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THE ROLE OF MERCURY IN THE CATALYSIS OF THE BETTENDORFF REACTION

by

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INTRODUCTION

The Bettendorff Reaction may be written

$$2\ As^{+++} + 3\ Sn^{++} = 2\ As^{o} + 3\,Sn^{+4}\ .$$

The reaction is usually carried out in strong hydrochloric acid solutions because it was found that it proceeds more rapidly the more concentrated the acid.

In 1933 King and Brown (1) reported an attempt to analyze qualitatively for arsenic and mercury in the same solution by the addition of $SnCl_2$. Mercury is reduced very rapidly by the reagent while arsenic is reduced rather slowly. They assumed that rapid filtration of the Hg^o and Hg_2Cl_2 first formed would be followed by the appearance of the characteristic brown colloid of As^o in the clear filtrate at a later time. That no such colloid was produced led to the discovery that mercury serves to increase the rate of the reduction of the arsenic by the $SnCl_2$. In their paper they describe a method for the determination of very small quantities of mercury by its effect on this reaction.

It was suggested at the time that this was an example of an induced reaction. However, in 1939 the same workers (2) presented experimental evidence indicating that the reaction was in reality catalyzed by the mercury and that elemental mercury was the catalytic agent.

The present work was carried out in an attempt to elucidate to some extent the kinetics of the reaction between arsenious ion and stannous ion, catalyzed and uncatalyzed.

REVIEW OF LITERATURE

With the exception of those pertaining to its analytical applications very few papers have appeared in the literature which deal solely with the Bettendorff reaction. The original work of Bettendorff did not concern itself with the kinetics of the reaction.

Durrant (3) carried out a series of experiments intended to elucidate the kinetics of the reaction but some of his conclusions are questionable. He showed the irreversible nature of the reaction by boiling finely divided arsenic with solutions of stannic chloride in the presence of hydrochloric acid of varying concentration and in no case did the resulting solution produce a precipitate with mercuric chloride. He also proved that the anhydrous chlorides, $AsCl_3$ and $SnCl_2$, would not react with one another. Introduction of water into the anhydrous system gave an immediate heavy crusting of arsenic.

Another interesting experiment carried out by Durrant indicated that the arsenic first formed in the reaction was the yellow modification (not well known at the time) and that under certain conditions unknown to him, it was extracted by carbon disulfide. According to Sidgwick (4) this is the least stable, lowest-density form of arsenic. It may be obtained by sudden cooling of the heated vapor and is soluble in carbon disulfide. It is probable that the initial formation of this modification of arsenic is partly responsible for the induction period observed during the present study.

For the purpose of this discussion Durrant's kinetic work may be separated into two phases, the study of the initial portion of the reaction and the study of the remaining portion. The interpretation of the former is acceptable whereas that of the latter is not. Durrant does not make a distinction between these two phases. He suggests that calculations are more appropriately based on the earlier stages of the reaction which is true in the absence of an induction period. In the event that there is an induction period these results should not be projected to the later stages of the reaction.

A turbidimetric analytical procedure was used in the investigation of the first stage of the reaction, using a synthetic standard consisting of a suspension of lead sulfide. Nine runs were made with combinations of concentrations of stannous and arsenious ions, N, N/2, and N/3. For those runs in which the initial concentration of stannous ion varied it was found that the time required for the sample to match the tint of the standard was inversely proportional to the square root of the concentration of the stannous ion. For those runs in which the initial concentration of the arsenious ion was varied it was found that the time required for the sample to match the tint of the standard was inversely proportional to the square of the concentration of the arsenious ion. Durrant therefore proposed that the rate of the reaction varied as the square of the concentration of the arsenious ion and as the square root of the concentration of the stannous ion.

This situation may be analyzed mathematically. Let C_1^o and C_2^o equal the initial concentrations of As^{+++} and Sn^{++}, respectively, expressed in normality. Under the conditions of the experiment the reaction has undoubtedly gone no more than one per cent to completion by the time it reaches the tint of the standard so we can say that throughout the course of the measured reaction the concentrations have not changed. We may therefore write the equation

$$d\,(As^o)/dt = k\,(C_1^o)^m(C_2^o)^n \quad . \tag{1}$$

On integration this becomes for any one run

$$(As^o) = k\,(C_1^o)^m(C_2^o)^n\, t$$

or

$$t = (As^o)/k\,(C_1^o)^m(C_2^o)^n \; . \tag{2}$$

The standard being the same for all measurements, (As^o) is a constant for all runs at the time of measurement. If C_1^o is held constant and C_2^o varied for several runs the time required for the sample to match the standard will be inversely proportional to $(C_2^o)^n$, and if C_2^o remains constant and C_1^o is varied the time will be inversely proportional to $(C_1^o)^m$. Durrant found $n = 1/2$ and $m = 2$ as indicated above. The mathematical treatment of his data confirms his interpretation.

Durrant's study of the later portion of the reaction was similar to that of the former. Keeping the initial concentration of one reactant constant he varied the initial concentration of the other reactant for three runs. The analytical method involved filtration to remove As^o followed by titration of the filtrate with N/4 $KMnO_4$. Reference to Table 3 in his paper shows that he made three errors which produced results in agreement with what he would have predicted. The first error involves a confusion of normalities. Since arsenic undergoes a three electron change in its reaction with stannous ion and a two electron change in its reaction with permanganate the normality of the arsenic solution is different for the two reactions. He apparently does not make a differentiation. This leads to the second error because he compares the amount of permanganate used in the titration to the amount that should be used in theory when the reaction is one-third complete, and his theoretical values are incorrect because of the confusion in normalities. The third error arises when he assumes that the ratio of the times for the reaction to go to one-third of completion on varying the initial concentration of one reactant should bear the same ratio suggested in the experiment previously described. Since he is now dealing with the integrated form of the general case of equation 1 the very special conditions which allowed the simplified assumption no longer obtain.

A fourth error was also made that does not appear in his data and that is a lack of appreciation of the induction period which adds to both numerator and denominator in the ratio of times. When studying the initial portion of the reaction he was actually studying the induction period so this did not influence those results.

Durrant suggests from his study that chloride ion "acts as a first power" which is not in accord with the data obtained in the present work. He arrives at his conclusion from the results of a number of runs in which the only variable is the concentration of the hydrochloric acid, C_1, C_2, C_3 etc. From these data he calculates for each concentration of hydrochloric acid a <u>first order rate constant</u>, k_1, k_2, k_3, etc. The ratios of these constants are then computed $^{k_1}/k_2$, $^{k_2}/k_3$, $^{k_3}/k_4$, etc. He then computes another series of ratios. The numerators of these ratios are the sums of the chloride ion concentration due to the arsenic trichloride and that due to the <u>difference</u> in chloride concentration resulting from the change in hydrochloric acid concentration.

The denominators are the concentration of chloride ion due to the arsenic trichloride. Letting C_{c1} be the concentration of chloride due to the arsenic trichloride the latter ratios may be written

$$\frac{(C_1-C_2)+C_{c1}}{C_{c1}},\quad \frac{(C_2-C_3)+C_{c1}}{C_{c1}},\quad \frac{(C_3-C_4)C_{c1}}{C_{c1}},\ \text{etc.}$$

Writing Cl'/Cl for these latter ratios the following values are obtained:

N HCl	$k \times 10^2$	k_n/k_{n+1}	Cl'/Cl
10.09	21.2		
		1.57	7.09
8.10	13.5		
		2.83	3.55
7.25	4.76		
		1.37	1.54
7.09	33.43		
		2.35	2.08
6.77	1.46		
		1.54	1.58
6.60	0.944		
		2.16	1.88
6.34	0.436		
		3.22	2.66
6.11	0.293		
		10.0	5.28
4.85	0.0293		

He suggests that discrepancies at high hydrochloric acid concentrations are due to incomplete ionization of the hydrochloric acid, while those at low concentrations are due to incomplete ionization of the arsenic trichloride. It is noted that the aggregates of the ratios, 25.04 for k_n/k_{n+1} and 25.66 for Cl'/Cl, are nearly equal and thus, "as is seen, the aggregate acceleration is directly proportional to the increase of chloride concentration."

There are several factors that are overlooked in the preceding argument. Although the chloride ion concentration is indeed changing, so also is the hydrogen ion concentration. In the present work it was found that rather than accelerating the reaction, chloride has a retarding effect at higher concentrations. Moreover, as the concentration of hydrochloric acid increases there is a concurrent increase in its mean ionic activity coefficient accompanied by a decrease in the activity of water (5, 6).

Qualitatively, Durrant's experimental results are concordant with those obtained during this work. There is no basis for quantitative comparison because of the differences that occur in all variables.

No other kinetic studies of the reduction of arsenic to the elementary state appear in the literature. Babko and Marchenko (7) have reported the effect of bromide and iodide ions on the reduction of arsenious ion by Sn(II), Cr(II), and $Ca(H_2PO_2)_2$, but the abstract does not imply that any kinetic information was obtained.

Several papers have appeared on the reduction of As(III): (1) polarographically (8, 9, 10); (2) electrolytically from nitrobenzene (11), ether (12), anhydrous acetic acid (13), and aqueous hydrochloric acid using copper as a carrier (14); by hydrogen in an electrodeless discharge in the vapor phase (15); by sodium amalgam (16); and by tin amalgam (17). However, none has dealt with the kinetics of the reaction concerned.

The kinetics of several reactions in which stannous ion is used as a reductant have been studied. The reaction between stannous ion and ferric ion has received a great deal of attention. Kahlenberg (18) appears to have been the first to report on the kinetics, suggesting that the reaction was

$$Fe_2Cl_6 + SnCl_2 \longrightarrow 2\ FeCl_2 + SnCl_4$$

and that his data, indicating a second order reaction, verified the Guldberg-Waage Law of Mass Action. In an article published in the following year, Noyes (19) claimed that the reaction was really of the third order, the first reaction to be observed of order higher than two. He recalculated some of Kahlenberg's data to support this hypothesis, and suggested that the equation should be written

$$2\ FeCl_3 + SnCl_2 \longrightarrow 2\ FeCl_2 + SnCl_4\ .$$

Timofeew and his successors (20), in order to test Bronsted's theory of the effect of added electrolytes, studied the reaction in the presence of various concentrations of NaCl and, finding the reaction rate increased with increasing concentration of NaCl, used this as evidence in support of the theory. Since that time, however, it has been established that chloride has a powerful accelerating effect on the reaction. Krishna (21) varied the ionic strength with non-halide salts and found in all cases that the rate diminished with increasing ionic strength. Assuming the validity of Bronsted's equation, this evidence supported Weiss' argument that the reaction actually occurred between $SnCl_4^{--}$ and Fe(III) and, being step-wise, was second-order. Weiss also maintained that the reaction was second order in chloride due to the equilibrium

$$SnCl_2 + 2\,Cl^- \rightleftharpoons SnCl_4^{--}$$

Duke and Pinkerton (23) studied the halide dependence of the reaction and concluded that the reaction was principally fourth-order in chloride, with however, a third-order contributing effect. They also found that in the presence of bromide third-order, and in the presence of iodide second-order, halide dependence predominated. In a reinterpretation of the work of Duke and Pinkerton, Duke and Peterson (24) observed that the chloride dependence is better described as fourth- and fifth-order rather than third- and fourth-order.

Gorin (25) studied the same reaction in perchloric acid medium (in the absence of chloride ions) and found the rate to be slower by a factor of 10^5 - 10^6 under comparable conditions. His data fit the rate equation

$$d(Sn^{++})/dt = k(Fe^{+++})(Sn^{++})/(H^+)^2$$

and from this and supporting evidence he favors a mechanism the first two steps of which are the hydrolysis of Fe(III). The initial step is supposed to be a rapid equilibrium, followed by a slow rate-determining equilibrium. The other rate-determining step consists of an electron transfer from the Sn(II) to the Fe(III) accompanied by a transfer of two hydroxyl radicals in the opposite direction. The $Sn(OH)_2^+$ intermediate is presumed to react rapidly.

Another reaction which is first-order with respect to Sn(II) is the reduction of U(VI) in hydrochloric acid solution studied by Moore (26). It is interesting to note that qualitatively there is a correlation between some of his data and that found in the present study, comments on which appear under the discussion. A spectrophotometric study of the individual reactants and the reaction mixture showed interaction absorption, leading to the conclusion that an interaction complex exists between U(VI) and Sn(II) composed of one U(VI) and one Sn(II) (with accompanying anions, of course).

Haight (27), and Haight and Sager (28) have studied the reduction of perchlorate ion by Sn(II) catalyzed by tungstate and molybdate, respectively. The former reaction is apparently zero-order in Sn(II) and the rate equation suggested is

$$d(Sn^{++})/dt = k(WO_4^{=})(ClO_4^{-}) \ .$$

An inverse dependence on the square of the chloride ion concentration is indicated. The proposed rate equation for the molybdate-catalyzed reaction is rather more complicated, the expression being

$$d(Sn^{++})/dt = \frac{K(Sn^{++})^{3/2}(ClO_4^{-})^{3/2}(Mo^{t})^{1/2}}{1 + 4K'(ClO_4^{-})} \ .$$

In both of these reactions the mechanism suggested includes a reduction by Sn(II) of a complex between ClO_4^- and the catalyst involving a two-electron transfer. Since the reaction does not occur (except in concentrated acid and at elevated temperatures) in the absence of a catalyst the mechanisms are probably as unusual as suggested, and it is unlikely that there is a basis for comparison with the present work.

Exchange studies between Sn(II) and Sn(IV) in aqueous HCl (29, 30) and in absolute ethanol (31) suggest (1) that exchange occurs between chloro-complexes of Sn(II) and Sn(IV), and (2) that there exists an unsymmetrical interaction complex containing one Sn(II), one Sn(IV) and from six (in ethanol) to ten chloride ions. Craig and Davidson (30), using a high-intensity Hg-arc, found the exchange was accelerated on exposure to radiation of wavelength 365 millimicrons. This wavelength is longer than the upper absorption edges of either Sn(II) or Sn(IV) but falls in the region of interaction absorption, indicating that perhaps this interaction complex is also the transition state.

