IV can be correlated by means of any one of the three empirical equations shown below. The differences in the equations is brought about by variations in the importance placed on complexing and hydrolysis of the thallium.

$$(6) \qquad R/ab = 0.004 + 0.41(SO_4^=) + 0.93(SO_4^=)^2$$

$$(7) \qquad R/ab = 0.004 + \frac{9.27(H^+)^2(SO_4^=)^2 + 40.8(SO_4^=)^2}{[(H^+)^2 + K_1(H^+) + K_1K_2][1 + K_4(SO_4^=)]}$$

$$(8) \qquad R/ab = 0.004 + \frac{0.7(H^+)^2(SO_4^=) + 12(H^+)^2(SO_4^=)^2}{[(H^+)^2 + K_1(H^+) + (H^+)^2K_3(SO_4^=)][1 + K_4(SO_4^=)]}$$

where,

$$K_1 = \frac{(TlOH^{++})(H^+)}{(Tl^{+++})} \quad , \quad K_2 = \frac{(TlO^+)(H^+)}{(TlOH^{++})}$$

$$K_3 = \frac{(TlSO_4^+)}{(Tl^{+++})(SO_4^=)} \quad \text{and} \quad K_4 = \frac{(TlSO_4^-)}{(Tl^+)(SO_4^=)} \ .$$

The number 0.004 appearing in each equation is the value of the rate constant in perchloric acid when $\mu = 3.68$, and $(H^+) = 2.90$ M.

Equation (6) implies that the species of thallium(I) and (III) do not change with variations of sulfate and hydrogen ion concentration. It agrees with the experimental data of Table III but the calculated rate constants deviate from the experimental values of Table IV at low hydrogen ion concentrations. The assumption made in the derivation of this equation was that there were negligible changes in the hydrolysis of thallium(III) and the complexing of thallium(I) and (III) by sulfate ion over the range of hydrogen ion and sulfate ion concentrations used in the study. This is inconsistent with the data of Bell and George (35) on sulfate complexes of thallium(I) and with Biedermann's (36) work on hydrolysis of thallium(III) ions at high acidities. For these reasons it is believed that Equation (7) or (8) more accurately describes the reaction system.

It is evident from the much higher rate of electron exchange in sulfuric acid that the hydrolyzed species proposed (6,7) for the exchange mechanism in perchloric acid solutions are not the principal exchanging species in sulfuric acid. It seems reasonable to assume, however, that these hydrolyzed species are important concentration-wise in light of studies on the hydrolysis of thallium(III). Biedermann (36) has recently published values for the first and second hydrolysis constants which indicate the importance of $TlOH^{++}$ and TlO^+ ions in solutions of thallium (III) even at high acidities.

Several workers have shown that some complexing will occur in sulfuric acid solutions containing thallium ions. Moeller (37) has shown that a comparison of the average solubility product constants of thallium(III) oxide in the presence of sulfate ion with those obtained in other systems indicates that some complexing occurs. He also states that complex formation between thallium(III) and sulfate ion is extensive but not as extensive as that between thallium(III) and chloride ion.

The work of Drucker (36) and the more recent work of Bell and George (35) indicates that in solutions of thallium(I) sulfate, the complex species $TlSO_4^-$ is present in significant concentrations.

In light of the above considerations it is believed that the important species of thallium(III) species are Tl^{+++}, $TlOH^{++}$, TlO^+ and perhaps $TlSO_4^+$. The major species of thallium(I) are Tl^+ and $TlSO_4^-$. These assumptions lead to the following relations:

Let a = Total concentration of monovalent thallium.

Let b = Total concentration of trivalent thallium.

Then,

$$(9) \qquad a = (Tl^+) + (TlSO_4^-) = Tl^+ \left[1 + K_4(SO_4^{--})\right]$$

and, if only hydrolysis of thallium(III) is considered,

$$(10) \qquad b = (TlO^+) + (TlOH^{++}) + Tl^{+++} = Tl^{+++} \frac{\left[(H^+)^2 + K_1(H^+) + K_1K_2\right]}{(H^+)^2}$$

If complexing of thallium(III) with sulfate ion is extensive, then

$TlSO_4^+$ will be important concentration-wise and,

$$(11)\quad b = Tl^+ + TlOH^{++} + Tl^{+++} + TlSO_4^+ = Tl^{+++}\,\frac{[(H^+)^2 + K_1(H^+) + K_1K_2 + (H^+)^2K_3(SO_4^=)]}{(H^+)^2}$$

It is evident from Figure 3 that sulfate ion enters the rate law with a power greater than one. This indicates that some species other than those considered above were entering the reaction, although its concentration may be very small. Some examples are the higher complexed species such as $Tl(SO_4)_2^{-1}$, $Tl(SO_4)_2^{-3}$ and $TlOSO_4^{-1}$.

The following expression is one of several possible combinations which is compatible with this view and leads to Equation (7).

$$(12)\quad R = k_1[(TlSO_4^-)][(TlSO_4^+)] + k_2[Tl^+][Tl(SO_4^=)_2^{-3}]$$

If one uses the following definition:

$$K_5 = \frac{Tl(SO_4^=)_2^{-3}}{(TlSO_4^-)\,(SO_4^=)^2}$$

and remembers that k_o, the specific rate constant for the observed rate, is defined as R/ab, it is evident that substituting in Equation (12) for a and b [Equations (9) and (10)] the following expression will be obtained:

$$(13)\quad k = \frac{k_1K_2K_4(H^+)^2(SO_4^=)^2 + k_2K_1K_2K_4K_5(SO_4^=)^2}{[(H^+)^2 + K_1(H^+) + K_1K_2]\,[1 + K_4(SO_4^=)]} + k_o$$

where k_o is the rate in the absence of sulfate ion. This treatment

requires that $TlSO_4^+$ be important in the exchange and that it does not contribute significantly to the total thallium(III) concentration. Equation (13) can also be written in the following form:

$$(14) \quad k = \frac{A(H^+)^2(SO_4^{=})^2 + B(SO_4^{=})^2}{[(H^+)^2 + K_1(H^+) + K_1K_2]\,[1 + K_4(SO_4^{=})]} + k_0$$

Since K_1 has been estimated from other work (7) to have a value of 6.4, it was necessary only to determine values for K_2 and K_3. The best fit (Figure 4) resulted when $K_2 = 1$ and $K_3 = 2$. Equation (14) has been rearranged to the following form:

$$(15) \quad F = \frac{k\,[(H^+)^2 + K_1(H^+) + K_1K_2]\,[1 + K_4(SO_4^{=})]}{(SO_4^{=})^2} = A(H^+)^2 + B$$

A graph (Figure 4) of F versus $(H^+)^2$ has been prepared. From the slope, A = 9.27, and, from the intercept, B = 49.8. Equation (7) is obtained by substituting these values in Equation (14). When hydrogen ion concentration is constant, Equation (14) can be written:

$$(16) \quad k = \frac{C(SO_4^{=})^2}{1 + K_4(SO_4^{=})} + k_0$$

where

$$C = \frac{A(H^+)^2 + B}{(H^+)^2 + K_1(H^+) + K_1K_2} .$$

In Figure 5 a plot of $k[1 + 2(SO_4^{=})]$ versus $(SO_4^{=})^2$ has been made using the data of Table III. From the slope of the plot the value of C (3.66) can be obtained. This value is in good agreement with the calculated value of 3.81.

