A STUDY OF THE ELECTRON EXCHANGE REACTION BETWEEN TIN(II) AND TIN(IV) IN AQUEOUS SULFURIC ACID SOLUTIONS

By

Gilbert Gordon

A THESIS

Submitted to the School for Advanced Graduate Studies of
Michigan State University of Agriculture and Applied Science
in partial fulfillment of the requirements
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Department of Chemistry

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Approved Carl H. Brubaker, Jr.

ABSTRACT

The kinetics of the exchange reaction between tin(II) and tin(IV) in aqueous sulfuric acid were studied in the temperature range of 25 °C. to 50 °C. Experiments were designed to determine the effect of variation in concentration of tin(II), tin(IV), sulfate, hydrogen, and chloride ions.

It was found that the reaction is first order with respect to tin(II) and tin(IV), and that the effect of increased hydrogen ion is to decrease the rate of exchange, and the effect of increased sulfate ion is to increase the rate of exchange. The predominant tin species appear to be $SnOH^{+}$ and $Sn(SO_4)_2$. A combination of the following exchange processes

$$^{*}SnO(SO_4)_2^{=} + SnOH^{+} \rightleftharpoons SnO(SO_4)_2^{=} + {}^{*}SnOH^{+}$$

or

$$^{*}Sn(OH)_3^{+} + SnSO_4 + SO_4^{=} \rightleftharpoons Sn(OH)_3^{+} + {}^{*}SnSO_4 + SO_4^{=}$$

and

$$^{*}SnO(SO_4)_2^{=} + SnSO_4 \rightleftharpoons SnO(SO_4)_2^{=} + {}^{*}SnSO_4$$

lead to

$$R/ab = 0.674(H^{+})^{-2} + 0.0725(SO_4^{=})(H^{+})^{-1}$$

The addition of chloride ion to the reaction mixture in 3.00 $\underline{M}$ sulfuric acid increased the rate by a factor of 100. The reaction can be described by the following exchange process

$$*SnCl_6^{=} + SnCl_4^{=} \rightleftharpoons SnCl_6^{=} + *SnCl_4^{=}$$

which leads to

$$R = 4.94[Cl^-][Sn(II)][Sn(IV)]$$

The chloride ion concentration probably appears in the rate expression because $SnCl_3^-$ is most likely the major tin(II) species.

Spectrophotometric examination of aqueous solutions of tin(II) in perchloric and sulfuric acids have been interpreted in terms of the hydrolysis of Sn^{++}. A hydrolysis constant equal to 24.5 has been evaluated. The absorption spectra of tin(IV) solutions and tin(II)-tin(IV) solutions in 3.00 $\underline{M}$ sulfuric acid and tin(II)-tin(IV) solutions in sulfuric acid containing 1.00 $\underline{M}$ chloride ion (3.99 $\underline{M}$ H^+) are given. The spectra have been interpreted in terms of an interaction dimer containing one atom of tin(II) and one atom of tin(IV).

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INTRODUCTION

The availability of isotopic tracers has made possible the study of exchange reactions between different oxidation states of the same element in which the initial and final states are identical. The exchange reaction

$$Sn(II) + Sn^{*}(IV) \rightleftharpoons Sn^{*}(II) + Sn(IV)$$

was studied in aqueous sulfuric acid in the temperature range of 25 to 50 degrees Centigrade. The primary interest is in connection with reactions which may proceed either by direct transfer of several electrons or alternatively by the stepwise exchange of one electron at a time. The exchange reaction was studied kinetically by the use of radioactive tracer in an attempt to elucidate a mechanism for the electron transfer process. The catalytic effect of chloride ion was also studied such that a comparison of the reactions in sulfuric acid and sulfuric acid containing chloride could be made. The ultraviolet absorption spectra of tin(II) in perchloric and sulfuric acids and of tin(II) - tin(IV) mixtures in sulfuric and hydrochloric acids were also studied in an attempt to predict quantitatively the behavior of the aqueous tin species.

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* By common usage, these asterisks indicate radioactive tracers.

HISTORICAL AND THEORETICAL CONSIDERATIONS

Historical

Tin metal has been known since the time of the ancients when it was known as diabolus metallorum-the devil of the metals (1). The physical properties of tin metal have been elucidated in recent years to facilitate its use in electroplating and alloying. Few studies have been made of the properties of tin(II) and tin(IV) in aqueous media other than hydrochloric acid solutions. The ions, tin(II) and tin(IV) hydrolyze readily and even in the presence of chloride ion, hydrous tin oxide is known to precipitate.

The well-known nature of SnO is closely associated with the tendency of tin(II) to undergo extensive hydrolysis in aqueous solutions. Denham and King (2) have studied the $SnO-SO_3-H_2O$ system at 25 °C. Several solid phases, including $SnSO_4 \cdot SnO$ and $SnSO_4$ were isolated but the data do not indicate the formation of any aqueous tin(II) sulfate complexes.

Studies of the conductance (3, 4) of aqueous sulfuric acid solutions containing tin(II) sulfate suggest that two types of complexes are formed, although these studies in very dilute solutions $\sim 2 \times 10^{-3}$ M Sn(II) , in the absence of excess acid, suggest complete dissociation. The hydrolysis of tin(II) can be described by several equations (5, 6, 7)

1) $Sn^{++} + H_2O \rightleftharpoons SnOH^{+} + H^{+}$

2) $2\ Sn^{++} + 2\ H_2O \rightleftharpoons Sn_2(OH)_2 + 2\ H^{+}$

Dimer and polymer formation (Equation 2) is always favored in solutions of low acidities as in the case of Fe(III) (8). However, the emf. studies of Gorman (9) show that the variations of the equilibrium quotient with ionic strength are consistent with Equation (1). At 25 °C, the constant is given as 0.02.

It appears that when tin(IV) sulfate dihydrate is dissolved in dilute sulfuric acid, the species, $SnSO_4^{++}$, are formed (10). In more concentrated solutions of sulfuric acid, higher complexing occurs. Brubaker (11, 12) has studied solutions of tin(IV) in sulfuric acid spectrophotometrically and these data indicate that the following reactions take place:

3) $SnSO_4^{++} + SO_4^{=} \rightleftharpoons Sn(SO_4)_2$ k_1

4) $Sn(SO_4)_2 + H_2SO_4 \rightleftharpoons H_2Sn(SO_4)_3$ k_2

The ratio of $Sn(SO_4)_2/SnSO_4^{++}$ is ~ 100 in 3.00 M sulfuric acid. The absorbancy index for $SnSO_4^{++}$, obtained by comparison of data in perchloric and sulfuric acids and in view of the findings (10) that $SnSO_4^{++}$ is the predominant species in dilute sulfuric acid, is approximately 2500. The complex acid suggested in Equation (4) is present in very low concentrations in 3.00 M sulfuric acid.

In an attempt to clarify reactions in which several electrons are transferred, Brubaker and Court (13) have studied the oxidation of tin(II) with cerium(IV) in sulfuric acid, with most of their data being collected at 0 °C. The following mechanism is consistent with the second-order reaction which occurs at moderate sulfate ion concentrations:

5) $SnSO_4 + Ce(SO_4)_3^{=} \rightleftharpoons$ tin intermediate

6) tin intermediate $+ Ce(SO_4)_3^{=} \rightleftharpoons SnSO_4^{++} + 2\ Ce(SO_4)_2^{=}$

Equally probable products for reaction (5) could be $SnSO_4^{+}$ + $Ce(SO_4)_2^{-}$ + $SO_4^{=}$ or a complex, $SnCe(SO_4)_X^{6-2X}$. The experimental evidence is compatible with the possibility of the "intermediate" existence of Sn(III), but the data do not exclude the other possibilities shown above.

Boyle, <u>et al.</u>, (14) have shown that γ-rays can catalyze the reaction between Fe(III) and Sn(II) in sulfuric acid. It is of some interest that the data can be interpreted by the formation of transient intermediates, of Sn(I) and Sn(III). These unstable intermediates, however, are then destroyed by reaction with other γ-induced radicals.

Weiss (15) has shown, that in the reduction of ferric chloride by tin(II) salts, the tin(II) chloride enters as the complex anion, $SnCl_4^{=}$, in a two stage reaction of a simple electron transfer process.

7) $Fe(III) + SnCl_4^{=} \rightleftharpoons Fe(II) + SnCl_4^{-}$

8) $Fe(III) + SnCl_4^{-} \rightleftharpoons Fe(II) + SnCl_4$

This is consistent with the observation of Duke and Pinkerton (17) that a minimum of three chlorides are necessary for the activated complex to yield any appreciable reaction rate. The reaction rate is greatly depressed when large amounts of tin(II) are present, at constant chloride ion concentration, due to complexing and the removal of halide ions. Davidson and co-workers (18) have studied the interaction between tin(II) and tin(IV) in hydrochloric acid solutions. A mixed solution of tin(II) and tin(IV) absorbs light of longer wave lengths than either solution alone. The observed absorbancy is proportional to the product of the tin concentrations (Equation 9).

$$9) \qquad A_i\left[\lambda, \mathrm{Sn(II)}, \mathrm{Sn(IV)}\right] = k_i \lambda \left[\mathrm{Sn(II)}\right]\left[\mathrm{Sn(IV)}\right]$$

The absorption spectra of tin(II) solutions did not obey Beer's law and this was probably due to the presence of 1-5% of tin(IV) in the solution studied. The result of equation (9) implies that the species responsible for the interaction absorption is a complex of tin(II) - tin(IV) and not a complex containing a single atom of tin(III). The absorption spectra of the interaction complex are characteristic of the long wave length tails of electron transfer bands (19).

Kinetic (18) and photochemical (20) studies on the above system, suggest that the optical interaction complex is unsymmetrical and that exchange takes place through this complex. The activation energy of 11 kcal. suggests that this is the minimum amount of energy necessary to activate the interaction complex into a configuration in which exchange can occur.

Meyer and Kahn (21) have studied the exchange reaction $SnCl_2$ + $Sn^*Cl_4 \rightleftharpoons Sn^*Cl_2 + SnCl_4$ in absolute ethyl alcohol. The reaction is first order with respect to tin(II) and tin(IV) chloride concentration. In accord with their kinetic data, they have postulated these reactions as contributing to the mechanism

10) $Sn^*Cl_4 \rightleftharpoons Sn^*Cl_3^+ + Cl^-$ (rapid)

11) $SnCl_2 + Cl^- \rightleftharpoons SnCl_3^-$ (rapid)

12) $SnCl_3^+ + SnCl_3^- \rightleftharpoons Cl_2SnCl_2Sn^*Cl_2$ (rapid)

13) $Cl_2SnCl_2Sn^*Cl_2 \rightleftharpoons Sn^*Cl_2 + SnCl_4$ (rate determining)

If the exchange occurs as suggested, the $SnCl_2$ could approach the $SnCl_4$ in such a way as to form an activated complex consisting of two tetrahedral units sharing two chlorine atoms along a common edge, thus necessitating steric orientation before exchange could occur.

Theoretical

The rate of exchange can be studied by independent variation of the concentrations of each of the reactants by use of the logarithmic form of the first order exchange law (22, 23)

$$14)\qquad \ln\left[I - X/X_{\infty}\right] = -R\frac{(a+b)}{(ab)}t$$

Equation (14) represents growth of activity with time in the initially inactive material, where X and $X(\infty)$ represent the activity of the initially inactive material at time t and infinite time. R is the observed rate, and if it has a simple power dependence upon a and b, one can write

$$15)\qquad R = k[a]^{\alpha}[b]^{\beta}$$

where k may be the specific rate reaction rate constant, and α and β represent the reaction order with respect to a and b.

The semilog plot of (1-f), where $f = X/X_{\infty}$, against t should be linear and can be used to calculate $t_{\frac{1}{2}}$ graphically. R can then be evaluated from the slope of this curve, or more conveniently,

$$16)\qquad R = \frac{ab}{a+b}\cdot\frac{0.693}{t_{\frac{1}{2}}}$$

At complete exchange (approximately 10 half-lives) the specific activity of both reactants will be identical. It is also possible to determine the reaction order with respect to hydrogen ion or sulfate ion concentrations, using the preceding procedure if all other concentrations are maintained constant.

The Arrhenius equation is found to fit the rate measurements on a large number of reactions at various temperatures. Deviations from the equation imply that the reaction is complex andthat several equilibria or steps may be involved. The derivation of the equation can be found in standard texts on kinetics [e.g. 24] and only the logarithmic form is shown here,

$$17) \qquad \ln k = -\ln \frac{R}{ab} = -\frac{Ea}{RT} + C$$

where k is the apparent rate constant, Ea the activation energy, R the gas constant, and T is the absolute temperature. Thus, if a graph of ln k against 1/T is linear, Ea can be determined from the slope.

To obtain an empirical formula for a complex, the method of "continuous variation" elaborated by Job (25) is useful. The method is based upon the relationship that on mixing two reagents forming an additive complex, to a fixed total concentration, the concentration of the complex is a maximum when the reagents are in the stoichiometric proportions in which they appear in the complex. Plotting a suitable physical or chemical property of the complex against the concentration of reagent should give a maximum at the ratio corresponding to the formation of the complex. This simple relationship is complicated if more than one complex is formed. Vosburgh and Cooper (26) have pointed out some of the properties of special cases in which two complexes are formed. Katzin (27) has elaborated upon Job's method for the case of three complexes determined spectrophotometrically. Using the difference in absorption and restricting the system to the wave lengths at which the complexes absorb more strongly than the uncomplexed material, a graph of ΔA[*] against the fraction of one component will intersect the abscissa at zero and one. The curve between must possess one or more maxima and/or minima i.e.,

$$18) \qquad \frac{d(\Delta A)}{dx} = 0,$$

at one or more points.

Errors

For each set of measurements, statistical considerations may be applied only when the total number of observations is high. Thus, all samples have been counted for a minimum of 10,000 counts and a background count with a standard deviation less than the deviation in the samples was used. Calculation of the standard deviation requires the use of arithmetically combined quantities. If one defines a quantity G which is a function of A and B, which have a standard deviation[†] σ_A and σ_B respectively, then the standard deviation of the result, σ_{AB}, can be given approximately by

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[*] ΔA is defined as the difference between the absorbancy observed for the mixture and the sum of the absorbancies of each component separately.

[†] σ_X is defined as the square root of the arithmetic mean of the squares of all the deviations from the average value, thus $\sigma_X{}^2 = \frac{1}{m} \sum_i^m (\bar{X} - X_i)^2$.

19) $$\sigma_{AB}^{2} = \left[\sigma_{A} \frac{dG_{(A,B)}}{dA}\right]^{2} + \left[\sigma_{B} \frac{dG_{(A,B)}}{dB}\right]^{2}$$

Thus, if the function were A/B,

20) $$\sigma_{A/B} = \frac{A}{B} \left\{ \frac{\sigma_{A}^{2}}{A^{2}} + \frac{\sigma_{B}^{2}}{B^{2}} \right\}^{1/2}$$

It is also possible to estimate the maximum error due to radioassay in the rate constant for an exchange reaction as a function of the extent of exchange. Davidson (28) has shown that the solution for the optimum degree of exchange to minimize this error can be found. In the case in which a decrease of activity is observed in the initially active component,

21) $$s = R_{(a,b)}\left[\frac{a+b}{ab}\right](t)$$

where a is the concentration of component A and b is the concentration of component B. Equation 21 can be rewritten

22) $$s = \frac{Rt}{b} + \frac{Rt}{a}$$

Thus, s is the sum of the number of exchanges for each component present. Now, if we define x as the activity of component A at the time t and a* as the initial activity of A, and let z = x/a* then,

23)‡ $$-\frac{d\,(\ln s)}{d\,(\ln z)} = \frac{1 + (a/b)\exp(s)}{S} = S_{(s)}$$

---

‡ Since $\sigma_s = |ds/dz|\,\sigma_z$, and the error occurring is mainly due to radioassay technique, not statistical counting error,
$$-\frac{d \ln s}{d \ln z} = \left[\frac{\sigma_s}{S}\right]\left[\frac{Z}{\sigma_z}\right]$$

It is possible to obtain a family of curves, one for each a/b ratio, by plotting $S_{(s)}$ against s. By choosing times or ln(1-f) values corresponding to the minimum in this curve, the error in the rate constant, R, can be minimized. Similarly, in the case in which the activity increases in a component that was originally inactive, one obtains

$$24) \qquad \frac{d \ln (s)}{d \ln (y/y(\infty))} = \frac{\exp(s) - 1}{S}$$

and only one curve is observed for all mole fractions. Use of optimum degree of exchange and calculation of the standard deviation for each point , depending on the number of samples taken and the minimum ln(1-f) value, the standard deviation in R (Table I) can be calculated.

TABLE I

STANDARD DEVIATION AS A FUNCTION OF (1-f)

Lowest (1-f) value	0.450	0.350	0.550	0.450	0.350	0.350
Number of samples	10	10	9	9	9	8
R (in %)	5.26	6.48	4.12	5.60	6.56	6.67

EXPERIMENTAL

Materials

The isotope used in the kinetic studies was the 112 day $_{50}Sn^{113}$, which decays by K-electron capture to an excited state of $_{49}In^{113}$. This decays to the ground state with a half-life of 1.73 hours by emission of a 0.39_2 M.e.v. gamma ray (29). All samples were mounted and γ-counted in new one-dram screw-cap vials, in a well-type NaI(Tl) scintillation counter.

The radioactive tin was a sample of neutron activated tin metal from the Oak Ridge reactor (30). It was obtained as a hydrochloric acid solution of tin(IV). Besides Sn^{113} activity, this contained the 2.7 year beta active Sb^{113} isotope. The sample was diluted to 10 ml. with 6 M hydrochloric acid, 4.64 mg. Sb^{+3} and 2.5 gm. of oxalic acid were added. The solution was heated to boiling and hydrogen sulfide was bubbled into the solution until Sb_2S_3 precipitated. The supernatant liquid was removed by centrifugation and the above procedure was repeated twice.

Concentrated nitric acid was added to the supernatant liquid to decompose the oxalic acid present. This solution was then heated with concentrated sulfuric acid for 250 hours and diluted with water to give a solution of active tin(IV) for the exchange experiments.

An aluminum absorption curve was made by mounting a sample two centimeters below the 1.1 inch mylar (1.5 mg./sq. cm.) window of a Tracerlab G-M tube. The observed break in this absorption curve at

110 ± 2 mg./cm.^{2} corresponds to an electron energy of 0.37 ± 0.01 M.e.v. (31) in exact agreement with that expected from a k-conversion electron from 0.31 M.e.v. gamma ray from metastable indium.

A lead absorption curve was made on the same sample and a lead half thickness of 2.77 ± 0.04 gm./sq.cm. corresponding to a gamma energy of 0.39 ± 0.01 M.e.v. (31) was observed.

The half-life was determined by comparison to an aqueous sample of Co^{60} in the scintillation counter. The half-life was observed to be 113 ± 2 days which is in good agreement with the value of 112 days reported in the literature.

Throughout this experimental work, the sulfuric and hydrochloric acids used were DuPont A. R. grade and the 70% perchloric acid was Mallinckrodt A. R. grade. Aqueous solutions of these acids were standardized with carbonate-free sodium hydroxide which had been standardized against potassium acid phthalate, using phenolphthalein as the indicator.

Stannous sulfate solutions were prepared indirectly, using the method of Noyes and Toabe (32). Pure cupric oxide was dissolved by boiling it with an excess of dilute sulfuric acid. To this copper sulfate solution, a threefold excess of 20 mesh granular tin was added. It was found that in sulfuric acid concentrations of 3 M to 5 M the displacement reaction

25) $$\mathrm{Sn(0) + Cu(II) \rightleftharpoons Cu(0) + Sn(II)}$$

occurred. If the mixture was kept at 100 °C for two hours, the reaction proceeded to completion without complication. Lower acid concentrations lead to rapid hydrolysis, whereas at sulfuric acid concentrations above 5 M, rapid hydrogen evolution occurs. These situations made regulation of the tin(II) concentration rather difficult. Solutions of tin(II) are readily oxidized by air, therefore, all preparations were carried out in an atmosphere of specially purified nitrogen. A drawing of the apparatus used to prepare, purify and store tin(II) solutions is given in Figure 1. Mallinckrodt, pre-purified nitrogen was passed over copper wire in a tube furnace (A) at 450 °C. and then passed over activated copper (B) which had been deposited on kieselguhr (33). According to Meyer (33), this activated copper is capable of reducing the oxygen content to less than 10^{-8} moles/liter. The purified nitrogen was bubbled through two pyrogallol towers (D, E) to act as purifiers if the electricity should fail, or to act as indicators if the activated copper were to become exhausted. The pyrogallol solutions were prepared by the dissolution of 30 gm. of Merck N. F. pyrogallic acid in 300 ml. of water and made alkaline by the addition of potassium hydroxide pellets. A third tower (F) contained 300 ml. of 3 M sulfuric acid which was used to maintain constant water vapor pressure in the gas phase. This was necessary to minimize volume changes during storage of tin(II) and tin(II) - tin(IV) mixtures. Previous to preparation of tin(II) solutions, the apparatus was completely assembled, evacuated to a pressure less than 20 mm. of mercury and filled with purified nitrogen. This operation was re-

PREPARATION & STORAGE OF AQUEOUS Sn^{II}

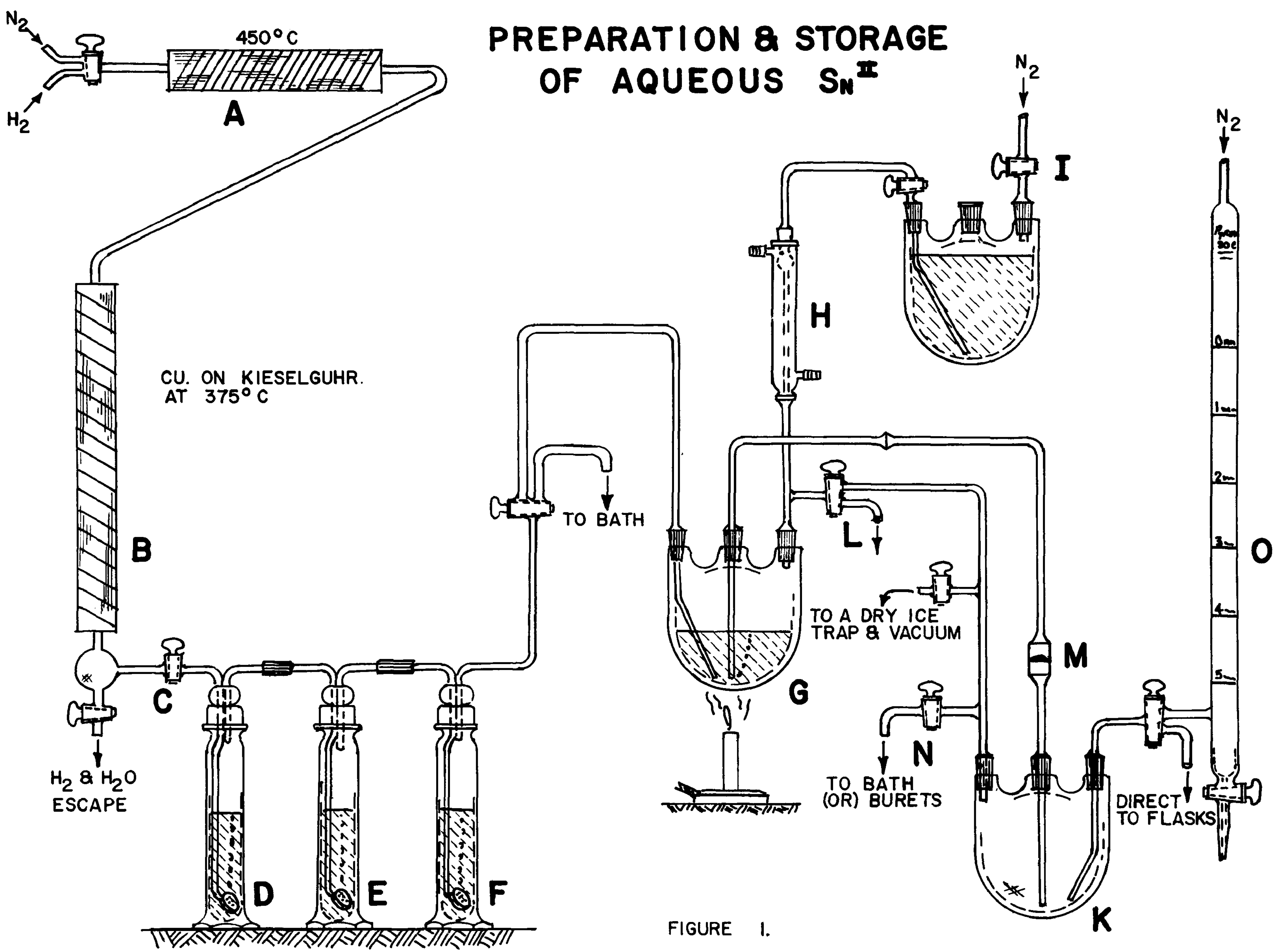

FIGURE 1.

peated twice. Calculated volumes of copper sulfate and sulfuric acid were added to reaction vessel (G) via the condenser (H) under a positive pressure of nitrogen. The system was closed to the atmosphere and evacuated twice as above. Nitrogen was bubbled through the solution for 10-20 hours, after which a threefold excess of Baker C. P. Analyzed 20 mesh tin was added through condenser (H). The system was re-evacuated and nitrogen was bubbled through the solution, until one atmosphere pressure was obtained. The reaction mixture was heated for two hours (twice the time necessary for the blue color of cupric ion to disappear) and cooled under nitrogen atmosphere. The freshly prepared tin(II) solution was diluted to the proper volume with distilled water contained in flask (I). The water in flask (I) was prepared by cooling freshly boiled distilled water under an atmosphere of the specially prepurified nitrogen. After dilution, the tin(II) solution remained in contact with tin metal for ten hours to reduce any tin(IV) formed. The tin solution was transferred to the storage flask (K) by reducing the pressure in the storage flask, closing stopcock (L) and increasing the nitrogen pressure. A fritted glass filter (M), midway between the reaction vessel and the storage vessel, facilitated the removal of excess tin and copper metals. After the transfer operation, flask (K) was usually at a pressure less than one atmosphere. Continuous nitrogen flow equalized the pressure throughout the system and also served to mix completely the tin(II) solutions. The nitrogen was vented through stopcock (N) to flasks in the constant temperature bath.