Electromotive force measurements have been the source of data for three investigations of the chloro-complexes of Sn(II) (32, 33, 34). Considering the formation of possible complexes

$$Sn^{++} + n\ Cl^{-} \rightleftharpoons SnCl_{n}^{2-n}$$

with equilibrium constants

$$K_n = (SnCl_n^{2-n})/(Sn^{++})(Cl^{-})^n$$

there is general agreement that the value of K_2 is larger than the others. Duke and Courtney (33) and Prytz (32) offer substantial values for K_4, while Vanderzee and Rhodes (34) maintain there is no evidence for more than an insignificant value. Their reinterpretation of Duke and Courtney's data supports their argument. Hydrolysis of Sn(II) and the complexing of the hydrolytic product are also proposed by Vanderzee and Rhodes according to the equations

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

and

$$Sn(OH)^+ + n\ Cl^- \rightleftharpoons Sn(OH)Cl_n^{1-n}$$

for which the equilibrium constants

$$h = (Sn(OH)^+)\ (H^+)/(Sn^{++})$$

and

$$D_n = (Sn(OH)Cl_n^{1-n})/(Sn(OH)^+)(Cl^-)^n$$

are evaluated. These values are small compared to those of K_n and the rather large concentration of H^+ used in the current work would render them of negligible importance.

A number of investigators have taken the position that a complex of Sn(III) is formed in many reductions involving Sn(II). The only direct experimental evidence for this intermediate oxidation state was offered by Ball and co-workers (35). The technique employed, the magneto-optic method of analysis, has however, completely lost its stature among the scientific community.

The literature on the action of mercury as a catalyst is quite extensive and almost every conceivable mechanism has been proposed in one case or another. A complete review of the subject is beyond the scope of this paper. Citations of research related to the current work will be found in the discussion.

EXPERIMENTAL PROCEDURE

Reagents

The As_2O_3 and $KHC_8H_4O_4$ were Primary Standard Grade reagents. All other reagents used were of Analytical Reagent Grade, supplied by reputable manufacturers.

Preparation of Solutions

7N HCl, 7N $HClO_4$, 7N LiCl, 1.5N $SnCl_2$(in 7N HCl), and 1.5N As_2O_3(in 7N HCl) were prepared using a small excess of the reagent in each case. They were then standardized and a calculated additional amount of solvent was added to produce the desired concentration. Each solution was then restandardized.

The $HgCl_2$ solution was made by weighing out 2.729 g. $HgCl_2$ which was then transferred to a 100 ml. volumetric flask, dissolved in HCl and diluted to the mark with HCl. Subsequent dilutions were made using the usual volumetric techniques.

All of the other solutions were prepared by following the directions in the texts by Willard and Furman (36) or by Diehl and Smith (37).

Standardization of Solutions

The following diagrams illustrate the standardization relationships among the several solutions. The procedures followed in each instance may be found below according to the numbers on the diagrams.

$$\begin{tikzcd}
 & 1.5N\ Sn^{++} \arrow[d, leftrightarrow, "(2)"] & & \\
As_2O_3 \arrow[r, leftrightarrow, "(1)"] & Ce^{+4} \arrow[r, leftrightarrow, "(4)"] & 0.1N\ AsO_2^{-} \arrow[r, leftrightarrow, "(5)"] & I_3^{-} \\
 & 1.5N\ As^{+3} \arrow[u, leftrightarrow, "(3)"'] & &
\end{tikzcd}$$

$$\begin{tikzcd}
 & 7N\ HClO_4 \arrow[d, leftrightarrow, "(7)"] & & \\
KHC_3H_4O_4 \arrow[r, leftrightarrow, "(6)"] & 0.1N\ NaOh \arrow[r, leftrightarrow, "(9)"] \arrow[d, leftrightarrow, "(8)"] & 0.1N\ HCl \arrow[d, leftrightarrow, "(10)"] & \\
 & 7N\ HCl \arrow[r, leftrightarrow, "(11)"] & 0.1N\ AgNO_3 \arrow[r, leftrightarrow, "(12)"] \arrow[d, leftrightarrow, "(13)"] & 7N\ LiCl \\
 & & 0.05N\ KCNS &
\end{tikzcd}$$

Procedures 1, 5, 6, 10, and 13 may be found in texts by Willard and Furman (36) or Diehl and Smith (37).

(2) Some solid $NaHCO_3$ and 50 ml. of H_2O were put into a 250 ml. erlenmeyer flask. To remove dissolved oxygen, 10 ml. of 6N HCl were then added while the solution was stirred with a magnetic stirring device. Three ml. of Sn^{++} solution were transferred to the flask by means of a pipette, three drops of 0.025M

ferroin indicator were added, and the resulting solution titrated with Ce^{+4} solution. CO_2 from a cylinder was passed through the flask during the entire procedure.

(3) A three ml. sample of As^{+3} was transferred by means of a pipette into a 250 ml. erlenmeyer flask containing 100 ml. of H_2O. Four drops of 0.01M OsO_4 and two drops of 0.025M ferroin were added and the resulting solution was titrated with Ce^{+4} solution. The normality obtained was multiplied by 3/2 to obtain the normality of the solution for its reaction with Sn^{++}.

(4) Two burettes, one containing 0.1N AsO_2^- solution and the other 0.1N Ce^{+4} solution, were mounted on a burette stand. About 40 ml. of the AsO_2^- solution were delivered into a flask containing 50 ml. H_2O, 10 ml. 1N H_2SO_4, four drops of 0.01M OsO_4, and two drops of 0.025M ferroin, and the resulting solution was titrated with Ce^{+4} solution.

(7) Five ml. of the 7N $HClO_4$ solution were transferred to a 100 ml. volumetric flask and diluted to the mark with H_2O. After mixing well, 10 ml. aliquots were titrated with 0.1N NaOH as in procedure (6).

(8) The procedure used was the same as described in (7).

(9) The procedure used was the same as indicated in (6) except that the HCl was measured from a burette.

(11) Five ml. of the 7N HCl were transferred to a 100 ml. volumetric flask and diluted to the mark with H_2O. After mixing well, 10 ml. aliquots were titrated according to procedure (10).

(12) The procedure used was the same as described in (11).

The $HgCl_2$ solution was not standardized.

The 7N HCl, 1.5N Sn^{++}, and 1.5N As^{+3} were standardized prior to beginning the series of experiments and also when the series was completed.

	Initial	Final
HCl	7.00 N	6.94 N
Sn^{++}	1.503N	1.502N
As^{+3}	1.499N	1.496N

The 1.5N Sn^{++}, 1.5N As^{+3}, 7N LiCl, and 7N $HClO_4$ solutions were stored in glass stoppered bottles. Before standardizing the Sn^{++} solution the volume above the solution was swept out with CO_2, and every time the bottle was opened thereafter to remove a sample, a slow stream of CO_2 was passed into the bottle to prevent air oxidation.

The 7N HCl was stored in a five gallon bottle fitted with a siphon to remove the solution. When not in use both ends of the siphon were clamped.

The 0.1N AsO_2^- solution was stored in a three liter bottle fitted with a manual bulb-type pumping device for removing the solution. An Ascarite-filled bulb was inserted between the bulb and the bottle to prevent the entrance of CO_2. When not in use both ends were sealed with rubber tubing and clamps.

The other solutions were kept in tightly stoppered bottles stored in lockers.

Apparatus

The apparatus consisted essentially of two parts, the constant temperature bath and the reaction vessel plus accoutrements.

Constant temperature bath

A cylindrical steel can (d = 16 in., h = 16 in.) was filled with sand to a depth of 5 in. A cylindrical pyrex vessel (d = 12 in., h = 12 in.) was placed concentrically in the can on the sand. The space between the can and the pyrex vessel was filled with insulating material to within one inch of the top of the pyrex vessel. Nine feet of 1/4 inch copper tubing was wound into a flat coil and placed on the bottom of the pyrex vessel and a piece of rubber tubing attached to each end. One of the pieces of rubber tubing was connected to a pressure reduction valve attached to a cylinder of CO_2. The other piece of rubber tubing was connected to the reaction vessel through a stopcock and a pyrex T-tube, which in turn was connected to a pressure gauge.

Since the ambient temperature was sometimes higher than the bath temperature, another two foot length of 1/4 inch copper tubing through which circulated cold tap water, was put in the bath.

The thermoregulator was an adjustable mercurial type made by the Philadelphia Scientific Glass Company (type LW-912), and heating was accomplished with a 300 watt blade-type immersion heater. Both heater and thermoregulator were plugged into a Fisher-Serfass electronic relay. The water in the bath was stirred by a two inch stainless steel stirring blade driven by a high speed electric motor. The blade was canted at an angle of 30° from the vertical and forced the water across the heating element onto the thermoregulator situated about four inches behind it.

The temperature of the bath was read from a 0 - 100°C. thermometer having 0.1° graduations using a magnifying burette reader. This working thermometer was calibrated against an E. H. Sargent thermometer, IR 7213, certified by the National Bureau of Standards, certificate number 149083. The National Bureau of Standards certified thermometer was accompanied by a table of correction factors for 20°, 30°, and 40°C., among others, but not for 25° or 35°C. Corrections for these temperatures were made by interpolation.

The reaction vessel

The reaction vessel was a 500 ml. round-bottom pyrex flask having three vertical necks with \$ 24/40 ground glass female joints. The center neck was fitted with a stirring assembly. This consisted of a male \$ joint having a cylindrical ground glass bore through which a ground glass stirring rod was inserted, using glycerine as a lubricant. The end of the stirring rod would accept a variety of stirring bars, a two inch plastic bar being used in all runs. The stirring rod was turned by a heavy-duty two-speed Waco motor, the lower speed (300 r.p.m.) being used in all runs.

The second neck was connected to the CO_2 source as described in the first paragraph of the preceding section. The CO_2 was passed through the copper tubing in the constant temperature bath to insure against an alteration of the temperature of the reacting system by the CO_2 which was at a lower temperature as it left the cylinder.

The third neck was fitted with a number five rubber stopper through which an eight millimeter hole was bored. This hole was closed with a piece of eight millimeter glass rod. When solutions were being added the whole stopper was removed. In order to take samples during the run only the glass rod was removed and the lower portion of a 10 ml. pipette inserted into the hole. Since the bulb of the pipette was larger than the hole, by pressing the bulb against the stopper the CO_2 pressure inside the reaction vessel forced the sample up into the pipette. After removing the pipette the glass rod was replaced.

The Reaction System

The reaction system consisted of 7N HCl, 1.5N As_2O_3 (in 7N HCl), and 1.5N $SnCl_2$(in 7N HCl). For runs in which the H^+ and Cl^- ion concentrations were varied, 7N LiCl and 7N $HClO_4$ respectively, were added. In the runs in which the mercury-catalyzed reaction was studied, 10^{-3}M $HgCl_2$(in 6M HCl) was added.

Three blank runs were made, two to test the stability of the Sn^{++} in the solution under reaction conditions, and one to test the stability of the As^{+3}. Over a period of eleven hours for Sn^{++} and four hours for As^{+3} no detectible change occurred.

The reaction was carried out under CO_2 as were the titrations so that the only exposure of the solution to the atmosphere was during the transfer of the pipette from the reaction vessel to the titration vessel.

Procedure for a typical run

The reaction vessel was flushed with a slow stream of CO_2 for a period of at least two hours before each run. The solvent, As^{+3} solution, and catalyst when used, were added, the stirrer started, and the system allowed to come to thermal equilibrium with the thermostat. Then the Sn^{++} solution was added, t = 0 being taken as the time at which the meniscus passed a certain mark in the bulb of the pipette used for delivery. Ten ml. samples were then removed as described above. The sample was delivered into a flask containing a mixture of 35 ml. H_2O, 10 ml. 6N HCl, and 20 ml. saturated $NaHCO_3$ which had just been added to remove dissolved oxygen. This dilution effectively stops the reaction. Starch-KI solution was added and the resulting solution titrated with I_3^- to the usual blue end-point. Throughout the procedure CO_2 was passed through the flask and the solution was stirred with a magnetic stirrer. Immediately following the run the I_3^- used was standardized against AsO_2^- solution.

Since the solution was relatively acidic the I_3^- did not oxidize the As^{+3}, and the reaction with the As^0 was sufficiently slow that the blue starch-I_2-I^- color persisted for about five minutes at the end point. The procedure was checked potentiometrically with Sn^{++} alone and with a mixture of Sn^{++} and As^0. The results were in excellent agreement with those obtained using the starch-KI indicator.

TREATMENT OF DATA

After completing the preliminary work on the analytical method and reasonable solution conditions, the reaction was run several times to obtain data to be used to find a suitable rate expression. A crude differential curve of the data ($\Delta Sn^{++}/\Delta t$ vs. t) displayed an initial rise to a maximum followed by a continuous decrease. This indicated a simple induction period, an auto-catalytic reaction, a series of consecutive reactions, or some more complicated process. Reference to original articles cited in Frost and Pearson (38) allowed the rapid rejection of a number of possibilities.

Preliminary turbidimetric experiments pointed to the possibility of an auto-catalytic reaction, although the results were uncertain. This could be described by an equation similar in form to that used by Krishna and Ghosh (39) for the Fe(II)-Ag(I) system, viz.,

$$-d(Sn^{++})/dt = k_1(Sn^{++})(As^{+3}) + k_2(Sn^{++})(As^{+3})(As^{o}) \qquad 3$$

Using equivalent concentrations of Sn(II) and As(III) (true for most runs) and setting $(Sn^{++})_i = (As^{+3})_i = a$ eq./l. and $(As^{o})_t = x$ eq./l., equation 3 becomes

$$dx/dt = k_1(a-x)^2 + k_2(a-x)^2(x) \qquad 4$$

which on integration gives

$$1/(a-x) + [k_2/(k_1+k_2a)] \ln [(k_1+k_2x)/(a-x)] = (k_1+k_2a)t + c \qquad 5$$

Letting $r = k_2/k_1$ and rearranging equation 5 we obtain

$$1/a(1-x/a) + [r/(1+ra)] \ln [(1+rx)/(1-x/a)] = k_1(1+ra)t + C' \qquad 6^*$$

Using the data from the first three runs, equation 6 was tested using different values of r, and for r = 63.4 a straight line was obtained for the interval 2 - 87% reaction (Fig. 1). The reaction was only followed to 87% completion. Below about 2% reaction (under these conditions) there is apparently an induction period. The value of k_1 was determined from the slope and k_2 from r and k_1.

This linearity implied the applicability of equation 3 and it was decided to apply three experimental tests to the equation.

