1974

Investigation of Several Aspects of the Landolt Reaction

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Recommended Citation

Behnke, Peter A., "Investigation of Several Aspects of the Landolt Reaction" (1974). *All NMU Master's Theses*. 264.
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AN INVESTIGATION OF SEVERAL ASPECTS
OF THE LANDOLT REACTION

by

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B. S., Northern Michigan University

A Thesis

Submitted in Partial Fulfillment of the

Requirements for the Degree of

Master of Arts in Chemistry

School of Graduate Studies

Northern Michigan University

Marquette

August 1974

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Abstract

A number of aspects of the Landolt reaction were investigated. The dependence of the reaction time on the reactants changed as the solvent polarity was decreased by adding 1,4-dioxane. A linear relationship was found between the initial pH of the solution and the reaction time. A computer simulation of the reaction using rate expressions found in the literature was found to agree with the experimental results only after modification of the rate constants for the rate expressions of the three reactions which comprise the Landolt reaction. A description of a simple apparatus for storing air sensitive materials is also included. Suggestions of further work are listed as well as a survey of the past work on the reaction.

Acknowledgements

I would like to take this opportunity to dedicate this study to the constant support and many self-sacrifices of my wife, Pam, throughout both the research and the writing of this thesis. I would also like to thank Dr. David W. Kingston for his continued help and guidance which aided the completion of the study in innumerable ways, Jim Knight for his diligence in maintaining all of the equipment associated with it, and the staff of the West Science Computer terminal for their help and suggestions with the computer programs used in it.

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Historical Introduction

In 1886, H. Landolt investigated the kinetics of a reaction between sulfurous acid and iodic acid(20). The reaction was well-suited for kinetic studies since the endpoint of the reaction was distinctly denoted by the formation of the dark blue iodine-starch complex. Through his studies Landolt reported that the reaction consisted of three individual reactions. The first reaction, Eq. (1), is slow and initiates the overall reaction by generating

$$IO_3^- + 3SO_3^= \longrightarrow 3SO_4^= + I^- \qquad (1)$$

iodide ions. The second reaction, Eq. (2), is also slow; however, it depends on the first reaction for iodide ion. If iodide ion is supplied as one of the initial reactants,

$$IO_3^- + 5I^- + 6H^+ \longrightarrow 3H_2O + 3I_2 \qquad (2)$$

the velocity of the second reaction becomes greater than the velocity of the first reaction. In this case, the rate of the overall reaction is dependent only on reaction two, Eq. (2). The third reaction, Eq. (3), is nearly instantaneous.

$$I_2 + SO_3^= + H_2O \longrightarrow 2I^- + 2H^+ + SO_4^= \qquad (3)$$

In addition, Landolt derived an expression, Eq. (4), for determining the length of the reaction, where t is the time of the overall reaction until the first appearance of

$$t = K_T/(C_S^{.904} \times C_I^{1.642}) \tag{4}$$

the iodine-starch complex, C_S is the initial concentration of sulfite ions, C_I is the initial concentration of iodate ions and K_T is a constant for the temperature, T. Table I contains values of K_T at various temperatures in degrees Centigrade. K_T has the value listed in Table I when the concentration terms are expressed in moles/liter and the time is in minutes.

Table I - Values for the Constant K_T

Temperature	5	10	15	20	25	30	35	40
K_T	796	692	597	524	443	381	244	304

In general for any temperature, T, Eq. (5) can be used to determine the value of K_T. In honor of his initial work

$$K_T = 906.05 - 23.01t + 0.1888t^2 \tag{5}$$

on the reaction, Eqs. (1), (2), and (3) are collectively referred to as the Landolt reaction and the distinct appearance of the endpoint of the reaction is called the Landolt effect(21).

An investigation by J. Eggert showed that the reaction time was nearly independent of the initial sulfite concentration; and was inversely proportional to the square of the hydrogen ion concentration and inversely proportional to the iodate concentration(7). He found that the time of the reaction could be determined from the rate constants, K_1 and K_2 of Eqs. (1) and (2). The time of the reaction is given by Eq. (6).

$$t = (1/(K_2-K_1))\ln(K_2/K_1) \qquad (6)$$

A. Skrabal confirmed Eggert's results stating that the time of the reaction was proportional to the concentrations of the reactants as shown by Eq. (7). Eq. (7) is true only

$$t \propto [SO_3^=]/[IO_3^-][H^+]^2[I^-]^2 \qquad (7)$$

when the initial concentrations of all reactants are large compared with the sulfite concentration. If this is not the case, the reaction time is proportional only to the concentration of sulfite. He also determined the rate expression for the first reaction, Eq. (8) and the rate expression for the second reaction, Eq. (9). The rate

$$-d[IO_3^-]/dt = K_1[H^+][IO_3^-][SO_3^=] \qquad (8)$$

$$-d[IO_3^-]/dt = K_2[H^+]^2[IO_3^-][I^-]^2 \qquad (9)$$

constants, K_1 and K_2, have values of 9.8×10^2 and 5.4×10^8 at a temperature of 16° C. and are expressed in $l^2 moles^{-2} min^{-1}$ and $l^4 moles^{-4} min^{-1}$ respectively(29).

The first reaction, Eq. (1) is monomolecular with respect to both iodate and sulfite. The rate constant for the reaction at various pH values and at a temperature of

25° C. is listed in Table II. The rate constant is for the rate expression having units of time in minutes and concentration units of moles/liter(33).

Table II - Rate Constant for the Iodate-Sulfite Reaction

pH	Rate Constant
9 - 10	0.002
5.0	40.
2.0	230.

