A KINETIC STUDY OF THE OXIDATION OF IRON (II) BY CHLORINE

THESIS BY

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ABSTRACT

The kinetics of the oxidation of iron (II) by aqueous chlorine has been investigated spectrophotometrically at an ionic strength of 1.00 M. In solutions with $[H^+] = 0.05 - 1.00$ M, $[Cl^-] = 0.10 - 1.00$ M, $[Fe^{++}] = 10^{-5} - 10^{-4}$, $[Cl_2] = 10^{-5} - 10^{-4}$ M, $[Fe^{+++}]_0 = 0.00 - 10^{-4}$ F, the rate law is $d[Fe^{+++}] / dt = k_1 [Fe^{++}] [Cl_3^-] + k_3 [Fe^{++}] [Cl_2]$; $k_1 = 1510 (\pm 150) M^{-1} sec.^{-1}$, $k_3 = 316 (\pm 30) M^{-1} sec.^{-1}$, and $R_{25} / [Fe^{++}] [Cl_2] = 10^{9.47} \exp (-9,320/RT)$. There is no apparent ferric inhibition of the reaction and the data suggest an iron (IV) intermediate. Small amounts of copper (II) catalyse the reaction and the data suggest a mechanism involving a copper (I) intermediate, since ferric ion inhibits the reaction. In solutions with $[H^+] = [Cl^-] = 1.00$ M, $[Fe^{+++}]_0 = 0.00 - 4.40 \times 10^{-5}$ M, and $[Cu^{++}]_0 = 10^{-6} - 10^{-4}$ M, the data are consistent with the additional rate term: $k_{11}[Fe^{++}] [Cu^{++}] (1 / 1 + k_{12}[Fe^{+++}] / \bar{k}_{14}[Cl_2])$; $k_{11} = 370 (\pm 20) M^{-1} sec.^{-1}$, and $k_{12} / \bar{k}_{14} = 0.14 (\pm 0.02)$ at 30.0°.

HISTORICAL

The mechanism of the reaction

$$2Fe^{++} + Cl_3^- \text{ (or } Cl_2) \longrightarrow 2Fe^{+++} + 3Cl^- \text{ (or } 2Cl^-) \qquad (1)$$

is of interest because it may proceed through an iron (IV) intermediate:

$$Fe^{++} + Cl_3^- \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 3Cl^- + Fe\ (IV) \qquad (2)$$

$$Fe^{++} + Cl_2 \underset{k_4}{\overset{k_3}{\rightleftharpoons}} 2Cl^- + Fe\ (IV) \qquad (3)$$

$$Fe^{++} + Fe\ (IV) \xrightarrow{k_5} 2Fe^{+++} \qquad (4)$$

or as suggested by Taube (1) through a chlorine radical:

$$Fe^{++} + Cl_3^- \underset{k_7}{\overset{k_6}{\rightleftharpoons}} Fe^{+++} + Cl_2^- + Cl^- \qquad (5)$$

$$Fe^{++} + Cl_2 \underset{k_9}{\overset{k_8}{\rightleftharpoons}} Fe^{+++} + Cl_2^- \qquad (6)$$

$$Fe^{++} + Cl_2^- \xrightarrow{k_{10}} Fe^{+++} + 2Cl^- \qquad (7)$$

Carter and Davidson (2) have reported that the reaction path $Fe^{++} + Br_3^- \longrightarrow Fe^{+++} + Br^- + Br_2^-$ is prefered to the reaction path $Fe^{++} + Br_3^- \longrightarrow Fe\ (IV) + 3Br^-$. Connick and Awtrey (3) have made preliminary studies of the iron (II) - chlorine reaction and reported a second order rate constant approximately the same as for the iron (II) - bromine reaction, although no attempt was made to identify the active chlorine species or to establish the existence of an iron (IV) intermediate. I have found that it is possible to measure the rate of reaction (1) by observing the increase with time of the concentration of the iron (III) ion spectro-

photometrically when the reagents are present at concentrations in the range 10^{-5} - 10^{-4} M. The kinetic results have been interpreted as demonstrating the existence of two active chlorine species, Cl_2 and Cl_3^-, and suggest an iron (IV) intermediate.