(1) Since the equation is symmetrical with respect to (Sn^{++}) and (As^{+3}), doubling the concentration of Sn^{++} in one experiment and then As^{+3} in another ought to produce the same results. The test was a failure and an analysis of the test indicated three factors operating against its success: a) the solutions of Sn^{++} and As^{+3} were prepared by dissolving

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*Subsequently F will refer to the left side of equation 6.

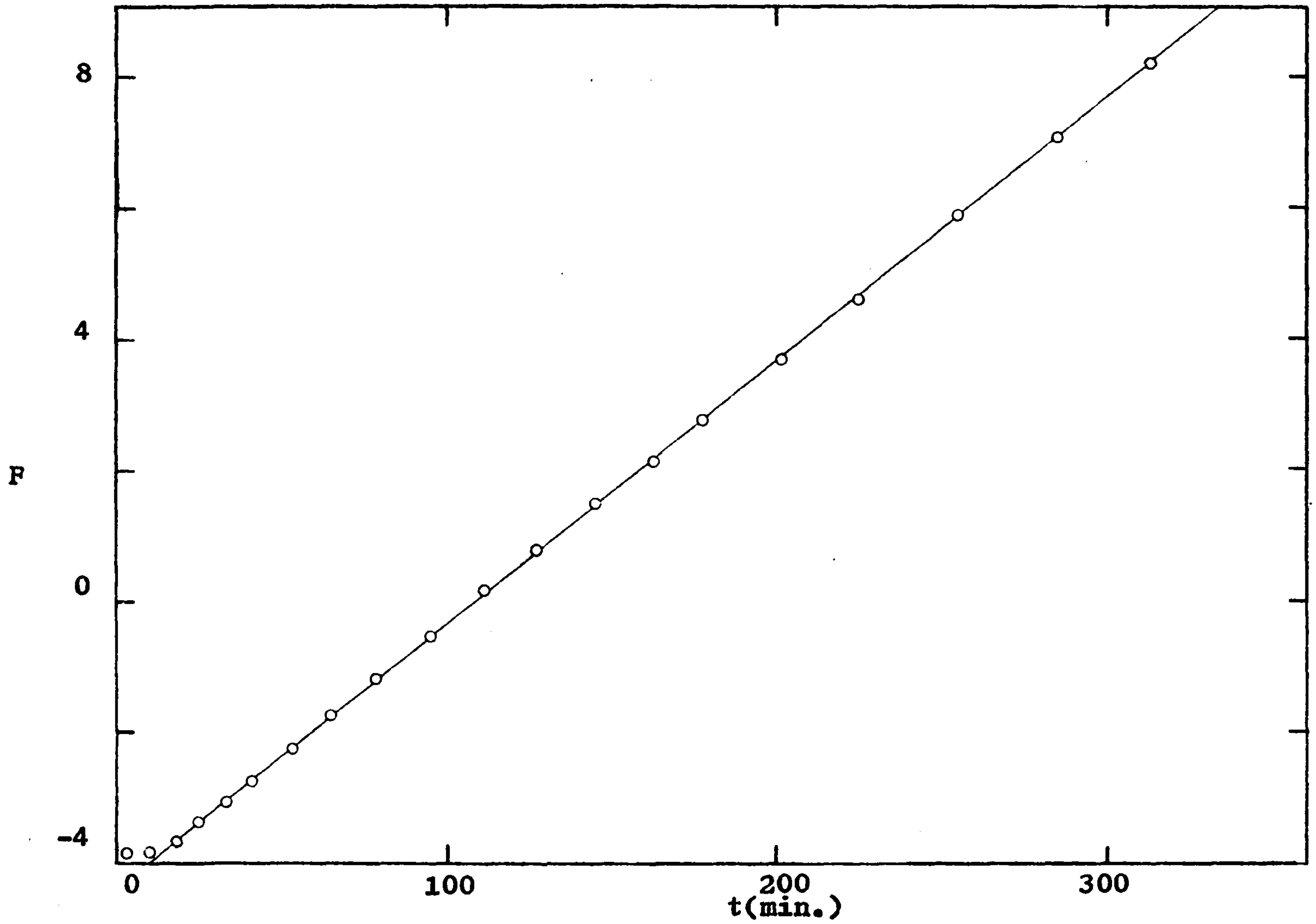

Figure 1. Graph of experimental data using integrated rate equation (F = left side of equation 6, p. 27); r = 63.4; $(Sn^{++})=(As^{+3})=$ 0.0685N; $(H^{+}) = (Cl^{-}) = 7N$

$SnCl_2 \cdot 2H_2O$ and As_2O_3 in 7N HCl (the concentration used as solvent for the reaction) so that the concentration of H^+ and Cl^- were probably different in the two runs; b) since I didn't have an independent method for the determination of As^{+3} it was, in the case of excess Sn^{++}, found by taking the difference between two large numbers; and c) the influence on the induction period due to the changes in concentration could not be predicted. The induction period in the case of excess Sn^{++} was substantially longer than in the case of As^{+3}, which is in agreement with Durrant's (3) results.

(2) If an excess of As^o were present in the reaction mixture, the differential equation 3 would degenerate to

$$dx/dt = k^o(a-x)^2$$

in which

$$k^o = k_1 + k_2(As^o)$$

and which on integration becomes

$$1/(a-x) = k^ot + C \ .$$

In a reaction carried out under these conditions a plot of $1/(a-x)$ vs. t produced a line having a very slight upward curvature which, because of the limited excess of As^o, can be interpreted as confirming the equation. (cf. Figure 2)

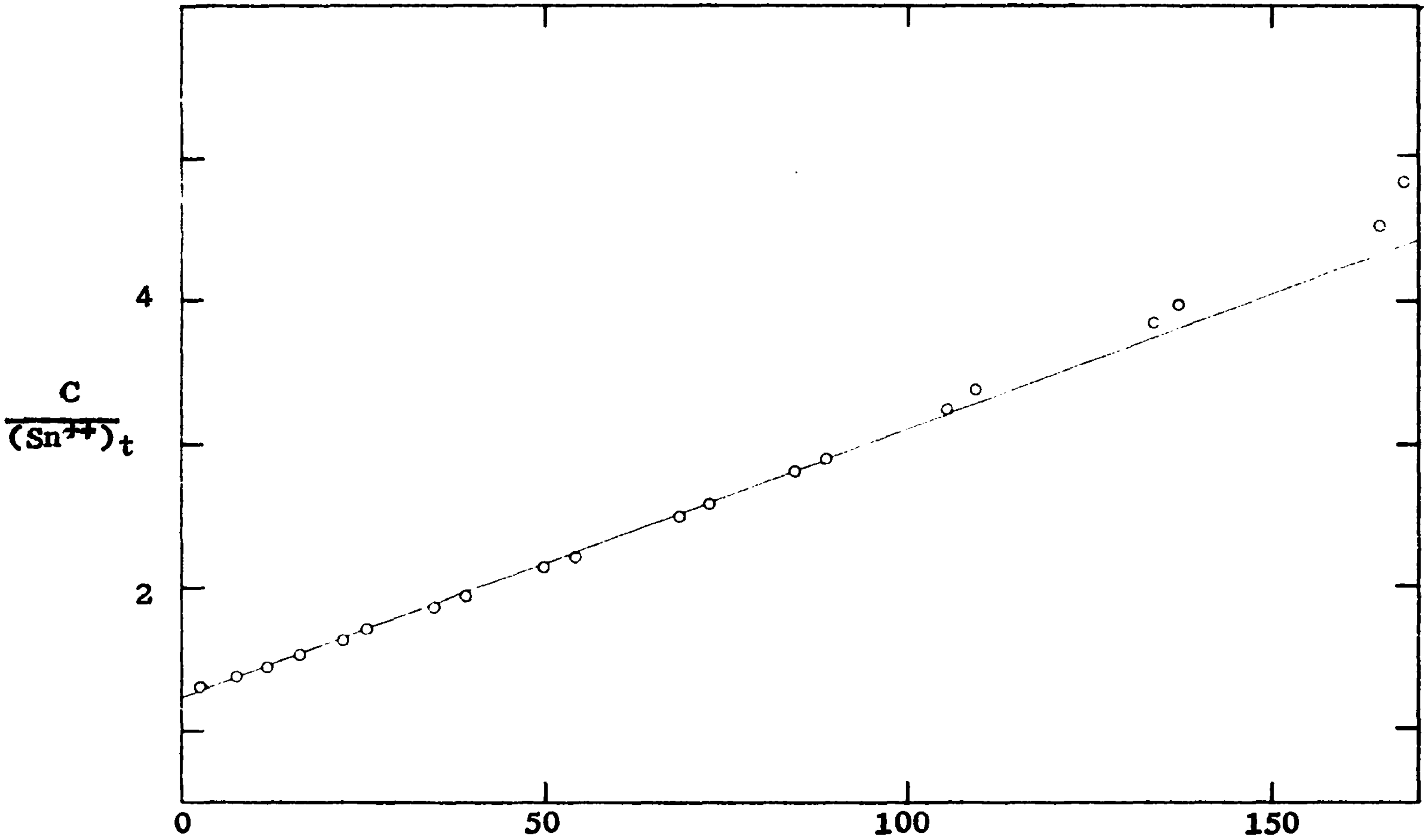

Figure 2. Graph of experimental data using integrated form of equation 3; in presence of limited excess of As^{o} (see paragraph 2, p. 29) $(Sn^{++})_i = (As^{+3})_i$; $(H^{+}) = (Cl^{-}) = 7N$; T = 25°C.

(3) If an excess of both As^o and As^{+3} were present the differential equation would degenerate to

$$dx/dt = k'(a-x)$$

in which $k' = k_1(As^{+3}) + k_2(As^{+3})(As^o)$

which on integration becomes

$$\ln(a-x) = k't + C$$

In each of two reactions carried out under these conditions a straight line was obtained by plotting ln(a-x) vs. t (Figure 3).

A number of runs were then made varying the concentrations of various constituents of the solution, the concentration of the mercury catalyst, and the temperature to determine the effects of each. (Figures 4, 5, 6, 7).

An attempt was made to obtain the values of k_1 and k_2 by graphically differentiating the curves in Figures 4, 5, 6, and 7 using a tangentimeter. If we rearrange equation 4 we obtain

$$\frac{d(x/a)/dt}{(1-x/a)^2} = k_1a + k_2a^2(x/a) \; . \qquad 7$$

Plotting the left side of equation 7 against x/a a straight line should be obtained with slope k_2a^2 and intercept k_1a. This procedure met with a notable lack of success for the most part. The fact that the curve x/a vs. t has a point of inflection makes it very difficult to draw the best line through

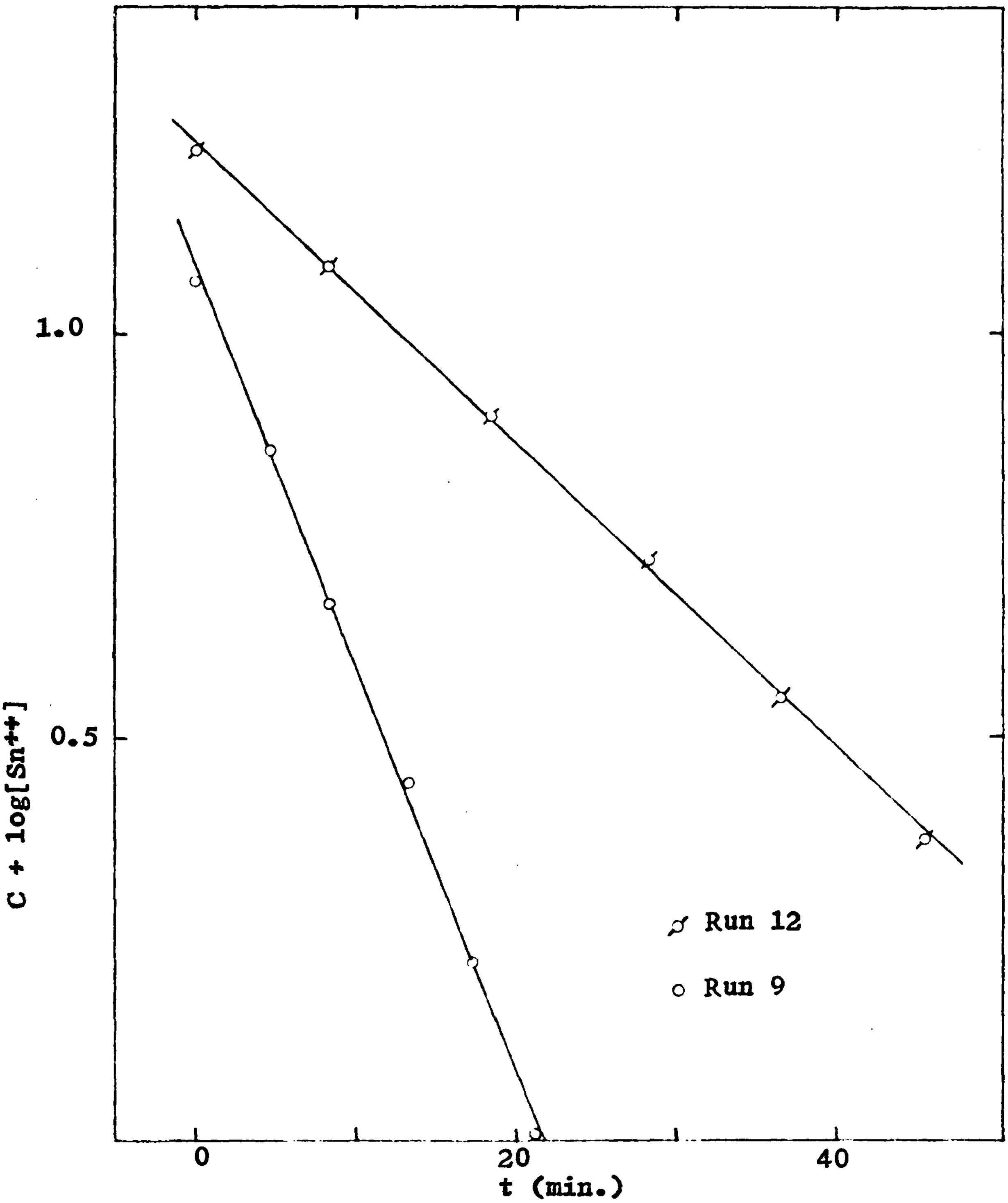

Figure 3. Graph of experimental data using first order rate equation (cf. p. 31). Excess As^{+3} and As^{0} present in reaction mixture; $(H^{+}) = (Cl^{-}) = 7N$; T = 25°C.