Nitrogen was bubbled through buret (O) for ten minutes prior to filling the buret with tin(II) solution. The buret was rinsed twice with tin(II) solution, which had been forced into it by use of excess nitrogen pressure. Measured volumes of solution were removed from the buret under an atmosphere of nitrogen. For tin(II) and hydrogen ion concentrations see Table II.

TABLE II

SN(II) PREPARATION

Code	ml. 0.138 M Cu	ml. Conc. H_2SO_4 Acid	Final Concentration M (H^+)	M Sn(II)	M Sn(IV)
2SD	75 ml.	50 ml.	2.214	0.0257	0.0015
2SF	160 ml.	60 ml.	2.406	0.0250	0.0013
2SG	150 ml.	100 ml.	3.448	0.0325	0.0024
2SH	250 ml.	75 ml.	2.307	0.0418	0.0021
2SI	300 ml.	75 ml.	2.980	0.0643	0.0007
2PA	300 ml.*	200 ml.†	1.710	0.0182	0.0000
2SJ	175 ml.	75 ml.	2.036	0.0298	0.0006
2SK	250 ml.	100 ml.	3.227	0.0364	0.0030
2SL	300 ml.	100 ml.	4.254	0.0484	0.0034

* 0.05 M $Cu(ClO_4)_2$ † 70% $HClO_4$

Three methods were used for the preparation of tin(IV) sulfate in aqueous sulfuric acid solutions. An evaluation of these methods appears in the discussion section of the report.

(I) Stannic hydroxide was prepared from Mallinckrodt stannic chloride pentahydrate by precipitating the tin with concentrated ammonia solution. The stannic hydroxide thus obtained was repeatedly washed and digested with distilled water until no chloride ions could be detected in the washings. These purifications required twenty to thirty days. The precipitate was stored under water until needed. The precipitate was dissolved in 3 M sulfuric acid and evaporated on the steam bath until $Sn(SO_4)_2 \cdot 2\ H_2O$ (12, 34) began to crystallize. Complete crystallization occurred on cooling. The stannic sulfate dihydrate was dissolved in aqueous sulfuric acid of appropriate concentrations. Duplicate determinations were made for tin and acid concentrations. Solutions of stannic sulfate prepared by this method were unstable, with respect to formation of white tin(IV) oxide, and were undesireable for use in prolonged kinetic studies.

(II) Hydrogen trisulfatostannate(IV) monohydrate was prepared by the reaction of Baker C. P. Analyzed 20 mesh tin in concentrated sulfuric acid at 190 °C (35). Subsequent fuming of this solution almost to dryness served to coagulate any colloidal sulfides that appeared and these were removed by filtration through fritted glass filter after dissolution of the tin sulfate in hot sulfuric acid. Fuming almost to dryness, filtering and re-dissolving were repeated twice. The resulting salt was hydroscopic and had the composition corresponding to hydrogen trisulfatostannate(IV) monohydrate.

Anal. Calcd. for $H_2Sn(SO_4)_2 \cdot H_2O$: Sn, 27.8; H, by titration, 0.47. Found: Sn, 27.8; H, by titration, 0.48.
Solutions prepared from this compound by heating it with dilute acid were less desireable for kinetic studies, due to hydrolysis, than those prepared by method (III).

(III) Stable solutions of stannic sulfate were prepared by dissolution of 0.2 moles of hydrogen trisulfatostannate(IV) monohydrate in one liter of boiling sulfuric acid. These solutions were kept at the boiling point (with addition of concentrated sulfuric acid to maintain constant volume) for 200-300 hours. After this prolonged heating, the solutions were diluted to 10-12 M acid and analyzed. Further dilution resulted in solutions which were stable with respect to hydrolysis for more than 60 days.

All attempts to prepare stable solutions of tin(IV) in perchloric acid by methods similar to those used for the preparation of tin(IV) sulfate were unsuccessful. Dissolution of freshly precipitated metastannic acid was also unsuccessful. Even dissolved crystalline hydrogen trisulfatostannate(IV) monohydrate was unstable in perchloric acid.

Mallinckrodt A. R. grade oxalic acid was recrystallized from distilled water, dried in vacuo over concentrated sulfuric acid, and ground to a fine powder.

Mallinckrodt analytical reagent grade lithium sulfate monohydrate was recrystallized from distilled water as the monohydrate. The purified salt was dried in vacuo for 24 hours and then in an oven at 180 °C.

for 48 hours in order to prepare the white anhydrous form.

Lithium perchlorate was prepared from Mallinckrodt analytical reagent grade lithium carbonate by the addition of perchloric acid in a slight excess. The solution was evaporated on a steam bath. After cooling, the salt was separated by filtration and recrystallized from distilled water seven times. The salt was dried over anhydrous lithium perchlorate which had been dried in vacuo over concentrated sulfuric acid. In this manner, lithium perchlorate, trihydrate was obtained. A sample of the trihydrate was dried in vacuo over concentrated sulfuric acid, and then heated at 200 °C. for several days. The loss of weight corresponded to that calculated for three moles of water.

The tin(II) concentration was obtained by titration in an atmosphere of carbon dioxide with 0.07 N iodine solution. Prior to each series of titrations, the iodine solution was standardized with arsenous oxide in a bicarbonate buffered medium using freshly prepared starch solution as the indicator (36). The stability of a properly prepared and preserved iodine solution is illustrated by the experience of Washburn (37) who found that the normality of an iodine solution that had been in frequent use during an interval of two months changed less than 0.002%. The sensitivity of starch as an indicator corresponds to an iodine concentration of 2×10^{-5} N. Thus, the concentration of the most dilute tin(II) solutions could be known better than five parts per thousand. The total tin concentrations were evaluated by a modification of Farnsworth's method (38) in which the absorption of a dispersion of tin(II) toluene 3-4 dithiolate was measured at 536 mμ. Matheson Coleman and Bell reagent grade thioglycollic acid was used to reduce the tin species to tin(II), Santomerse SX* was the dispersing agent, and Eastern Chemical Company toluene 3-4 dithiol was used to form the red complex with tin. A standard tin solution containing 393 γ tin/ml. was prepared to be used as a reference. Aliquots of the standard solution, when treated as indicated, were found to obey Beer's law. Dithiol reagent was freshly prepared before each determination by dissolving approximately 0.03 gms. of dithiol in 10 ml. of 2% NaOH. The addition of two drops of thioglycollic acid increased the stability of the dithiol reagent from several hours to several days.

Previous workers (38, 39) have noted poor stability for the tin dithiol complexes. The author has been able to observe stabilities (no spectral changes) of greater than 36 hours by maintaining the following concentrations in the final solution: Sulfuric acid concentration equal to 0.21 ± 0.05 M and tin concentrations from 0.8 to 8.0 γ/ml. A known volume of the appropriate solutions, three reference solutions (100-500 λ of stock solution), the calculated amount of sulfuric acid and 3 drops of thioglycollic acid were thoroughly mixed and diluted to 20 ml. Five drops of Santomerse SX were added, and one half milliliter of dithiol reagent were added, and the solutions were mixed very carefully. The solutions were diluted with water to 25 ml. and the absorbancy determined at 536 mμ. Distilled water, treated as above was used as the reference solution.

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* Trademark, Montsanto Chemical Company

Kinetic Studies

The exchange studies were carried out in solutions with the molar ionic strength of 4.98 except for the series used to study very high hydrogen and sulfate ions, where it was necessary to vary the ionic strength also. The actual kinetic studies were carried out in 100 ml. volumetric flasks. All glassware used was carefully cleaned, dried, heated, blown out with purified nitrogen, and stoppered before use. For all samples, except those in which tin concentrations were varied, the total tin concentration was 2.58×10^{-2} M. Preliminary studies indicated that the half lives would be rather long (300-600 hours), thus it was necessary to keep a stream of nitrogen flowing into the reaction vessels which were stored in a constant temperature bath.

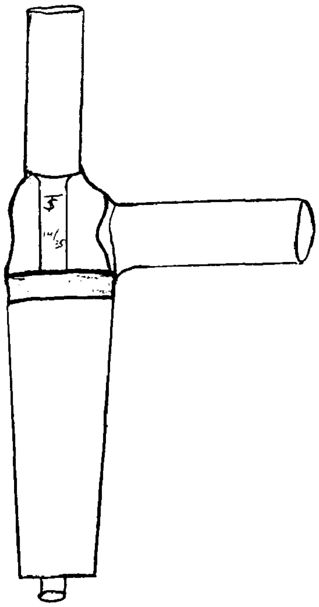

Figure 2

A 14/35 Ŧ male joint was fitted with a 6 mm. glass inlet and an outlet tube (see Figure 2). The vertical tubing served as the gas inlet, and the horizontal tubing served as an outlet to the next inlet tube. Four such adaptors were placed in series. Four series of adaptors came from one common manifold. By maintaining a positive nitrogen pressure above the liquids continuously, it was possible to maintain 10^{-2} M tin(II) solutions for periods up to 100 hours without detectable oxidation.

Previous to each run, the glass-stoppered 100 ml. volumetric flasks were placed into the bath and flushed with nitrogen for 6-8 hours before the addition of any solutions. The solutions used, and the volumes of each were calculated using equations 63-85 in Appendix B. The volumes of sulfuric acid, the volumes of minor acids, the volumes of lithium salts, and the water were added in that order. The flasks were replaced into the constant temperature bath and were cooled and flushed with nitrogen. The calculated volume of tin(IV) was added, and the flasks were flushed with purified nitrogen for 45-60 minutes. The calculated volumes of tin(II) solutions were added under a constant flow of nitrogen. The flasks were stoppered, inverted 10 times and were replaced into the constant temperature bath and flushed with nitrogen. At this point, the flasks contained approximately 96 ml. The reaction flasks were allowed to come to thermal equilibrium for twelve hours. After attaining equilibrium (see Table III), three ml. of Sn^{113} were added and the flasks were inverted 10 times to insure thorough mixing. The flasks were placed in the bath again and nitrogen flow was begun immediately. Zero time was taken as the time when one-half of the activity had drained into the flask. The overall mixing procedure took less than 20 seconds.

As soon as possible, after mixing, the tin(II) concentration was determined iodometrically and the absorption spectrum was measured (see Table III). Data from kinetic runs were recorded only when the absorption spectra and tin(II) concentrations remained constant for two half lives.

TABLE III

TIN(II) CONCENTRATION AND ABSORPTION SPECTRA AS A FUNCTION OF TIME FOR A TYPICAL EXCHANGE EXPERIMENT

t(hrs.)	M[Sn(II)]	$A_{250\ m\mu}$	$A_{270\ m\mu}$
0.5	0.0126	1.89	0.189
50.0	0.0126	1.89	0.192
100.0	0.0127	1.87	0.191
300.0	0.0126	1.87	0.189
600.0	0.0127	1.88	0.193
900.0	0.0127	1.89	0.191

Separation Procedure

(I) Oxalic acid was used to precipitate stannous oxalate. The separation was effected by adding 2 ml. of reaction solution to a small beaker containing 1 gm. of powdered oxalic acid and 2 ml. of saturated oxalic acid solution. To insure complete precipitation, even when tin(II) concentrations were lowered to 0.005 M, 1 ml. of 0.100 M tin(II) in 2.00 M hydrochloric acid was added. The solutions were stirred rapidly with a magnetic stirrer for two minutes and filtered through a stainless steel filter with a removeable chimney and holding 22 mm. Whatman No. 42 paper. The rate of filtration was controlled by an aspirator connected to a micro bell jar with a ground flange and opening for the steel funnel. The filtrate was collected in a 10 ml. volumetric flask. The beaker and precipitate was washed with two 2 ml. samples of saturated oxalic acid solution. The filtrate and washing were diluted to 10 ml. with water and mixed thoroughly. Four ml. samples were withdrawn and were mounted for γ-counting in new 1-dram screw-cap vials. The samples were counted 20-24 hours after separation to insure that equilibrium was established with the In^{113m} present. Periodically, duplicate samples were taken to determine the sampling error.

The precipitation of stannous oxalate was satisfactory for samples containing less than 0.6 M chloride ion. Above 0.6 M chloride ion, the precipitation was kinetically hindered by the chloride and a second method of separation was utilized.

(II) Cesium hexachlorostannate(IV) was precipitated in the high chloride samples. The exchange reaction in the sample was quenched by the addition of 2 ml. of reaction solution to 1 ml. of 0.087 M cesium chloride in 11 M hydrochloric acid. The solution was stirred for 60 seconds and filtered through the same apparatus as in method (I). The filtrate was collected directly in a 1-dram screw-cap vial. The beaker and precipitate were washed with 1 ml. of concentrated hydrochloric acid. Duplicate samples gave results which agreed within expected counting statistics.

The cesium hexachlorostannate samples were not counted until 20-24 hours after separation; the In^{113m} activity at this time indicates the amount of Sn^{113} present in the filtrate.

It is possible to obtain equilibrium activities, i.e. activities when $t = \infty$, by taking samples after ten half lives. With very long half lives, or as in this case where possible oxidation becomes a factor, a calculated value for the activity must be used. This method has been used successfully by several authors (18, 40) and was also used, in part, in this study. Since the decrease of activity in an initially active component was observed, (1-f) has been rewritten

$$26) \qquad (1-f) = \frac{X - [1 - \bar{n}(II)]X_o}{\bar{n}(II)X_o}$$

Where X is the activity at any time, t, $\bar{n}(II)$ is the average mole fraction of tin(II) in the sample, and X_o is the initial activity of the radioactive component.

The (1-f) values, Appendix A, pp. 80-102, have been calculated using Equation (26). To facilitate future calculations, the c/s(IV) values listed in Appendix A have been calculated using

$$27) \qquad c/s(IV) = X - [1 - \bar{n}(II)]\,X_o$$

and the c/s(IV) when $t = \infty(c)$ are

$$28) \qquad c/s(IV)_{\infty} = [\bar{n}(II)][X_o]$$

thus

$$29) \qquad (1-f) = \frac{c/s(IV)}{c/s(IV)\,\infty}$$

All other counts recorded are the counting rates observed per 4 ml. vial and have been corrected for background. These are marked as c/s(II) and since observed activities at t $= \infty$ were used, these are marked "observed".

The activities of three samples prepared from aliquots of the same active solution were the same within the counting error, indicating satisfactory reproducibility of the radio-assay technique. For the exchange experiments, samples were counted for a minimum of 10,000 counts.

It is necessary for the ionic strength of the medium to remain constant for the study of complicated equilibrium in order to try to eliminate activity coefficients as variables. Any limitation that this method may have is certainly outweighed by this advantage.

In order to vary the hydrogen, sulfate, or chloride ions and to maintain constant ionic strength it was necessary to consider the bisulfate ion dissociation as a function of ionic strength. The thermodynamic dissociation constant of the bisulfate ion is defined as

$$30) \qquad K_2 = \frac{(a_{H^+})(a_{SO_4^=})}{(a_{HSO_4^-})} = \frac{(C_{H^+})(C_{SO_4^=})}{(C_{HSO_4^-})} \cdot \frac{(y_{H^+})(y_{SO_4^=})}{(y_{HSO_4^-})}$$

and since it is difficult to measure individual activity coefficients, one defines

$$31) \qquad y_R = \frac{(y_{H^+})(y_{SO_4^=})}{(y_{HSO_4^-})}$$

and values of y_R are available from Smith's (41) Raman spectral data as a function of the molarity of sulfuric acid based upon K_2(at 25 °C.) $= 0.0104$ (41). From which a value of $y_R = 0.00531$ is obtained for

3.00 M sulfuric acid.

Thus,

$$32)\qquad 1.96 = \frac{(\underline{M}_{H^+})(\underline{M}_{SO_4^=})}{(\underline{M}_{HSO_4^-})} = K_{2C}$$

Concentrations of the sulfuric acid species may be defined in terms of K_{2c}, and the ionic strength which is defined as

$$33)\qquad \mu = \frac{1}{2} \sum_{all}^{i} \underline{M}_i \, (Z_i)^2$$

where $\underline{M}_i$ is the molarity of species (i) with charge Z_i. Using the method described by Young and Blatz and assuming that the addition of lithium sulfate, lithium perchlorate, lithium chloride or perchloric acid do not alter the correspondence of K_{2c} to μ, concentrations of various species can be evaluated by use of Equations (63-85) in Appendix B. For the addition of any of these salts it is assumed that they are completely ionized. Brubaker has shown (10, 11, 12) that the predominant tin(IV) species in 3.00 M sulfuric acid are neutral species and should not affect the ionic strength. If these assumptions about the tin(IV) species were incorrect, with the total tin concentration equal to 2.58×10^{-2} M, an error of less than 1% would show up in the K_{2c} for sulfuric acid.

The qualitative absorption spectra were run on a Beckman DK-2 recording spectrophotometer. All of the quantitative spectra were measured with a line operated Beckman model DU spectrophotometer equipped with a photomultiplier. Matched, stoppered 1 cm. quartz cells and a blank solution corresponding to each sample were used and the cells were calibrated after each series of measurements. No change in the absorbancy was observed on exposure of tin(IV) or tin(II) solutions to the ultraviolet beam in the spectrophotometer for periods up to thirty minutes. Sample cells were filled and emptied until constant absorbancies were observed. Immediately after recording the absorbancy, the concentration of the tin(II) was determined iodometrically. Samples in which more than 1% oxidation had occurred were discarded and new samples were examined.

Electromigration studies were carried out on one-half by 10 inch strips of Eaton-Dikeman No. 652 electrophoresis paper using the apparatus described by Brubaker (12). The apparatus was modified such that a purified nitrogen atmosphere could be maintained over the tin(II) samples to minimize oxidation.

RESULTS

Spectrophotometric Observations

A detailed spectrophotometric study of tin(II) and tin(IV) was carried out simultaneously with the radioactive exchange studies between the two oxidation states. The absorption results precede the kinetic results. Figure 3 exhibits the absorption spectra in 3.00 M sulfuric acid of (A) 2×10^{-3} M Sn(II); (B) 1×10^{-3} M Sn(IV), prepared by dissolution of $Sn(SO_4)_2 \cdot 2\ H_2O$ in 3.00 molar sulfuric acid; (C) 2×10^{-3} M Sn(IV), prepared by prolonged heating with sulfuric acid (method III) and diluted to 3.00 M sulfuric acid.

The general shape of the tin(II) absorption curve was similar to that observed by Court (39). A minimum occurs in the absorption curve if the solution contains little or no tin(IV) contamination. As the tin(IV) concentration in the tin(II) increases, the absorption at the minimum increases. At about 10% tin(IV) concentration, a 6-10 mμ plateau is observed, followed by a steep rise. The exact position of this minimum is also a function of the hydrogen ion, with shifts to lower wave lengths observed as the hydrogen ion increases.

Aqueous sulfuric acid solutions of tin(II) were found to obey Beer's law (from 230 - 260 mμ) to ± 1%, as the tin(II) was varied from 5×10^{-4} M to 2×10^{-2} M.