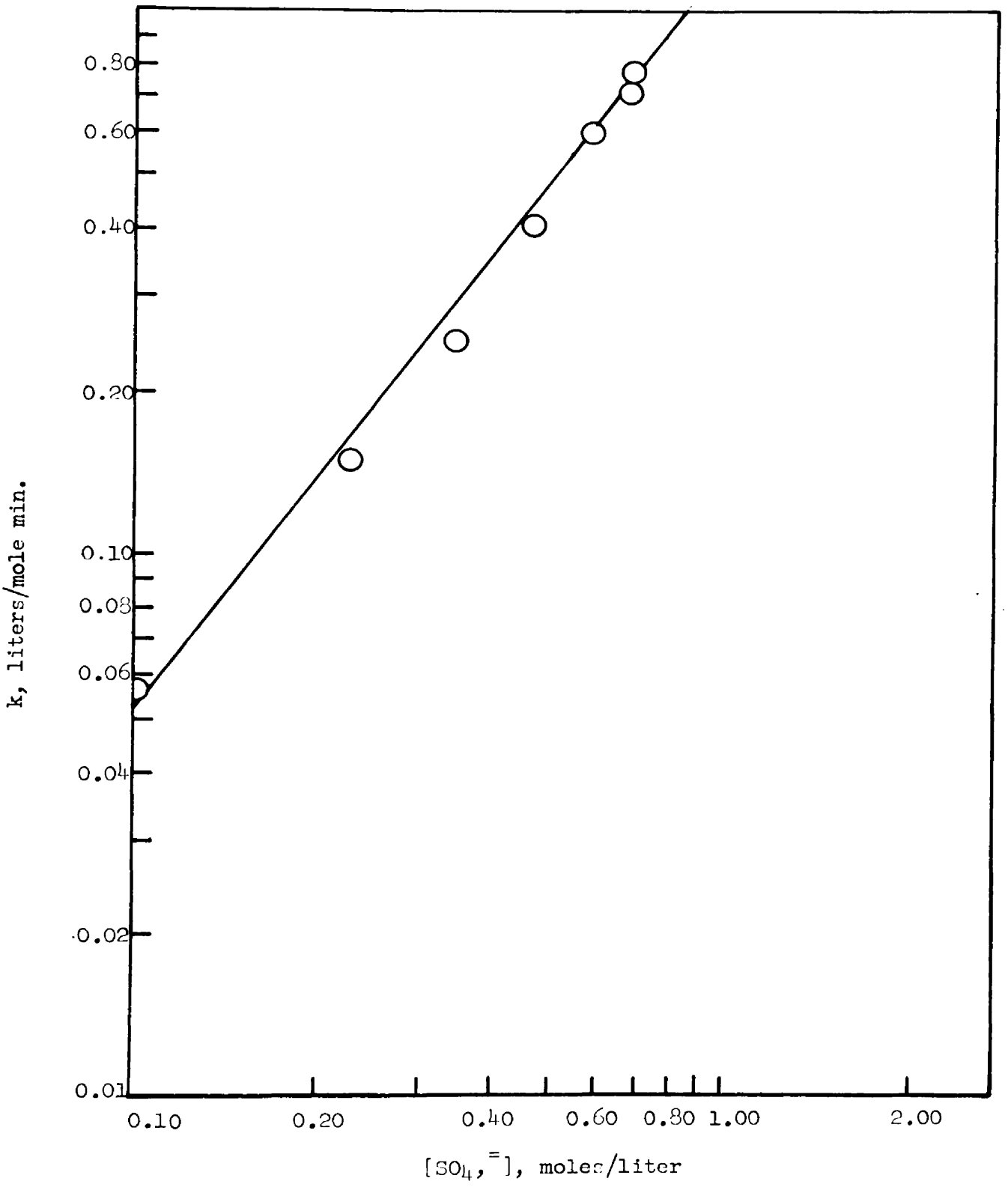

Figure 3. Dependence of Exchange Rate on Concentration of Sulfate Ion.

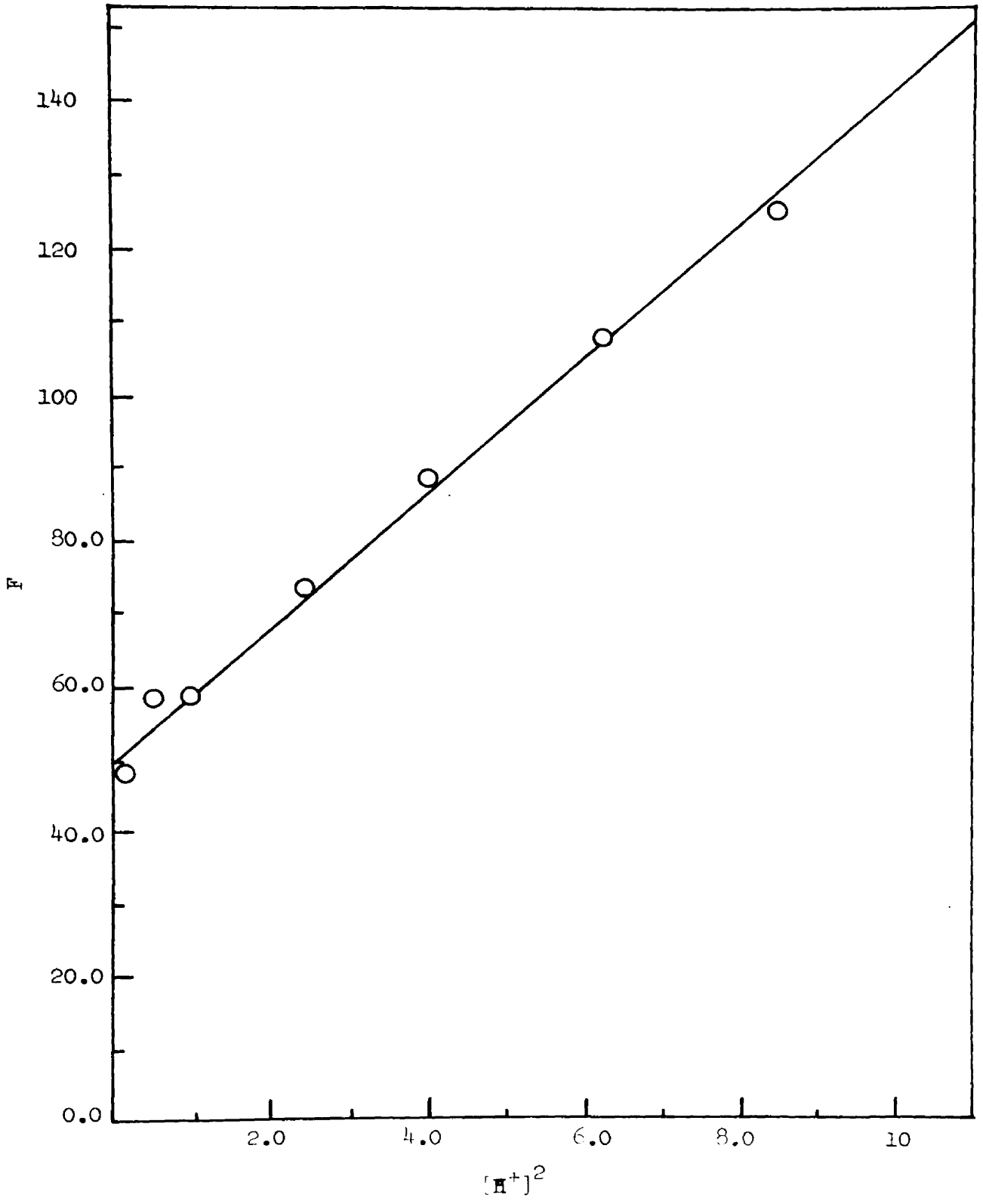

Figure 4. Dependence of Exchange Rate on Concentration of Hydrogen and Sulfate Ions. [Equation (15)]

If one considers that $TlSO_4^+$ is present in appreciable quantity and contributes significantly to the thallium(III) concentration, substitution of a and b from Equations (9) and (11) in Equation (12) yields

$$(18) \quad k = \frac{K' (H^+)^2 (SO_4^=) + K(H^+)^2 (SO_4^=)^2}{[(H^+)^2 + (H^+)K_1 + K_1K_2 + (H^+)^2 K_3(SO_4^=)] [1 + K_4(SO_4^=)]} + k_o$$

If K' and K'' have values of 0.7 and 12 respectively, then this is Equation (8). The values of the complexing and hydrolysis constants are different from those of Equation (7). If one uses Biedermann's (36) values of K_1 and K_2, 0.077 and 0.071 respectively, the above equation is more consistent with the experimental data of this study than is Equation (7). The value used for K_2 in this case differs considerably from the value of 6.4 which was reported by Hodson (7). The value of two for K_4 is consistent with the value obtained from the work of Bell and George (35), if their value of 23 for infinite dilution is corrected to an ionic strength of 3.68. K_5 is assumed equal to K_4 (21).