EXPERIMENTAL

Materials - Ferrous ammonium sulfate (0.2g.) was dissolved in 500 ml. 1.00 M HCl, the solution was degassed with dry nitrogen and stored under nitrogen in a storage buret. The ferrous ion was determined coulometrically with bromine. There was no measurable air oxidation of this solution in a two month period. An aqueous chlorine solution was prepared by bubbling dry chlorine gas through a 1.00 M HCl solution. The ca. 10^{-3} M solution was stored under nitrogen in a storage buret. Ferric ammonium sulfate (0.10g.) was dissolved in 250 ml. 1.00M HCl. The actual $[Fe^{+++}]_0$ was determined spectrophotometrically prior to the reaction.

Procedure - A measured amount of the ferrous solution was placed in a 10 cm. quartz cell with appropriate volumes of the reagents: 1.00 M HCl, 1.00 M $HClO_4$, 1.00 M NaCl, and 0.0010 M Fe^{+++}. The solution was brought to 30.0° and diluted to 30 ml. by rapid addition of the chlorine solution; the cell was stoppered and shaken for 10 sec. The zero time point was taken when all the chlorine had been added. The cell was then placed in the thermostatted cell compartment of a Cary model 14 spectrophotometer, using as a blank another cell containing all the components except the chlorine; absorption due to the trichloride ion and aqueous chlorine was less than 5 percent of the

ferric ion absorption at 335 mμ. The first optical density reading was usually obtained about 20 seconds after mixing and the half time of a typical experiment was about one minute. The response time of the spectrophotometer to small changes in the optical density was less than one second.

Extinction coefficients - The formal extinction coefficients, $\epsilon = A/[Fe^{+++}]l$ of various ferric solutions were measured and are listed in Table I.

Table I

Formal extinction coefficients, ϵ, of ferric iron at λ = 335mμ in various solutions.

$[H^+]$	$[Cl^-]$	T	ϵ
1.00 M	1.00 M	30.0°	2090
0.10	1.00	30.0	1900
0.05	1.00	30.0	1895
1.00	0.50	30.0	1511
1.00	0.10	30.0	695
1.00	1.00	15.0	1783

The data of Sherrill and Izard (4) and of Zimmerman and Strong (5) at μ = 1.00 M, T = 25.0°, give $K_{Cl_3^-} = [Cl_3^-]/[Cl_2][Cl^-] = 0.176\ M^{-1}$. This value was used in this research at 30.0°.

RESULTS AND DISCUSSION

All reaction rates were measured at the constant ionic strength of 1.00 M, maintained with sodium and perchlorate ions. The concentrations of ferrous, ammonium, sulfate ions, and of chlorine made a negligable contribution to the ionic strength. The slope of the optical density - time curve was determined at 25 seconds and this value was used as the initial rate, $R_{25"}$. These initial rates are given in Table II along with other pertinent reaction data. Check experiments showed that there

was no photochemical reaction due to the light of the spectrophotometer. The rate constants were independant of the hydrogen ion concentration over the limited range studied.

Table II

$[Fe^{++}]_{25}$	$[Cl_2]_{25}$	$[Fe^{+++}]_{25}$	R_{25}	$[Fe^{++}][Cl_2]$	$R_{25}/[Fe^{++}][Cl_2]$
	M X 10^5		M sec^{-1} X 10^7	M^2 X 10^{10}	$M^{-1}sec^{-1}$ X 10^{-2}
		T = 30.0°, $[Cl^-]$ = 1.00 M			
8.34	0.12	0.41	0.43	0.83	5.17
8.01	0.44	0.74	1.34	2.96	4.53
4.09	0.52	0.29	2.25	1.80	12.50
3.32	0.95	1.05	2.35	2.69	8.74
7.36	0.57	1.39	2.39	3.54	6.75
7.07	0.76	1.68	2.66	4.60	5.78
7.16	1.12	1.59	3.49	6.80	5.13
6.58	1.29	2.17	4.30	7.24	5.95
5.97	1.75	2.78	5.50	8.90	6.18
5.55	1.93	3.20	7.56	9.10	8.31
8.65	2.70	4.47	10.38	19.80	5.24
3.80	0.74	2.68	1.29	2.39	5.39
7.98	0.58	3.25	1.91	3.92	4.87
3.51	1.29	2.97	2.25	3.86	5.83
7.99	1.05	9.23	2.25	7.12	3.12
7.87	0.65	5.10	2.30	4.33	5.32
7.26	1.04	5.62	3.49	6.38	5.47
7.23	1.12	3.77	3.82	6.88	5.56
6.85	1.63	4.17	4.79	9.52	5.03
6.87	1.52	6.14	5.64	8.85	6.37
6.04	2.20	4.97	6.12	11.30	5.41
7.41	2.29	10.00	6.94	14.40	4.82
		T = 30.0°, $[Cl^-]$ = 0.05 M			
3.95	0.83	0.42	0.79	3.00	2.64
7.60	0.71	1.15	2.51	4.94	5.08
6.82	1.06	1.93	2.58	6.61	3.90
2.97	2.78	1.40	4.69	7.57	6.20
6.45	1.56	2.30	4.83	9.23	5.24
6.37	2.29	2.38	5.95	13.40	4.44
		T = 30.0°, $[Cl^-]$ = 0.10 M			
3.51	0.89	0.86	1.01	3.06	3.30
7.05	1.09	1.70	2.59	7.55	3.43
7.48	0.60	1.27	1.30	4.41	2.95
2.63	2.49	1.74	2.73	6.45	4.23
6.14	2.06	2.60	3.17	12.40	2.56
6.69	1.51	2.06	3.45	9.90	3.49