This work is in agreement with Davidson's (18) observation that a decrease of chloride ion displaces the tin(II) absorption to lower wave lengths. The measurements at very low chloride ion (20 Cl^-/Sn(II))

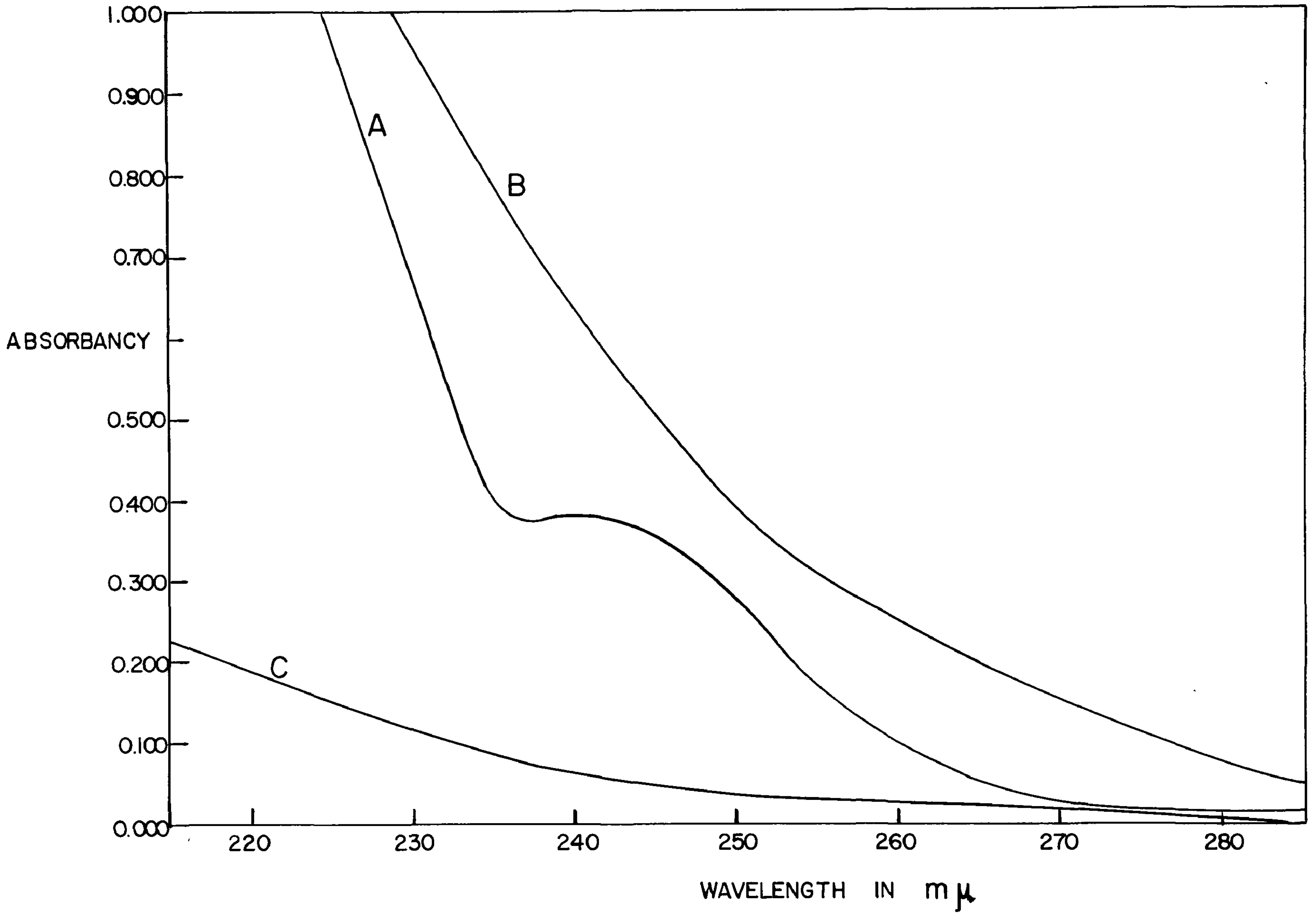

FIGURE 3. ULTRA-VIOLET SPECTRA OF TIN(II) AND TIN(IV) SULFATE, IN 3.00 **M** SULFURIC ACID
(A) 2×10^{-3} **M** Sn(II), (B) 1×10^{-3} **M** Sn(IV), (C) 5×10^{-3} **M** Sn(IV)

were made at 240 - 260 mμ, whereas at higher chloride ion concentrations, absorbancies were measured around 300 mμ.

In contrast to the failure of Beer's law, observed for dilute solutions of tin(II) in 3.00 to 10.00 M chloride by deMaine and deMaine (42), all of the tin(II) solutions followed Beer's law to ± 2%.

It was necessary to correct the tin(II) solutions for the tin(IV) present and the absorption spectra of tin(II) solutions containing more than 2% tin(IV) were found to disobey Beer's law, unless they were so corrected. Careful preparation of tin(II) resulted in less than 2% tin(IV) and little or no correction was necessary. The absorption spectra of these solutions were found to follow Beer's law very well from 230 - 260 mμ.

The log of the "observed" molar absorbancy index, where the absorpancy index is defined as

$$34) \qquad a_{(obs)} = A_{(obs)}/C(Sn(II)) \; ,$$

has been plotted as a function of wave length between 220 mμ and 260 mμ for perchloric and sulfuric acids. These absorption spectra, for solutions of tin(II) in perchloric acid, are shown in Figure 4. Figure 5 illustrates some typical absorption spectra for tin(II) solutions in sulfuric acid. Qualitatively, the curves in Figures 4 and 5 appear to be quite similar. The hydrogen ion concentration was calculated for the sulfuric acid solutions, using the data of Smith (41), and Figure 6 shows $a_{(obs)}$ at 230, 240 and 250 mμ as a function of the calculated hydrogen ion concentration.

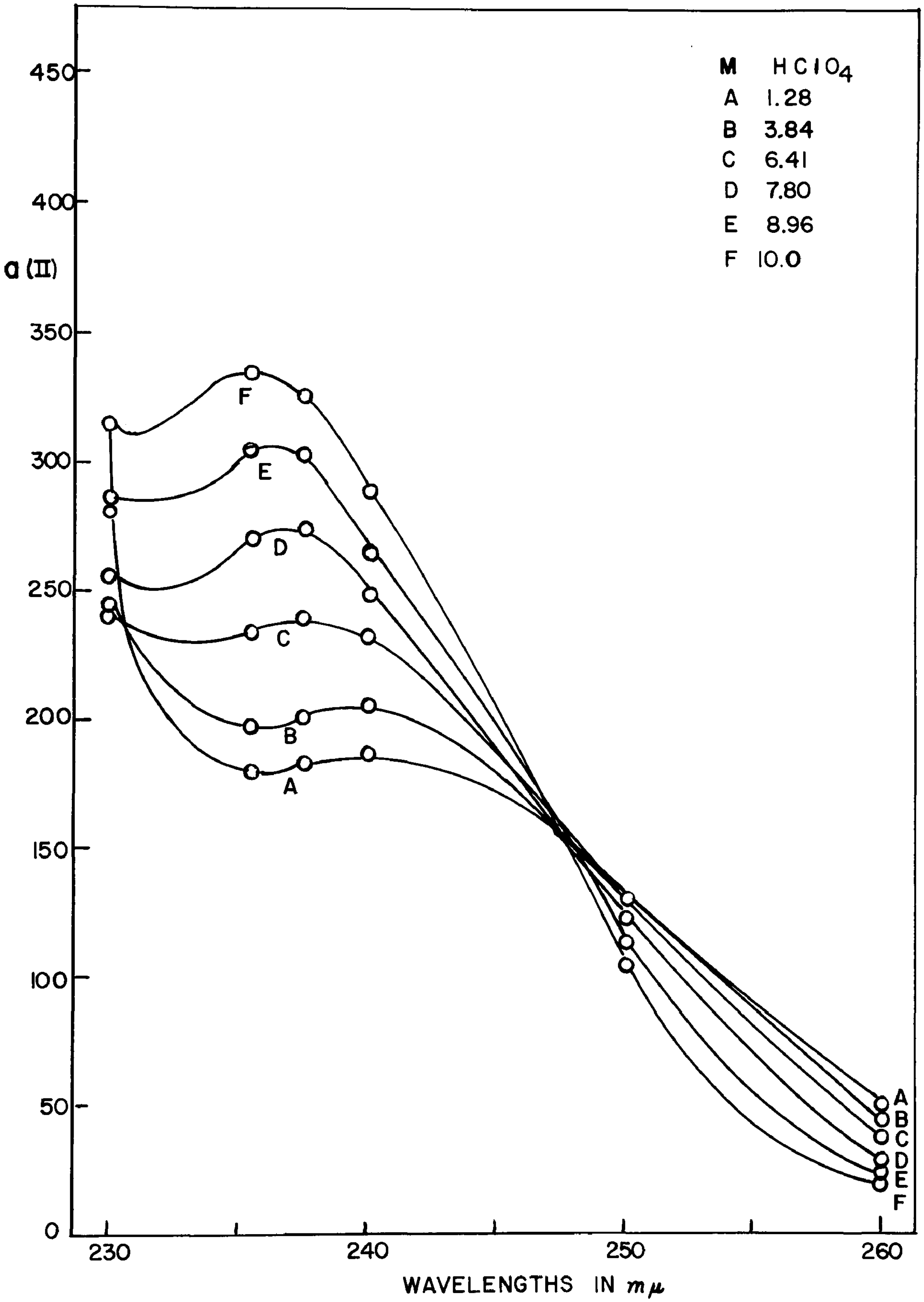

FIGURE 4. THE ABSORBANCY INDEX OF TIN (II) IN PERCHLORIC ACID AS A FUNCTION OF WAVELENGTH.

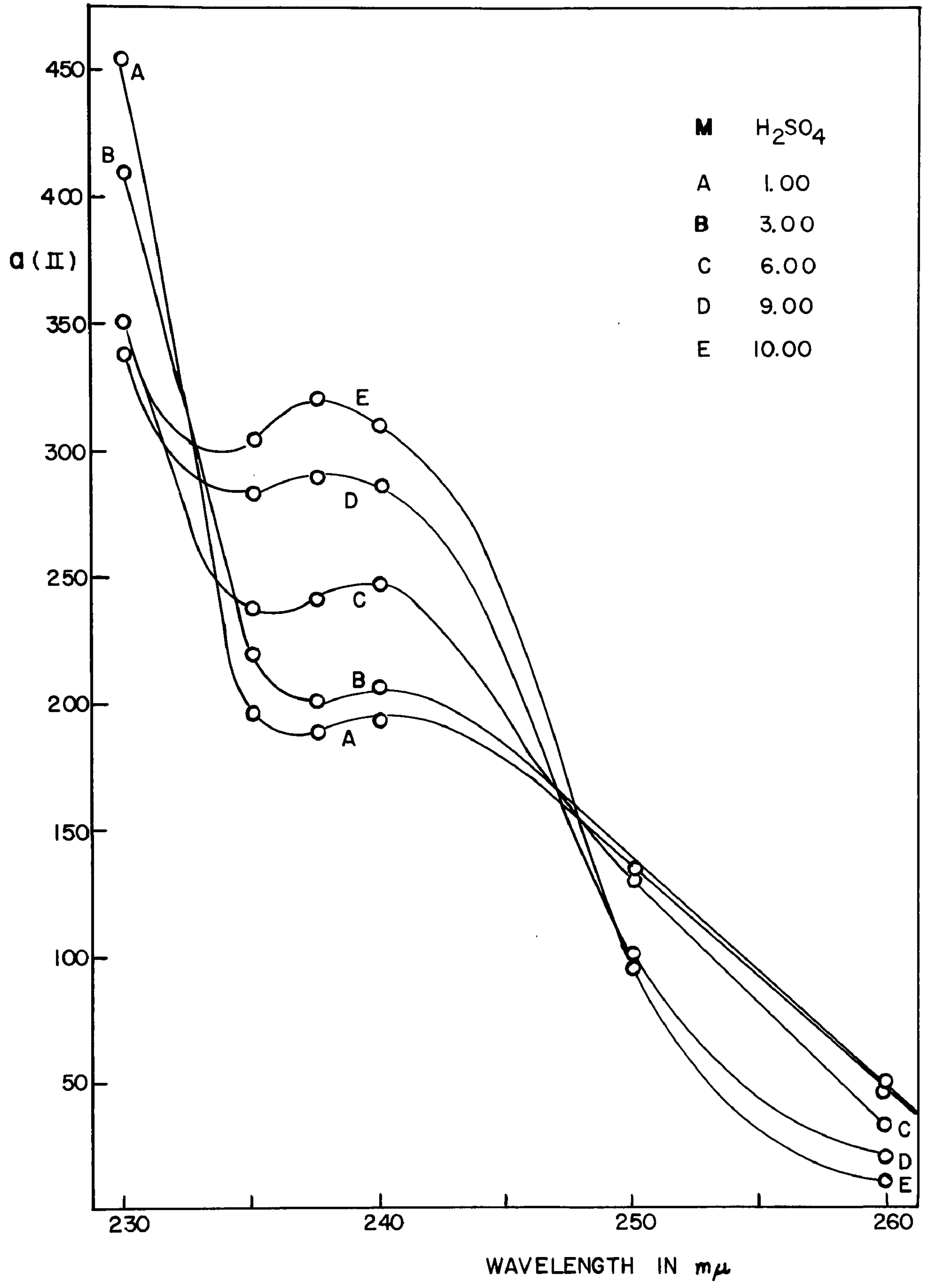

FIGURE 5. THE ABSORBANCY INDEX OF TIN (II) IN SULFURIC ACID AS A FUNCTION OF WAVELENGTH.

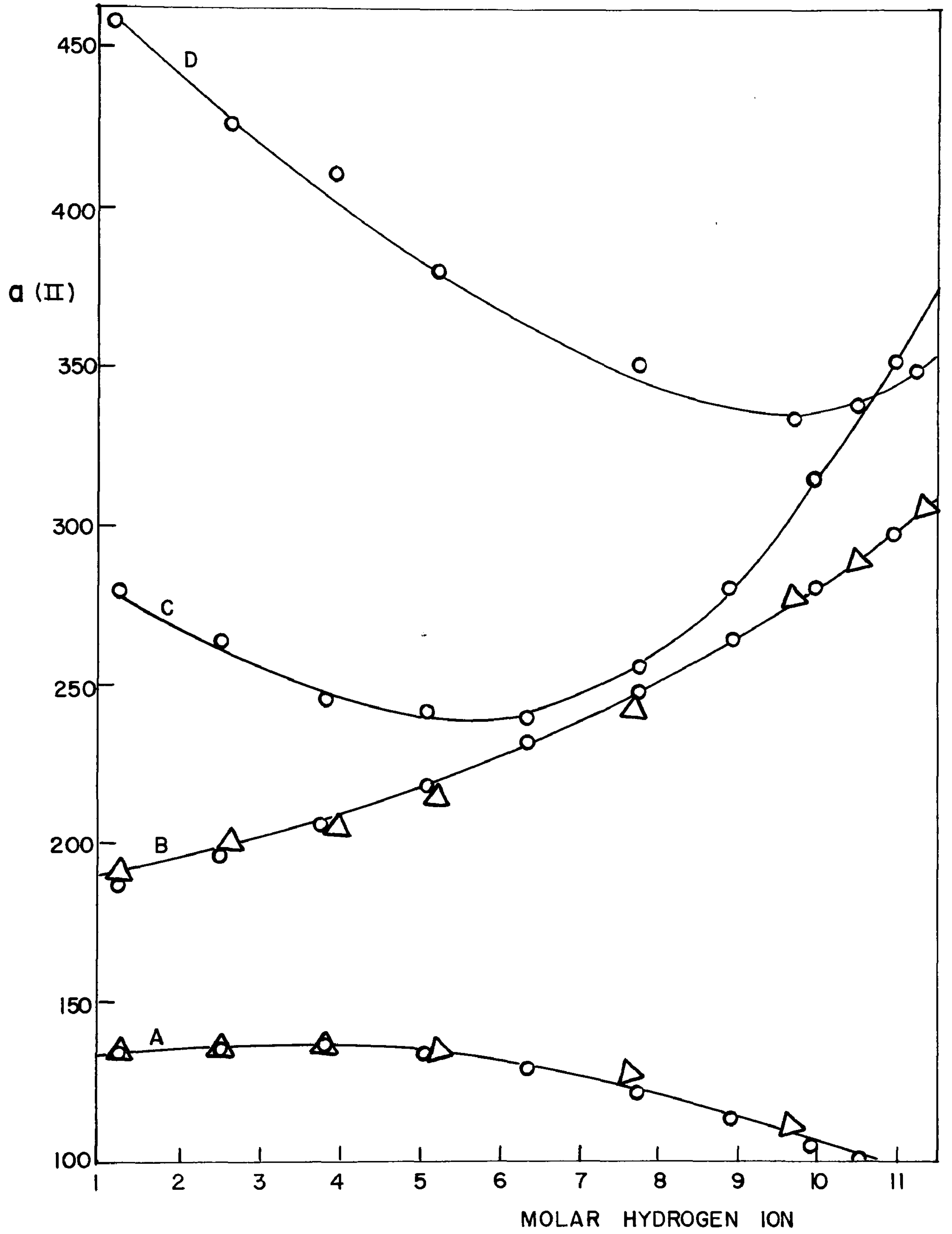

FIGURE 6. THE ABSORBANCY INDEX OF TIN(II) AS A FUNCTION OF HYDROGEN ION CONCENTRATION.

(A) ○ $HClO_4$ SOLUTIONS AT 250 mμ ; △ H_2SO_4 SOLUTIONS AT 250 mμ
(B) ○ $HClO_4$ SOLUTIONS AT 240 mμ ; △ H_2SO_4 SOLUTIONS AT 240 mμ
(C) $HClO_4$ SOLUTIONS AT 230 mμ ; (D) H_2SO_4 SOLUTIONS AT 230 mμ

At 240 and 250 mμ, the absorption spectra of tin(II) are virtually identical in both sulfuric and perchloric acids, suggesting the following type of equilibrium:

35) $$Sn^{++} + H_2O \rightleftharpoons SnOH^{+} + H^{+} \qquad K_1$$

If a_1 is the absorbancy index for $SnOH^+$, and a_2 is the absorbancy index for Sn^{++}, we can assume that $a_{\infty} = a_2$, and that $a_o = a_1$. Now, if we also assume that $SnOH^+$ and Sn^{++} are the only "colored" species observed at 240 mμ, we can write

36) $$a_{(obs)} = \left\{a_1[SnOH^+] + a_2[Sn^{++}]\right\}\left\{C_{(Sn)}\right\}^{-1}$$

then

37) $$\frac{a_{(obs)} - a_o}{a_{\infty} - a_o} = \frac{\left(a_1[SnOH^+] + a_2[Sn^{++}] - a_o C_{(Sn)}\right)/\left(C_{(Sn)}\right)}{a_2 - a_1}$$

and using K_1 from equation (35) and the definition of a_{∞} and a_o, we can write

38) $$\frac{a_{(obs)} - a_o}{a_{\infty} - a_o} = \frac{a_1K_1/(H^+) + a_2 - a_1[K/(H^+) + 1]}{[a_2 - a_1][(K/H^+) + 1]}$$

Equation (38) can be inverted and rewritten as

39) $$\frac{a_{\infty} - a_o}{a_{(obs)} - a_o} = 1 + K/(H^+)$$

The value $a_o = 179$ is obtained by extrapolation of curve B in Figure 6 to zero hydrogen ion concentration. A plot of

$[a_\infty - a_o]/[a_{(obs)} - a_o]$ as a function of hydrogen ion yields a good straight line if $a_\infty = 320$. K_1 is determined from the slope and is 24.5 ± 0.05. These data are summarized in Table (IV).

If the species present can be adequately described by Equation (35), then the spectra of tin(II) in perchloric acid at 230 mμ should also follow this description. Thus, let

$$40)\qquad a'_{(obs)} = \frac{a'_1[K_1/(H^+)] + a'_2}{[K_1/H^+] + 1}$$

where a' denotes the absorbancy index at 230 mμ. Since K_1 has been evaluated, it can be substituted in Equation (40) and by subsequent rearrangement, we obtain Equation (41).

$$41)\qquad [a'_{(obs)}][1 + K_1/H^+] = [a'_1K_1/H^+] + a'_2$$

A plot of $[a'_{(obs)}][1 + \frac{K_1}{H^+}]$ as a function of $[K_1/H^+]$ is linear with a slope, $a'_1 = 300$ and an intercept, $a'_2 = 250$. These spectrophotometric data are summarized in Table (V).

The proposed mathematical model which quantitatively describes the equilibrium between $SnOH^+$ and Sn^{++} can also be used qualitatively to explain the general shape of the tin(II) spectra. Since the maximum in the absorption spectra appears to be in the vicinity of 240 mμ and the absorbancy index for $SnOH^+$ increases toward shorter wave length, a minimum could occur when these two curves were added together, and this minimum would be expected to shift toward shorter wave lengths as the hydrogen ion increased, because the absorption due to Sn^{++} would be

TABLE IV

THE "OBSERVED" ABSORBANCY INDEX AND VARIOUS OTHER DERIVED QUANTITIES FOR 2.00 x 10^{-3} $\underline{M}$ TIN(II) IN ACID SOLUTION AT 240 mμ

$\underline{M}$ (H^+)	a_{obs}	($1/H^+$)	$\frac{a_{\infty} - a_o}{a_{obs} - a_o}$
1.00	185	1.000	23.5
1.40	187_5	0.714	16.6
1.60	190	0.625	14.1
2.00	192	0.500	10.8
3.00	199	0.333	7.05
4.00	207	0.250	5.05
5.00	217	0.200	3.74
6.00	227	0.167	2.94
7.00	238	0.142	2.39
8.00	251	0.125	1.96
9.00	265	0.111	1.64
10.00	281	0.100	1.38
11.00	298	0.091	1.18

TABLE V

THE "OBSERVED" ABSORBANCY INDEX AND VARIOUS OTHER DERIVED QUANTITIES FOR 2.00 x 10^{-3} M TIN(II) IN PERCHLORIC ACID AT 230 mμ

M (H^+)	$a_{(obs)}$	(K_1/H^+)	$[a'_{(obs)}]/[1 + K_1/H^+]$
1.30	285	19.9	5860
2.62	269	10.9	2940
3.30	262	8.4	2200
3.99	255	7.1	1810
4.61	250	6.3	1575
5.27	246	5.65	1390
5.90	243	5.15	1250
6.52	241	4.75	1145
7.18	239	4.41	1051
7.76	240	4.16	1000
8.27	242	3.96	959
8.82	245	3.78	926
9.30	250	3.63	910
9.76	259	3.51	910

increasing and that due to $SnOH^+$ decreasing.

The spectra of tin(II) in sulfuric acid at 230 mμ suggest that some highly "colored" tin(II) species is formed in dilute sulfuric acid, and that similar species to those observed in perchloric acid exist in more concentrated sulfuric acid. This suggests possible ion-pair formation between the partially hydrolized species, $SnOH^+$, and $SO_4^=$ or HSO_4^-. No suitable mathematical model has been found that can describe these data.

Curves B and C in Figure 3 are representative of the absorption spectra observed for solutions of Sn(IV) in 3.00 M sulfuric acid. The absorbancy index for $Sn(SO_4)_2 \cdot 2\ H_2O$ as a function of sulfuric acid concentrations have been reported (11), and those observed in curve B are in agreement with these values reported in the literature. It is also reported that these solutions are somewhat unstable, becoming cloudy in less than a week, and finally, hydrous white tin(IV) oxide is precipitated.