Both Equation (7) and Equation (8) are inconsistent with the work of Moeller (37) who indicates that K_3 is large. However, Equation (8) is consistent with the potential studies of Noyes and Garner (21) and others (22) who indicated that $K_3 = K_4$. The values of the specific rate constants predicted by Equation (8) are listed with the experimental values of Tables III and IV. The calculated values agree within experimental error with the experimental values of both tables. It is believed that Equation (8) more accurately represents the processes which were observed in this study than either Equation (6) or (7).

Any of the indicated combination of the following exchange processes will lead to an equation of the same form as Equation (7) or (8).

(a) $^{*}TlSO_4^{+} + Tl^{+}$ k_1 $TlSO_4 + {}^{*}Tl^{+}$

or

(b) $^{*}Tl^{+3} + TlSO_4^{-}$ k_1 $Tl^{+3} + {}^{*}TlSO_4^{-}$

and

(c) $^{*}Tl(SO_4^{=})_2^{-} + TlSO_4^{-}$ k_2 $Tl(SO_4)_2^{-} + {}^{*}TlSO_4^{-}$

(d) $^{*}Tl(SO_4)_2^{-3} + Tl^{+}$ k_2 $Tl(SO_4)_2^{-3} + {}^{*}Tl^{+}$

or

(e) $^{*}Tl\ SO_4^{+} + Tl(SO_4)_2^{-3}$ k_2 $Tl\ SO_4^{+} + Tl(SO_4)_2^{-3}$

($^{*}Tl$ is radioactive Tl^{204})

The large increase in the rate of reaction in sulfuric acid might be caused by the favorable charge effects between positive and negative exchanging species. For this reason equations (b) and (e) above would be favored.

It might be pointed out that the existence of negatively charged thallium(I) species might very well be the reason for the lack of reaction between cerium(IV) and thallium(I). This would still not explain why the reaction is so slow in perchloric acid.

D. Variation of Exchange Rate with The Concentration of Sulfuric Acid

A few experiments were carried out in which the ionic strength was allowed to vary. In order to do this, the amount of sulfuric acid present was varied, resulting in a corresponding variation in the

concentrations of the hydrogen and sulfate ions. The results and conditions are listed in Table V.

TABLE V

DEPENDENCE OF EXCHANGE RATE ON SULFURIC ACID CONCENTRATION
Tl(I) = 0.0100 M, Tl(III) = 0.0108 M

Number of Runs	(H_2SO_4) M	(H^+) M	(SO_4^{--}) M	μ	k l/mole-minutes
1	2.38	3.16	0.79	4.06	0.78
4	2.19	2.90	0.70	3.68	0.77
1	1.53	2.00	0.46	2.55	1.00
1	1.21	1.56	0.35	2.00	1.08
1	0.36	0.45	0.10	0.65	1.25

acid concentration. It was found that they rise more rapidly than sulfuric acid concentration. It was found that they rise more rapidly than predicted by Equations (6), (7) or (8) which would indicate that the decrease in ionic strength brings about a corresponding increase in the rate of exchange.

E. Variations of the Exchange Rate with Temperature

Variations in the rate of exchange have been measured at three different temperatures for solutions containing 0.0100 M thallium(I) and 0.0108 M thallium(III) and 2.19 M sulfuric acid. The results are shown in Table VI.

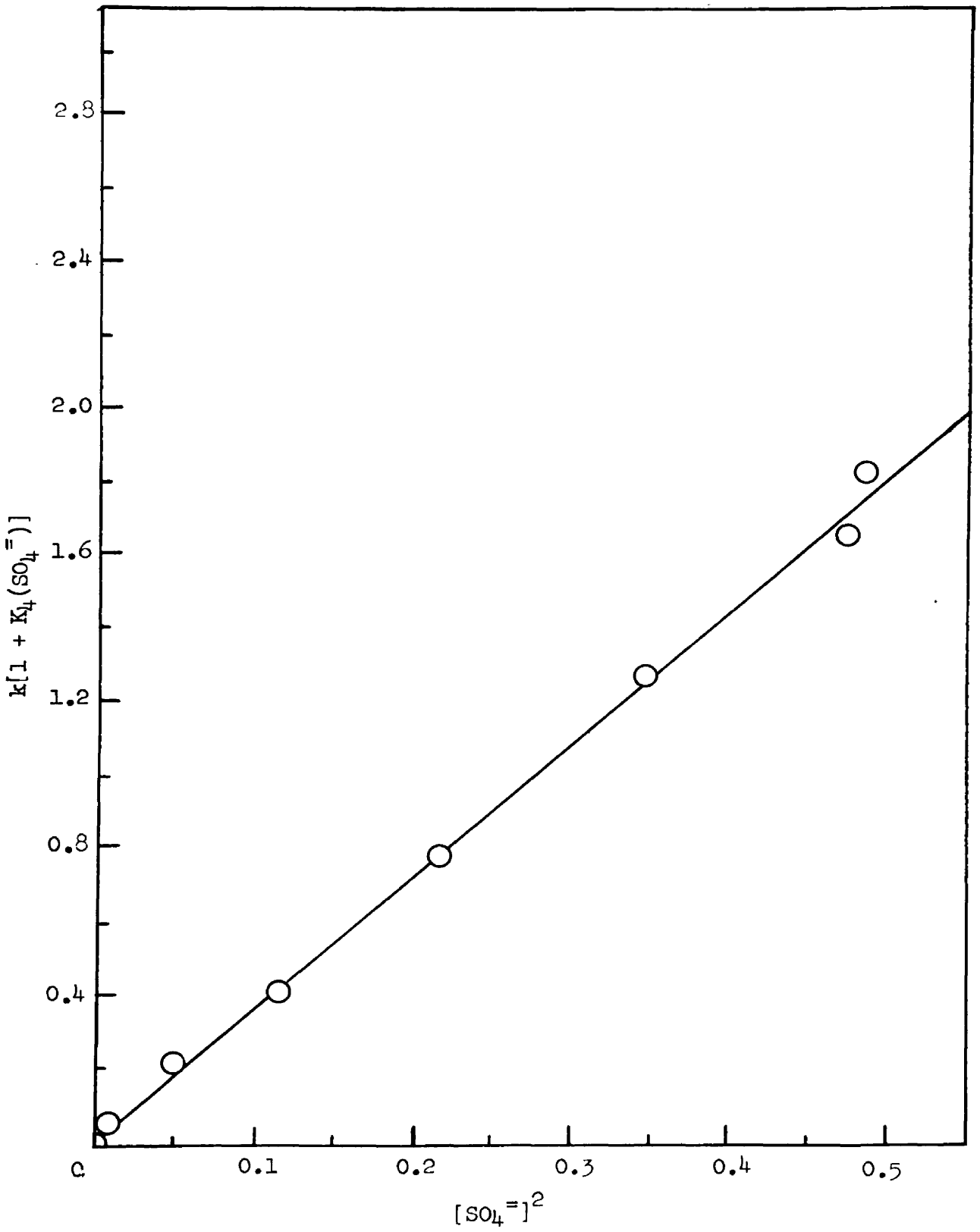

Figure 5. Dependence of Exchange Rate on Concentration of Sulfate Ion. [Equation (16)]

TABLE VI

DEPENDENCE OF RATE OF EXCHANGE ON TEMPERATURE
$\mu = 3.68$; $(H^+) = 2.90$ M; Tl(I) = 0.0100 M; Tl(III) = 0.0108 M; $(H_2SO_4) = 2.19$ M

Temperature °C	k (liter/mole-min.)
0.0	0.086
10.0	0.22
24.9	0.77

An Arrhenius plot of this data was made (Figure 6) wherein k is plotted against the reciprocal of the absolute temperature, T. The slope of this line gives values of E_a/R (3100) (see Equation (5) "Theoretical" section of this thesis). It was decided that no useful purpose could be accomplished by calculating an activation entropy because of the complex nature of the reaction; indeed one can scarcely justify a calculation of activation energy in this case.