Table II (cont.)

$T = 15.0^{o}$, $[Cl^{-}] = 1.00$ M

8.12	0.54	0.63	0.62	3.74	1.66
3.70	1.41	0.67	1.29	4.44	2.91
7.89	1.02	0.86	1.68	5.86	2.87
3.28	2.73	1.10	1.91	7.61	2.51
7.52	1.67	1.23	2.52	10.70	2.35
7.18	2.50	1.57	3.09	15.30	2.02

$[H^{+}] = 0.10$ M and 0.05 M excluded from the table.

These initial rates at a fixed chloride ion concentration fit the second order rate equation

$$d[Fe^{+++}]/dt = \bar{k}[Fe^{++}][Cl_2] \qquad (8)$$

The quantity $\bar{k}$ increases with increasing chloride ion concentration. This suggests that both Cl_2 and Cl_3^{-} are effective as oxidants, and that the rate equation is:

$$d[Fe^{+++}]/dt = k_1[Fe^{++}][Cl_3^{-}] + k_3[Fe^{++}][Cl_2] \qquad (9a)$$

$$R_{25}/[Fe^{++}][Cl_2] = k_3 + k_1 K_{Cl_3^{-}}[Cl^{-}] \qquad (9b)$$

Table III

Slope of a plot of R_{25} vs. $[Fe^{++}][Cl_2]$ at $[Cl^{-}] = 1.00$, 0.50, and 0.10 M

$K_{Cl_3^{-}}[Cl^{-}]$	Slope $M^{-1}sec.^{-1}$	T
0.0176	320	30.0^{o}
0.088	476	30.0
0.176	570	30.0
0.176	230	15.0

In Fig. 1, the quantity R_{25} is plotted vs. $[Fe^{++}][Cl_2]$ to display the second order rate character of the reaction. The average slopes at a fixed chloride ion concentration are listed in Table III and plotted vs. $K_{Cl_3^{-}}[Cl^{-}]$, as suggested by Eq. 9b, in Fig. 2. A straight line fit to the data in Fig. 2 was determined by least squares and is shown as a solid line; the slope and intercept with their probable errors are $k_1 = 1510 (\pm 150)\ M^{-1}sec.^{-1}$ and $k_3 = 316 (\pm 30)\ M^{-1}sec.^{-1}$.

The data are not sufficiently detailed to permit determination of the temperature coefficient of the rate constants k_1 and k_3. For the overall rate constants $R_{25}/[Fe^{++}][Cl_2]$ at $[H^+] = [Cl^-] = 1.00$ M at 30.0° and 15.0°,

$$R_{25}/[Fe^{++}][Cl_2] = 10^{9.47}\exp(-9,320/RT) \qquad (10)$$

INHIBITION

There was no demonstrable inhibition by added ferric ion over the limited range studied; it was impractical to attempt high initial ferric ion concentration because of the high absorbtivities of the ferric ion and its chloride complexes. Thus there is no positive evidence for the chlorine radical reaction path of Eqs. 5, 6, and 7. On the other hand the plot of $R_{25}/[Fe^{++}][Cl_2]$ of Fig. 2 shows a small negative curvature. This would be expected if the reaction proceeded through an iron (IV) intermediate via reactions (2), (3), and (4), since chloride ion can act as an inhibitor by back reaction with Fe (IV) (reverse of reactions (2) and (3). The above chain of reasoning is clearly not conclusive, and it is not possible to determine with certainty whether Cl_2^- or Fe (IV) is the important intermediate. Experiments at very high chloride ion concentration might distinguish between the two mechanisms.