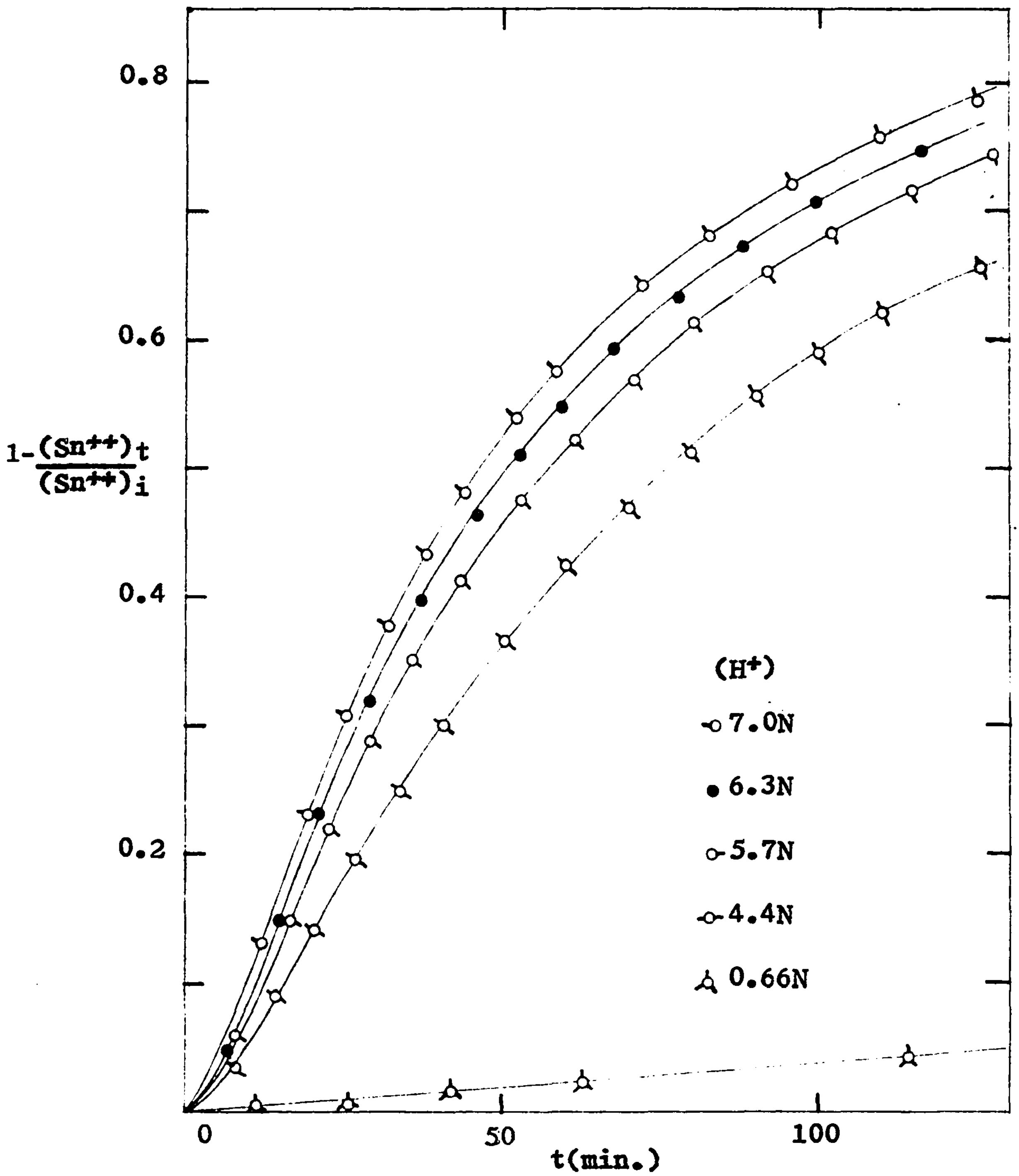

Figure 4. Hydrogen ion variation (catalyzed) $(Sn^{++})_i = (As^{+3})_i = 0.0685N$; $(Cl^-) = 7N$; $(Hg) = 5.43 \times 10^{-6}M$; $T = 25^{\circ}C$.

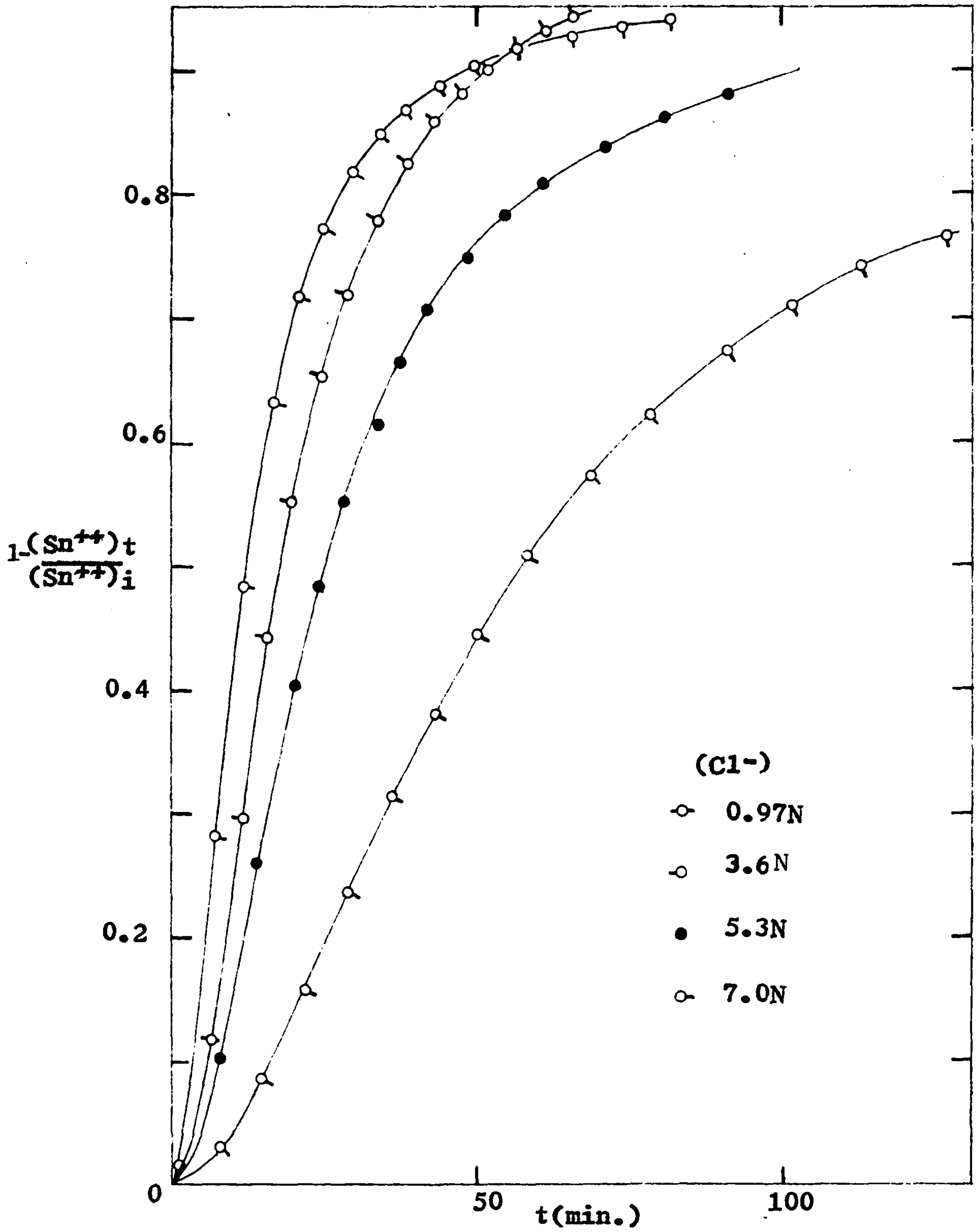

Figure 5. Chloride ion variation (uncatalyzed); $(Sn^{++})_i$ = $(As^{+3})_i$ = 0.0950N; (H^+) = 7N; no Hg; T = 25°C.

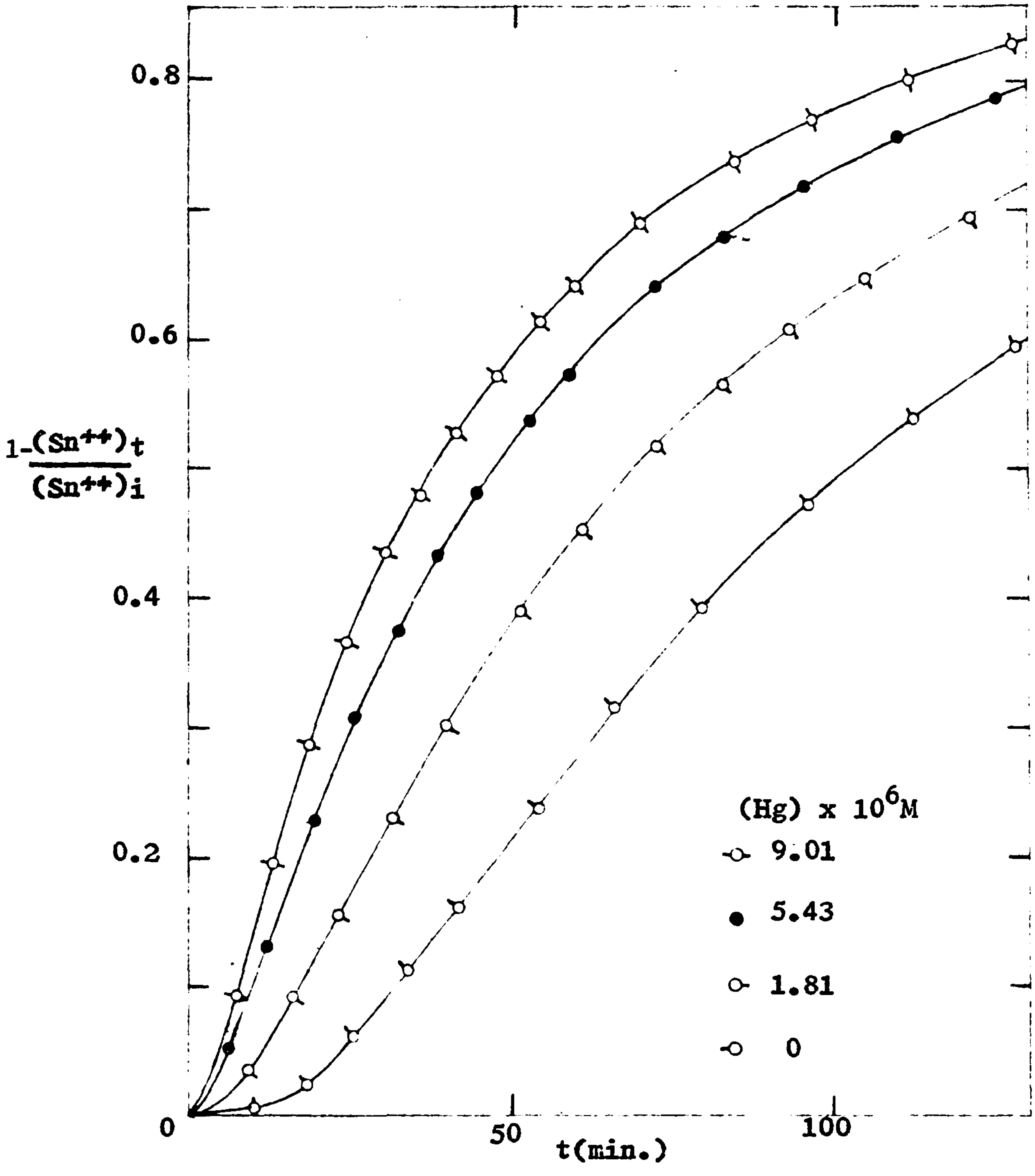

Figure 6. Hg variation; $(Sn^{++})_i = (As^{+3})_i = 0.0685N$; $(H^+) = (Cl^-) = 7N$; T = 25°C.

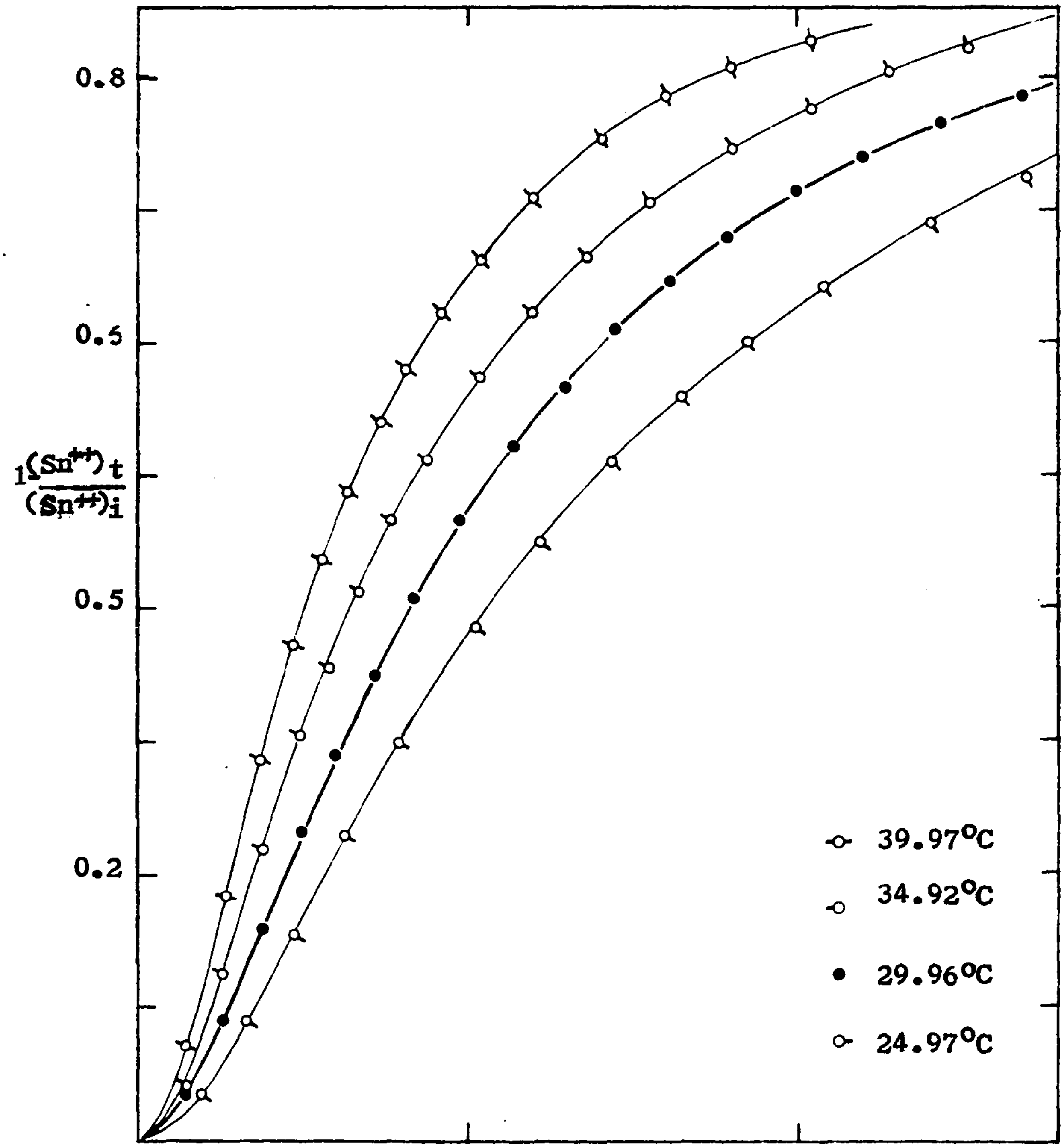

Figure 7. Temperature variation; (catalyzed) $(Sn^{++})_i$ = $(As^{+3})_i$ = 0.0685N; (H^+) = $Cl^-)$ = 7.0N; (Hg) = 1.81×10^{-6}M

the experimental points. Also, as x/a approaches zero, the points cannot be linear because of the induction period.