F. Variation of Exchange Rate with Chloride Concentration

The exchange rate was studied in a series of solutions in which various amount of chloride ion were present. The chloride ion was added as hydrochloric acid. Hydrogen ion concentration and the ionic strength were constant throughout the series of experiments. In order to do this the sulfuric acid concentration was varied slightly. This variation was never more than 1.4 percent and was neglected in the treatment of the data. The data are summarized in Table VII.

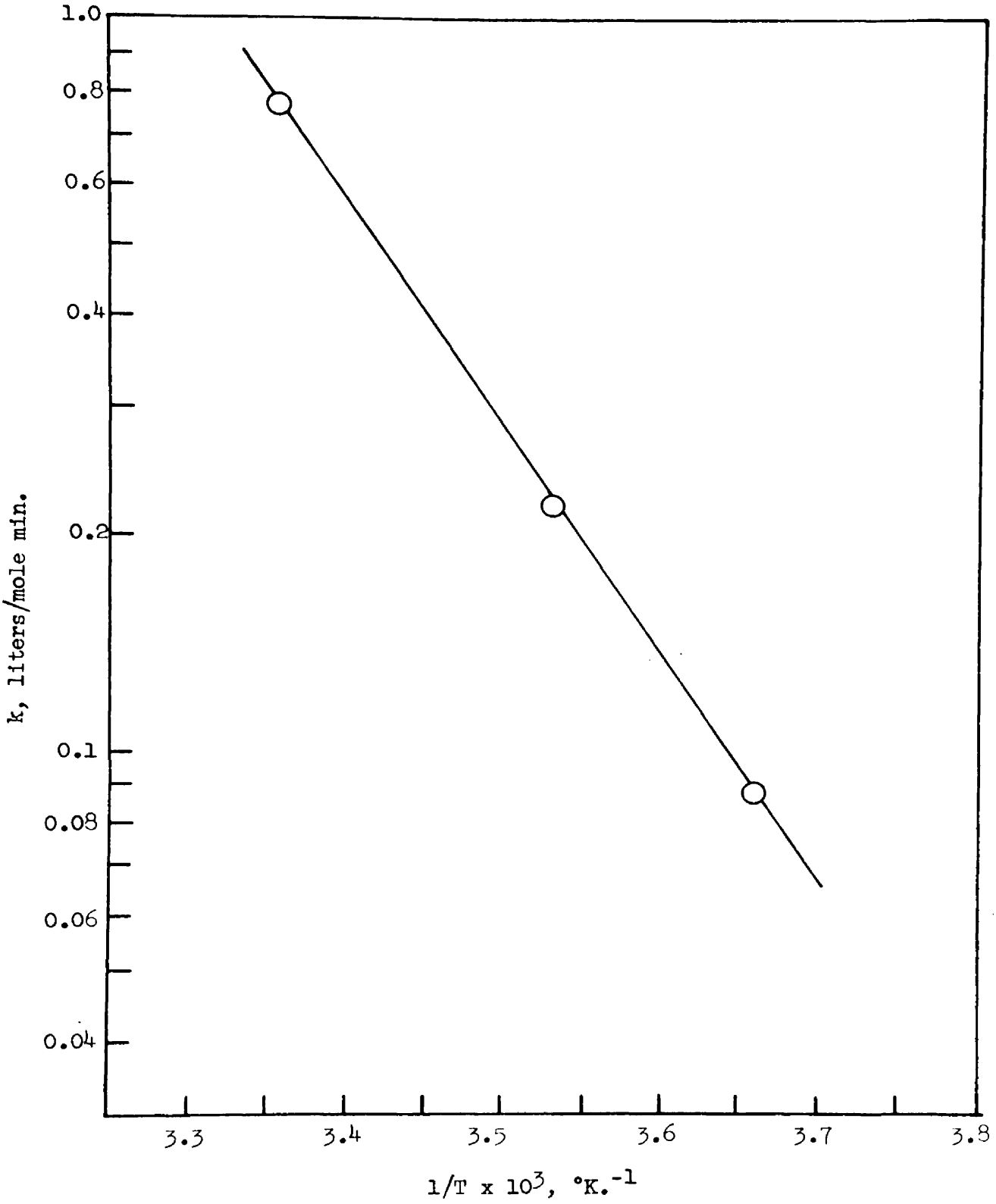

Figure 6. Arrhenius Plot for Thallium(I)-Thallium(III) Exchange in Sulfuric Acid Solution.

TABLE VII

DEPENDENCE OF EXCHANGE RATE ON CHLORIDE CONCENTRATION
μ = 3.68; (H^+) = 2.90 M; Tl(I) = 0.0100 M; Tl(III) = 0.0108 M

Number of Runs	Cl^- M	k Liter/mole-min.	Average Deviation X 10^3
4	-	0.77	9.0
1	0.0001	0.70	-
3	0.001	0.71	11.0
2	0.002	0.67	20.0
1	0.003	0.62	-
2	0.005	0.41	13.0
2	0.008	0.22	8.0
3	0.010	0.12	0.27
1	0.015	0.018	-
2	0.020	0.0023	0.20
2	0.030	0.0019	0.30
2	0.040	0.0040	0.20
2	0.045	0.0059	0.30

A log plot of k versus $\frac{(Cl^-)}{[Tl(III)]}$ is shown in Figure 7. It can be seen that the rate falls off as the concentration of chloride increases until the chloride concentration is approximately equal to the thallium (III) concentration. The rate then falls off even more rapidly until the chloride concentration is slightly more than twice the thallium(III) concentration. In this range the trend is reversed and an increase in chloride concentration brings about an increase in the rate of exchange up to 0.095 M chloride ion.

Solutions prepared with chloride concentration greater than 0.045 M contained a precipitate and were not examined further.

Dodson et al., (9,39,40) found that chloride ion and cyanide ion had similar effects on the rate of this exchange in perchloric acid.