Preliminary exchange studies in sulfuric acid indicated that the half lives would be on the order of hundreds of hours. Thus, it was essential to obtain tin(IV) species whose absorption spectra would remain constant for this period of time. It was assumed that a change in the absorption would be an indication that the species were changing, and, therefore, the rates of exchange observed would be meaningless. Figure 7 shows how the absorption spectra of these tin solutions change with time. No Tyndall beam was observed for the first 60 hours. By 75 hours, a Tyndall beam was visible and at 100 hours, a visible

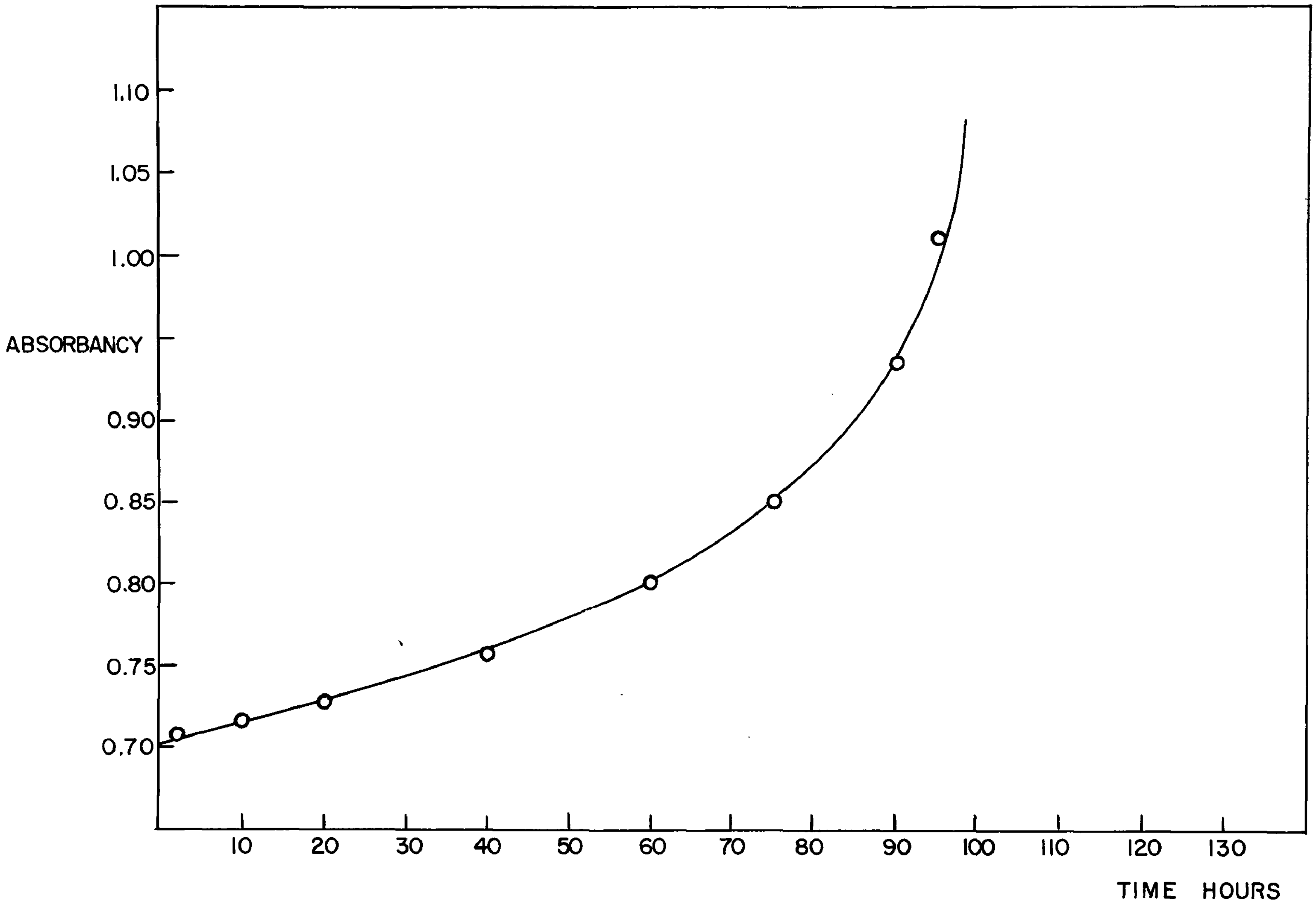

FIGURE 7. ULTRA-VIOLET ABSORBANCY OF $Sn(SO_4)_2 \cdot 2H_2O$ IN 3.00 **M** H_2SO_4 AS A FUNCTION OF TIME

precipitate was observed.

Very small absorbancy indices were observed for solutions of tin(IV) that had been boiled in sulfuric acid for prolonged periods of time [curve C, Figure 3]. The absorption spectra did not change with time, i.e., the absorbancy index was constant for 800 hours.

Both tin(IV) solutions were observed to obey Beer's law although the curves did not intercept the abscissa at zero, which is indicative of more than one tin species being present.

The absorption spectra of mixed solutions of tin(II) and tin(IV) were dependent on the history of the tin(IV) species present. The mixed solutions, in all cases, absorbed more energy than the sum of the absorptions of the individual components. All of the following spectra were studied in 3.00 M sulfuric acid, except for the studies which were 1.00 M in chloride ion, and these solutions were 3.99 M in hydrogen ion (the H^+ concentration of 3.00 M sulfuric acid). The interaction spectra for two different tin preparations will be treated separately.

Dissolution of $Sn(SO_4)_2 \cdot 2\ H_2O$ in 3.00 M sulfuric acid provides solutions in which the tin(IV) spectra change with time (see Figure 7), but the spectra are reproduceable, at any given time after dissolution. Thus, the absorbancies were determined fifteen minutes after the solutions were mixed. The absorbancy indices for the tin(II) and tin(IV) were the same order of magnitude (424, and 630 @ 240 mμ) and suggest that these solutions will support the model proposed by Davidson (18) for the tin(II) - tin(IV) - chloride system. Equation (9) defines this relationship and Figure 8 displays some of the data that support Equation (9). These data indicate that the interaction absorption is that of a dimeric species, formed by

$$42) \qquad Sn(II) + Sn(IV) \rightleftharpoons Sn(II)Sn(IV)$$

and not the formation of an intermediate species,

$$43) \qquad Sn(II) + Sn(IV) \rightleftharpoons 2\ Sn(III)$$

If Equation (43) were correct, a plot of $[C(II) \cdot C(IV)]^{\frac{1}{2}}$ against $A_{(obs)}$ would be linear, but this is not the case (Figure 8). Mathematically, the system can be described by $A_{e} = k[C(II) - C(D)][C(IV) - C(D)]$, where C(II) and C(IV) refer to the molar concentration of tin(II) and C(D) is the molar concentration of the interaction dimer. However, the use of Equation (9) implies that the concentration of interaction species must be very low (although it may have a rather large absorbancy index) because the cross terms seem to be negligible.

Several solutions, containing tin in both oxidation states, were prepared using tin(IV) that had been boiled in sulfuric acid for 250 hours. Since the absorbancy indices of these tin(IV) solutions were very low, it was possible to use the method of continuous variation to study the complex formation. A graph of Δ A as a function of the tin(II) - tin(IV) ratio is exhibited in Figure 9 . A maximum occurs in this graph at a ratio of 1:1 which supports the formation of an interaction dimer. Variation of sulfuric acid concentration affects the absorbancy indices of the individual species, but Δ A remained

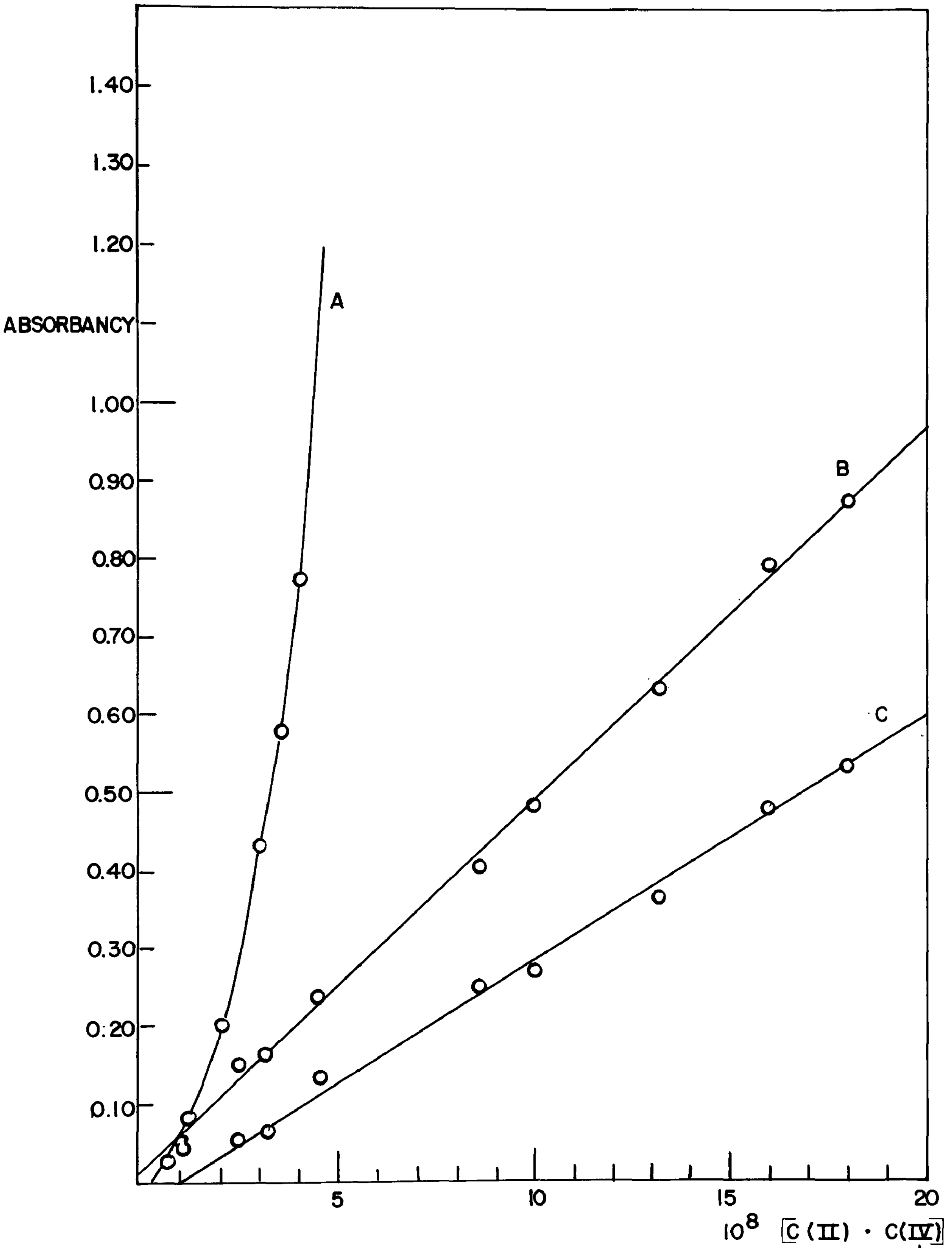

FIGURE 8. (A) ABSORBANCY AS A FUNCTION OF $(C(II)\,C(IV))^{1/2}$ AT 240 mμ
(B) ABSORBANCY AS A FUNCTION OF C(II) C(IV) AT 240 mμ
(C) ABSORBANCY AS A FUNCTION OF C(II) C(IV) AT 260 mμ

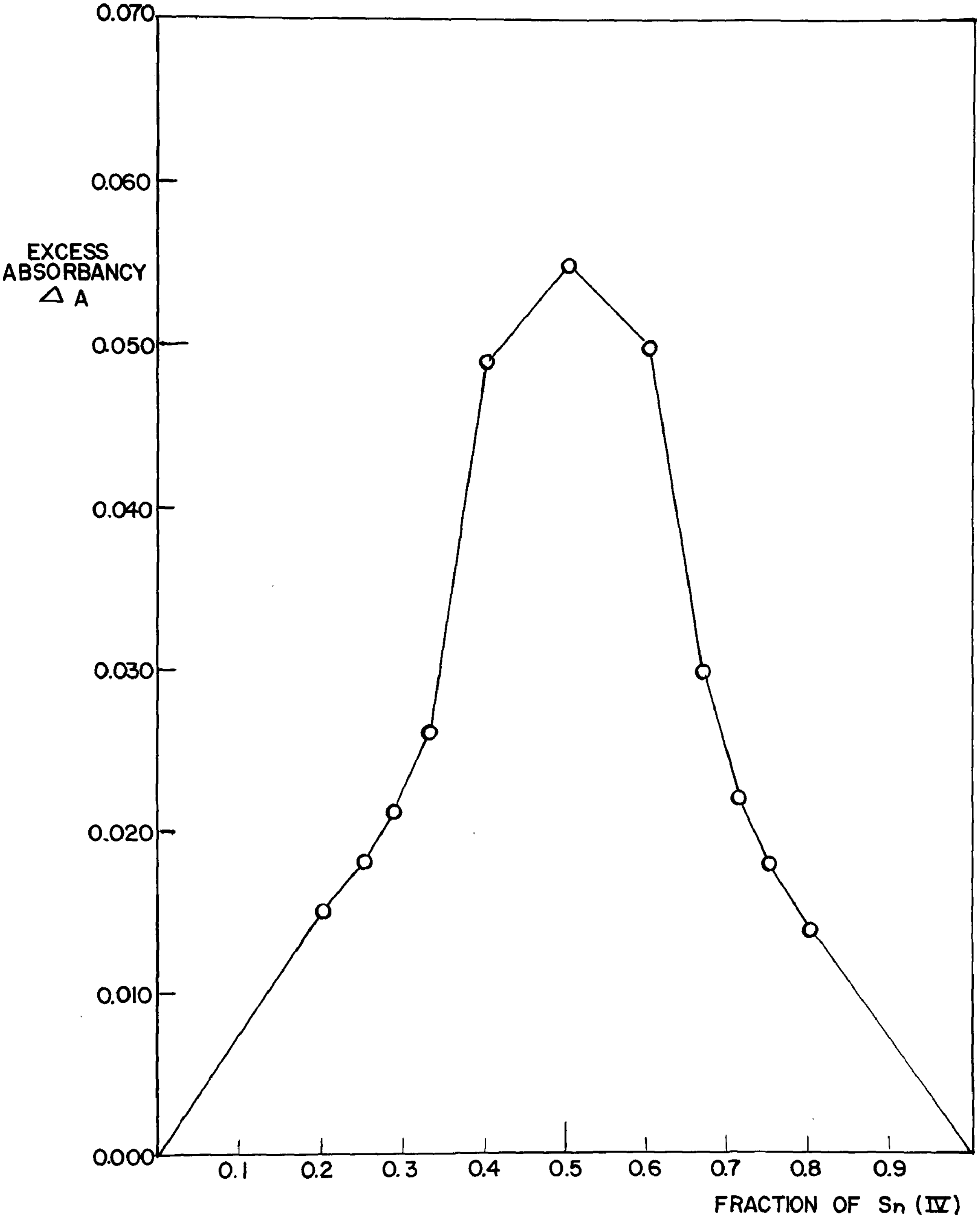

FIGURE 9. EXCESS ABSORBANCY AS A FUNCTION OF TIN COMPOSITION. 2.5×10^{-3} M TOTAL TIN IN 3.00 M H_2SO_4

constant, even though the sulfuric acid concentration was varied from 2.5 to 4.5 M.

Evidence for complex formation between tin(II) and tin(IV) in hydrochloric acid solutions has been given by Davidson (18), and in a series of papers by de Maine and de Maine (42). Analysis of these spectra indicate that the observed enhancement is due to interaction between tin(II) and tin(IV) species. Figure 10, curve B exhibits a graph of Δ A against the tin(II) - tin(IV) ratio in 1 M chloride. In conformity with Davidson's results, a maximum is observed at a ratio of one to one, indicating an interaction dimer.

Kinetic Observations

Variation of the concentration of each reactant is necessary to determine the order of that component with respect to the overall exchange rate. Figures 11, 12 shows some typical graphs of log(1-f) against t for several runs. Curves A and B, Figure 11 include data from the oxalate precipitation of tin(II). Curves B and C, Figure 12 give a comparison of the half lives obtained by the two different precipitation methods. Curve B is typical of the oxalate precipitate in high chloride, curve A is from the cesium precipitation of tin(IV) for the same run, and curve C is typical of other runs in which tin(IV) was precipitated.

Values of the exchange rate R were computed from the half time obtained from graphs, such as those in Figures 11 and 12. It has been shown by Prestwood and Wahl (46) that incomplete separation or partial

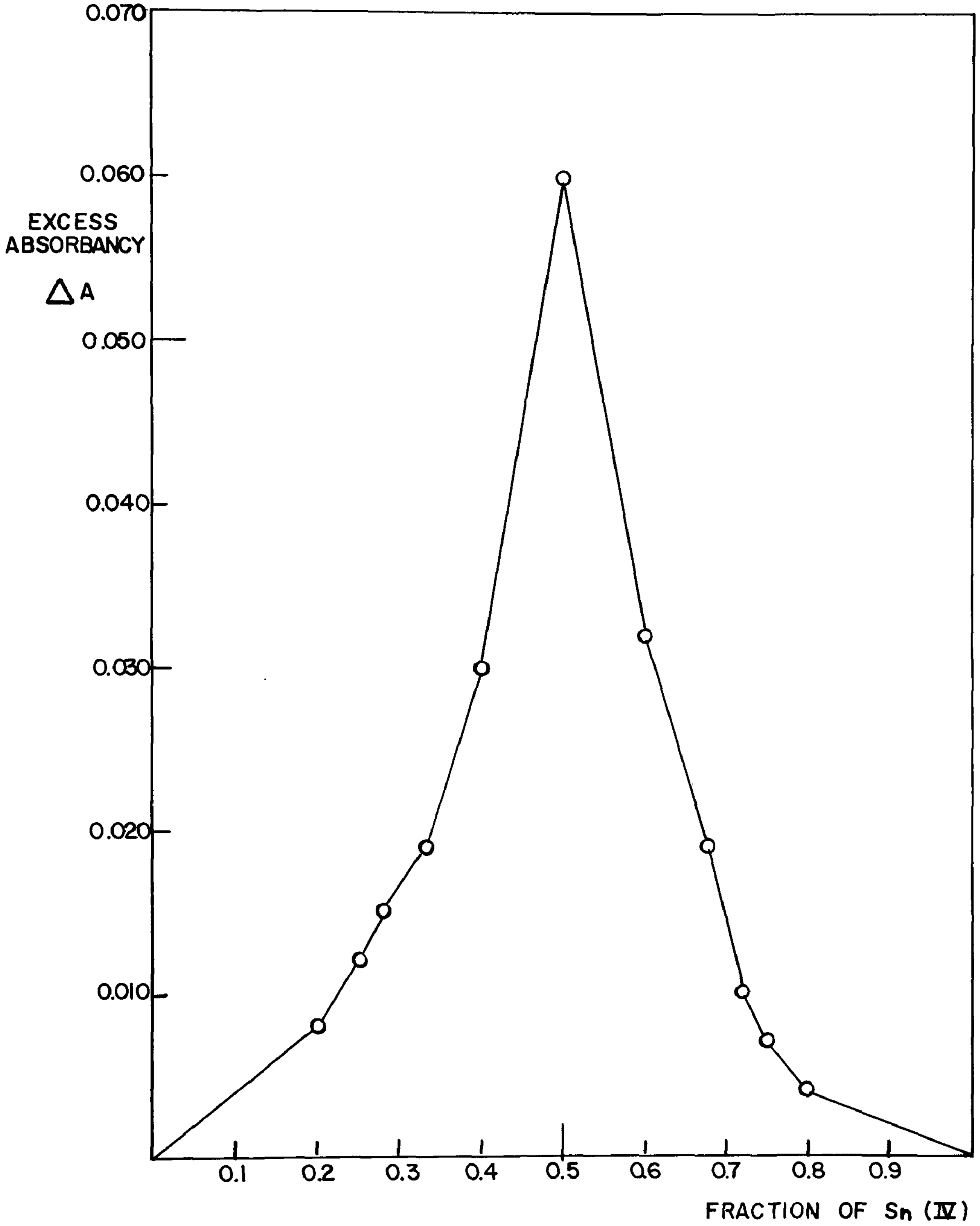

FIGURE 10. EXCESS ABSORBANCY AS A FUNCTION OF TIN COMPOSITION. 2.5×10^{-3} M TOTAL TIN IN, 1.00 M HCl, WITH 3.99 M H^+ AND 0.79_5 M $SO_4^=$.