Equation 6 was then employed, using as first approximations the values of r, i.e. k_2/k_1, found by the preceding procedure. Under these circumstances a straight line was always obtained above 50% reaction. Extrapolating this linear portion to lower values of t enabled one to estimate the direction and magnitude of the change in r that would be required to give very nearly a straight line. If r were too high the points at low t would fall below the extrapolated line and if too low they would fall above the extrapolated line. The slope of the linear portion above 50% reaction is quite insensitive to changes in r so only one point had to be recalculated to determine the value of r for the second approximation. It was never necessary to go beyond a third approximation.

When mercury was added to the solution it was assumed that equation 3 would take the form

$$-d(Sn^{++})/dt = k_1(Sn^{++})(As^{+3}) + k_2(Sn^{++})(As^{+3})(As^{o}) + k_3f(Hg)(Sn^{++})(As^{+3}) + k_4f'(Hg)(Sn^{++})(As^{+3})(As^{o}) \qquad 8$$

i.e., the mercury would increase the rates of extant paths of reaction. Since f(Hg) and f'(Hg) are constants for any given run equation 8 may be rearranged to give

$$-d(Sn^{++})/dt = [k_1+k_3f(Hg)]\ (Sn^{++})(As^{+3}) + [k_2+k_4f'(Hg)]\ (Sn^{++})(As^{+3})(As^{o}) \qquad 9$$

and letting

$$k_1' = k_1 + k_3f(Hg) \qquad 10$$

and

$$k_2' = k_2 + k_4f'(Hg) \qquad 11$$

this becomes

$$-d(Sn^{++})/dt = k_1'(Sn^{++})(As^{+3}) + k_2'(Sn^{++})(As^{+3})(As^{o}) \qquad 12$$

which is of the same form as equation 3 and on integration becomes equation 6 with k_1' replacing k_1 and k_2' replacing k_2. k_1' and k_2' were determined as were k_1 and k_2. It is obvious from equations 10 and 11 that plotting k_1' and k_2' vs. $(Hg)^n$ will produce straight lines when n is the proper order for mercury. These graphs (Figures 8, 9) indicate n for the k_3 term is 2/3 while for the k_4 term it is one. The slopes of these lines are k_3 and k_4 which may thus be evaluated. (Table 1)

Knowing the value of n, equation 8 may be converted to the more definitive form

$$-d(Sn^{++})/dt = k_1(Sn^{++})(As^{+3})+k_2(Sn^{++})(As^{+3})(As^{o})+k_3(Hg)^{2/3}(Sn^{++})(As^{+3})+k_4(Hg)(Sn^{++})(As^{+3})(As^{o}) \qquad 13$$

The values of the several rate constants under various solution conditions are to be found in Tables 1 - 7.

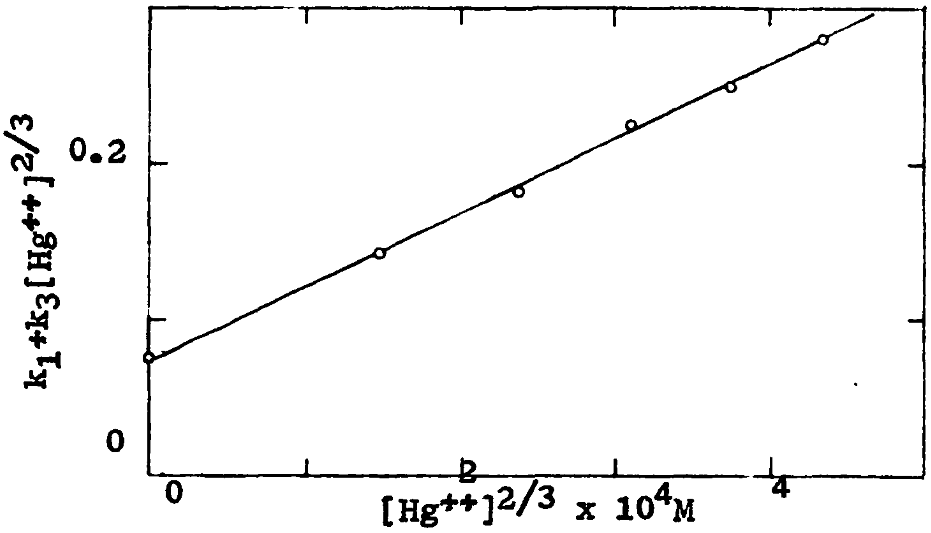

Figure 8. Variation of k_1' with (Hg); (cf. equations 10, 12 and 13, p. 38); $(Sn^{++})_i = (As^{+3})_i = 0.0685$; $(H^+) = (Cl^-) = 7N$; T = 25°C

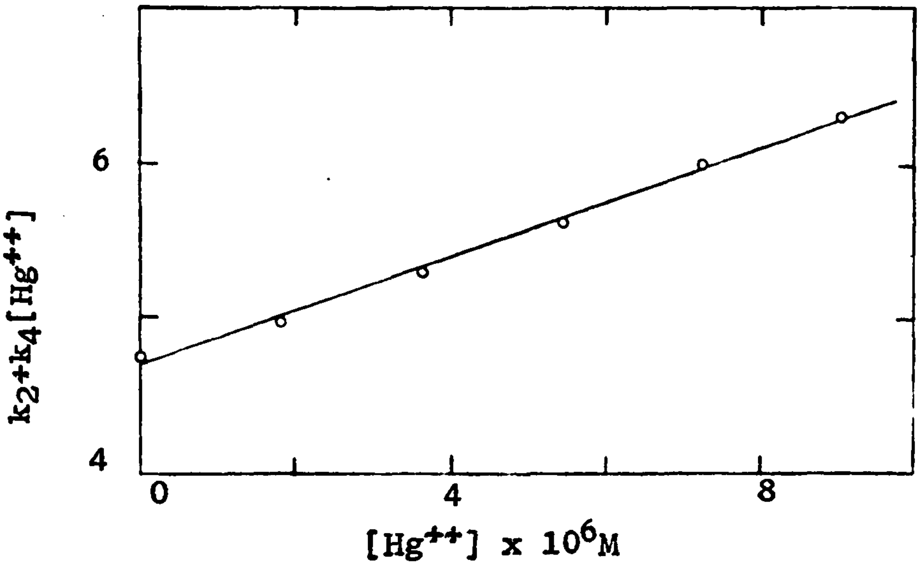

Figure 9. Variation of k_2' with (Hg); (cf. equations 11, 12 and 13, p. 38); $(Sn^{++})_i = (As^{+3})_i = 0.0685N$; $(H^+) = (Cl^-) = 7N$; T = 25°C.

Table 1. Mercury variation; $(Sn^{++})_i = (As^{+3})_i = 0.0685N$; $(H^+) = (Cl^-) = 7N$; $T = 25^oC$.

(Hg) x 10^6M	k_1'*	k_2'*
1.81	0.142	4.98
3.62	0.183	5.30
5.43	0.225	5.62
7.23	0.250	6.00
9.01	0.280	6.30

*k_1' expressed in liters-eq.$^{-1}$-min.$^{-1}$. k_2' expressed in liters^2-eq.$^{-2}$-min.$^{-1}$. From these values, $k_3 = 974$ (liters/mole)$^{5/3}$min.$^{-1}$ and $k_4 = 1.06 \times 10^6$ (liters/mole)^{3}min.$^{-1}$

Table 2. Chloride variation; $(Sn^{++})_i = (As^{+3})_i = 0.0950N$; $(H^+) = 7N$; $T = 25^oC$. (no Hg)

(Cl^-) moles-liter^{-1}	k_1*	k_2*
7.0	0.099	4.20
5.2	0.226	10.4
3.5	0.400	23.8
0.88	0.176	21.0

*k_1 expressed in liters-eq.$^{-1}$-min.$^{-1}$; k_2 expressed in liters^2-eq.$^{-2}$-min.$^{-1}$

Table 3. Chloride variation (catalyzed); $(Sn^{++})_i = (As^{+3})_i =$ 0.0685N; (H^+) = 7N; (Hg) = 5.43 x 10^{-6}M; T = 25°C.

(Cl^-) moles/liter	k_1'*	k_2'*
7.0	0.225	5.62
5.7	0.410	9.45
4.4	0.674	17.9
0.66	0.248	24.6

*k_1' expressed in liters-eq.$^{-1}$-min.$^{-1}$. k_2' expressed in liters^2-eq.$^{-2}$-min.$^{-1}$

Table 4. Hydrogen ion variation; $(Sn^{++})_i = (As^{+3})_i =$ 0.0950N; (Cl^-) = 7.0N; T = 25°C.; (no Hg)

(H^+) moles/liter	k_1*	k_2*
7.0	0.099	4.20
6.1	0.084	3.82
5.2	0.066	2.94
3.5	0.038	1.50
1.7	0.0104	2.66

*k_1 expressed in liters-eq.$^{-1}$-min.$^{-1}$. k_2 expressed in liters^2-eq.$^{-2}$-min.$^{-1}$

Table 5. Hydrogen ion variation (catalyzed); $(Sn^{++})_i$= $(As^{+3})_i$= 0.0685N; (Cl^-)= 7.0N; (Hg) = 5.43 x 10^{-6}M; T = 25°C.

(H^+) moles/liter	k_1'*	k_2'*
7.0	0.225	5.62
6.3	0.212	4.53
5.7	0.185	4.55
4.4	0.150	2.86
0.67	0.0034	0.0455

*k_1' expressed in liters-eq.$^{-1}$-min.$^{-1}$. k_2' expressed in liters^2-eq.$^{-2}$-min.$^{-1}$

Table 6. Temperature variation; $(Sn^{++})_i$=$(As^{+3})_i$= 0.0685N; (H^+)= (Cl^-)= 7.0N; (no Hg)

Temp. (°C.)**	k_1*	k_2*
24.97	0.075	4.75
29.96	0.098	6.35
34.92	0.123	8.00
39.97	0.160	9.89

*k_1 expressed in liters-eq.$^{-1}$-min.$^{-1}$. k_2 expressed in liters^2-eq.$^{-2}$-min.$^{-1}$

**Temperatures to ± 0.05°C.

Table 7. Temperature variation (catalyzed); $(Sn^{++})_i$=$(As^{+3})_i$= 0.0685N; (H^+)= (Cl^-)= 7N; (Hg)= 1.81 x 10^{-6}M

Temp. (°C.)**	k_1'*	k_2'*
24.97	0.142	4.98
29.96	0.186	6.50
34.92	0.234	8.16
39.97	0.306	10.7

*k_1' expressed in liters-eq.$^{-1}$-min.$^{-1}$. k_2' expressed in liters^2-dq.$^{-2}$-min.$^{-1}$

**Temperatures to ±0.05°C.

Arrhenius' equation

$$d \ln k/dT = E_a/RT^2$$

in its integrated form

$$\ln k = -E_a/RT + C$$

may be utilized for determining the experimental activation energies. If we plot log k_1 and log k_2 vs. $1/T$, E_{a_1} and E_{a_2}, respectively, may be evaluated by simply multiplying the slope of the line so obtained by 2.303R (Figure 10). Since the (Hg) was the same for each run in the temperature variation study, E_{a_3} may be determined in the same manner by plotting log $k_3(Hg)^{2/3}$ (i.e. $\log(k_1' - k_1)$)vs. $1/T$ (Figure 10). In theory, E_{a_4} could be obtained by a similar procedure. Unfortunately, the difference between k_2' and k_2 is about of the same magnitude as the error involved in determining either one of them and it is obvious that this makes any estimate relatively worthless (cf. Table 7).