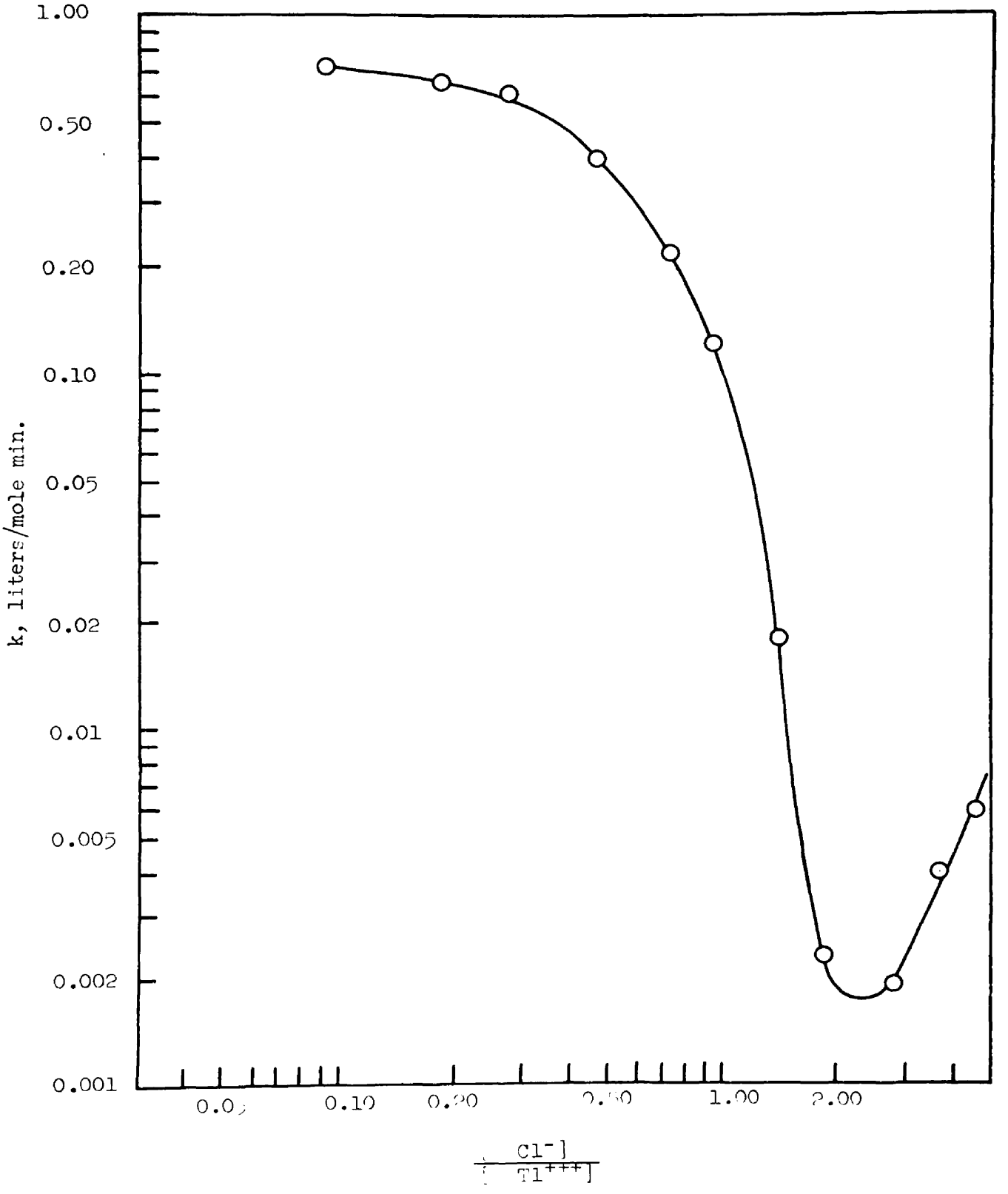

Figure 7. Dependence of Exchange Rate on Concentration of Chloride Ion.

They found a minimum for the reaction at a chloride to thallium(III) ratio of 1 to 1.5.

Thallium(III) forms a series of complexes with chloride ion. Values for the formation constants have been given by Benoit (18) and are shown below.

$$K_I = \frac{TlCl^{++}}{[Tl^{+++}]\,[Cl^-]} = 10^{7.1}$$

$$K_{II} = \frac{[TlCl_2^+]}{[TlCl^{++}]\,[Cl^-]} = 10^{6.6}$$

$$K_{III} = \frac{[TlCl_3]}{[TlCl_2^+]\,[Cl^-]} = 10^{5.5}$$

$$K_{IV} = \frac{[TlCl_4^-]}{[TlCl_3]\,[Cl^-]} = 10^{2.9}$$

Using these constants, attempts were made to fit various equations to the data. In no case could a reasonably good fit be obtained by considering that the chloride ion is complexing the thallium(III) ions and forming a nonexchanging species.

Benoit's (18) values were obtained in dilute solutions and the great difference in ionic strengths would change the values of formation quotients (concentration equilibrium constants) for the chloride complexes but during the study of the data it became apparent that in order to explain the data, formation quotients of the order of 10^4 for K_1 would be required. A method employed by Dodson for the cyanide study (39) was used in order to determine the ratio of the first and second equilibrium quotients.

When the formation quotients are large it can be shown from mass balance that:

$$\frac{K_{II}}{K_I} = \gamma \frac{(\gamma - 1 + y)}{(2 - \gamma - y)}.$$

where γ (gamma) is the ratio of total chloride to that of total thallium(III) and y is the ratio of uncomplexed thallium(III) to total thallium(III). If one assumes that $TlCl^{++}$ and $TlCl_2^{+}$ do not react and that for $\gamma < 2$, higher complexes are not important concentrationwise then $y = k/k_o$; where k is the second order rate constant and k_o is the same constant in the absence of chloride. Using Equation (19) it was found that the average of five values for the ratio K_{II}/K_I was 0.02 ± 0.006 (compare with Benoit's value of 0.0025). If one uses this calculated value, solves the above equation for y, values of k, using $k_o = 0.77$ can be calculated and are listed in Table VIII.

TABLE VIII

A COMPARISON OF THE CALCULATED VALUES OF THE RATE CONSTANT WITH EXPERIMENTAL VALUES FOR $\gamma < 2$

K(Calculated) l/mole-min.	K(Experimental) l/mole-min.	Cl^- M
0.77	0.77	0.000
0.70	0.71	0.001
0.63	0.67	0.002
0.56	0.62	0.003
0.42	0.41	0.005
0.22	0.22	0.008
0.11	0.12	0.010
0.071	0.018	0.015

The calculated value for Cl^- = 0.003 M is off by approximately ten percent as compared to the experimental value. A glance at Figure 7 shows that the experimental value does not fall on the smooth curve drawn through the data and the curve passes through 0.57 for 0.003 M chloride ion, indicating that the experimental value may be in error. Otherwise, these data indicate that up to 0.010 M Cl^- the assumptions used in this analysis are valid.

The wide deviation of the calculated value for 0.015 M chloride ion from the experimental value again emphasizes the complex nature of this reaction. At this concentration of chloride ion the assumptions made in this treatment are no longer sufficient.

Qualitatively one suspects that the mono and dichloro complexes of thallium(III) do not exchange with thallium(I) species in these solutions. Probably either the tri- or the tetrachloro (or both) complex may react.

Dodson (40) has shown that continued increase in chloride concentration increases the rate of this exchange (in perchloric acid medium) to a value several orders of magnitude greater than the rate in the absence of chloride. He indicated that thallium(I) chloride complexes enter into the reaction at the higher chloride concentrations (0.5 M).

In light of the complex nature of the exchange in the sulfuric acid media in the absence of chloride, it is not surprising that the presence of chloride greatly increases the complexity of the exchange mechanism and a quantitative treatment of the data is not possible with the information which is available on the thallium(I) and thallium(III) chloro- complexes.

VII. SUMMARY AND CONCLUSIONS

It has been found that the electron exchange reaction between thallium(I) and thallium(III) is first order with respect to each of the oxidation states of the element in aqueous sulfuric acid solutions. The rate of exchange was found to be 200 times that in perchloric acid solutions of comparable ionic strengths. The dependence of the rate of exchange on sulfate ion concentration indicates that the increase in the rate in sulfuric acid solutions is due to the participation in the exchange of complex sulfate species of both thallium(I) and thallium(III). Three empirical rate equations were shown, each of which satisfactorily explains the dependence of the rate on hydrogen and sulfate ion concentrations. However, it is believed that the data are most accurately represented by equation (8), since this equation includes variations in the concentrations of the hydrolyzed and complex sulfate species of both thallium(I) and thallium(III). The unusual dependence of the rate in sulfuric acid solution on chloride ion concentration is qualitatively explained by the formation of nonexchanging mono- and dichloro-complexes of thallium(III), and then higher chloro-complexes entering into the exchange to bring about an increase in the rate at high chloride concentrations. It is believed that the unusual effect that hydrochloric and sulfuric acids have on the rate of redox reactions between thallium(I) and thallium(III) and other reagents can be qualitatively explained by the relative magnitudes of the stability constants of thallium(I) and thallium(III) chloride and sulfate complexes.

The stability constant for the monochlorothallium(I) and monosulfatothallate(I) complex ions are very nearly equal. The formation of the sulfatothallate(I) complex upon the addition of sulfuric acid to a hydrochloric acid solution of thallium(I) chloride would be an explanation for the retarding effect that sulfuric acid has on the rate of reaction of thallium(I) and cerium(IV). In the reduction of thallium(III) by titanium(III) or iron(II), the high stability of the chloride complexes of thallium(III) as compared with the sulfate complex and the relatively low reactivity of $TlCl^{++}$ and $TlCl_2^{+}$ combine to slow the reduction in the presence of chloride. The reason for the fast rate of reduction in pure sulfuric acid solutions (e.g., when titanium(III) is used) could be due to the formation of thallium(III) sulfate complexes which react rapidly with the reducing agent.