COPPER CATALYSIS

While developing a procedure for the coulometric titration of ferrous iron with electrolytically generated chlorine using an amperometric endpoint, Farrington, Schaefer, and Dunham (6) observed that the rate of reaction between iron (II) and chlorine was catalysed by small amounts of cupric ion. I have studied this effect briefly at one initial concentration of Cl^- ion, Fe^{++} ion, and Cl_2, and at two different ferric ion concentrations. Two features of the copper catalysis are immediately apparent in Fig. 3, which displays the results of a series of runs in which the Cu^{++} concentration was varied. The course of any one reaction is first order in ferrous ion concentration, and the reaction is slowed markedly by added ferric ion. The data suggest a mechanism involving a copper (I) intermediate, observed by Cher and Davidson (7) for the iron (II)-oxygen reaction. The data are consistent with the following mechanism:

$$Fe^{++} + Cu^{++} \underset{k_{12}}{\overset{k_{11}}{\rightleftharpoons}} Fe^{+++} + Cu^{+} \qquad (11)$$

$$Fe^{++} + Cl_3^- \xrightarrow{k_1} Fe^{+++} + Cl_2^- + Cl^- \qquad (12)$$

$$Fe^{++} + Cl_2 \xrightarrow{k_3} Fe^{+++} + Cl_2^- \qquad (13)$$

$$Fe^{++} + Cl_2^- \xrightarrow{k_{13}} Fe^{+++} + 2Cl^- \qquad (14)$$

$$Cu^{+} + Cl_2 \xrightarrow{\bar{k}_{14}} Cu^{++} + Cl_2^- \qquad (15)$$

Reactions 1 and 3 initiate the uncatalysed reaction, while reaction 11 initiates the catalysed reaction. The resulting Cu^+ ions can either react with a chlorine species (14), or undergo the back reaction 8 which would account for the inhibition by Fe^{+++} ions. Reactions 1 and 3

would allow for the downward curvature of the first-order plots. By applying the steady state condition to Cu^{+} ions and Cl_2^- ions the rate law of the assumed mechanism is

$$-d[Fe^{++}]/dt = k_1[Fe^{++}][Cl_3^-] + k_3[Fe^{++}][Cl_2] + k_{11}[Fe^{++}][Cu^{++}](1/1 + k_{12}[Fe^{+++}]/\bar{k}_{14}[Cl_2]) \quad (16a)$$

$$-d\ln[Fe^{++}]/dt = k_1[Cl_3^-] + k_3[Cl_2] + k_{11}[Cu^{++}](1/1 + k_{12}[Fe^{+++}]/\bar{k}_{14}[Cl_2]) \quad (16b)$$

The slopes of the $-\ln[Fe^{++}]$ vs. time plots were determined at 20 seconds due to slight error in the zero time point. Pertinent results are listed in Table IV. The values of the constants used are: $k_1 = 1510\ M^{-1}sec^{-1}$, $k_3 = 316\ M^{-1}sec^{-1}$, and $K_{Cl_3} = 0.176\ M^{-1}$.

Table IV

Copper catalysis at $Cu^{++} = 10^{-6} - 10^{-4}$ M, $[Fe^{++}]_0 = 6.57 \times 10^{-5}$ M, and $[H^+] = [Cl^-] = 1.00$ M at 30.0°.

$[Cl_2]_0$	$k_1[Cl_3^-] + k_3[Cl_2]$	$[Cu^{++}]$	$[Fe^{+++}]_0$	$-d\ln[Fe^{++}]/dt$
M X 10^5	sec^{-1} X 10^2	—— M X 10^5 ——		sec^{-1} X 10^2
3.15	1.56	0.33	0.00	1.85
2.60	1.59	0.67	0.00	1.41
3.17	1.57	1.00	0.00	1.85
3.22	1.59	5.00	0.00	3.68
3.22	1.59	10.00	0.00	5.23
	1.58 ave.			
2.65	1.31	0.33	4.35	1.22
2.76	1.37	0.67	4.40	1.34
2.76	1.37	1.00	4.46	1.61
2.91	1.43	5.00	4.38	3.18
2.71	1.34	10.00	4.42	4.38
	1.36 ave.		4.38 ave.	