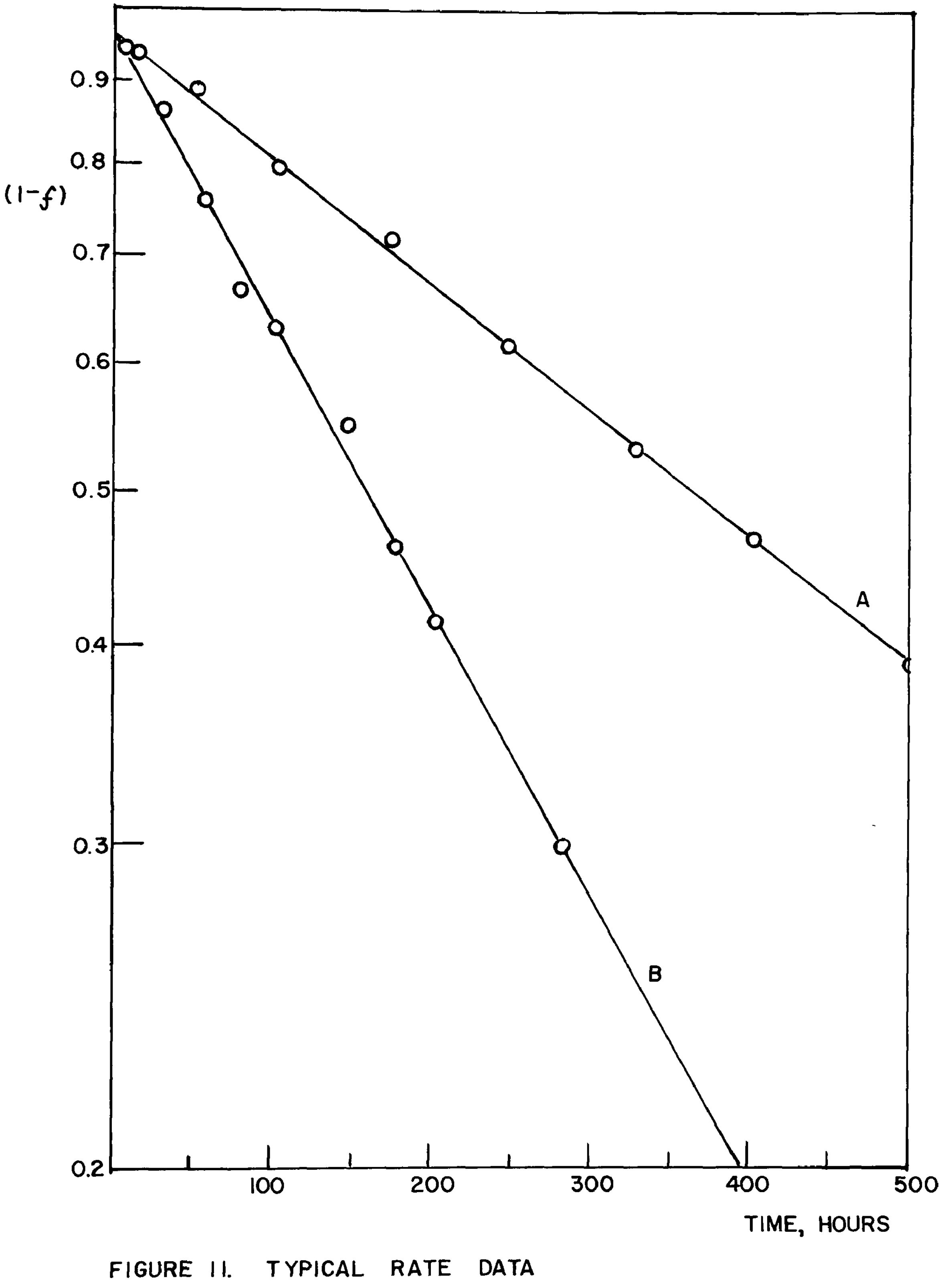

FIGURE 11. TYPICAL RATE DATA

(A) 3.00 **M** H_2SO_4, (B) 0.077$_5$ **M** Cl^- IN 3.00 **M** H_2SO_4

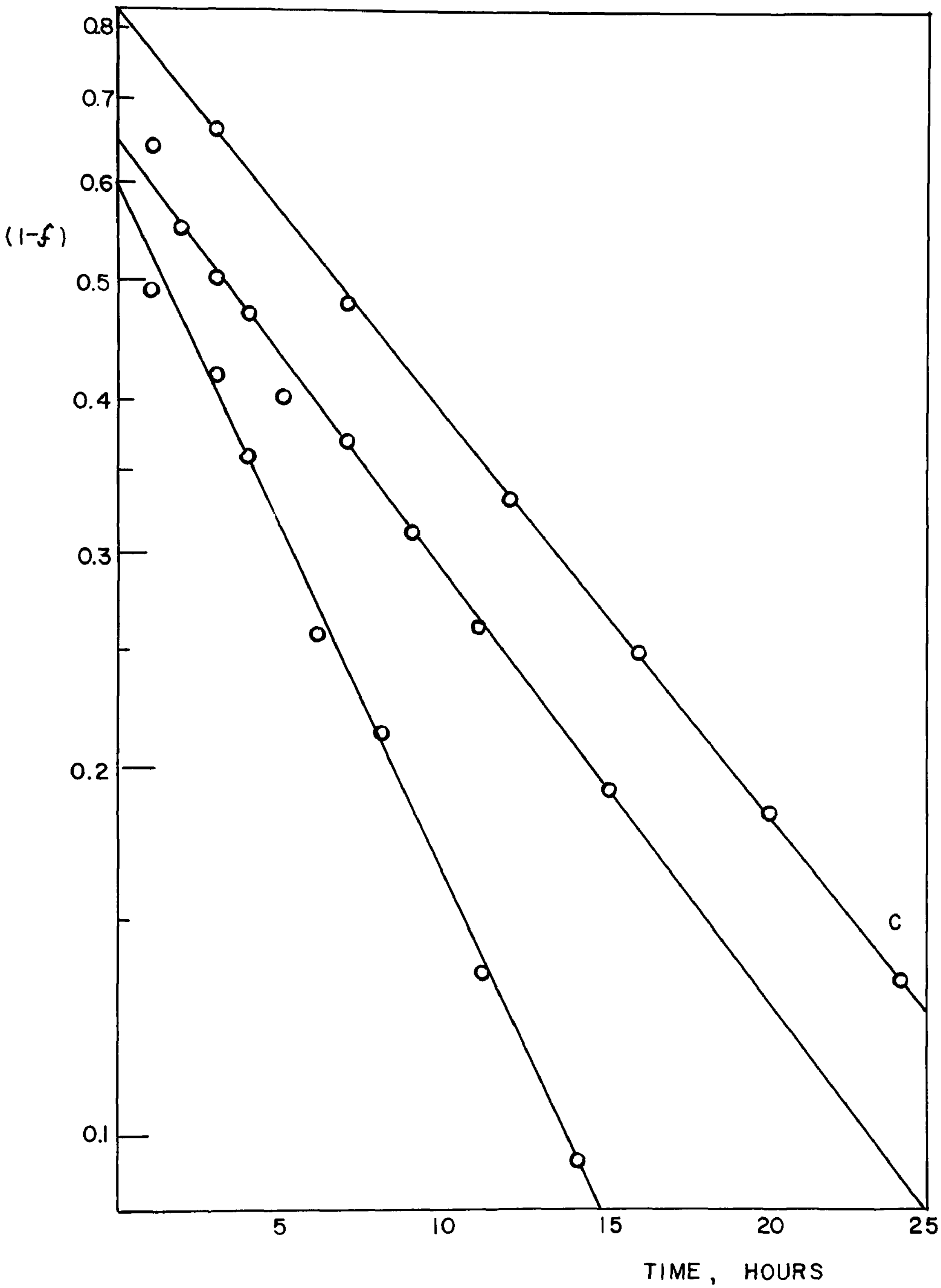

FIGURE 12. TYPICAL RATE DATA FOR PRECIPITATION FROM TWO DIFFERENT MEDIA.

(A) Cs_2SnCl_6 FROM 1.00 **M** Cl^-

(B) Cs_2SnCl_6 FROM 0.60 **M** Cl^-

(C) SnC_2O_4 FROM 0.60 **M** Cl^-

catalysis of an exchange reaction by the separation method does not affect the value of R determined in this way, provided these affects are reproducible in each run. In these experiments, the apparent zero time exchange for the cesium precipitation of tin(IV), i.e., the value of 100 X/X_{∞} at $t = 0$, averaged about 45%.

The agreement of duplicate runs (curves B and C, Figure 12) by two different methods and the statistical agreement with the predicted exchange law is a good indication that the method is justified.

A log-log plot of the rate of exchange, from independent variation of tin(II) and tin(IV) concentrations, against tin concentration gave the expected linear relationship. When the tin(IV) concentration was maintained constant, and tin(II) varied, it was found that $\alpha = 0.98_9 \pm 0.04$. Constant values of tin(II) and variation of tin(IV) concentration resulted in $\beta = 0.99_4 \pm 0.01_5$. The constant k or R/ab can be evaluated for 3.00 M sulfuric acid (3.00 M hydrogen ion and 0.99 M sulfate ion) from the above data. Table VI summarizes these data. A value of 0.0621 ± 0.0017 liters/mole-hour was obtained for R/ab.

In order to evaluate the effect of hydrogen ion on the rate of exchange, a series of experiments were made in which the ionic strength was maintained at 4.98 and the sulfate ion concentration was kept at 0.99 M. The equations used to satisfy these conditions are listed in Appendix B. A summary of these data appear in Table VII, where C(Sn) is the total M tin concentration. The variation of R can be shown in a log-log plot of the rate constant against hydrogen ion[‡] concentration, where a slope of -1.5 ± 0.1 was observed. An increase in the

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[‡] Calculated hydrogen ion concentration as evaluated on page 28

TABLE VI

DEPENDENCE OF EXCHANGE RATE ON CONCENTRATION OF TIN(II) AND TIN(IV)

$(H^+) = 3.99$ M; $(SO_4^{=}) = 0.99$ M; $\mu = 4.98$

[Sn(II)] M	[Sn(IV)] M	l. mole^{-1} hrs.$^{-1}$ k(obs)	k(I)	k(II)
0.0077_7	0.0129	0.062	0.061	0.062
0.0097	0.0126	0.061	0.061	0.062
0.0104	0.0129	0.064	0.061	0.062
0.0129	0.0129	0.062	0.061	0.062
0.0156	0.0129	0.060	0.061	0.062
0.0129	0.0066_3	0.064	0.061	0.062
0.0129	0.0086_1	0.062	0.061	0.062
0.0129	0.0106	0.062	0.061	0.062
0.0129	0.0129	0.064	0.061	0.062
0.0129	0.0205	0.063	0.061	0.062

TABLE VII

DEPENDENCE OF EXCHANGE RATE ON THE CONCENTRATION OF HYDROGEN ION

$\mu = 4.98$; $(SO_4^{=}) = 0.99$ M; C(Sn) $= 0.0258$ M

$[H^+]$	$[H_2SO_4]$	$[HClO_4]$	$[Li_2SO_4]$	$[LiClO_4]$	l. moles^{-1} hrs.$^{-1}$		
M	M	M	M	M	k(obs)	k(I)	k(II)
3.30	2.31	0.34_5	0.34_5	—	0.082	0.083	0.084
3.60	2.61	0.20_0	0.20_0	—	0.072	0.073	0.072
3.99	3.00	—	—	—	0.060	0.062	0.061
4.40	3.21	0.21	—	0.57	0.054	0.054	0.051
4.80	3.43	0.38	—	0.18	0.047	0.047	0.045
5.00	3.53	0.48	—	—	0.045	0.044	0.042

TABLE VIII

DEPENDENCE OF EXCHANGE RATE ON THE CONCENTRATION OF SULFATE ION

$\mu = 4.98$; $(H^+) = 0.99$; C(Sn) $= 0.0258$ M

$[SO_4^{=}]$	$[H_2SO_4]$	$[HClO_4]$	$[LiClO_4]$	$[Li_2SO_4]$	l. moles^{-1} hrs.$^{-1}$		
M	M	M	M	M	k(obs)	k(I)	k(II)
0.70	2.12	1.17	0.29	—	0.057	0.057	0.056
0.80	2.42	0.77	0.19	—	0.058	0.059	0.057
0.99	3.00	—	—	—	0.060	0.062	0.061
1.20	3.21_5	—	—	0.42_5	0.065	0.065	0.064
1.30	3.32	—	—	0.63_0	0.066	0.066	0.065
1.40	3.42	—	—	0.83_0	0.066	0.067	0.067

hydrogen ion concentration decreased the rate of exchange. The variations in hydrogen ion were limited by two factors: (a) the tin(IV) spectra were stable as a function of time only above 3.00 M hydrogen ion; (b) an ionic strength of 4.98 limited the maximum hydrogen ion at 5.00 M. Data appear later in which the ionic strength, μ, was allowed to vary and hydrogen ion concentrations up to 6.67 M were obtained. The rate law can now be written:

$$44) \qquad R = \frac{k[Sn(II)][Sn(IV)]}{[H^+]^{1.5}}$$

The effect of variation in sulfate ion is shown in Table VIII. These data indicate that the effect of sulfate ion is very small, but would correspond to a value of 0.25 ± 0.04 in the mathematical expression for the rate law,

$$45) \qquad k(I) = \frac{R}{ab} = \frac{0.496\,[SO_4^{=}]^{0.25}}{[H^+]^{1.5}}$$

Due to the insolubility of tin(IV) in perchloric acid, it was impossible to diminish the sulfate ion concentration below 0.70 M at constant ionic strength and constant hydrogen ion concentration. Constant ionic strength limited the maximum sulfate ion concentration to 1.40 M. In order to study the effect of higher hydrogen and sulfate ions than were allowed with $\mu = 4.98$, a series of measurements were made in which the ionic strength was allowed to vary from run to run. These results are tabulated in Table IX. The value, k(obs), is the apparent rate constant calculated from the observed half life (see Equation (16))

TABLE IX

DEPENDENCE OF EXCHANGE RATE ON THE CONCENTRATION OF HYDROGEN AND SULFATE IONS AT 25.0 °C.; C(Sn) = 0.0258 M

$[H^+]$ M	$[SO_4^=]$ M	$[\mu]$ M	$[H_2SO_4]$ M	$[HClO_4]$ M	$[LiClO_4]$ M	$[Li_2SO_4]$ M	l. moles^{-1} hrs.$^{-1}$ k(obs)	k(I)	k(II)
4.95	1.21	6.16	3.75	--	--	--	0.046	0.047	0.046
5.08	1.24	6.32	3.85	--	--	--	0.043	0.046	0.044
5.99	1.43	7.39	4.57	--	--	--	0.043	0.068	0.036
5.74	1.40	7.71	4.07	2.27	0.57	--	0.039	0.039	0.038
5.42	1.73	8.00	4.12	--	--	0.42_5	0.044	0.045	0.046
6.40	1.52	8.10	4.40	0.48_6	--	--	0.033	0.034	0.034
6.67	1.53	8.20	4.52	0.61_5	--	--	0.031	0.032	0.032
5.57	1.94_5	8.77	4.25	--	--	0.63_0	0.045	0.045	0.047
5.70	2.15	9.51	4.38	--	--	0.83_0	0.045	0.044	0.048

and k(I), will be discussed later.

It can be seen that the exponents chosen in Equation (45) agree with the experimental results rather well. The values obtained in this mathematical expression for the rate constant indicate that the exchange is due to several equilibria or steps.

It is necessary to correlate the experimental variable in a rate law which will not only be mathematically correct, but that can be interpreted in terms of a mechanism for the exchange reaction. The following equation:

$$46) \qquad k(II) = \frac{R}{ab} = \frac{0.674}{[H^+]^2} + \frac{0.0725\,[SO_4^=]}{[H^+]}$$

also adequately describes the data. Values of k(II) have been evaluated in the previous tables for comparison with k(obs).

Attempts to fit the experimental observations to alternative mathematical models give less satisfactory agreement. A discussion will follow in which the effects of hydrolysis and complexing of the tin will be fitted to this model.

Variations in the rate of exchange have been studied at three different temperatures for solutions containing 2.58 x 10^{-2} $\underline{M}$ total tin in 3.00 $\underline{M}$ sulfuric acid. The plots of ln(1-f) against t gave the anticipated linear relationship at 25.0 °C. and 37.8 °C. Figure 13 illustrates the data observed at 49.7 °C. The absorption spectra remained constant for 50-60 hours, followed by an increase in the optical density as a function of time. At 400 hours a visible precipitate

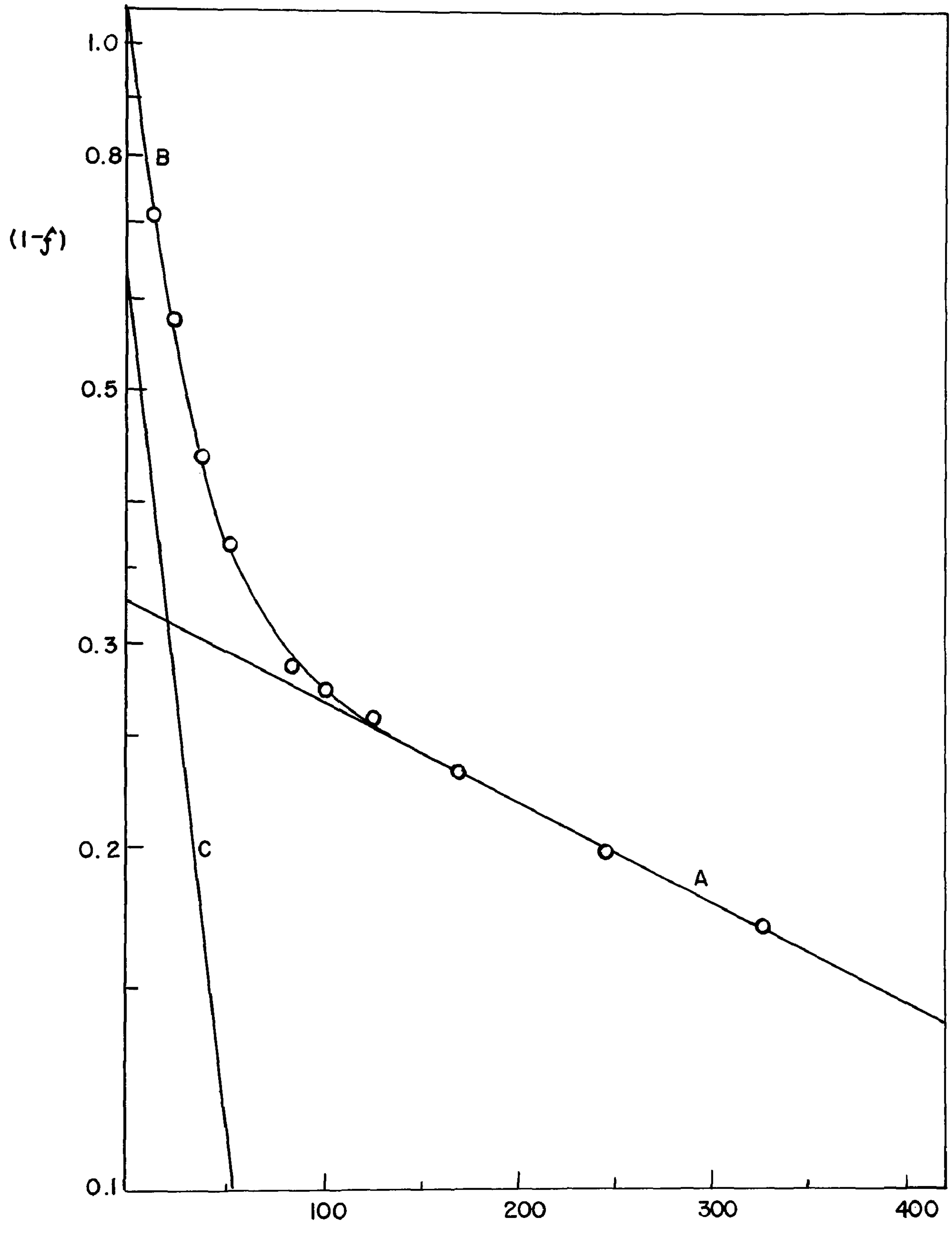

FIGURE 13. LOG. (1-f) AS A FUNCTION OF TIME AT 49.7°C
0.0129 M Sn(II) AND Sn(IV), 3.99 M H^+, AND 0.99M $SO_4^=$

of unknown composition (but presumably hydrous tin(IV) oxide) appeared in the reaction flasks.

Curve A in Figure 13 is linear and suggests that two processes are taking place at different rates. Graphical subtraction of curve A (extrapolated to zero time) from curve B results in curve C which is also linear. Perhaps it is fortuitous that B is linear, but this does suggest that two different species are involved in the electron exchange and that equilibrium between these species is kinetically slow. If this were the case, the exchange rate could be determined for each process from the slope of curves A and B. The other possibility is that curve A represents a decrease in the rate of exchange due to the formation of a very slow--or non-exchanging hydrolyzed species.

Although an Arrhenius plot of these data would be meaningless, due to the lack of linearity of the McKay plot, it is of interest that the exchange rate determined from curve B gives a linear Arrhenius plot, when combined with the data from the other two temperatures, with a slope, Ea equal to 1900 cal./mole. These data are summarized in Table X.

TABLE X

DEPENDENCE OF EXCHANGE RATE ON TEMPERATURE
$\mu = 4.98$; 3.00 $\underline{M}$ H_2SO_4; $(H^+) = 3.99$;
$(SO_4^=) = 0.99$ $\underline{M}$; C(Sn) $= 0.0258$ $\underline{M}$

Temp.	k(A)	k(B)	k(C)
25.0 °C.	0.062	--	--
37.8 °C.	0.211	--	--
49.5 °C.	0.0844	0.750	1.37_8

Catalysis of the Exchange Rate by Chloride Ion

A series of experiments were carried out in which the chloride ion was varied from 0.01 to 1.2 M. The equations used to calculate the 3.99 M hydrogen ion and ionic strength of 4.98 are listed in Appendix B. The total tin concentration was maintained at 2.58×10^{-2} M. Chloride ion was added as hydrochloric acid for solutions containing less than 0.5 M Cl^-, and above 0.5 M Cl^-, mixtures of lithium chloride and hydrochloric acid were added. These data are summarized in Table XI. A log plot of k(obs) against the chloride ion concentration is shown in Figure 14. It can be seen that chloride ion has a negligible effect on the rate exchange below 0.02 M. The rate increases rapidly beyond this point and straightens out (with a slope of 1.0) above 0.5 M chloride ion. At chloride concentrations below 0.5 M, the rate of exchange is not first order with respect to tin(II) or tin(IV) concentrations (see Table XII, p. 62).