An exact evaluation of the error in the values of the various constants is impossible because of the subjective judgment in determining at what value of r the plot of F (equation 6) vs. t becomes the 'best' straight line. Empirically, a change in r of about 10% tends to change the slope of the line ($k_1(1 + ra)$) by about 1% in the same direction as the change in r. Since $k_1 = \text{slope}/(1 + ra)$ and ra

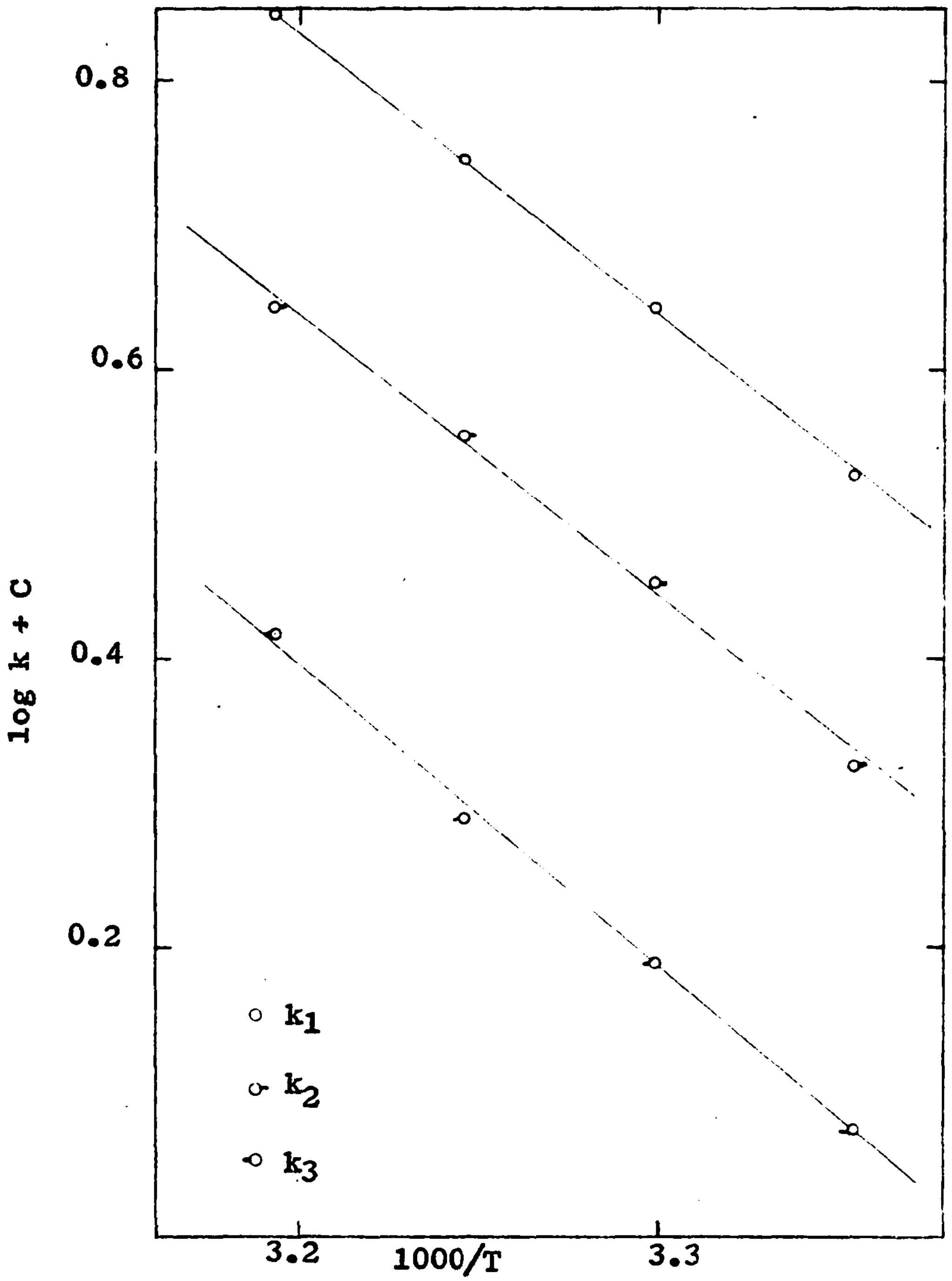

Figure 10. Temperature dependence of rate constants; (cf. equation 13, p. 38) $(Sn^{++})_i = (As^{+3})_i =$ 0.0685N $(H^+) = Cl^-) =$ 7N

has values ranging from 1.4 to 9, the addition of one in the denominator tends to decrease the effect on k_1 of changes in r so that, in general, a change of about 10% in r results in a change in k_1 of about 5 - 7% in the opposite direction. Also, since $k_2 = rk_1$ and r and k_1 change in opposite directions a 10% change in r results in a 3 - 5% change in k_2 in the same direction as the change in r. From this one would expect k_2 to be more reliable than k_1, and my estimate of the error of k_1 is ±7% and of k_2 about ±5%.

There is no particular advantage in calculating k_1 values from the raw data and determining that value of r which produces the smallest standard deviation (or similar statistical or mathematical processes) in the series of k_1 values so calculated because of the relative insensitivity of k to r and the number of significant figures available from the experimental data.

DISCUSSION

The discussion will be centered on an attempt to subject the available information to an analysis leading to a gross mechanistic interpretation. It is to be constantly borne in mind that the nature and extent of this information seriously diminishes the probability that the mechanisms to be proposed reflect the true course of events. The value of such a review lies in the construction of models which may be experimentally tested and some of the tests the author intends to perform are outlined later.

The usual starting point from which a mechanism is developed is the rate equation which fits the experimental data. Assuming the validity of the experimental data, a mechanism cannot be correct in all its particulars if it does not lead to an equation consistent with that data. The converse is, of course, not true, i.e., even though the mechanism may lead to an equation consistent with the experimental data, it may portray a quite erroneous picture (cf. Addendum). We must therefore support our mechanistic conjectures with correlative information derived from two sources, a) qualitative and quantitative experiments conducted during the study that are not directly related to the delineation of the rate equation, and b) the literature dealing with similar systems or processes.

The present study has indicated that the reaction between As(III) and Sn(II) in hydrochloric acid can be described by equation 3 and that if we add mercury to the system recourse must then be had to equation 13. The k_1 term in these equations leads one to think in terms of a relatively simple bimolecular reaction between some form of As(III) and Sn(II) involving, perhaps, a one electron transfer, followed by other more rapid steps leading to As^o and Sn(IV). Under similar circumstances reactions in which Sn(II) is the reducing agent are strongly catalyzed by chloride ions and only slightly, if at all, affected by hydrogen ions. At low chloride ion concentrations an increase in the chloride ion concentration has an accelerating effect on the present reaction also. However, at higher chloride ion concentrations an increase in the chloride ion concentration has a retarding effect on the reaction, while an increase in the hydrogen ion concentration has an accelerating effect under all conditions (Figures 11, 12, 13, 14). The anion exchange studies of Nelson and Kraus (40) show that at high hydrochloric acid concentration As(III) is adsorbed on anion exchange resins, probably due to the formation of complexes of the nature $AsCl_4^-$. Clusius and Haimerl (41) have shown that $H^{35}Cl$ exchanges chloride very rapidly with $AsCl_3$. All of this would indicate the equilibria

$$As(u) + H^+ \rightleftharpoons As(r) + Cl^- \rightleftharpoons As(u)$$

and

$$Sn(u) + Cl^- \rightleftharpoons Sn(r)$$

in which (u) signifies an unreactive species and (r) a reactive species.

The fact that As(III) and Sn(II) occur in each part of the rate equation 13 in the same form, and that the influences of hydrogen ion and chloride ion are qualitatively similar for the catalyzed reaction and the uncatalyzed reaction suggests that the mechanisms of all paths are grossly similar, the intimate differences being due to the effect of the As^o and Hg. The Arrhenius activation energies for the three terms for which they can be evaluated are:

k_1 $E_{a_1} = 9{,}500 \pm 800$ cal./mole

k_2 $E_{a_2} = 8{,}900 \pm 600$ cal./mole

k_3 $E_{a_3} = 9{,}100 \pm 900$ cal./mole

Since these values are the same (within experimental error) and there are large differences among the values of the rate constants from which they are obtained it is reasonable to conclude that the primary difference resides in the entropy of activation. A possible alternative to this explanation would be that the rate constants differ because the reactive species are different and present in the solution in widely varying quantities due to the several equilibrium constants that control their concentrations. This would, of course, require that the activation energies be similar by chance. It would also require that the dependence with respect to hydrogen ion and/or chloride ion would have to be different, and it can be seen from Figures 11-15 that qualitatively this is not so.

The presence of As^o in the second term of equation 13 is probably the result of a heterogeneous catalytic mechanism. Gutman's data (15) lends support to this possibility in that it pointed to the adsorption of $AsCl_3$ by elementary As under the conditions of his experiments. Taylor (42) has also reported the adsorption of an arsenic compound, AsH_3, on arsenic in its autocatalytic decomposition. It would, therefore, seem logical to propose for the mechanism corresponding to the second term in equation 13 a loose adsorption of the reactive form(s) of As(III) on the surface of the As^o (loose enough so that the concentration of As(III) on the surface is determined by the concentration of As(III) in the solution) followed by the diffusion of the Sn(II) to the adsorbed As(III), reaction similar to the bimolecular process of the first term, and diffusion of the Sn product away.

From the fact that the reaction has been described as taking place on the surface of the arsenic one might conclude that the As^o dependence should not be first order. A reasonable explanation for this can be offered. The As^o particles

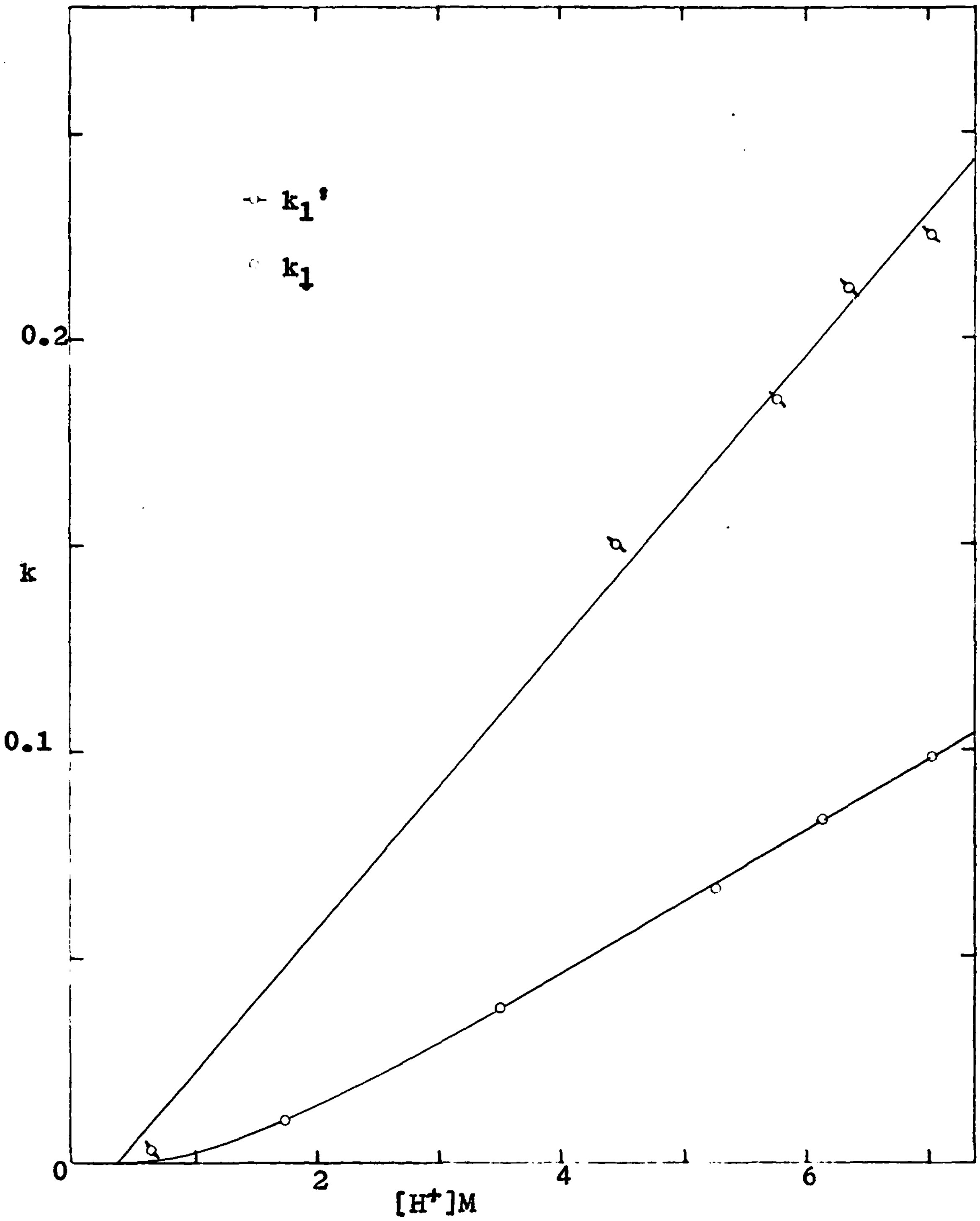

Figure 11. Variation of k_1 and k_1' with $[H^+]$; (cf. equations 10 and 13, p. 38). For k_1 evaluation, $(Sn^{++})_i$ = $(As^{+3})_i$ = 0.0950N; for k_1', evaluation, $(Sn^{+})_i$ = $(As^{+3})_i$ = 0.0685N. In both cases (Cl^-) = 7N, T = 25°C.