The slopes, listed in Table IV, are plotted vs. $[Cu^{++}]$, as suggested by Eq 16b, in Fig. 4. A straight line fit to the data was determined, using as the intercept the average value of $k_1[Cl_3^-] + k_3[Cl_2]$; the two slopes are 370 $M^{-1}sec^{-1}$ (for $[Fe^{+++}]_0 = 0.00$) and 304 $M^{-1}sec^{-1}$ (for $[Fe^{+++}]_0 = 4.38 \times 10^{-5}$ M). These values permit the determination

of k_{11} and $k_{12}/\bar{k}_{14}$. At 30.0° these values with their probable errors are: k_{11} = 370 (± 20) $M^{-1}sec^{-1}$ and $k_{12}/\bar{k}_{14}$ = 0.14 (± 0.02). The data are not sufficiently detailed to permit determination of the temperature coefficient of the rate constant k_{11}. The rate constants k_1 and k_3 are quite consistent with the data plotted in Fig. 4 when the values are extrapolated to $[Cu^{++}]$ = 0.00 M. It was not possible to obtain data for $[Cu^{++}]$ greater than 10^{-4} M since the half time of the reaction at these concentrations was on the order of 5 seconds.

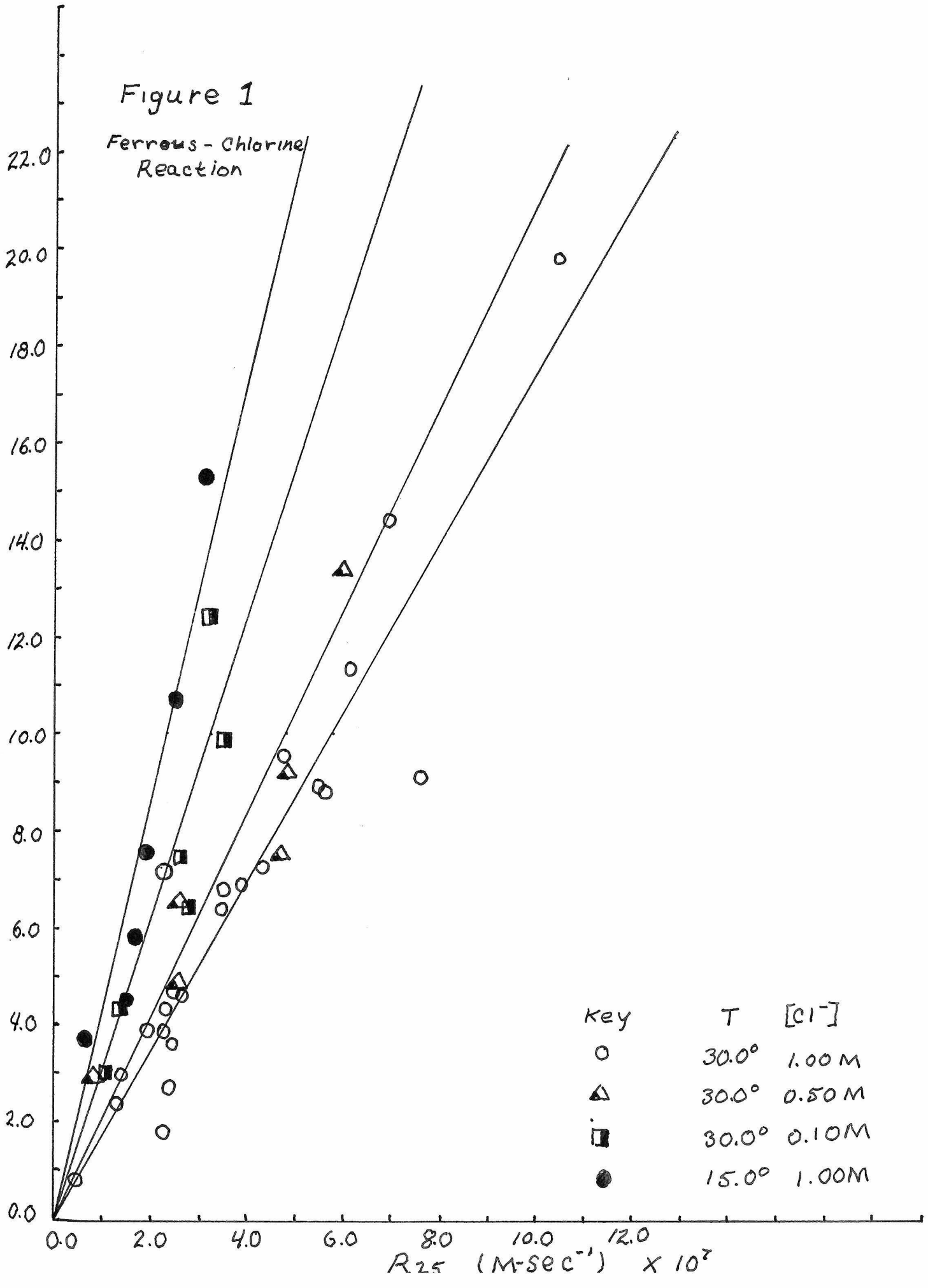
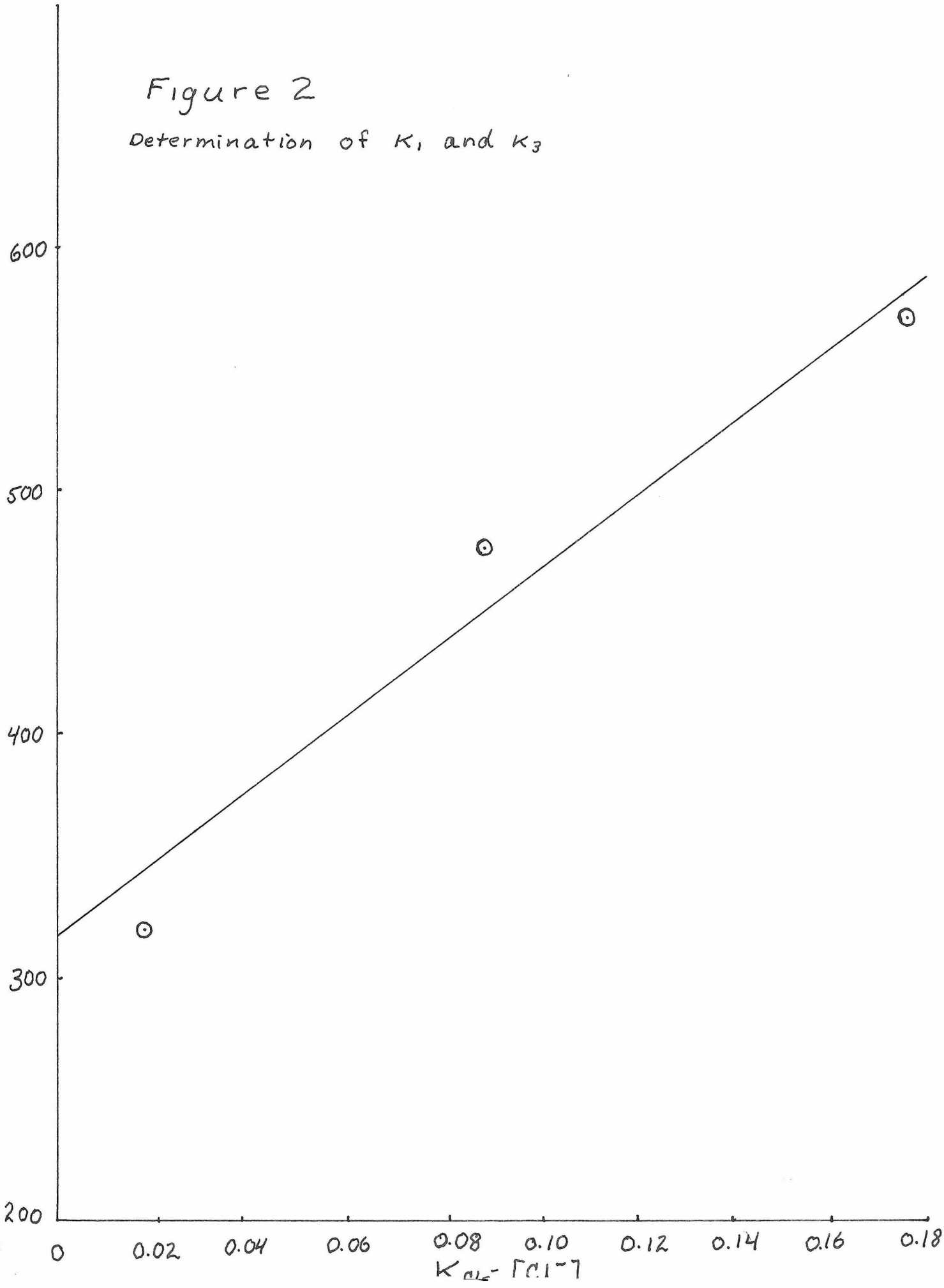