Both tin(II) and tin(IV) are known to form a series of complexes with chloride ion. Vanderzee and Rhodes have studied the equilibrium between tin(II) and chloride ion, reporting the following:

47) $$K_1 = \frac{(Sn^{++})(Cl^-)}{(SnCl^+)} = 0.0714$$

48) $$K_2 = \frac{(SnCl^+)(Cl^-)}{(SnCl_2)} = 0.281$$

49) $$K_3 = \frac{(SnCl_2)(Cl^-)}{(SnCl_3^-)} = 0.96_2$$

50) $$K_4 = \frac{(SnCl_3^-)(Cl^-)}{(SnCl_4^=)} \gtrsim 5$$

TABLE XI

CATALYSIS OF EXCHANGE RATE BY CHLORIDE ION
$\mu \simeq 4.98$; (H$^+$) $\simeq 3.99$ M; C(Sn) $= 0.0258$ M

[Cl$^-$] M	[H$_2$SO$_4$] M	[HCl] M	[LiCl] M	l. moles^{-1} hrs.$^{-1}$ k(obs)
0.015	2.98	0.015	—	0.0632
0.030	2.97	0.030	—	0.0809
0.060	2.94	0.060	—	0.1162
0.077_5	2.92	0.077_5	—	0.154
0.103_3	2.90	0.103_3	—	0.215
0.120	2.88	0.210	—	0.298
0.129	2.87	0.129	—	0.325
0.150	2.85	0.185	—	0.472
0.193_7	2.81	0.193_7	—	0.691
0.200	2.80	0.200	—	1.058
0.258_2	2.74	0.258_2	—	1.078
0.300	2.73	0.260	0.04_0	1.283
0.516_3	2.70	0.416	0.10_0	2.59
0.600	2.68	0.460	0.14_0	3.00
0.900	2.46	0.720	0.18_0	4.62
1.20	2.28	0.960	0.24_0	5.72

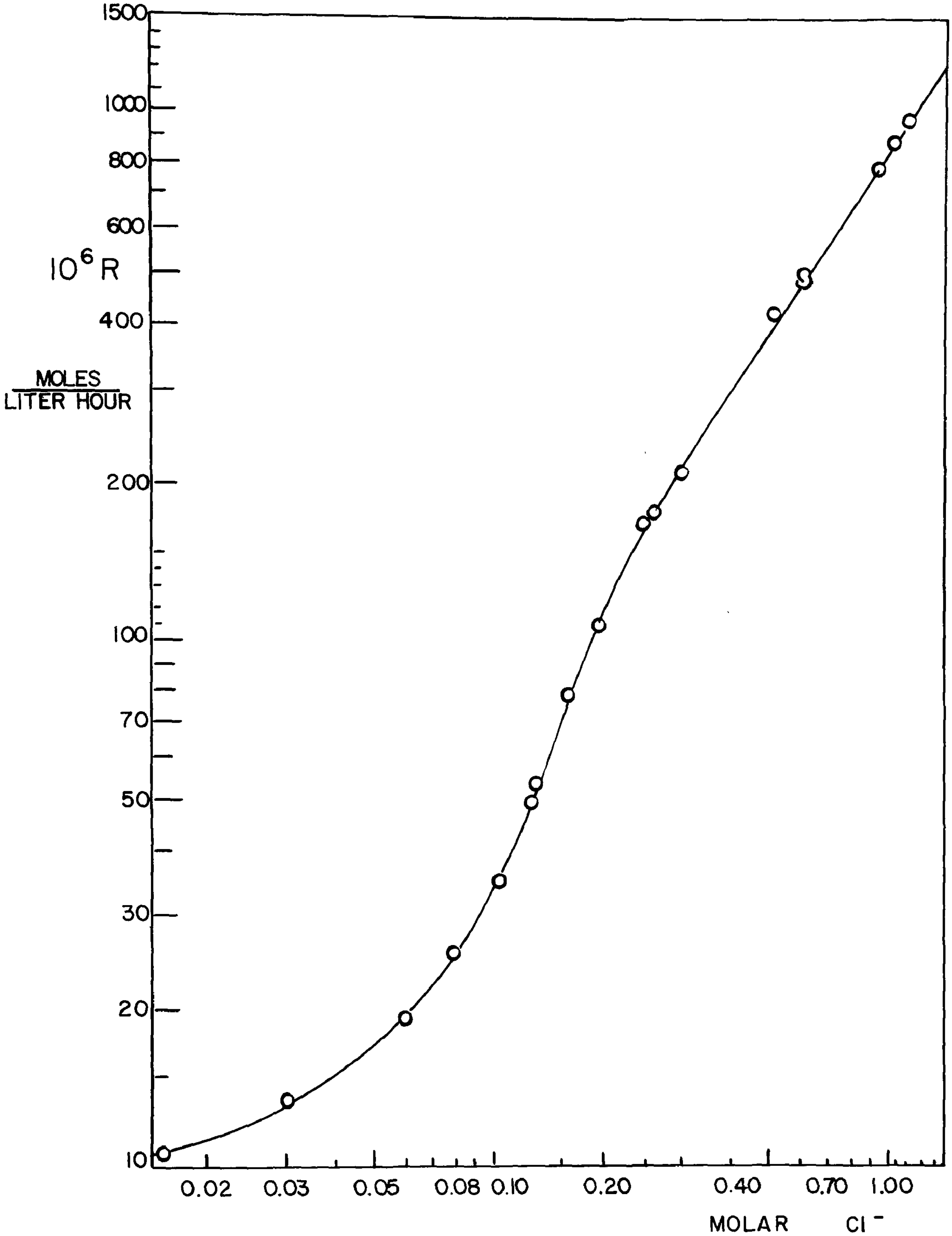

FIGURE 14. EXCHANGE RATE AS A FUNCTION OF CHLORIDE ION CONCENTRATION $C_{Sn(II)} = 0.0258$ M

Several values have been listed in the literature for the overall formation constant, β_6, for $SnCl_6^=$.

$$51) \qquad \beta_6 = \frac{[SnCl_6^=]}{[Sn(IV)][Cl^-]^6}$$

Prytz (44) has reported $\beta_6 = 0.82$ and a value of $\beta_6 = 4.00$ has been listed by Smith (45). Unfortunately the individual equilibrium constants have not been evaluated.[‡] Using the constants from Equations (47-50) attempts were made to find equations which could satisfactorily represent the unusual tin(II) and tin(IV) orders at low chloride ion concentrations. E.m.f. studies (44, 45) seem to indicate that under the conditions studied at least 2 and probably 3 Cl^- are completely complexed to the Sn(II). No suitable mathematical model has been found which would represent the rate data and evaluate a reasonable constant for the tin(IV)--chloride equilibrium.

The effect of independent variation of tin concentration on the rate of exchange was studied in 1.00 M chloride solutions (3.99 M H^+, $\mu = 4.98$). The McKay plots were linear and the constants, α and β, from Equation (37) were evaluated with $\alpha = 1.00 \pm 0.02$ and $\beta = 0.99 \pm 0.04$. These data are summarized in Table XIII.

The effect of temperature on the rate of exchange 1.00 M chloride was also studied at 3 different temperatures. Once again, a non-linear McKay plot was observed at 49.7 °C. (see Figure 15). The original

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[‡] Appendix C contains a survey of solvents that would be appropriate to study the formation constants, k_6, k_5, for the Sn(IV)-Cl system at various acidities and chloride ion concentrations.

curve A is non-linear for the first 140 hours. Beyond this a linear curve B is obtained. Graphical subtraction of the extrapolated curve B results in a linear curve C. This suggests that once again the higher temperature has accelerated the hydrolysis of the Sn(IV) and this hydrolyzed species is either extremely slow to exchange or possibly does not exchange. The log of the rate, calculated from the slope of curve C, and the data from other temperatures was plotted as a function of 1/T. The resulting Arrhenius plot is linear with Ea = 2260 cal.-mole^{-1}. These data are summarized in Table XIV.

Due to the complexity of the systems being studied, no further activation energies have been calculated.

TABLE XII

CATALYSIS OF EXCHANGE RATE BY CHLORIDE ION WITH VARIATION IN TOTAL TIN CONCENTRATION

$\mu = 4.98$; $(H^+) = 3.98$ M

$[Sn(II)]$ M	$[Sn(IV)]$ M	$[Cl^-]$ M	l. moles^{-1} hrs.$^{-1}$ k(obs)
0.0128	0.0100	0.129	0.245
0.0128	0.0129	0.129	0.325
0.0096_0	0.0129	0.129	0.405
0.0055	0.0134	0.200	1.98
0.0085	0.134	0.200	1.46
0.0125_3	0.0134	0.200	1.05_8
0.0195	0.0134	0.200	0.69_2

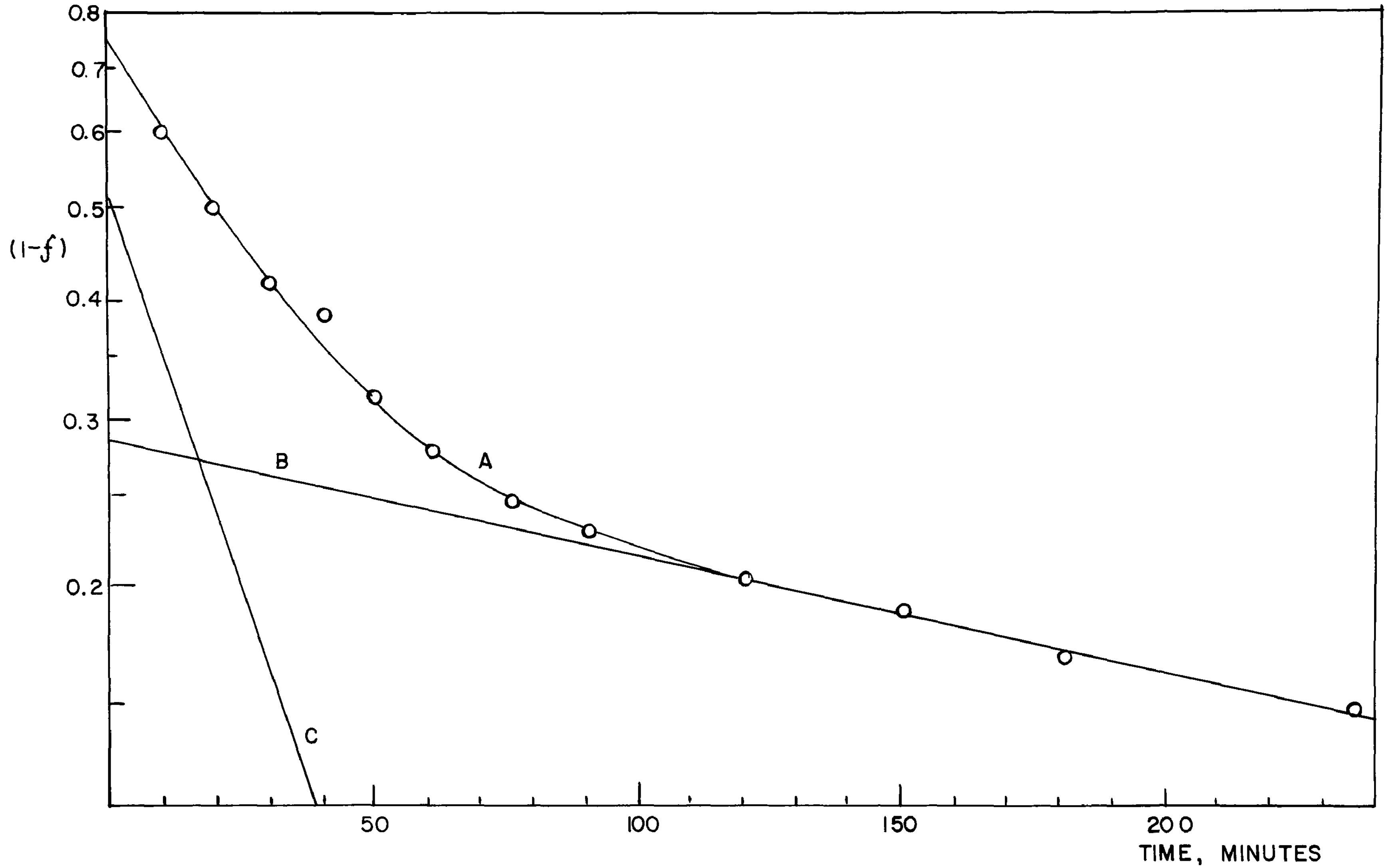

FIGURE 15. LOG (1-f) AS A FUNCTION OF TIME AT 49.7°C 0.0129 **M** Sn (II) AND Sn(IV) 1.00 **M** Cl^-, 3.99 **M** H^+, AND 0.079_5 **M** $SO_4^=$.

TABLE XIII

DEPENDENCE OF THE EXCHANGE RATE ON CONCENTRATION OF TIN(II) AND TIN(IV)

$(H^+) = 3.99$ M; $(Cl^-) = 1.00$ M

[Sn(II)] M	[Sn(IV)] M	l. moles^{-1} hrs.$^{-1}$ k(obs)
0.0048_7	0.0131_5	4.34
0.0088_5	0.0131_5	4.38
0.0129	0.0129	4.58
0.0171	0.0133	4.39
0.0126	0.0053	4.56
0.0126	0.0093	4.40
0.0126	0.0178	4.42

TABLE XIV

DEPENDENCE OF EXCHANGE RATE ON TEMPERATURE

$\mu = 4.98$; $(H^+) = 3.99$ M; $(Cl^-) = 1.00$ M

Temperature	l. moles^{-1} hrs.$^{-1}$
25.0 °C.	4.58
37.8 °C.	19.3
49.5 °C.	88.5

DISCUSSION

It was found that the reaction between tin(II) and tin(IV) in sulfuric acid was first order with respect to both oxidation states of tin. Variation of R/ab with concentration of sulfuric acid at constant sulfate ion concentration shows that the rate of exchange decreases with increasing hydrogen ion. This suggests that hydrolysis of at least one species is occurring, and that the more hydrolyzed species exchange more rapidly.

The spectral data, from the study of aqueous tin(II) dissolved in perchloric and sulfuric acid, have been interpreted in terms of the equilibrium between $SnOH^{+}$ and Sn^{++} and the hydrolysis constant equal to 24.5 has been evaluated for this process. This value differs from the value determined by Gorman (9) who used e.m.f. measurements to determine the hydrolysis constant. His value was calculated from a graph of the log of the equilibrium constant as a function of the square-root of the ionic strength. The graph was extrapolated to zero ionic strength, and this resulted in a value of 0.02 for the equilibrium constant. Gorman's data indicate that the equilibrium constant increases rapidly as the ionic strength of the medium is increased. Since the spectrophotometric results were not calculated on the basis of constant ionic strength, his data have been extrapolated to an ionic strength corresponding to that from the lowest concentration of perchloric acid used.

Gorman's extrapolated value and the spectrophotometric value are then of the same order of magnitude.

If activity coefficients are selected from ions of the same charge and valence type as the $SnOH^{+}$ and the Sn^{++} involved in the equilibrium, once again the two values are of the same order of magnitude.

In the electromigration studies of tin(II) dissolved in perchloric or sulfuric acids, only migration to the cathode was observed, suggesting that the predominant or most mobile species present in aqueous solutions of divalent tin are cationic. The spectrophotometric interpretation is in agreement with this observation.

Although, at present, the equilibrium constant has not been determined for the tin(II)-sulfate equilibrium, a critical examination of the data of Denham and King (2) indicates that no higher tin(II) complexes than $SnSO_4$ are formed in the $SnO-SO_3-H_2O$ system. This is in agreement with the assumption (13) that $SnSO_4$ is the highest tin(II)-sulfate complex present in sulfuric acid.

Solutions of tin(IV) in sulfuric acid have been prepared by two different methods which result in solutions with very different behavior, both with respect to the intensity of the absorption spectra and the formation of hydrous tin(IV) oxide as a function of time.

Dissolution of stannic sulfate dihydrate in aqueous sulfuric acid results in solutions that are unstable with respect to the precipitation of the hydrous oxide. It has been shown (11, 12) that $SnSO_4^{++}$ and $Sn(SO_4)_2$ are the predominant species present in 3.00 M sulfuric acid and it appears that SnO^{++} is not an important species under these conditions. Brubaker (10) was unable to correlate his hydrolysis data for tin(IV) in sulfuric acid with partially hydrolyzed species such as $Sn(OH)_2^{++}$, $Sn(OH)^{+3}$, but the data were in accord with the formation of $SnSO_4^{++}$. It seems highly improbable that there are actually hydrated stannic ions (Sn^{+4}) in such dilute sulfuric acid.

Furthermore, little else is reported in the literature about changes in tin(IV) species which occur as hydrogen and sulfate ion concentrations are varied, although such information is essential to the description of the aqueous tin(IV) system. If some SnO^{++} were in equilibrium with $SnSO_4^{++}$, it is very possible that this partially hydrolyzed species would hydrolyze further before the $SnSO_4^{++}$.

The absorbancy index for $SnSO_4^{++}$ has been evaluated (12) and is about 2500 at 240 mμ. Thus, even small amounts of $SnSO_4^{++}$ should be visible spectrophotometrically. Oxidation of tin(II) solutions in sulfuric acid results in a decrease, not an increase in the intensity of the aborption spectra. Since tin(II) solutions are less highly "colored" originally than tin(IV) solutions containing predominantly $SnSO_4^{++}$, and a decrease in intensity is observed for the absorption spectra, it appears that a partially hydrolyzed tin(IV) species is being formed upon oxidation. Complete oxidation of dilute tin(II) solutions also results in the formation of a precipitate containing hydrolyzed tin(IV) species. Previous work has shown that if a sulfate complex of tin(IV) were formed, this would probably be a soluble one.

It is apparent that boiling of tin(IV) solutions in concentrated sulfuric acid for prolonged periods of time results in more highly complexed tin species. The absorbancy of these tin solutions drops by a factor of 50 after prolonged heating and subsequent dilution. Samples from the stable tin(IV) solutions have been stored and observed for more than 9 months. Two such solutions were 12 *M* and 5.7 *M* in sulfuric acid. The absorption spectra of these solutions were constant throughout the 9 month period, and no precipitate was visible. Subsequent dilution of these solutions to give 3 *M* sulfuric acid resulted in stable solutions. Samples of the original stable tin(IV) that had been diluted to 3 *M* sulfuric acid showed no change in the absorption during a 10 week period.

It certainly seems plausible to assume that part of the reason for the decrease in intensity of the absorption spectra and increase in stability is due to the formation of $Sn(SO_4)_2$ and possibly $Sn(SO_4)_3^{=}$. However, since the absorbancy index for $Sn(SO_4)_3^{=}$ is very large (12) and in light of the very low intensity absorption observed, it appears that $Sn(SO_4)_2$ is the predominant sulfate complex. If $SnO^{\#}$, or an equilibrium mixture of $SnSO_4^{\#}$ and $SnO^{\#}$, or other hydrolyzed species is responsible for the formation of the precipitate when sulfuric acid solutions of $Sn(SO_4)_2 \cdot 2\,H_2O$ are aged, it is highly probable that boiling sulfuric acid would convert any hydrolyzed tin(IV) species to either $Sn(SO_4)_2$ or $SnOSO_4$.

There seems to be little question that prolonged heating of tin(IV) in sulfuric acid results in the formation of the tin(IV) sulfate complex $Sn(SO_4)_2$.

This does not preclude the existence of other species such as

SnO^{++}, $SnOH^{+3}$, $SnSO_4^{++}$, and $Sn(SO_4)_3^{=}$, but it certainly suggests that if these species are present, they are not predominant.

Equation (46),

$$k = 0.674(H^+)^{-2} + 0.0725(SO_4^{=})(H^+)^{-1} \tag{46}$$

implies that the predominant species of tin(II) and tin(IV) do not change with the variation in sulfate (0.70-2.15 M) and hydrogen (3.30-6.40 M) ions used in the exchange experiments. This also may indicate that only one predominant species is present in each oxidation state.

$SnOH^+$ is probably the major tin(II) species present in 3.00 M sulfuric acid. The hydrolysis constant would predict this for solutions that were low in hydrogen ion, and as the concentration of hydrogen ion increased, thus increasing the Sn^{++} concentration, the sulfate ion concentration would also increase followed by the formation of $SnSO_4$.

From the preceding discussion, $Sn(SO_4)_2$ seems to be the predominant tin(IV) species. Thus, if a is the total tin(II) concentration, and b is the total tin(IV) concentration, let

$$a = (SnOH^+) = Sn^{++}\left[K_1/H^+\right] \tag{52}$$

$$b = (Sn(SO_4)_2) = Sn^{+4}\left[K_aK_b(SO_4^{=})^2\right] \tag{53}$$

and,

$$K_1 = \frac{(SnOH^+)(H^+)}{(Sn^{++})} \quad , \quad K_2 = \frac{(SnSO_4)}{(Sn^{++})(SO_4^{=})}$$

$$K_a = \frac{Sn(SO_4)_2}{(SnSO_4^{++})(SO_4^{=})} \quad , \quad K_b = \frac{(SnSO_4^{++})}{(Sn^{+4})(SO_4^{=})}$$

$$K_c = \frac{SnOSO_4}{(SnO^{++})(SO_4^{=})} \quad \text{and} \quad K_d = \frac{(SnO^{++})(H^+)^2}{(Sn^{+4})}$$

Thus, a combination of the following exchange processes will be consistent with the mathematical model that has been presented.

54) $$*SnO(SO_4)_2^{=} + SnOH^+ \rightleftharpoons SnO(SO_4)_2^{=} + *SnOH^+$$

or

55) $$*Sn(OH)_3^+ + SnSO_4 + SO_4^{=} \rightleftharpoons Sn(OH)_3^+ + *SnSO_4 + SO_4^{=}$$

and

56) $$*SnO(SO_4)_2^{=} + SnSO_4 \rightleftharpoons SnO(SO_4)_2^{=} + *SnSO_4$$

Several species, such as $SnO(SO_4)_2^{=}$, $Sn(OH)_3^+$, and $SnSO_4$ have been suggested as important in the exchange, even though the foregoing discussion indicates that they do not contribute significantly to the total tin concentration.

Thus, a combination of Equations 54 or 55 and 56 results in Equation 57,

57) $$R/ab = k(II) = k_1'(H^+)^{-2} + k_2'(SO_4^{=})(H^+)^{-1}$$

with k_1' and k_2' being composites of rate and equilibrium constants, and if $k_1' = 0.674$ and $k_2' = 0.0725$, then this is Equation (46).

In the absence of further information regarding the hydrolysis and formation constants for the tin(II) and tin(IV) systems, it would be meaningless to attempt to postulate mechanisms which would try to take these phenomenon into effect. Certainly equilibrium studies are suggested, with the hope of finding a more complete model.

The rate of exchange was much more rapid in sulfuric acid solutions that contained chloride ion than was the rate of exchange in pure sulfuric acid solutions. Chloride ion has a very small effect on the rate of exchange below 0.02 M chloride ion (2.58×10^{-2} M total tin), but the rate increases rapidly as the chloride ion concentration increased. The rate of exchange is increased by a factor of 100 as the chloride concentration changes from 0.01 to 1.2 M. In all of the exchange experiments that contained chloride ion, the ionic strength was 4.98 and the hydrogen ion concentration was 3.99 M.

The data in Table XIII show that the rate of exchange in 1.00 M chloride is first order with respect to both tin(II) and the tin(IV) concentrations, and when the chloride concentration is greater than 0.5 M, the rate of exchange is also first order in chloride ion, i.e.,

$$R = k[\mathrm{Sn(II)}][\mathrm{Sn(IV)}][\mathrm{Cl^-}] \tag{50}$$

Although an increase in the rate of exchange is observed as the chloride ion concentration increases from 0.01 to 0.5 M, the reaction is not first order with respect to the tin(II), tin(IV), or the chloride ion concentration and in view of the complete lack of information regarding the individual formation constants for the tin(IV)-chloride equilibrium, only a qualitative explanation can be offered in this region.

In experiments containing 0.129 M chloride ion, the rate of exchange was of an order much less than one for the tin(II), and of an order slightly greater than one for the tin(IV). In this region (0.01 to 0.5 M chloride ion), the rate of exchange is about 3/2 order with respect to chloride ion. These data suggest that the exchange reaction is proceeding by two paths or that several equilibria are involved.

For low acidities, e.g. the 3.99 M hydrogen ion used in these experiments, and low chloride ion concentrations (less than 0.1 M), the equilibrium amount of $SnCl_4^=$ and $SnCl_6^=$ complexes is small, and if the rate of formation of these complexes is slow, the rate of exchange is often determined by the rate of formation of the complexes, and not the exchange process itself.

Most of the previous workers have considered that exchange occurs between $SnCl_4^=$ and $SnCl_6^=$, not only because they are the best known and predominant species of the two oxidation states under the conditions studied, but also because one can easily visualize a symmetric transition state in which the electron transfer is facilitated.

One can calculate the concentration of $SnCl_6^=$ using Smith's constant (45) of 4.00 for the formation of hexachlorostannate ion, and it appears that $SnCl_6^=$ may be the major tin(IV) species present in 1.00 M chloride.

In the electromigration studies of aqueous tin(II) solutions which contained chloride ion, little or no migration was observed for solutions containing less than 0.1 M chloride ion. When the solution was 0.5 M in chloride ion, some migration to the anode was observed and in 1.00 M chloride ion, only migration to the anode was observed, suggesting that the major or most mobile species present in these solutions are anionic. The formation constant for the reaction $Sn^{++} + 3\,Cl^- \rightleftharpoons SnCl_3^-$ is 48 (43). Thus it appears that $SnCl_3^-$ could be the major tin(II)-chloride complex in 1.00 M chloride ion.