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APPENDICES

APPENDIX I

Raw Kinetic Data on The Study

of

The Electron Exchange Reaction Between

Thallium(I) and Thallium(III)

INDEX TO APPENDIX I

TABLE IX

Run Number	Tl(I) M	Tl(III) M
1 Aa	0.0100	0.0108
1 Ab	0.0100	0.0108
1 Ac	0.0100	0.0108
1 Ad	0.0100	0.0108
1 B	0.0100	0.0058
1 Ca	0.0100	0.0018
1 Cb	0.0100	0.0018
1 D	0.0050	0.0108
1 Ea	0.0010	0.0108
1 Eb	0.0010	0.0108
1 F	0.0050	0.0058
1 G	0.0200	0.0108

TABLE X

Run Number	$HClO_4$ M
2 A	0.0001
2 B	0.001
2 C	0.010
2 D	0.100
2 E	0.50
2 F	1.00
2 Ga	1.50
2 Gb	1.50
2 H	2.00
2 I	2.50
2 J	2.89
2 K	3.50

TABLE XI

Run Number	$[H^+]$ M
2 A	2.50
2 b	2.00
2 Ca	1.56
2 Cb	1.56
2 D	1.00
2 E	0.70
2 F	0.45

TABLE XII

REFER TO TABLE V OF THESIS

Run Number	u
4 A	4.06
4 B	2.55
4 C	2.00
4 D	0.65

TABLE XIII

REFER TO TABLE VI OF THESIS

Run Number	Temperature °C.
5 A	0.0
5 B	0.0
5 C	10.0
5 D	10.0

TABLE XIV

REFER TO TABLE VII OF THESIS

Run Number	α_1^*
6 A	0.0001
6 Ba	0.001
6 Bb	0.001
6 Ca	0.002
6 Cb	0.002
6 D	0.003
6 Ea	0.005
6 Eb	0.005
6 Fa	0.008
6 Fb	0.008
6 Ga	0.010
6 Gb	0.010
6 H	0.015
6 Ia	0.020
6 Ib	0.020
6 Ja	0.030
6 Jb	0.030
6 Ka	0.040
6 Kb	0.040
6 La	0.045
6 Lb	0.045

TABLE IX

STUDY OF THE EFFECT OF VARIATIONS IN TOTAL THALLIUM CONCENTRATIONS ON THE EXCHANGE RATE

Run and Sample No.		Specific Activity	Time (Min.)	Run and Sample No.		Specific Activity	Time (Min.)
1 Aa	1	0.685	2.0	1 Ab	1	0.851	1.0
	2	0.936	4.0		2	2.72	10.0
	3	3.09	30.0		3	4.28	20.0
	4	3.35	32.0		4	5.53	30.0
	5	6.10	90.0		5	6.51	40.0
	6	6.07	92.0		6	7.90	50.0
	7	7.96			7	8.83	60.0
	8	7.95			8	10.57	70.0
					9	12.87	70.0
					10	13.82	
					11	13.68	
1 Ac	1	1.30	2.0	1 Ad	1	1.75	2.0
	2	3.74	17.0		2	4.47	20.0
	3	5.38	27.0		3	5.08	30.0
	4	6.76	42.0		4	6.45	42.0
	5	8.85	63.0		5	7.03	50.0
	6	9.43	78.0		6	7.78	60.0
	7	12.80			7	8.39	70.0
	8	12.75			8	8.87	90.0
					9	11.82	
					10	11.23	
1 B	1	2.11	2.0	1 Ca	1	1.76	3.0
	2	4.00	15.0		2	13.84	116.0
	3	5.55	26.0		3	23.06	
	4	6.83	35.0		4	22.66	
	5	7.84	45.0				
	6	8.43	60.0				
	7	10.24	70.0				
	8	11.11	80.0				
	9	15.03					
	10	15.54					

TABLE IX - Continued

Run and Sample No.		Specific Activity	Time (Min.)	Run and Sample No.		Specific Activity	Time (Min.)
1 Gb	1	1.78	2.0	1 D	1	2.41	3.0
	2	4.16	20.0		2	4.46	16.0
	3	6.83	40.0		3	6.43	30.0
	4	8.50	56.0		4	8.48	47.0
	5	10.84	76.0		5	10.85	61.0
	6	11.91	91.0		6	11.13	70.0
	7	13.11	110.0		7	12.10	82.0
	8	18.12			8	16.99	
	9	18.39			9	16.56	
1 Ha	1	1.53	2.0	1 Hb	1	0.673	3.0
	2	2.05	113.0		2	1.00	22.0
	3	2.52			3	1.19	40.0
					4	1.41	55.0
					5	1.52	75.0
					6	1.66	91.0
					7	1.75	110.0
					8	2.19	
					9	2.24	
1 F	1	3.85	3.0	1 G	1	1.33	5.0
	2	7.24	28.0		2	2.42	11.0
	3	9.44	44.0		3	3.18	20.0
	4	10.90	60.0		4	4.05	29.0
	5	13.50	82.0		5	4.64	38.0
	6	15.31	103.0		6	5.52	48.0
	7	17.16	120.0		7	5.96	60.0
	8	25.01			8	7.52	
	9	25.78			9	7.42	

TABLE X

STUDY OF RATE IN PERCHLORIC-SULFURIC ACID MIXTURES

Run and Sample No.	Specific Activity	Time (Min.)	Run and Sample No.	Specific Activity	Time (Min.)
2 A 1	0.749	2.0	2 B 1	0.917	3.0
2	1.09	5.0	2	2.71	15.0
3	3.05	20.0	3	4.48	31.0
4	3.14	22.0	4	5.63	47.0
5	4.50	36.0	5	10.41	
6	5.35	51.0	6	10.06	
7	9.26		7	10.90	
8	9.26		8	10.55	
2 C 1	0.988	2.0	2 D 1	0.854	1.0
2	2.88	12.0	2	2.80	10.5
3	4.65	23.0	3	5.21	25.0
4	7.09	42.0	4	6.54	36.0
5	9.14	66.0	5	7.82	47.0
6	10.15	90.0	6	9.31	60.0
7	14.34		7	15.47	
8	14.08		8	14.52	
			9	15.03	
			10	15.29	
			11	14.92	
2 E 1	1.19	3.0	2 F 1	1.05	2.0
2	2.94	15.0	2	2.30	20.0
3	4.27	27.0	3	4.22	51.0
4	5.33	37.0	4	5.16	69.0
5	5.79	46.0	5	5.96	86.0
6	7.09	60.0	6	6.85	110.6
7	7.74	71.0	7	7.15	120.0
8	12.56		8	10.66	
9	13.15		9	10.52	

TABLE X – Continued

Run and Sample No.		Specific Activity	Time (Min.)
2 Ca	1	0.967	3.0
	2	1.86	16.0
	3	2.72	33.25
	4	3.13	40.0
	5	3.52	50.0
	6	4.03	60.0
	7	4.47	70.0
	8	5.10	85.0
	9	5.61	100.0
	10	6.70	130.0
	11	12.74	
	12	12.95	
2 H	1	0.919	2.0
	2	3.82	95.0
	3	4.29	156.0
	4	5.23	212.0
	5	6.37	270.0
	6	7.16	330.0
	7	7.69	390.0
	8	10.77	
	9	10.55	
2 J	1	0.610	(Hrs.) 0.03
	2	0.600	0.05
	3	1.83	13.85
	4	2.35	36.0
	5	2.36	36.0
	6	3.44	61.75
	7	3.52	61.82
	8	11.73	
	9	11.65	

Run and Sample No.		Specific Activity	Time (Min.)
2 Cb	1	0.828	2.0
	2	2.78	40.0
	3	3.90	71.0
	4	4.71	100.0
	5	5.00	150.0
	6	6.90	171.0
	7	6.67	175.0
	8	7.01	191.0
	9	10.26	
	10	10.31	
2 I	1	1.11	(Hrs.) .05
	2	9.18	19.0
	3	9.12	19.0
	4	12.00	
	5	12.40	
2 K	1	0.785	(Hrs.) 0.05
	2	0.966	0.33
	3	0.725	0.60
	4	0.943	1.10
	5	0.946	3.30
	6	1.58	16.23
	7	2.06	27.35
	8	3.02	45.11
	9	4.27	64.00
	10	4.86	94.0
	11	4.79	94.0
	12	13.19	
	13	12.88	