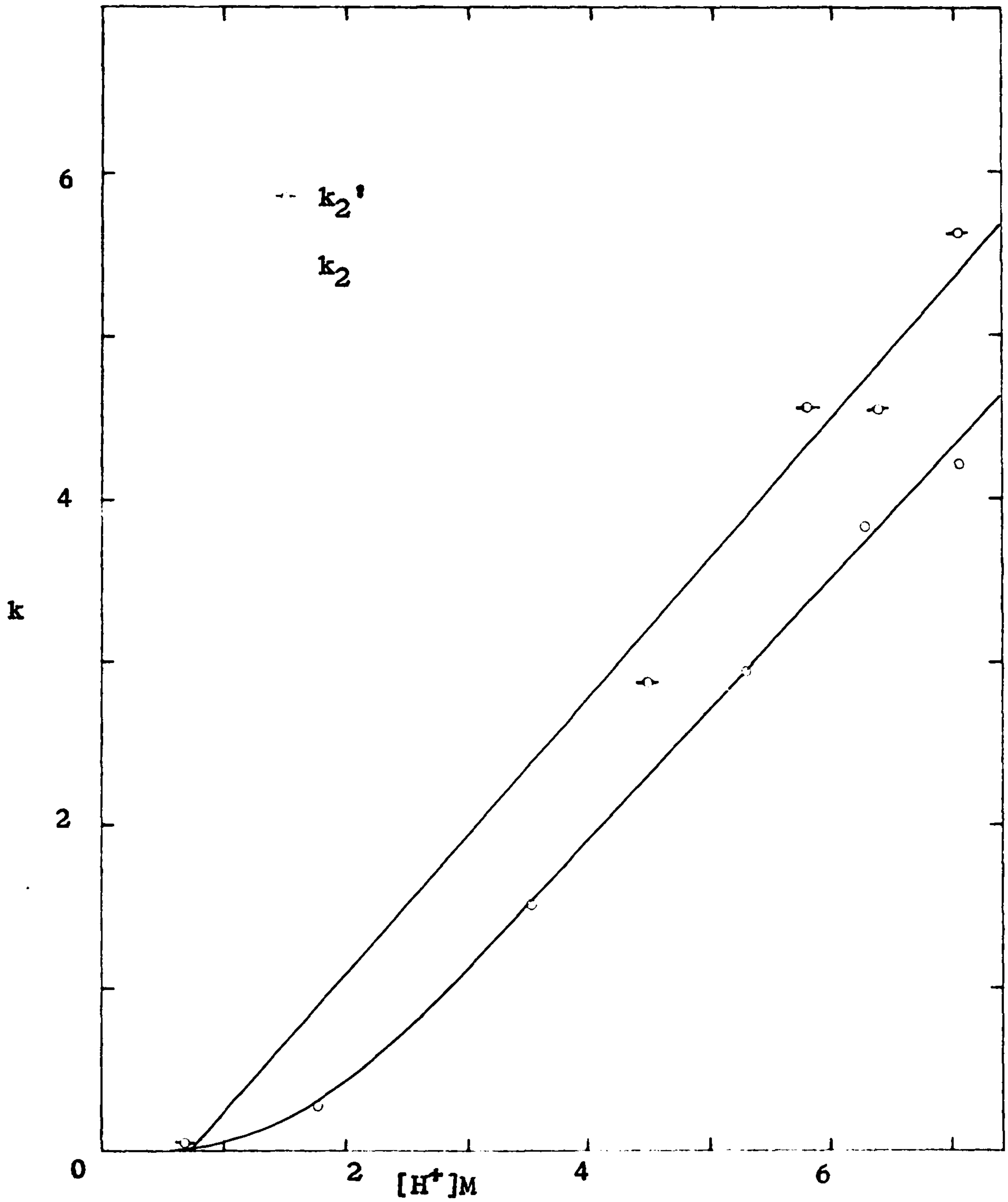

Figure 12. Variation of k_2 and k_2' with $[H^+]$; (cf. equations 11 and 13, p. 38). For k_2 evaluation, $(Sn^{++})_i = (As^{+3})_i = 0.0950N$; for k_2' evaluation $(Sn^{++})_i = (As^{+3})_i = 0.0685N$. In both cases $(Cl^-) = 7N$, $T = 25^oC$.

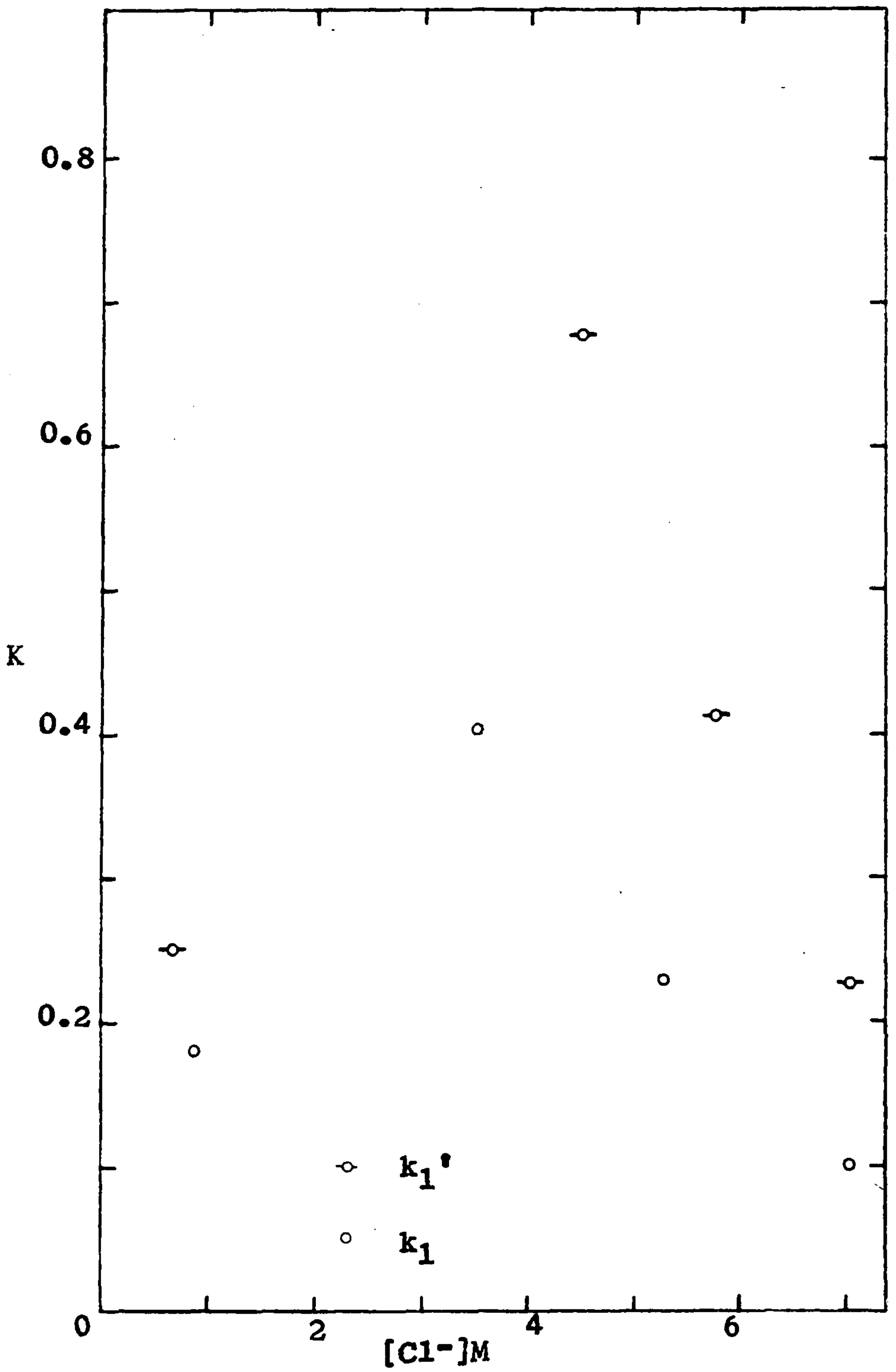

Figure 13. Variation of k_1 and k_1' with $[Cl^-]$; (cf. equation 10 and 13, p. 38). For k_1 evaluation, $(Sn^{++})_i = (As^{+3})_i = 0.0950N$; for k_1' evaluation, $(Sn^{++})_i = (As^{+3})_i = 0.0685N$. In both cases $(H^+) = 7N$, $T = 25^oC$.

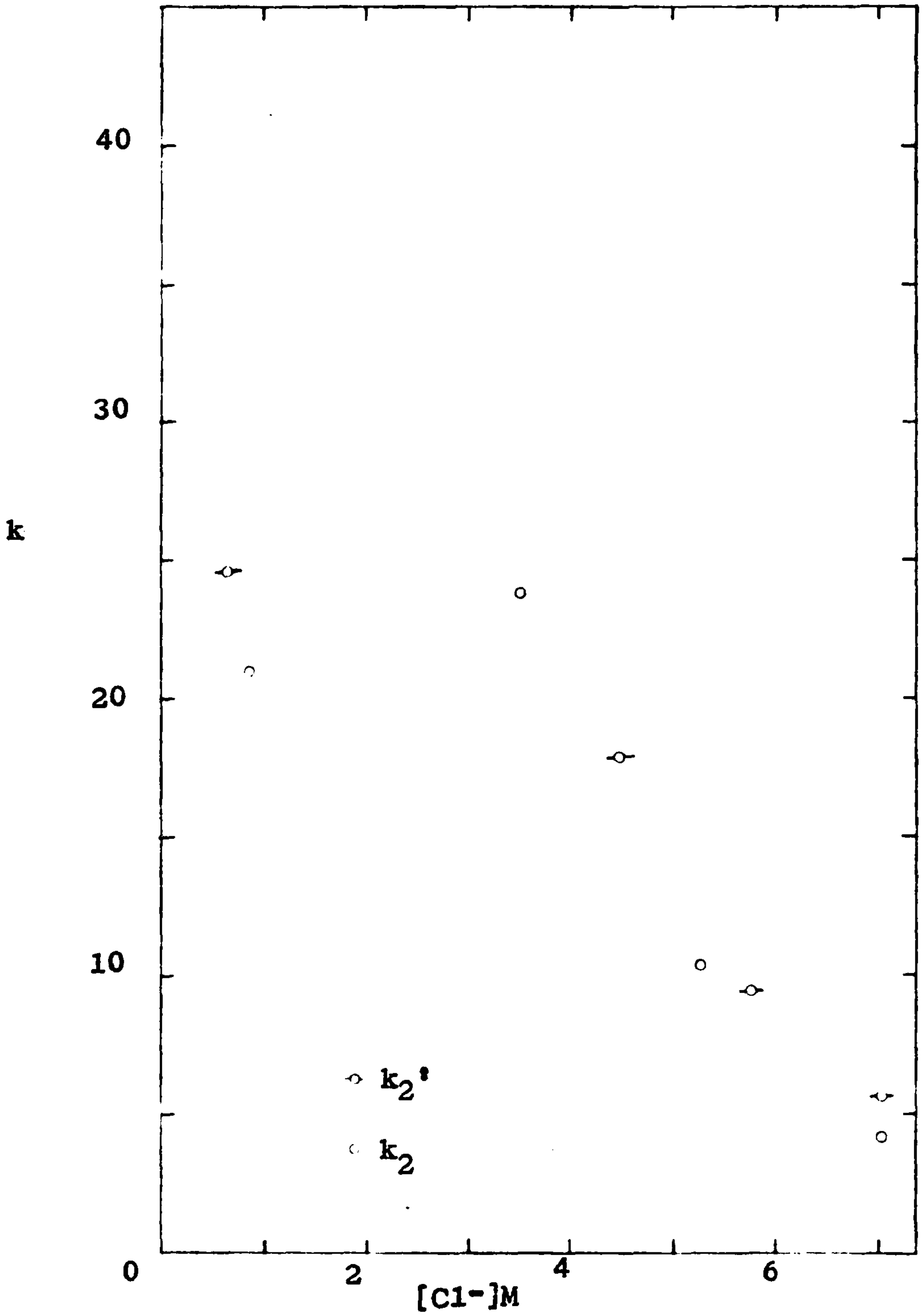

Figure 14. Variation of k_2 and k_2' with $[Cl^-]$; (cf. equations 11 and 13, p. 38). For k_2 evaluation, $(Sn^{++})_i = (As^{+3})_i = 0.0950N$; for k_2' evaluation, $(Sn^{++})_i = (As^{+3})_i = 0.0685N$. In both cases $(H^+) = 7N$, $T = 25^{\circ}C$.

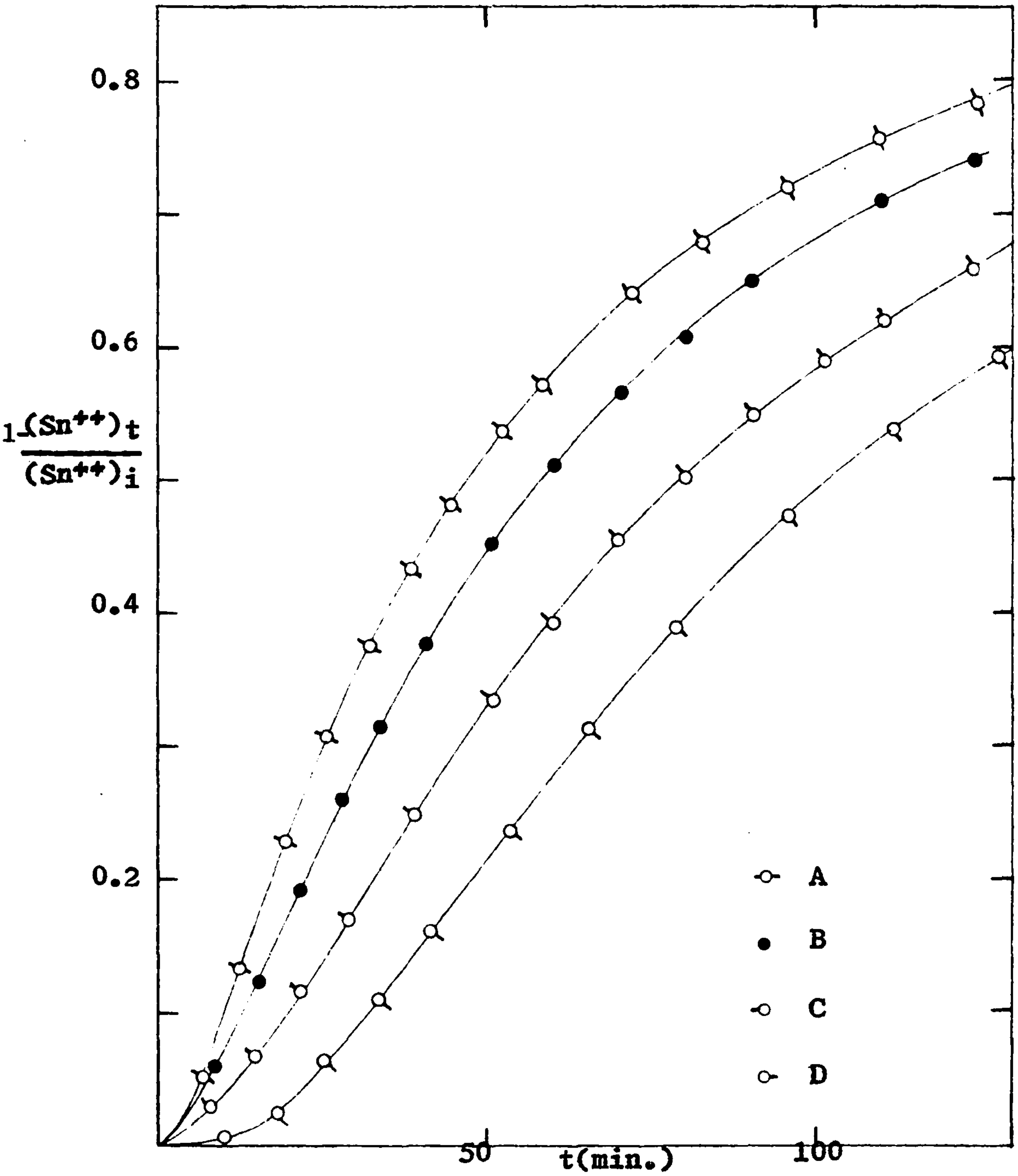

Figure 15. Effect of pre-reaction between Sn(II) and Hg(II) before adding As(III). A, no pre-reaction; B, 26 min. pre-reaction; C, 248 min. pre-reaction; D, no Hg added. $(Sn^{++})_i = (As^{+3})_i = 0.0685N$; $(H^+) = (Cl^-) = 7N$; (Hg^{++}) (except for D) = $5.43 \times 10^{-6}M$; T = 25°C.

were so small that a microscopic examination did not reveal their complete geometric details. However, they had the appearance of thin platelets which reflected flashes of incident light as they rotated when the suspension was agitated. If we assume that they grow as platelets by extension of their longer sides and take as our model a thin rectangular solid of dimensions $a \simeq b >>> c$, then the surface/volume ratio R takes the form

$$R = (2ab + 2ac + 2bc)/abc = 2/a + 2/b + 2/c$$

This means that R is controlled primarily by the smallest dimension, so that in the growth process R would remain almost constant, the more so the larger a and b. Expressed mathematically

$$dR = \left(\frac{\partial R}{\partial a}\right)_{b,c} da + \left(\frac{\partial R}{\partial b}\right)_{a,c} db + \left(\frac{\partial R}{\partial c}\right)_{a,b} dc$$

Assuming $dc = 0$

$$-dR = (1/a^2)da + (1/b^2)db$$

proving that for given changes in a and b, R decreases less the larger are a and b. Also, since 2/c is much larger than either 2/a or 2/b, changes in a and b will have almost no effect on R.