Figure 1
Ferrous - Chlorine Reaction
22.0
20.0
18.0
16.0
14.0
12.0
10.0
8.0
6.0
4.0
2.0
0.0
0.0
2.0
4.0
6.0
8.0
10.0
12.0
R_{25} (M-sec^{-1}) X 10^7
Key
T
[Cl$^-$]
30.0° 1.00 M
30.0° 0.50 M
30.0° 0.10M
15.0° 1.00M

Figure 2

Determination of K_1 and K_3



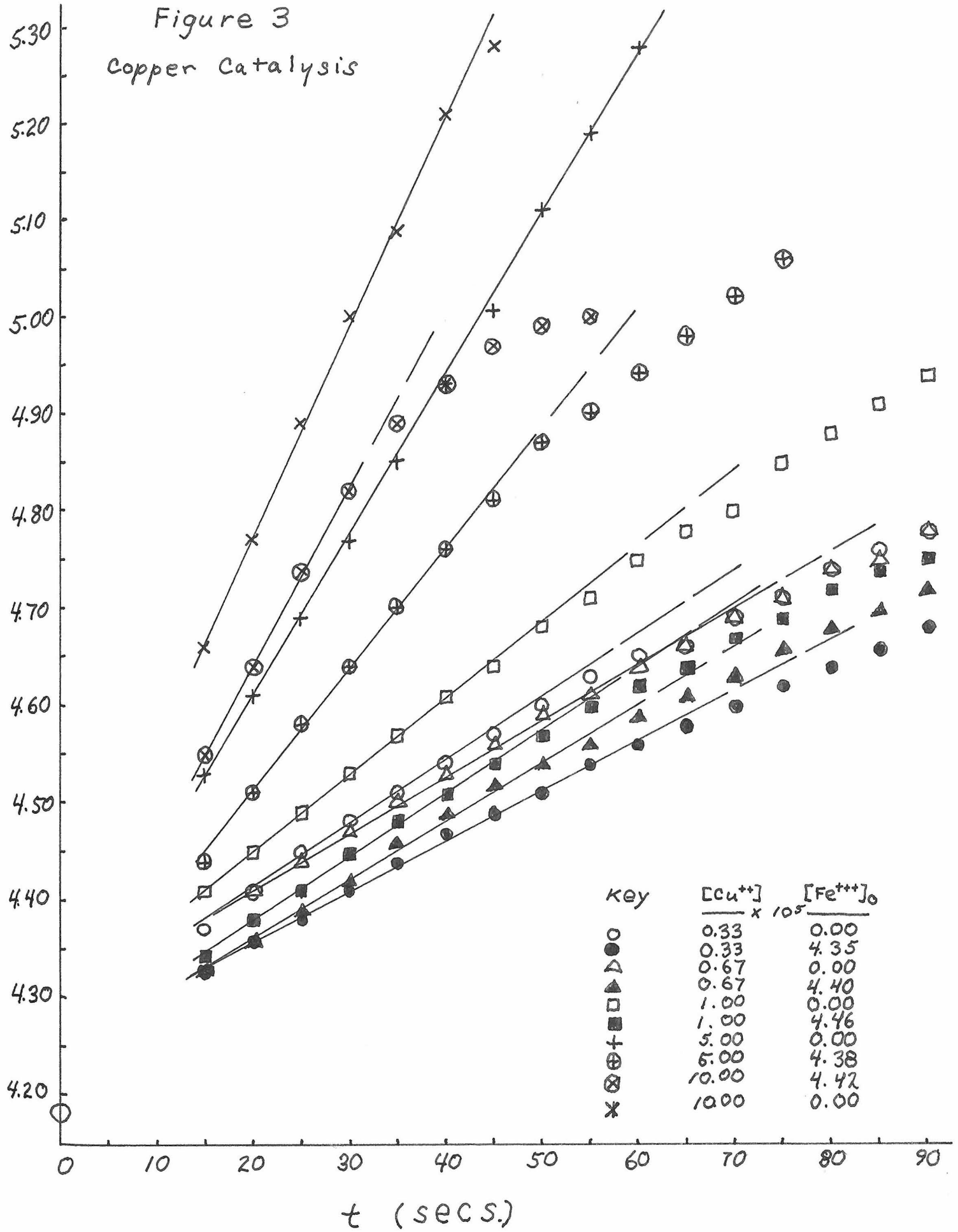
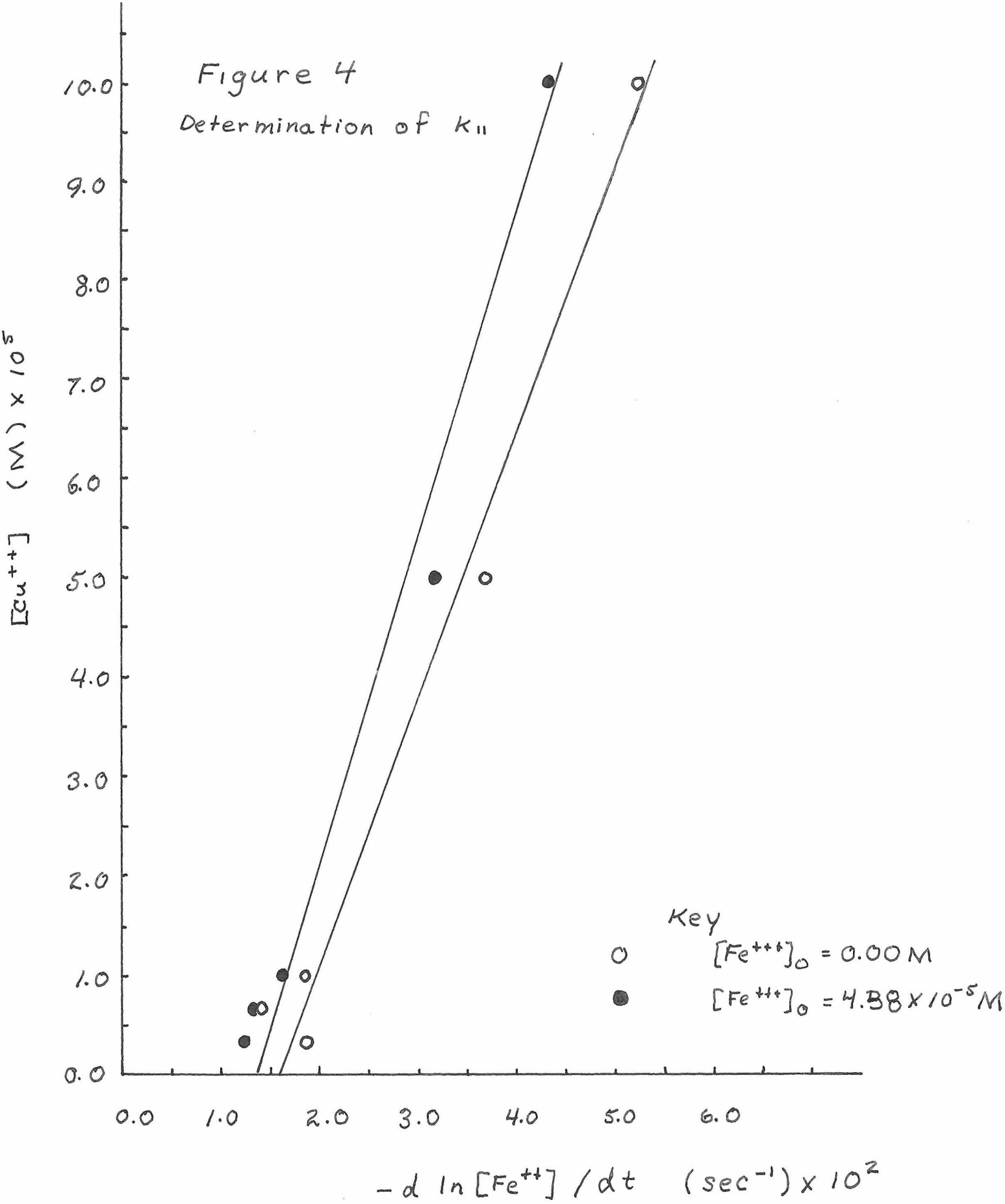


Figure 3
Copper Catalysis
5.30
5.20
5.10
5.00
4.90
4.80
4.70
4.60
4.50
4.40
4.30
4.20
0
10
20
30
40
50
60
70
80
90
t (secs.)
Key
[Cu++] x 10^5
[Fe+++]o
0.33 0.00
0.33 4.35
0.67 0.00
0.67 4.40
1.00 0.00
1.00 4.46
5.00 0.00
5.00 4.38
10.00 4.42
10.00 0.00

Figure 4

Determination of k_{11}



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