TABLE XI

STUDY OF THE EFFECT OF HYDROGEN ION ON THE EXCHANGE RATE

Run and Sample No.		Specific Activity	Time (Min.)	Run and Sample No.		Specific Activity	Time (Min.)
3 A	1	1.29	2.5	3 B	1	1.36	2.0
	2	3.82	17.0		2	3.62	15.0
	3	4.14	19.0		3	4.98	25.0
	4	6.38	35.0		4	5.99	35.0
	5	8.30	57.0		5	7.16	47.0
	6	8.63	64.0		6	8.25	60.0
	7	12.62			7	8.99	70.0
	8	11.98			8	11.22	
					9	11.12	
3 Ca	1	1.49	2.0	3 Cb	1	1.09	1.0
	2	3.35	11.0		2	3.47	13.0
	3	5.02	22.0		3	4.62	20.0
	4	6.16	30.0		4	5.77	30.0
	5	7.40	40.0		5	6.33	35.0
	6	8.27	50.0		6	7.19	45.0
	7	9.02	63.0		7	10.84	
	8	9.51	70.5		8	10.66	
	9	11.32					
	10	11.44					
3 D	1	1.16	1.0	3 E	1	1.61	2.0
	2	3.11	9.0		2	3.17	7.0
	3	4.43	15.0		3	5.16	16.0
	4	5.26	20.0		4	6.67	24.0
	5	6.52	30.0		5	7.33	30.0
	6	7.43	39.9		6	10.68	
	7	10.39			7	10.55	
	8	10.62					
3 F	1	1.83	2.0				
	2	5.48	15.0				
	3	7.54	25.0				
	4	8.88	36.0				
	5	9.64	45.0				
	6	11.26					
	7	11.27					

TABLE XII

STUDY OF THE EFFECT OF VARYING IONIC STRENGTH ON THE RATE OF EXCHANGE

Run and Sample No.		Specific Activity	Time (Min.)	Run and Sample No.		Specific Activity	Time (Min.)
4 A	1	1.67	3.0	4 B	1	1.47	2.0
	2	3.90	15.0		2	4.20	17.0
	3	6.32	37.0		3	5.15	25.0
	4	6.87	46.0		4	6.55	37.0
	5	12.45			5	7.63	50.0
	6	12.39			6	8.78	64.0
					7	9.09	73.5
					8	9.77	92.0
					9	11.49	
					10	10.68	
4 C	1	1.61	3.0	4 D	1	1.31	2.0
	2	4.46	21.0		2	4.85	17.0
	3	5.56	30.0		3	6.31	30.3
	4	6.62	40.0		4	7.32	40.0
	5	7.13	50.0		5	8.98	60.0
	6	8.06	60.0		6	10.72	
	7	8.84	80.0		7	11.12	
	8	9.73	140.0				
	9	10.93					
	10	11.10					

TABLE XXXI

STUDY OF THE EFFECT OF TEMPERATURE ON RATE OF EXCHANGE

Run and Sample No.		Specific Activity	Time (Min.)	Run and Sample No.		Specific Activity	Time (Min.)
5 A	1	0.858	2.0	5 B	1	0.872	3.0
	2	1.42	30.0		2	2.11	60.0
	3	2.70	90.0		3	2.96	110.0
	4	2.98	91.0		4	4.18	177.0
	5	2.73	120.0		5	4.09	179.0
	6	3.48	151.0		6	5.08	240.0
	7	4.05	180.0		7	5.11	240.0
	8	12.39			8	6.28	330.5
	9	12.43			9	6.29	331.0
					10	12.68	
					11	13.19	
5 C	1	1.14	4.0	5 D	1	0.945	2.5
	2	2.65	37.0		2	2.41	32.5
	3	3.98	67.0		3	3.91	62.5
	4	4.71	96.0		4	4.96	91.5
	5	5.93	128.0		5	5.95	123.0
	6	6.64	150.5		6	6.75	150.5
	7	7.73	202.0		7	7.99	201.5
	8	12.59			8	12.48	
	9	12.47			9	12.65	

TABLE XIV

STUDY OF THE EFFECT OF CHLORIDE ION ON THE RATE OF EXCHANGE

Run and Sample No.	Specific Activity	Time (Min.)	Run and Sample No.	Specific Activity	Time (Min.)
6 A 1	0.943	1.0	6 Ba 1	1.11	1.5
2	3.08	11.5	2	3.61	15.0
3	4.90	22.0	3	5.71	30.0
4	6.49	33.0	4	7.56	43.5
5	7.63	42.0	5	7.54	54.3
6	8.74	53.5	6	9.77	72.3
7	9.49	60.0	7	10.83	90.0
8	15.80		8	12.30	120.0
9	15.75		9	15.39	
			10	15.34	
6 Bb 1	0.866	1.0	6 Ca 1	1.03	1.0
2	2.63	10.8	2	3.00	14.0
3	4.23	19.8	3	4.55	25.0
4	5.92	31.8	4	5.76	35.0
5	7.27	39.8	5	7.35	46.0
6	8.52	60.0	6	7.45	55.0
7	9.05	64.8	7	8.74	66.0
8	10.47	85.0	8	10.19	81.0
9	11.53	110.0	9	13.98	
10	14.18		10	14.16	
11	14.66				
6 Cb 1	1.22	2.0	6 D 1	1.89	3.0
2	2.72	11.0	2	2.29	10.0
3	4.62	24.0	3	3.70	21.0
4	5.89	30.0	4	4.88	32.0
5	6.89	41.0	5	6.70	50.0
6	7.98	57.0	6	7.49	60.0
7	9.17	74.0	7	7.60	70.0
8	14.35		8	13.07	
9	14.37		9	13.31	
6 Bc 1	0.844	1.3	6 Bb 1	0.888	2.0
2	1.96	10.0	2	2.75	23.0
3	2.84	20.0	3	3.61	33.0
4	3.94	30.0	4	4.58	48.0
5	5.31	45.0	5	6.26	74.0
6	5.93	55.0	6	6.66	85.0
7	6.68	65.0	7	12.71	
8	8.42	98.0	8	12.27	
9	15.19				
10	15.07				
11	14.91				

TABLE XIV - Continued

Run and Sample No.		Specific Activity	Time (Min.)	Run and Sample No.		Specific Activity	Time (Min.)
6 Fe	1	0.785	2.0	A Fb	1	0.683	2.0
	2	1.02	5.0		2	1.58	13.0
	3	5.69	105.0		3	2.41	26.2
	4	7.30	190.0		4	2.81	36.0
	5	7.78	160.0		5	3.51	48.0
	6	14.80			6	3.87	60.0
	7	15.34			7	5.07	78.0
					8	14.43	
					9	14.64	
							(Hrs.)
6 Cm	1	0.768	1.0	6 Cb	1	0.723	0.02
	2	2.68	62.0		2	0.827	0.07
	3	3.92	116.0		3	2.61	1.2
	4	5.72	180.0		4	2.79	1.2
	5	6.65	230.0		5	3.56	1.8
	6	8.00	281.0		6	3.59	1.9
	7	8.56	315.0		7	4.74	2.6
	8	8.55	330.0		8	4.66	2.6
	9	8.46	337.0		9	5.55	3.3
	10	9.78	456.0		10	6.63	4.5
	11	15.01			11	6.54	4.5
	12	15.62			12	7.16	5.3
	13	15.23			13	8.06	6.3
					14	12.58	
					15	12.25	
			(Hrs.)				(Hrs.)
6 H	1	0.650	.08	6 Ia	1	0.693	0.5
	2	0.656	.08		2	1.26	16.2
	3	2.00	5.0		3	1.95	37.0
	4	1.97	5.0		4	2.59	61.0
	5	2.80	9.6		5	4.69	144.5
	6	2.78	9.6		6	4.58	144.5
	7	3.48	12.8		7	5.31	160.0
	8	3.47	12.8		8	6.75	241.0
	9	4.29	16.3		9	7.12	241.0
	10	4.19	16.3		10	7.10	267.0
	11	12.36			11	13.32	
	12	12.18					