The process that compensates for the decrease in R is the nucleation of new As^o particles which have very large R values. The nucleation process is most rapid at the beginning of the reaction when the R values of the already-formed As^o particles is diminishing most rapidly, i.e., when a and b are still small. As the reaction progresses the rate of nucleation decreases, but so also does the rate of change of R for the older particles. These two processes may then just counterbalance each other so that the surface area remains proportional to the volume and the volume proportional to the moles As^o/liter.

For the catalyzed form of the above reaction, i.e., the one described by the fourth term in equation 13 it is proposed that the Hg is adsorbed on the surface of the As^o particles. This is implied by the equation, of course, but there are two other reasons that lead to this conclusion:

1) The appearance of the As^o particles in the presence of Hg is different from that in its absence, exhibiting a more amorphous form in the former case.
2) The As^o formed a mirror on the walls of the reaction vessel in the absence of Hg but only slightly, and at the end of the reaction, in its presence.

This mechanism would require that the Hg remain on the growing As^o surface. The solubility of Hg in As is vanishingly small so that this is not surprising. This condition may also be maintained if the Hg acts as a two-dimensional gas on the surface of the As, what de Boer (43) calls 'supermobile adsorption' as proposed for the adsorption of Hg on charcoal at higher temperatures.

The adsorption of Hg on the surface of the As particles would lead naturally to first order dependence on Hg. The first order dependence on As^0 follows the same argument outlined for it above, although a different choice of model may be required.

The fact that Hg appears to the 2/3 power with k_3 is subject to two interpretations:

1) That there is surface catalysis due to the formation of free Hg, since the surface area is proportional to $(\text{volume})^{2/3}$ and the volume is proportional to (Hg).
2) That the reaction is more complex than indicated but that under the conditions of the experiments the complex equation degenerates to give $(\text{Hg})^{2/3}$.

It might appear contradictory at first glance to propose first order dependence for As^0 in the second term and 2/3 order dependence for Hg in the third term and suggest that surface catalysis is involved in both cases. However, the circumstances are quite different. We assume in the case of the As^0 that we are dealing with a dynamic system while the Hg system, after the very beginning of the reaction, is essentially static. For reasonably regular surfaces the surface area is proportional to (colume)$^{2/3}$ and the volume in turn is directly proportional to the concentration.

Although mercury is added to the reaction system as Hg(II) it is proposed that its catalytic action is due to Hg(O). The reduction of Hg(II) to Hg(I) by Sn(II) in hydrochloric acid solution is extremely rapid and the Hg(I) so formed is soluble to the extent used in the reaction. Armstrong and Halpern (44) have suggested that in the reduction of Tl(III) by Hg(I) the active reducing agent is Hg(O) produced by the disproportionation of Hg(I) which is presumed to be a non-rate determining step. Schwarzenbach and Anderegg (45) and Moser and Voigt (46) have determined the disproportionation constant

$$K = (Hg_2^{++})/(Hg^{++}) \simeq 85$$

and (45) found it to increase with increasing ionic strength. King (47) and Wolfgang and Dodson (48) have shown that the zero-time exchange is essentially complete for Hg(II) - Hg(I) in hydrochloric acid. The rate of reduction of Hg(I) would therefore not appear to be of great importance since the rapid dismutation that has been proposed would continually replenish the Hg(II) concentration and provide a very fast route to Hg(O).

Also, according to Patrick and Bachman (49) and Rosenberg and Stegeman (50) metallic mercury adsorbs Hg(I) ions which could lead to a more rapid direct reaction between Hg(I) and Sn(II) (autocatalysis).

Since the solubility of Hg(O) in pure water is about 3×10^{-7} g. at./1. (46, 51) and the total Hg in the system varies from 10^{-6} - 10^{-5} M one might expect that enough of the mercury would be dissolved atomically (assuming this species is ineffective as a catalyst) that a linear function of rate constant vs. (Hg) (see equations 10 and 11) would not be obtained. Hahn (52) points out, however, that in the catalytic gold reaction between Fe(II) and Ag(I) the limiting concentration of gold is diminished by a factor of 10^3 - 10^4 by the introduction of carrier nuclei. In the present reaction the elementary arsenic first formed could serve as the carrier nuclei to effectively decrease the solubility of the mercury.

A brief series of experiments was carried out to determine the effect of allowing the Sn(II) and Hg(II) to react for varying periods of time before the addition of As(III). The results are shown in Figure 15. It is obvious from these results that the catalytic effect diminishes with increasing time allowed for the pre-reaction of the Sn(II) and Hg(II). These experiments do not necessarily support the proposed mechanism, but on the other hand, neither do they refute it. One interpretation that can be made is that the decrease in catalytic activity is due to the aging or coagulation of the Hg particles leading to a smaller surface area for a given initial amount of mercury.

Since there is available no quantitative information on the activity coefficients of the ions in the reacting solutions one can only assume that they remain constant throughout the reaction. There should be relatively little change in the ionic strength of the solution throughout the course of the reaction because the reactants should be in complexes of relatively small charge and the ionic strength of the medium initially is high. If no complexes were involved there would be an increase in the ionic strength of about 1% for the complete reaction

$$3\ Sn^{++} + 2\ As^{+3} = 3\ Sn^{+4} + 2\ As^{o}$$

The data furnished by the hydrogen and chloride ion variations is not of such a nature to allow a mathematical formulation of their functions. This problem is further complicated by the fact that the activity coefficients of hydrogen ion and chloride ion probably change as their concentrations are changed, (even at constant ionic strength) since the literature suggests that pure aqueous solutions of the solutes LiCl, $HClO_4$, and HCl at the same concentrations have different activities. (These are the solutes used for varying the (H^+) and (Cl^-). They were chosen partly because their activity coefficients resembled one another more closely than any others that could be found.) According to Latimer (53), at the same concentrations $a_{HClO_4} > a_{HCl} > a_{LiCl}$.

In conclusion it should be pointed out that equation 13 represents the rate equation as elucidated by the present study. The general equation would take the form (assuming Hg^o as the catalyst and $\gamma_{Hg^o} = \gamma_{As^o} = 1$):

$$\begin{aligned} -d(Sn^{++})/dt = {} & k_1^o(Sn^{++})(As^{+++})(Sn^{++})(As^{+++})f_1(a_{H+})f_2(a_{Cl-}) + \\ & k_2^o(Sn^{++})(As^{+++})(Sn^{++})(As^{+++})f_3(a_{H+})f_4(a_{Cl^-}) \\ & \qquad (As^o) + \\ & k_3^o(Sn^{++})(As^{+++})(Sn^{++})(As^{+++})f_5(a_{H^+})f_6(a_{Cl^-}) \\ & \qquad (Hg)^{2/3} + \\ & k_4^o(Sn^{++})(As^{+++})(Sn^{++})(As^{+++})f_7(a_{H^+})f_8(a_{Cl^-}) \\ & \qquad (As^o)(Hg) \end{aligned} \qquad 14$$

which means that in equation 13 the k's have the significance

$$\begin{aligned} k_1 &= k_1^o(Sn^{++})(As^{+++})f_1(a_{H+})f_2(a_{Cl^-}) \\ k_2 &= k_2^o(Sn^{++})(As^{+++})f_3(a_{H^+})f_4(a_{Cl-}) \\ k_3 &= k_3^o(Sn^{++})(As^{+++})f_5(a_{H^+})f_6(a_{Cl-}) \\ k_4 &= k_4^o(Sn^{++})(As^{+++})f_7(a_{H+})f_8(a_{Cl-}) \end{aligned} \; .$$

Future Experiments

1. In order to determine the relative charges of the reacting species an ionic strength variation should be carried out.

2. From the ionic strength variation suitable conditions should be chosen for carrying out complete hydrogen and chloride ion variations so that their functions in equation 14 may be given precise mathematical form.

3. The conditions for evaluating the activation energy for the k_4 term in equation 13 should be found.

4. The experiments describing a pre-reaction between Hg(II) and Sn(II) for varying periods prior to the addition of As(III) (p.60) should be repeated in combination with a Hg variation to determine the relative effects on k_3 and k_4. This information should provide a more penetrating insight into the role that mercury plays in these two mechanisms.

5. A more detailed study of the effects of changes in the initial concentrations of the reactants should be made and this in turn requires a more complete analytical procedure. Information in the literature indicates that ion exchange procedures may be useful in this respect.

6. A complete spectrophotometric investigation of the reaction should be made. Exploratory spectrophotometric studies made while searching for an analytical procedure produced results that were quite unusual and may have been caused by the formation of interaction complexes in the reacting solution.

SUMMARY

The kinetics of the Bettendorff Reaction

$$3\,Sn^{++} + 2\,As^{+3} = 3\,Sn^{+4} + 2\,As^{o}$$

have been investigated. The data obtained are in agreement with the proposed rate equations

$$-d(Sn^{++})/dt = k_1(Sn^{++})(As^{+3}) + k_2(Sn^{++})(As^{+3})(As^{o})$$

for the uncatalyzed reaction, and

$$-d(Sn^{++})/dt = k_1(Sn^{++})(As^{+3}) + k_2(Sn^{++})(As^{+3})(As^{o}) + k_3(Hg)^{2/3}(Sn^{++})(As^{+3}) + k_4(Hg)(Sn^{++})(As^{+3})(As^{o})$$

for the reaction catalyzed by mercury. (cf. Addendum).

Results indicate that the reaction is catalyzed by chloride ion at low chloride ion concentration, but inhibited by chloride ion at higher chloride ion concentrations. Hydrogen ion acts as a catalyst at all concentrations.

A temperature variation study allowed the evaluation of the Arrhenius activation energies (subscripts correspond to the subscripts of the k's in equation 13).

$$E_{a_1} = 9{,}500 \pm 800 \text{ cal./mole}$$

$$E_{a_2} = 8{,}900 \pm 600 \text{ cal./mole}$$

$$E_{a_3} = 9{,}100 \pm 900 \text{ cal./mole}$$

The data did not permit the evaluation of E_{a_4}.

Further investigations to be carried out are outlined.

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ADDENDUM

While this paper was in the process of being written the author discovered that the differential equation used to describe the system studied is not unique for the majority of experiments carried out in the laboratory. The equation used in the evaluation of the data collected is of the form

$$dx/dt = k_1(a-x)(b-x) + k_2(a-x)(b-x)(x) \qquad 1A$$

in which

$a = (As^{+3})_o$

$b = (Sn^{++})_o$ (all concentrations expressed in

$x = (As^o)_t$ equivalents/liter)

$(a-x) = (As^{+3})_t$

$(b-x) = (Sn^{++})_t$

If $a = b$ this becomes

$$dx/dt = k_1(a-x)^2 + k_2(a-x)^2(x) \qquad 2A$$

and rearranging

$$dx/dt = (a-x)^2(k_1+k_2x) \quad . \qquad 3A$$

Using the same terminology the equation

$$dx/dt = k_1{*}(a-x)^2(b-x) + k_2{*}(a-x)(b-x)(x) \qquad 4A$$

under conditions $a = b$ becomes

$$dx/dt = k_1{*}(a-x)^3 + k_2{*}(a-x)^2(x) \qquad 5A$$

and rearranging

$$dx/dt = (a-x)^2[k_1{*}a + (k_2{*}-k_1{*})(x)] \qquad 6A$$

It is immediately obvious that for a series of experiments in which a is not varied (the majority of experiments here considered) equation 6A is kinetically indistinguishable from equation 3A. Also, the experiments in which both As(III) and As^o were present in large excess (cf. Figure 3) would produce the same results for either equation.

The information at hand that might serve to make an unambiguous choice possible is somewhat fragmentary. What little there is, however, points toward equation 1A as being more appropriate than equation 4A. Experiment 5 in the experiments proposed for the future should clarify the situation completely.

In the event that equation 4A proves to be correct the re-evaluation of the constants involved is simple since from equations 3A and 6A it can be seen that

$$k_1 = k_1{*}a$$

$$k_2 = k_2{*} - k_1{*}$$

or

$$k_1{*} = k_1/a$$

$$k_2{*} = k_2 + k_1/a \; .$$

Such a change would have no effect on the values of E_{a_1} and E_{a_3} but would change E_{a_2}. It would also, of course, require a reinterpretation of the gross mechanism suggested for the k_1 term and its relationship to the other terms in equation 13.