Since the fourth formation constant for tin(II) chloride is very small, and in light of the preceeding discussion, the data can be interpreted as follows: Let a equal the total concentration of divalent tin, and let b equal the total concentration of tetravalent tin, then

$$a = (SnCl_3^-) = K_7(Cl^-)^3(Sn^{++}) \tag*{59)}$$

$$b = (SnCl_6^=) = K_8(Cl^-)^6(Sn^{+4}) \tag*{60)}$$

where,

$$K_7 = \frac{(SnCl_3^-)}{(Sn^{++})(Cl^-)^3} \qquad \text{and} \qquad K_8 = \frac{(SnCl_6^=)}{(Sn^{+4})(Cl^-)^6}$$

thus, the following exchange process:

$${}^*SnCl_6^= + SnCl_4^= \rightleftharpoons SnCl_6^= + {}^*SnCl_4^= \tag*{61)}$$

leads to

$$R = k_1''(Cl^-)(a)(b) \tag*{62)}$$

with k_1'' being a composite of rate and equilibrium constants. If k_1'' equals 4.94, then for chloride ion concentrations above 0.5 M, the data in Tables XI and XIII are predicted to within 3%.

SUMMARY

The kinetics of the exchange reaction between tin(II) and tin(IV) in aqueous sulfuric acid were studied in the temperature range of 25 °C. to 50 °C. Experiments were designed to determine the effect of variation in concentration of tin(II), tin(IV), sulfate, hydrogen, and chloride ions.

It was found that the reaction is first order with respect to tin(II) and tin(IV), and that the effect of increased hydrogen ion is to decrease the rate of exchange, and the effect of increased sulfate is to increase the rate of exchange. The predominant tin species appear to be $SnOH^+$ and $Sn(SO_4)_2$. A combination of the following exchange processes

$$*SnO(SO_4)_2^= + SnOH^+ \rightleftharpoons SnO(SO_4)_2^= + *SnOH^+$$

or

$$*Sn(OH)_3^+ + SnSo_4 + SO_4^= \rightleftharpoons Sn(OH)_3^+ + *SnSO_4 + SO_4^=$$

and

$$*SnO(SO_4)_2^= + SnSO_4 \rightleftharpoons SnO(SO_4)_2^= + *SnSO_4$$

lead to

$$R/ab = 0.674(H\ )^{-2} + 0.0725(SO_4^=)(H^+)^{-1}$$

The addition of chloride ion to the reaction mixture in 3.00 M sulfuric acid increased the rate by a factor of 100. The reaction can be described by the following exchange process

$$*SnCl_6^{=} + SnCl_4^{=} \rightleftharpoons SnCl_6^{=} + *SnCl_4^{=}$$

which leads to

$$R = 4.94[Cl^-][Sn(II)][Sn(IV)]$$

The chloride ion concentration probably appears in the rate expression because $SnCl_3^-$ is most likely the major tin(II) species.

Spectrophotometric examination of aqueous solutions of tin(II) in perchloric and sulfuric acids have been interpreted in terms of the hydrolysis of Sn^{++}. A hydrolysis constant equal to 24.5 has been evaluated. The absorption spectra of tin(IV) solutions and tin(II) - tin(IV) solutions in 3.00 M sulfuric acid and tin(II)-tin(IV) solutions in sulfuric acid containing 1.00 M chloride ion (3.99 M H^+) are given. The spectra have been interpreted in terms of an interaction dimer containing one atom of tin(II) and one atom of tin(IV).

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APPENDICES

APPENDIX A

ORIGINAL KINETIC DATA

KINETIC STUDIES IN 3.00 M SULFURIC ACID, $\mu = 4.98$

TABLE XV

STUDY OF THE EFFECT OF VARIATIONS IN TIN(II) CONCENTRATIONS ON THE RATE OF EXCHANGE

	c/s(IV)*	(1-f)‡	t(hrs)
	30.72	0.980	13.82
0.0077 M Sn(II)	30.34	0.968	25.00
0.0129 M Sn(IV)	29.44	0.939	47.33
3.99 M H^+	28.28	0.902	78.62
0.99 M $SO_4^=$	26.68	0.851	126.91
$t_{\frac{1}{2}}$ = 540 hrs.	22.92	0.731	238.11
	19.72	0.629	359.11
	31.35	—	∞(c)
	30.29	0.964	13.85
0.0104 M Sn(II)	29.82	0.949	25.03
0.0129 M Sn(IV)	28.78	0.916	48.05
3.99 M H^+	27.46	0.874	78.65
0.99 M $SO_4^=$	25.79	0.821	126.95
$t_{\frac{1}{2}}$ = 481 hrs.	21.87	0.696	238.11
	20.83	0.664	271.37
	18.29	0.582	359.21
	31.42	—	∞(c)
	33.71	0.988	13.95
0.0129 M Sn(II)	32.41	0.950	25.83
0.0129 M Sn(IV)	31.42	0.921	48.08
3.99 M H^+	29.99	0.879	78.70
0.99 M $SO_4^=$	28.08	0.823	126.95
$t_{\frac{1}{2}}$ = 434 hrs.	23.41	0.686	238.17
	22.21	0.651	271.42
	19.11	0.560	359.17
	34.12	—	∞(c)

* $(X_\infty - X)$ in equation 27, page 26

‡ Value calculated on basis of mole fraction, equation 26, page 26

c Calculated

TABLE XV cont.

	c/s(IV)	(1-f)	t(hrs)
0.0156 M Sn(II) 0.0129 M Sn(IV) 3.99 M H^+ 0.99 M $SO_4^=$ $t_{\frac{1}{2}} = 409$ hrs.	41.17	0.981	13.97
	40.38	0.962	25.13
	39.49	0.941	48.13
	37.77	0.900	78.80
	35.34	0.842	127.00
	30.18	0.719	238.22
	29.04	0.692	271.47
	25.64	0.611	360.00
	41.97	—	∞(c)
0.0970 M Sn(II) 0.0126 M Sn(IV) 3.99 M H^+ 0.99 M $SO_4^=$ $t_{\frac{1}{2}} = 519$ hrs.	20.84	0.862	26.00
	19.32	0.799	58.00
	18.67	0.772	102.00
	17.97	0.743	153.00
	16.97	0.702	191.00
	15.72	0.650	240.00
	14.99	0.620	290.00
	13.30	0.550	360.00
	11.12	0.460	500.00
	24.18	—	∞(c)

TABLE XVI

STUDY OF THE EFFECT OF VARIATIONS IN TIN(IV) CONCENTRATIONS ON THE RATE OF EXCHANGE

	c/s(IV)	(1-f)	t(hrs)
0.0129 M Sn(II) 0.00663 M Sn(IV) 3.99 M H^+ 0.99 M $SO_4^=$ $t_{\frac{1}{2}} = 555$ hrs.	42.52	0.991	5.75
	41.71	0.972	17.75
	41.15	0.959	30.25
	40.25	0.938	51.43
	39.13	0.912	72.37
	38.06	0.887	93.95
	36.95	0.861	117.90
	32.31	0.753	212.32
	25.83	0.602	401.21
	42.91	—	∞(c)

TABLE XVI cont.

	c/s(IV)	(1-f)	t(hrs)
0.0129 M Sn(II) 0.0086 M Sn(IV) 3.99 M H^+ 0.99 M $SO_4^=$ $t_{\frac{1}{2}}$ = 518 hrs.	38.90	0.999	5.73
	38.24	0.982	17.73
	37.81	0.971	20.23
	36.53	0.938	51.45
	35.47	0.911	72.38
	34.58	0.888	93.95
	33.10	0.850	117.90
	31.07	0.798	212.13
	22.62	0.581	401.21
	38.94	---	∞(c)
0.0129 M Sn(II) 0.0106 M Sn(IV) 3.99 M H^+ 0.99 M $SO_4^=$ $t_{\frac{1}{2}}$ = 480 hrs.	33.99	0.954	5.70
	33.49	0.940	17.70
	32.82	0.921	30.20
	31.71	0.890	51.50
	30.96	0.869	72.40
	29.82	0.837	93.95
	28.86	0.810	117.90
	25.01	0.702	212.13
	35.63	---	∞(c)
0.0129 M Sn(II) 0.0129 M Sn(IV) 3.99 M H^+ 0.99 M $SO_4^=$ $t_{\frac{1}{2}}$ = 420 hrs.	25.86	0.967	26.00
	24.68	0.923	58.00
	21.93	0.820	102.00
	20.16	0.754	153.00
	18.91	0.707	191.00
	18.58	0.695	240.00
	15.88	0.594	290.00
	14.73	0.551	360.00
	11.64	0.435	500.00
	26.74	---	∞(c)
0.0129 M Sn(II) 0.0205 M Sn(IV) 3.99 M H^+ 0.99 M $SO_4^=$ $t_{\frac{1}{2}}$ = 330 hrs.	24.78	0.989	5.62
	24.11	0.962	17.62
	23.58	0.941	30.12
	22.48	0.897	51.31
	21.58	0.861	72.30
	20.85	0.832	93.88
	19.42	0.775	119.83
	15.81	0.631	212.13
	25.06	---	∞(c)

TABLE XVII

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

	c/s(IV)	(1-f)	t(hrs)
	52.61	0.910	50.00
0.0128 M Sn(II)	45.00	0.780	100.00
0.0130 M Sn(IV)	40.42	0.699	170.00
3.30 M H^+	34.28	0.594	245.00
0.99 M $SO_4^=$	28.80	0.499	325.00
$t_{\frac{1}{2}} = 328$ hrs.	25.37	0.439	400.00
	21.08	0.365	505.50
	57.60	---	∞(c)
	62.58	0.892	50.00
0.0126 M Sn(II)	56.21	0.800	100.00
0.0132 M Sn(IV)	50.77	0.723	170.00
3.60 M H^+	43.49	0.619	245.00
0.99 M $SO_4^=$	36.52	0.520	325.00
$t_{\frac{1}{2}} = 371$ hrs.	32.83	0.468	400.00
	26.76	0.381	505.00
	70.21	---	∞(c)
	58.33	0.912	50.00
0.0124 M Sn(II)	53.85	0.842	100.00
0.0134 M Sn(IV)	46.95	0.734	175.00
3.99 M H^+	35.82	0.560	350.00
0.99 M $SO_4^=$	31.02	0.485	450.00
$t_{\frac{1}{2}} = 430$ hrs.	25.58	0.400	550.00
	21.93	0.343	650.00
	17.14	0.268	800.00
	63.96	---	∞(c)
	57.25	0.878	50.00
0.0124 M Sn(II)	52.17	0.800	100.00
0.0134 M Sn(IV)	47.99	0.736	175.00
4.40 M H^+	38.93	0.597	350.00
0.99 M $SO_4^=$	31.63	0.485	450.00
$t_{\frac{1}{2}} = 498$ hrs.	28.76	0.441	550.00
	24.77	0.380	650.00
	65.21	---	∞(c)

TABLE XVII cont.

	c/s(IV)	(1-f)	t(hrs)
	57.68	0.890	50.00
0.0125 $\underline{M}$ Sn(II)	54.44	0.840	100.00
0.0133 $\underline{M}$ Sn(IV)	49.32	0.761	175.00
4.80 $\underline{M}$ H^+	40.77	0.629	350.00
0.99 $\underline{M}$ $SO_4^=$	35.65	0.550	450.00
$t_{\frac{1}{2}}$ = 575 hrs.	31.69	0.484	550.00
	29.10	0.449	650.00
	23.98	0.370	800.00
	64.81	——	∞(c)
	57.28	0.840	50.00
0.0124 $\underline{M}$ Sn(II)	54.50	0.799	100.00
0.0134 $\underline{M}$ Sn(IV)	49.18	0.721	175.00
5.00 $\underline{M}$ H^+	39.02	0.572	350.00
0.99 $\underline{M}$ $SO_4^=$	36.83	0.540	450.00
$t_{\frac{1}{2}}$ =603 hrs.	32.26	0.473	550.00
	29.06	0.426	650.00
	24.21	0.355	800.00
	68.21	——	∞(c)

TABLE XVIII

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

	c/s(IV)	(1-f)	t(hrs)
	57.41	0.890	50.00
0.0120 $\underline{M}$ Sn(II)	53.48	0.830	100.00
0.0132 $\underline{M}$ Sn(IV)	48.37	0.750	170.00
3.99 $\underline{M}$ H^+	43.50	0.675	245.00
0.70 $\underline{M}$ $SO_4^=$	38.36	0.596	325.00
$t_{\frac{1}{2}}$ =466 hrs.	33.56	0.521	400.00
	29.69	0.462	505.00
	64.48	——	∞(c)

TABLE XVIII cont.

	c/s(IV)	(1-f)	t(hrs)
	64.21	0.941	50.00
0.0128 M Sn(II)	57.99	0.849	100.00
0.0130 M Sn(IV)	52.63	0.773	170.00
3.99 M H^+	47.42	0.694	245.00
0.80 M $SO_4^=$	41.72	0.611	325.00
$t_{\frac{1}{2}}$ =456 hrs.	35.38	0.518	400.00
	30.80	0.451	505.00
	68.26	---	∞(c)
	63.50	0.929	50.00
0.0127 M Sn(II)	57.42	0.838	100.00
0.0131 M Sn(IV)	52.11	0.761	170.00
3.99 M H^+	46.41	0.678	245.00
0.99 M $SO_4^=$	39.00	0.571	325.00
$t_{\frac{1}{2}}$=447 hrs.	36.37	0.532	400.00
	31.49	0.460	505.00
	68.42	---	∞(c)
	58.66	0.880	50.00
0.0127 M Sn(II)	51.93	0.779	100.00
0.0131 M Sn(IV)	47.13	0.707	175.00
3.99 M H^+	34.53	0.518	350.00
1.20 M $SO_4^=$	29.33	0.440	450.00
$t_{\frac{1}{2}}$ =414 hrs.	24.80	0.372	550.00
	21.26	0.319	650.00
	16.53	0.248	800.00
	66.66	---	∞(c)
	56.62	0.871	50.00
0.0128 M Sn(II)	52.01	0.800	100.00
0.0130 M Sn(IV)	46.42	0.714	175.00
3.99 M H^+	34.07	0.524	350.00
1.30 M $SO_4^=$	29.12	0.448	450.00
$t_{\frac{1}{2}}$ =410 hrs.	23.99	0.369	550.00
	20.48	0.315	650.00
	15.28	0.235	800.00
	65.01	---	∞(c)

TABLE XVIII cont.

	c/s(IV)	(1-f)	t(hrs)
	58.43	0.880	50.00
0.0126 $\underline{M}$ Sn(II)	57.17	0.861	100.00
0.0132 $\underline{M}$ Sn(IV)	48.67	0.733	175.00
3.99 $\underline{M}$ H^+	29.55	0.445	350.00
1.40 $\underline{M}$ $SO_4^=$	30.68	0.462	450.00
$t_{\frac{1}{2}} = 405$ hrs.	26.56	0.400	550.00
	21.58	0.325	650.00
	16.27	0.245	800.00
	66.40	---	∞(c)

TABLE XIX

STUDY OF THE EFFECT OF SULFATE AND HYDROGEN IONS ON THE RATE OF EXCHANGE

	c/s(IV)	(1-f)	t(hrs)
	26.70	0.962	26.00
0.0129 $\underline{M}$ Sn(II)	24.28	0.875	58.00
0.0129 $\underline{M}$ Sn(IV)	23.50	0.847	102.00
4.95 $\underline{M}$ H^+	22.42	0.808	153.00
1.21 $\underline{M}$ $SO_4^=$	21.42	0.772	191.00
$\mu = 6.16$	19.75	0.712	240.00
$t_{\frac{1}{2}} = 578$ hrs.	18.37	0.662	290.00
	16.84	0.607	360.00
	14.04	0.506	500.00
	27.05	---	∞(c)
	58.93	0.952	25.00
0.0129 $\underline{M}$ Sn(II)	56.51	0.917	74.00
0.0129 $\underline{M}$ Sn(IV)	55.70	0.900	122.00
5.08 $\underline{M}$ H^+	51.53	0.830	175.00
1.24 $\underline{M}$ $SO_4^=$	46.61	0.737	245.00
$\mu = 6.32$	43.65	0.706	300.00
$t_{\frac{1}{2}} = 625$ hrs.	41.32	0.667	365.00
	36.02	0.584	460.00
	29.68	0.480	655.00
	25.39	0.410	792.00
	61.86	---	∞(c)

TABLE XIX cont.

	c/s(IV)	(1-f)	t(hrs)
0.0127 $\underline{M}$ Sn(II) 0.0131 $\underline{M}$ Sn(IV) 5.99 $\underline{M}$ H^+ 1.43 $\underline{M}$ $SO_4^=$ $\mu = 7.39$ $t_{\frac{1}{2}} = 630$ hrs.	26.50	0.991	26.00
	25.35	0.948	58.00
	24.36	0.911	102.00
	22.92	0.857	153.00
	21.21	0.793	191.00
	19.97	0.747	240.00
	18.32	0.685	290.00
	18.10	0.677	360.00
	15.54	0.581	500.00
	13.80	0.516	600.00
	26.74	—	∞(c)
0.0129 $\underline{M}$ Sn(II) 0.0129 $\underline{M}$ Sn(IV) 5.74 $\underline{M}$ H^+ 1.40 $\underline{M}$ $SO_4^=$ $\mu = 7.71$ $t_{\frac{1}{2}} = 690$ hrs.	63.44	0.929	23.00
	59.92	0.866	71.00
	57.31	0.841	118.00
	53.62	0.786	172.00
	51.39	0.753	242.00
	47.65	0.699	297.00
	42.71	0.625	362.00
	39.82	0.584	457.00
	33.35	0.489	652.00
		0.425	789.00
	68.15	—	∞(c)
0.0129 $\underline{M}$ Sn(II) 0.0129 $\underline{M}$ Sn(IV) 5.42 $\underline{M}$ H^+ 1.73 $\underline{M}$ $SO_4^=$ $\mu = 8.00$ $t_{\frac{1}{2}} = 605$ hrs.	63.14	0.904	25.00
	60.99	0.873	74.00
	56.77	0.811	121.00
	53.66	0.769	175.00
	48.75	0.698	245.00
	45.23	0.648	300.00
	41.28	0.592	365.00
	38.77	0.555	460.00
	34.77	0.497	655.00
	26.57	0.380	792.00
	69.92	—	∞(c)

TABLE XIX cont.

	c/s(IV)	(1-f)	t(hrs)
0.0129 M Sn(II) 0.0129 M Sn(IV) 6.40 M H^+ 1.52 M $SO_4^=$ $\mu = 8.10$ $t_{\frac{1}{2}} = 810$ hrs.	62.58	0.924	25.00
	60.89	0.897	74.00
	57.60	0.850	121.00
	56.43	0.815	175.00
	51.62	0.761	295.00
	48.84	0.770	300.00
	45.17	0.665	365.00
	42.36	0.624	460.00
	37.32	0.550	655.00
	31.85	0.470	792.00
	27.31	0.403	963.00
	67.77	——	∞(c)
0.0129 M Sn(II) 0.0129 M Sn(IV) 6.67 M H^+ 1.53 M $SO_4^=$ $\mu = 8.20$ $t_{\frac{1}{2}} = 865$ hrs.	62.67	0.889	25.00
	59.09	0.842	74.00
	56.83	0.806	121.00
	53.63	0.762	175.00
	51.93	0.735	245.00
	49.15	0.697	300.00
	46.12	0.640	365.00
	42.89	0.608	460.00
	37.47	0.532	655.00
	33.49	0.475	792.00
	29.12	0.413	963.00
	70.50	——	∞(c)
0.0129 M Sn(II) 0.0129 M Sn(IV) 5.57 M H^+ 1.94 M $SO_4^=$ $\mu = 8.77$ $t_{\frac{1}{2}} = 600$ hrs.	61.04	0.925	23.00
	58.08	0.880	71.00
	54.63	0.828	118.00
	51.54	0.781	172.00
	47.51	0.720	242.00
	44.42	0.072	297.00
	40.87	0.619	362.00
	36.86	0.558	457.00
	29.56	0.448	652.00
	26.20	0.397	789.00
	65.99	——	∞(c)

TABLE XIX cont.

	c/s(IV)	(1-f)	t(hrs)
	63.16	0.970	23.00
0.0120 $\underline{M}$ Sn(II)	59.76	0.918	71.00
0.0129 $\underline{M}$ Sn(IV)	55.15	0.846	118.00
5.70 $\underline{M}$ H^+	50.75	0.779	172.00
2.15 $\underline{M}$ $SO_4^=$	48.91	0.751	242.00
$\mu = 9.51$	46.47	0.697	297.00
$t_{\frac{1}{2}} = 595$ hrs.	41.15	0.631	362.00
	38.20	0.586	457.00
	30.19	0.403	652.00
	26.11	0.401	789.00
	65.12	---	∞(c)

TABLE XX

STUDY OF THE EFFECT OF TEMPERATURE ON THE RATE OF EXCHANGE

	c/s(IV)	(1-f)	t(hrs)
	43.79	0.823	25.00
0.0129 $\underline{M}$ Sn(II)	40.40	0.760	40.00
0.0129 $\underline{M}$ Sn(IV)	35.98	0.676	67.00
3.99 $\underline{M}$ H^+	30.93	0.581	90.00
0.99 $\underline{M}$ $SO_4^=$	26.31	0.495	118.00
37.8 °C	22.95	0.431	150.00
$t_{\frac{1}{2}} = 127$ hrs.	17.09	0.321	195.00
	12.91	0.243	245.00
		---	∞(c)
	43.92	0.809	25.00
0.0129 $\underline{M}$ Sn(II)	40.44	0.762	40.00
0.0129 $\underline{M}$ Sn(IV)	35.55	0.670	67.00
3.99 $\underline{M}$ H^+	32.24	0.608	90.00
0.99 $\underline{M}$ $SO_4^=$	26.27	0.495	118.00
37.8 °C	23.04	0.434	150.00
$t_{\frac{1}{2}} = 127$ hrs.	18.29	0.348	195.00
	12.05	0.228	245.00
		---	∞(c)

TABLE XX cont.

	c/s(IV)	(1-f)	t(hrs)
	46.00	0.746	14.00
0.0120 M Sn(II)	35.52	0.580	24.00
0.0132 M Sn(IV)	27.13	0.441	37.00
3.99 M H^+	22.02	0.360	50.10
0.99 M $SO_4^=$	17.76	0.290	75.00
49.5 °C	16.30	0.268	100.00
$t_{\frac{1}{2}}$=19 hrs.	15.31	0.251	125.00
	13.82	0.226	170.00
	11.42	0.187	245.00
	9.55	0.156	325.00
	61.13	---	∞(c)
	44.02	0.714	14.00
0.0127 M Sn(II)	35.50	0.576	24.00
0.0131 M Sn(IV)	26.89	0.436	37.00
3.99 M H^+	22.13	0.358	50.00
0.99 M $SO_4^=$	17.62	0.286	75.00
49.5 °C	16.81	0.272	100.00
$t_{\frac{1}{2}}$=20 hrs.	15.90	0.258	125.00
	14.23	0.231	170.00
	12.12	0.196	245.00
	10.32	0.168	325.00
	61.64	---	∞(c)