TABLE XIV – Continued

Run and Sample No.		Specific Activity	Time (Hrs.)	Run and Sample No.		Specific Activity	Time (Hrs.)
6 Ib	1	0.609	.03	6 Ja	1	0.72	0.5
	2	0.559	.06		2	0.94	5.0
	3	2.49	52.2		3	1.22	15.9
	4	2.40	52.2		4	1.30	16.0
	5	3.42	74.4		5	1.60	32.0
	6	3.24	74.5		6	2.21	48.0
	7	4.13	106.0		7	2.95	72.5
	8	4.33	106.0		8	3.30	95.5
	9	5.14	144.0		9	3.44	95.5
	10	5.27	144.0		10	4.35	139.8
	11	7.45	245.8		11	4.94	163.7
	12	7.48	245.8		12	6.39	236.0
	13	13.29			13	6.75	268.7
	14	13.13			14	7.80	320.0
					15	14.65	
					16	14.64	
6 Jb	1	0.612	0.01	6 Ka	1	0.666	0.01
	2	0.609	0.05		2	0.649	0.06
	3	2.70	74.0		3	0.974	6.0
	4	2.20	74.0		4	1.98	19.3
	5	4.10	145.3		5	2.06	19.4
	6	4.16	145.3		6	2.91	35.6
	7	6.22	246.9		7	3.85	51.8
	8	6.03	246.9		8	5.29	76.1
	9	6.37	295.5		9	6.28	98.5
	10	6.24	295.5		10	6.17	98.5
	11	12.68			11	7.06	122.6
	12	12.69			12	7.78	143.3
					13	14.96	
					14	14.33	

TABLE XIV - Continued

Run and Sample No.	Specific Activity	Time (Hrs.)
6 Kb 1	0.594	0.03
2	0.593	0.1
3	3.36	51.0
4	3.33	51.0
5	4.34	73.8
6	4.43	73.8
7	5.45	106.3
8	5.57	106.4
9	6.42	130.5
10	6.35	130.8
11	6.76	
12	13.10	
13	13.02	
6 Lb 1	0.554	0.05
2	0.553	0.10
3	4.30	49.5
4	4.23	49.5
5	5.71	72.0
6	5.82	72.0
7	7.27	104.0
8	7.09	104.0
9	7.10	108.5
10	7.08	108.5
11	8.15	128.5
12	8.19	128.5
13	12.81	
14	12.46	
6 La 1	0.702	0.03
2	0.709	0.08
3	0.931	2.42
4	0.856	2.45
5	1.24	6.5
6	1.25	6.5
7	1.76	10.8
8	1.77	10.8
9	2.20	16.2
10	2.15	16.3
11	2.97	23.9
12	2.86	24.0
13	3.25	28.2
14	3.21	28.2
15	3.50	30.8
16	3.39	30.8
17	4.84	48.0
18	4.85	48.0
19	5.74	60.0
20	5.68	60.0
21	6.61	72.0
22	6.37	72.0
23	6.93	81.4
24	7.24	81.4
25	7.64	91.6
26	7.53	91.6
27	15.45	
28	15.40	

APPENDIX II

PRELIMINARY EXPERIMENTS CARRIED OUT ON THE REACTION BETWEEN CERIUM(IV) AND THALLIUM(I)

The reaction between cerium(IV) and thallium(I) had been previously reported (1) to be slow in sulfuric acid but estimates of the half life indicated that it might be studied quantitatively.

Preparation of Solutions

Reagent grade ammonium hexanitratocerate(IV) was obtained from G. Frederic Smith Chemical Company. Fifty-five grams of this salt was dissolved in distilled water and 200 ml of 5 M ammonium hydroxide (Baker Chemical Company, Reagent Grade) was added. The flocculent cerium(IV) hydroxide precipitate was separated from the solution by filtration and washed repeatedly until no test for nitrate ion could be obtained in the filtrate. The hydroxide was then dissolved in 100 ml. of 8.4 M sulfuric acid. This solution was diluted to one liter volume and analysed. The total cerium concentration was obtained by the persulfate method as described in Hillebrand et al. (2). The cerium(IV) concentration was found by analysis, using As_2O_3 as a standard, a method described in Kolthoff and Sandell (3). The hydrogen ion concentration was obtained by treating an aliquot of the cerium(IV) sulfate solution with excess sodium oxalate, filtering and titrating the filtrate with standard sodium hydroxide using phenolphthalein as an indicator. The analysis of the stock solution gave the following results:

Ce(IV)	0.08299 M
Ce(III)	0.01260 M
(H^+)	1.567 M

A solution of 0.00956 M cerium(III) ion in 1.00 M sulfuric acid was prepared by reducing a 10 ml. sample of the above solution with 1 ml. of 3% hydrogen peroxide, evaporation to half its volume, addition of sufficient sulfuric acid to make the final solution 1.00 M in hydrogen ion and dilution to volume. A spectral study of the solution was made covering the range from 230-320 mμ. A maximum was found between 250 and 255 mμ. A portion of this solution was diluted to one tenth its volume with 1.00 M sulfuric acid and the spectrum obtained over the same range. Again a peak was obtained at 255 mμ. One molar sulfuric acid was used as a blank in the 1.0 cm silica cell.

The spectra of 9.56×10^{-3} and 9.56×10^{-2} M cerium(IV) solutions was obtained. Maximum absorption occurred at 315 mμ. A Beckman DU spectrophotometer was used in all cases for observing the spectra of these solutions.

Results and Discussion

A solution containing 1.00 M sulfuric acid and 0.0001 M cerium(IV) ion was prepared and stored under nitrogen to test the stability of the solutions over a period of several days.

Stability Study

Time	Dobs.
0 hrs.	0.565
24 hrs.	0.540
48 hrs.	0.530
14 days	0.492
16 days	0.490

Two series of solutions were prepared containing only cerium(IV) ions and sulfuric acid. These solutions were identical with the exception that one series was stored in clear bottles and the other in bottles which had been painted black. Both series were prepared with freshly distilled water (distilled in nitrogen atmosphere) and stored under a nitrogen atmosphere. The following results were obtained:

	Series Not Exposed to Light		Series Exposed to Light
	Dobs		Dobs
1	0.354	Time of	0.352
2	0.470	Mixing	0.470
3	0.588		0.585
1	0.336	3 Days	0.318
2	0.455		0.434
3	0.573		0.538
1	0.335	4 Days	0.310
2	0.455		0.425
3	0.572		0.535
1	0.327	15 Days	0.288
2	0.445		0.400
3	0.565		0.508

It was apparent that light accelerated the decomposition of the cerium(IV) solutions but its absence did not stop the reaction.

The possibility of running the reaction at high concentration was investigated. A solution containing approximately 0.1 M cerium(IV), 0.05 M thallium(I) and 210 M in sulfuric acid was prepared. Fifty milliliters of this solution gave no test for thallium(III) ion after being heated for 30 hours at 70° C, indicating that very little reaction had taken place. A second fifty milliliter sample of the solution was heated to 70° C and a piece of platinum foil 1 in.^{2} was placed in the

solution. The deep orange color of the cerium(IV) species slowly disappeared. After four hours the solution had a very pale yellow color. The solution gave a test for thallium(III) ion indicating that a reaction had occurred between cerium(IV) and thallium(I) in sulfuric acid in the presence of platinum.

Reaction Between Titanium(III) and Thallium(III)

A solution containing 0.005 M thallium(III) and 1.5 M sulfuric acid was prepared and stored under nitrogen. A solution containing approximately 0.01 M titanium(III) and 2 M sulfuric acid was prepared and stored under nitrogen. It was found that the reaction between titanium (III) and thallium(III) occurred rapidly and appeared to be complete in time of mixing.

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