KINETIC STUDIES WITH 3.99 M HYDROGEN ION, CATALYZED BY CHLORIDE ION, $\mu = 4.98$

TABLE XXI

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

	c/s(IV)*	(1-f)ǂ	t(hrs)
0.0129 M Sn(II) 0.0129 M Sn(IV) 3.99 M H^+ 0.015 M Cl^- $t_{\frac{1}{2}} = 425$ hrs.	28.22	1.033	26.00
	25.30	0.926	58.00
	24.56	0.899	102.00
	22.53	0.825	153.00
	20.49	0.750	191.00
	19.40	0.710	240.00
	18.14	0.664	290.00
	16.00	0.586	360.00
	27.32	---	∞(c)
0.0129 M Sn(II) 0.0129 M Sn(IV) 3.99 M H^+ 0.030 M Cl^- $t_{\frac{1}{2}} = 332$ hrs.	26.52	0.992	26.00
	23.10	0.864	58.00
	22.30	0.834	102.00
	19.44	0.727	153.00
	17.43	0.652	191.00
	16.07	0.601	240.00
	15.16	0.567	290.00
	13.58	0.508	360.00
	26.74	---	∞(c)
0.0129 M Sn(II) 0.0129 M Sn(IV) 3.99 M H^+ 0.060 M Cl^- $t_{\frac{1}{2}} < 231$ hrs.	24.43	0.911	26.00
	23.20	0.865	58.00
	19.58	0.730	102.00
	17.51	0.653	153.00
	16.41	0.612	191.00
	13.19	0.492	240.00
	11.53	0.430	290.00
	8.58	0.320	360.00
	26.82	---	∞(c)

* (X oo-X) in equation 27, page 26

ǂ Value calculated on basis of mole fraction, equation 26, page 26

c Calculated

TABLE XXI cont.

	c/s(IV)	(1-f)	t(hrs)
	38.01	0.943	6.00
0.0128 $\underline{M}$ Sn(II)	37.77	0.937	12.00
0.0129 $\underline{M}$ Sn(IV)	34.75	0.862	30.00
3.99 $\underline{M}$ H^+	30.72	0.762	55.00
0.0775 $\underline{M}$ Cl^-	27.13	0.673	79.00
$t_{\frac{1}{2}} = 174$ hrs.	25.56	0.634	100.00
	22.21	0.551	145.00
	18.70	0.464	175.00
	16.81	0.417	200.00
	40.31	---	∞(c)
	38.45	0.916	6.00
0.0129 $\underline{M}$ Sn(II)	36.27	0.864	12.00
0.0129 $\underline{M}$ Sn(IV)	32.45	0.773	30.00
3.99 $\underline{M}$ H^+	27.41	0.653	55.00
0.103$_3$ $\underline{M}$ Cl^-	26.66	0.635	79.00
$t_{\frac{1}{2}} = 125$ hrs.	22.38	0.533	100.00
	18.47	0.440	145.00
	15.45	0.368	175.00
	14.99	0.357	200.00
	41.98	---	∞(c)
	20.22	0.754	26.00
0.0129 $\underline{M}$ Sn(II)	15.90	0.593	58.00
0.0129 $\underline{M}$ Sn(IV)	10.75	0.401	102.00
3.99 $\underline{M}$ H^+	8.29	0.309	153.00
0.120 $\underline{M}$ Cl^-	5.28	0.197	191.00
$t_{\frac{1}{2}} = 90$ hrs.	4.18	0.156	240.00
	3.27	0.122	290.00
	1.66	0.062	360.00
	27.22	---	∞(c)
	31.68	0.897	6.00
0.0096 $\underline{M}$ Sn(II)	30.83	0.873	12.00
0.0129 $\underline{M}$ Sn(IV)	27.48	0.778	30.00
3.99 $\underline{M}$ H^+	21.05	0.596	55.00
0.129 $\underline{M}$ Cl^-	17.09	0.484	79.00
$t_{\frac{1}{2}} = 76$ hrs.	14.19	0.402	100.00
	11.73	0.332	145.00
	7.03	0.199	175.00
	6.08	0.172	200.00
	35.32	---	∞(c)

TABLE XXI cont.

	c/s(IV)	(1-f)	t(hrs)
	36.60	0.874	6.00
0.0128 M Sn(II)	35.26	0.842	12.00
0.0129 M Sn(IV)	31.49	0.752	30.00
3.99 M H^+	24.21	0.578	55.00
0.129 M Cl^-	18.97	0.453	79.00
$t_{\frac{1}{2}}$ = 83 hrs.	18.18	0.434	100.00
	12.35	0.295	145.00
	9.97	0.238	175.00
	8.75	0.209	200.00
	41.88	---	∞(c)
	42.53	0.929	6.00
0.0128 M Sn(II)	40.56	0.886	12.00
0.0100 M Sn(IV)	34.47	0.753	30.00
3.99 M H^+	26.82	0.586	55.00
0.129 M Cl^-	23.99	0.524	79.00
$t_{\frac{1}{2}}$ = 88 hrs.	20.00	0.437	100.00
	18.08	0.395	145.00
	11.86	0.259	175.00
	8.93	0.195	200.00
	45.78	---	∞(c)
	39.34	0.969	3.00
0.0128 M Sn(II)	35.28	0.869	7.00
0.0129 M Sn(IV)	33.90	0.835	12.00
3.99 M H^+	30.25	0.745	24.00
0.150 M Cl^-	28.22	0.695	27.00
$t_{\frac{1}{2}}$ = 57 hrs.	25.78	0.635	31.00
	22.17	0.546	49.00
	18.43	0.454	56.00
	15.51	0.382	74.00
	40.60	---	∞(c)
	35.32	0.854	6.00
0.0128 M Sn(II)	32.51	0.786	12.00
0.0129 M Sn(IV)	25.56	0.618	25.00
3.99 M H^+	23.16	0.560	30.00
0.193 M Cl^-	14.35	0.347	55.00
$t_{\frac{1}{2}}$ = 39 hrs.	9.97	0.241	79.00
	6.04	0.146	100.00
	41.36	---	∞(c)

TABLE XXI cont.

	c/s(IV)	(1-f)	t(hrs)
0.0055 M Sn(II) 0.0134 M Sn(IV) 3.99 M H^+ 0.200 M Cl^- $t_{\frac{1}{2}}$ = 18.5 hrs.	32.29	0.882	2.00
	28.88	0.789	5.00
	23.25	0.635	10.00
	19.18	0.524	17.00
	13.84	0.378	24.00
	11.13	0.304	30.00
	8.68	0.237	37.00
	5.49	0.150	50.00
	1.91	0.052	71.00
	36.61	---	∞(c)
0.0085 M Sn(II) 0.0134 M Sn(IV) 3.99 M H^+ 0.200 M Cl^- $t_{\frac{1}{2}}$ = 21.6 hrs.	41.83	0.857	2.00
	39.34	0.806	5.00
	35.48	0.727	10.00
	25.91	0.531	17.00
	20.09	0.424	24.00
	16.79	0.344	30.00
	15.32	0.314	37.00
	9.23	0.189	50.00
	5.08	0.104	71.00
	48.81	---	∞(c)
0.0125$_3$ M Sn(II) 0.0133 M Sn(IV) 3.99 M H^+ 0.200 M Cl^- $t_{\frac{1}{2}}$ = 25.2 hrs.	53.24	0.857	2.00
	50.57	0.814	5.00
	39.39	0.634	10.00
	35.66	0.574	17.00
	28.58	0.460	24.00
	23.73	0.382	30.00
	19.14	0.308	37.00
	14.66	0.236	50.00
	8.01	0.129	71.00
	62.13	---	∞(c)
0.0128 M Sn(II) 0.0129 M Sn(IV) 3.99 M H^+ 0.258$_2$ M Cl^- $t_{\frac{1}{2}}$ = 25 hrs.	32.38	0.772	6.00
	26.17	0.624	12.00
	17.36	0.414	25.00
	16.99	0.405	30.00
	9.27	0.221	55.00
	4.57	0.109	79.00
	2.30	0.055	100.00
	41.94	---	∞(c)

TABLE XXI cont.

	c/s(IV)	(1-f)	t(hrs)
	32.18	0.781	3.00
0.0128 $\underline{M}$ Sn(II)	29.54	0.717	7.00
0.0129 $\underline{M}$ Sn(IV)	25.79	0.626	12.00
3.99 $\underline{M}$ H^+	15.98	0.388	24.00
0.300 $\underline{M}$ Cl^-	14.91	0.362	27.00
$t_{\frac{1}{2}} = 21$ hrs.	13.60	0.330	31.00
	8.28	0.201	49.00
	5.93	0.144	56.00
	41.20	---	∞(c)
	69.95	0.924	2.00
0.0195 $\underline{M}$ Sn(II)	63.82	0.843	5.00
0.0134 $\underline{M}$ Sn(IV)	52.99	0.700	10.00
3.99 $\underline{M}$ H^+	46.25	0.611	17.00
0.200 $\underline{M}$ Cl^-	41.71	0.551	24.00
$t_{\frac{1}{2}} = 30.5$ hrs.	36.56	0.483	30.00
	31.41	0.415	37.00
	24.22	0.320	50.00
	14.08	0.180	71.00
	75.70	---	∞(c)
	24.15	0.587	6.00
0.0128 $\underline{M}$ Sn(II)	18.23	0.443	12.00
0.0129 $\underline{M}$ Sn(IV)	10.82	0.263	20.00
3.99 $\underline{M}$ H^+	9.54	0.232	25.00
0.516_3 $\underline{M}$ Cl^-	5.39	0.131	30.00
$t_{\frac{1}{2}} = 10.4$ hrs.	1.65	0.040	50.00
	0.34	0.008	100.00
	41.14	---	∞(c)
	27.93	0.662	3.00
0.0128 $\underline{M}$ Sn(II)	20.26	0.480	7.00
0.0129 $\underline{M}$ Sn(IV)	13.97	0.331	12.00
3.99 $\underline{M}$ H^+	5.61	0.133	24.00
0.600 $\underline{M}$ Cl^-	4.64	0.110	27.00
$t_{\frac{1}{2}} = 9.1_0$ hrs.	3.39	0.080	31.00
	0.89	0.021	49.00
		---	56.00
	42.20	---	∞(c)

TABLE XXI cont.

	c/s(II)*	(1-f)	t(hrs)
	29.79	0.643	1.05
0.0127 M Sn(II)	37.60	0.550	2.00
0.0131 M Sn(IV)	41.88	0.499	3.00
3.99 M H^+	44.37	0.469	4.00
0.60 M Cl^-	50.13	0.400	5.00
$t_{\frac{1}{2}} = 8.7_8$ hrs.	52.61	0.369	7.00
	57.48	0.312	9.00
	61.93	0.259	11.00
	67.50	0.192	15.00
	83.79	---	∞(o)
	32.11	0.616	1.03
0.0127 M Sn(II)	43.67	0.478	2.00
0.0131 M Sn(IV)	47.30	0.434	3.08
3.99 M H^+	49.85	0.404	4.00
0.90 M Cl^-	52.26	0.374	5.00
$t_{\frac{1}{2}} = 5.8_2$ hrs.	60.40	0.277	7.00
	64.91	0.223	9.00
	68.95	0.175	11.00
	74.00	0.112	15.00
	83.45	---	∞(o)
	27.58	0.670	0.50
0.0127 M Sn(II)	30.44	0.635	1.00
0.0131 M Sn(IV)	34.36	0.588	1.50
3.99 M H^+	39.31	0.529	2.00
1.20 M Cl^-	42.10	0.495	2.50
$t_{\frac{1}{2}} = 4.6_9$ hrs.	47.50	0.432	3.50
	51.38	0.385	4.50
	61.20	0.267	7.00
	70.50	0.155	10.50
	83.50	---	∞(o)

* Activity of 4 ml. sample corrected for background

o Observed

TABLE XXII

STUDY OF THE EFFECT OF VARIATION IN TIN(II) CONCENTRATIONS ON THE RATE OF EXCHANGE

	c/s(II)	(1-f)	t(hrs)
0.0048_7 M Sn(II) 0.0131_3 M Sn(IV) 3.99 M H^+ 1.00 M Cl^- $t_{\frac{1}{2}}=8.8_8$ hrs.	24.08	0.459	0.50
	25.08	0.437	1.00
	26.91	0.396	2.00
	28.11	0.368	3.00
	28.46	0.360	4.00
	30.02	0.326	5.00
	31.06	0.303	6.00
	32.71	0.264	8.00
	36.78	0.173	14.00
	39.05	0.120	17.00
	44.45	---	∞(o)
0.0088_5 M Sn(II) 0.0131_5 M Sn(IV) 3.99 M H^+ 1.00 M Cl^- $t_{\frac{1}{2}}=7.1_8$ hrs.	28.20	0.402	1.00
	29.95	0.365	2.00
	31.45	0.332	3.00
	32.47	0.310	4.00
	34.56	0.268	5.00
	37.00	0.215	6.00
	37.73	0.199	8.00
	40.42	0.139	11.00
	47.10	---	∞(o)
0.0171 M Sn(II) 0.0133 M Sn(IV) 3.99 M H^+ 1.00 M Cl^- $t_{\frac{1}{2}}=5.2_0$ hrs.	34.19	0.490	1.00
	38.90	0.420	2.50
	43.20	0.357	4.00
	49.90	0.257	6.00
	52.65	0.216	8.00
	58.00	0.135	11.00
	60.55	0.095	14.00
	67.00	---	∞(o)

TABLE XXIII

STUDY OF THE EFFECT OF VARIATION IN TIN(IV) CONCENTRATIONS ON THE RATE OF EXCHANGE

	c/s(II)	(1-f)	t(hrs)
	30.81	0.567	0.50
0.0126 M Sn(II)	33.21	0.434	1.00
0.0053 M Sn(IV)	33.76	0.524	2.00
3.99 M H^+	36.51	0.488	3.00
1.00 M Cl^-	39.74	0.444	4.00
$t_{\frac{1}{2}}=8.4_6$ hrs.	45.50	0.361	5.00
	48.94	0.323	6.00
	49.00	0.312	8.00
	57.21	0.195	14.00
	61.53	0.134	17.00
	71.22	---	∞(o)
	27.92	0.559	1.00
0.0126 M Sn(II)	33.33	0.474	2.00
0.0093 M Sn(IV)	36.65	0.420	3.00
3.99 M H^+	37.98	0.399	4.00
1.00 M Cl^-	40.70	0.355	5.00
$t_{\frac{1}{2}}=7.2_0$ hrs.	42.70	0.325	6.00
	46.00	0.271	8.00
	51.12	0.190	11.00
	63.15	---	∞(o)
	29.41	0.437	1.00
0.0126 M Sn(II)	35.42	0.323	2.50
0.0178 M Sn(IV)	37.80	0.276	4.00
3.99 M H^+	40.51	0.223	6.00
1.00 M Cl^-	43.54	0.167	8.00
$t_{\frac{1}{2}}=5.0_0$ hrs.	46.40	0.114	11.00
	48.94	0.066	14.00
	52.15	---	∞(o)

TABLE XXIV

STUDY OF THE EFFECT OF TEMPERATURE ON THE RATE OF EXCHANGE

	c/s(II)	(1-f)	t(hrs)
	29.99	0.484	0.50
0.0126 M Sn(II)	35.39	0.390	1.00
0.0132 M Sn(IV)	43.41	0.254	1.50
3.99 M H^+	44.84	0.228	2.00
1.00 M Cl^-	49.08	0.154	3.00
37.8 °C	50.79	0.126	3.50
$t_{\frac{1}{2}}$=1.46 hrs.	52.50	0.095	4.00
	54.52	0.060	5.00
	58.17	---	∞(o)
	30.57	0.474	0.50
0.0127 M Sn(II)	36.69	0.368	1.00
0.0131 M Sn(IV)	41.82	0.280	1.50
3.99 M H^+	46.96	0.192	2.00
1.00 M Cl^-	50.60	0.128	3.00
37.8 °C	64.75	---	3.50
$t_{\frac{1}{2}}$=1.39 hrs.	54.25	0.068	4.00
	55.51	0.046	5.00
	58.03	---	∞(o)

	c/s(II)	(1-f)	t(min.)
	32.85	0.575	10.00
0.0125 M Sn(II)	37.29	0.517	20.00
0.0133 M Sn(IV)	44.95	0.419	30.00
3.99 M H^+	47.35	0.388	40.00
1.00 M Cl^-	51.95	0.339	50.00
49.5 °C	54.42	0.296	60.00
$t_{\frac{1}{2}}$=18.2 mins.	58.46	0.245	75.00
	60.42	0.229	90.00
	61.59	0.203	120.00
	62.09	0.146	150.00
	64.71	0.103	180.00
	65.80	0.148	240.00
	77.31	---	∞(o)

TABLE XXIV cont.

	c/s(II)	(1-f)	
	32.85	0.575	10.00
0.0126 $\underline{M}$ Sn(II)	37.29	0.517	20.00
0.0132 $\underline{M}$ Sn(IV)	44.95	0.419	30.00
3.99 $\underline{M}$ H^+	47.35	0.388	40.00
1.00 $\underline{M}$ Cl^-	51.95	0.339	50.00
49.5 °C	54.42	0.296	60.00
$t_{\frac{1}{2}}$ 18.2 mins.	58.46	0.245	75.00
	60.42	0.229	90.00
	61.59	0.203	120.00
	62.09	0.196	150.00
	64.71	0.163	180.00
	65.80	0.148	240.00
	77.31	---	∞(o)

APPENDIX B

EQUATIONS USED TO CALCULATE SPECIES PRESENT IN KINETIC RUNS, APPENDIX A

(I) Constant hydrogen and sulfate ions--variation in tin concentration:

63) $\underline{M}_{SO_4^=} = X$

64) $\underline{M}_{HSO_4^-} = \underline{M}_{H_2SO_4} - X$

65) $\underline{M}_{H^+} = \underline{M}_{H_2SO_4} + X$

66) $\mu = \underline{M}_{H_2SO_4} + 2\,X$

67) $K_{2c} = 1.96 = (\underline{M}_{H^+})(\underline{M}_{SO_4^=})/(\underline{M}_{HSO_4^-})$

(II) (a) Hydrogen ion greater than 3.99 $\underline{M}$ with constant sulfate ion:
(b) Sulfate ion less than 0.99 $\underline{M}$ with constant hydrogen ion:

68) $\underline{M}_{SO_4^=} = X$

69) $\underline{M}_{HSO_4^-} = \underline{M}_{H_2SO_4} - X$

70) $\underline{M}_{H^+} = \underline{M}_{H_2SO_4} + \underline{M}_{HClO_4} + X$

71) $\mu = \underline{M}_{LiClO_4} + \underline{M}_{H_2SO_4} + \underline{M}_{HClO_4} + 2\,X$

and Equation (67)

(III) Sulfate ion greater than 0.99 $\underline{M}$:

72) $\underline{M}_{SO_4^=} = \underline{M}_{Li_2SO_4} + X$

73) $\underline{M}_{HSO_4^-} = \underline{M}_{H_2SO_4} - X$

74) $\underline{M}_{H^+} = \underline{M}_{H_2SO_4} + X$

75) $\mu = 3\,\underline{M}_{Li_2SO_4} + \underline{M}_{H_2SO_4} + 2\,X$

and Equation (67)

(IV) Hydrogen ion less than 3.99 M, with constant sulfate ion:

76) $\underline{M}_{SO_4^=} = \underline{M}_{Li_2SO_4} + X$

77) $\underline{M}_{HSO_4^-} = \underline{M}_{H_2SO_4} - X$

78) $\underline{M}_{H^+} = \underline{M}_{H_2SO_4} + X + \underline{M}_{HClO_4}$

79) $\mu = 3\,\underline{M}_{Li_2SO_4} + \underline{M}_{H_2SO_4} + 2X + \underline{M}_{HClO_4}$

and Equation (67)

(V) Hydrogen ion greater than 3.99 M, sulfate ion greater than 0.99, and u greater than 4.98:

80) $\mu = 2.204\,K + 0.66$

and Equations (67, 68, 69, 70, and 71)

(VI) Chloride ion greater than 0.1 M:

81) $\underline{M}_{SO_4^=} = X$

82) $\underline{M}_{HSO_4^-} = \underline{M}_{H_2SO_4} - X$

83) $\underline{M}_{H^+} = \underline{M}_{H_2SO_4} + \underline{M}_{HCl} + X$

84) $\underline{M}_{Cl^-} = \underline{M}_{HCl} + \underline{M}_{LiCl}$

85) $\mu = 2X + \underline{M}_{H_2SO_4} + \underline{M}_{HCl} + \underline{M}_{LiCl}$

and Equation (67)

APPENDIX C

SURVEY OF ORGANIC SOLVENTS FOR SOLVENT EXTRACTION OF TIN(IV)

A series of preliminary experiments were carried out for the purpose of choosing an organic solvent that would be suitable for distribution studies. The data are given in terms of the distribution coefficient K_D, where

$$K_D = \frac{\text{concentration in the organic phase}}{\text{concentration in the aqueous phase}}$$

TABLE

VARIATION OF THE DISTRIBUTION COEFFICIENT WITH HYDROCHLORIC ACID AND 0.0261 $\underline{M}$ Sn(IV)

Solvent	Molar Hydrochloric Acid				
	1.00	2.50	4.00	5.50	7.00
acetophenone	1.67_c	1.61_c	3.11_c	3.94_c	5.72_c
tri-n-butyl phosphate	3.46	3.20	3.13_c	4.02_c	8.35_c
methyl isoamyl ketone	0.15_e	0.85_e	1.08_e	2.47_y	3.82_y
methyl n-propyl ketone	1.13	3.37	4.15	m	m
cyclohexanone	3.54	5.09_y	6.41_v	m	m

c	Cloudy
e	Slight coloring in organic phase
y	Both phases yellow
m	Miscible
v	Greater than 20% volume change

No extraction was observed for the following solvents in 4.00 M hydrochloric acid (Sn(IV) $\simeq$ 0.0261 M):

chlorobenzene
chloroform
propylene chloride
n-butyl ether
tri-tolyl-phosphate
beta, beta'-dichloro-diethyl ether
di-isobutyl ketone
cyclohexane

Benzonitrile, methyl, n-amyl ketone, iso-amyl alcohol, and n-hexyl alcohol were also tried as solvents (4.00 M HCl, 0.0261 M Sn(IV)) but they were undesireable due to deep coloration of the organic layer and/or large volume changes.

No extraction was observed for 0.0261 M Sn(IV) in 5.00 M sulfuric acid with the following solvents:

methyl, isobutyl ketone
di-isobutyl ketone*
isoamyl ketone (v)
n-butyl ether
n-hexane
n-hexyl alcohol (v)*
acetophenone
benzonitrile
chloroform (p)
propylene chloride
methyl, isoamyl ketone
methyl, n-amyl ketone (y)
methyl, n-propyl ketone (v)
cyclohexanone (v)
cyclohexane
nitrobenzene
chlorobenzene
tri-n-butyl phosphate (v)*
beta,beta-dichlorodiethyl ether
tri-tolyl phosphate

Glycol, dimercapto acetate (available from Evans Chemetrics, 250 E. 43 Street, New York 17, New York) was also tried as a solvent. K_D was approximately constant (4.0 ± 0.2) using 2 - 6 M sulfuric acid. This solvent should be investigated more extensively.

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p Poor interface
v Volume change upon mixing
y Organic phase turned yellow in color
* Higher acid concentrations tried, also unsuccessful