Thiel and Meyer consider the first reaction to be a stepwise reduction of iodate to iodide with sulfite ion as the reducing agent. Their reaction scheme is

$$IO_3^- + SO_3^= \longrightarrow IO_2^- + SO_4^= \qquad (10)$$

$$IO_2^- + SO_3^= \longrightarrow IO^- + SO_4^=$$

$$IO^- + SO_3^= \longrightarrow I^- + SO_4^=$$

The sum of the three reactions is Eq.(1). This they contend shows that hydrogen ion does not directly participate in the first reaction. The hydrogen ion concentration does contribute indirectly by increasing the concentration of sulfurous acid present compared to the concentration of the bisulfite and sulfite species. Table III lists the relative percentages of sulfurous acid, bisulfite and sulfite ions at given values of pH. The reducing power of the three species is in the order of

$$H_2SO_3 \quad > \quad HSO_3^- \quad > \quad SO_3^=$$

At higher hydrogen ion concentrations the stronger reducing agent sulfurous acid, is present in greater concentration and the reaction velocity is greater.

Table III - Percentages of Sulfite Species Present at Various pH Values

Percentages of -			Solution pH
H_2SO_3	HSO_3^-	$SO_3^=$	
26.8	75.2	0.00133	2.25
17.0	83.0	0.00267	2.50
10.4	89.6	0.00514	2.75
6.10	93.9	0.00958	3.00
3.52	96.4	0.0175	3.25
2.01	98.0	0.0316	3.50
1.14	98.8	0.0567	3.75
0.644	99.2	0.101	4.00
0.363	99.4	0.180	4.25
0.204	99.4	0.321	4.50
0.115	99.3	0.570	4.75
0.0642	98.9	1.01	5.00

The rate expression for the reaction is Eq. (11). The rate constants have units of $l^2 moles^{-2} min^{-1}$ and $l^4 moles^{-4} min^{-1}$

$$-d[IO_3^-]/dt = 0.53\times10^{6}[H^+][HSO_3^-][IO_3^-] + 0.67\times10^{17}[H^+]^2[SO_3^=]^2[IO_3^-] \quad (11)$$

respectively and are for a temperature of 25° C. Skrabal reported that Eq. (11) holds over a range of pH 4 - 13 (31).

The second reaction in the Landolt reaction has been investigated thoroughly. The original and most extensive work was done by Saul Dushman(6). In fact, it is often referred to as the Dushman reaction. Dushman determined the rate of the reaction to be Eq. (12). The rate constants

$$-d[IO_3^-]/dt = 2.54\times10^{10}[IO_3^-][H^+]^2[I^-]^{1.9} + 1.70\times10^{10}[IO_3^-][H^+]^2[I^-][I_3^-] \quad (12)$$

are expressed in units of $l^{3.9}moles^{-3.9}min^{-1}$ and $l^4moles^{-4}min^{-1}$ and they are for a reaction run at 0° C. in an acetate-acetic acid buffer. A subsequent study determined the first rate constant also in an acetate-acetic acid buffer at 25° C. and found it to be 5.29×10^{10}. The rate constant is expressed in terms of liters, moles and minutes(28). The latest examination of the reaction was carried out in a buffer free solution. The rate expression is Eq. (13).

$$-d[IO_3^-]/dt = 7.6\times10^{10}[IO_3^-][H^+]^2[I^-]^2 + 5.5\times10^{10}[IO_3^-][H^+][I^-][I_3^-] \quad (13)$$

The rate constants have units of $l^4mole^{-4}min^{-1}$ and $l^3moles^{-3}min^{-1}$.

Historically there has been little question concerning the rate expression of the second reaction, the mechanism is still open to debate. In his original work (6), Dushman proposed the mechanism,

$$IO_3^- + 2I^- + 2H^+ \longrightarrow 2HOI + IO^- \qquad (14)$$

$$2HOI + IO^- \longrightarrow I_2 + H_2O + IO_2^-$$

Abel and Hilferding proposed Eq. (15) as a possible mechanism for the second reaction (1).

$$IO_3^- + H^+ \longrightarrow HIO_3 \qquad (15)$$

$$I^- + H^+ \longrightarrow HI$$

$$HIO_3 + HI \longrightarrow HIO + HIO_2$$

Bray and Liebhafsky proposed two possible mechanisms (5). The first mechanism is Eq. (16).

$$IO_3^- + I^- + 2H^+ \longrightarrow H_2I_2O_3 \qquad (16)$$

$$H_2I_2O_3 \longrightarrow I_2O_2 + H_2O$$

$$I_2O_2 + I^- \longrightarrow I_3O_2^-$$

The second mechanism, Eq. (17), is proposed to occur at low iodide concentrations.

$$IO_3^- + I^- + 2H^+ \longrightarrow H_2I_2O_3 \qquad (17)$$

$$H_2I_2O_3 \longrightarrow HOI + HIO_2$$

Probably the most conclusive study into the mechanism of the Dushman reaction was carried out by Morgan, Peard, and Cullis (23). They proposed that the mechanism of the reaction is

$$\begin{aligned} IO_3^- + H^+ &\longrightarrow IO_2^+ + OH^- \\ IO_2^+ + I^- &\longrightarrow IOIO \\ IOIO + I^- &\longrightarrow I^+ + 2IO^- \end{aligned} \tag{18}$$

At low concentrations of iodide Eq. (19) is considered the mechanism. From these two mechanisms they derived theoretically Eq. (13). At high iodide concentrations the IOIO

$$\begin{aligned} IO_3^- + H^+ &\longrightarrow IO_2^+ + OH^- \\ IO_2^+ + I^- &\longrightarrow IOIO \\ IOIO &\longrightarrow IO^+ + IO^- \end{aligned} \tag{19}$$

species is relatively long lived and can react with more iodide. As a result the second term in Eq. (13) becomes insignificant. When the iodide concentration is low the possibility of the IOIO complex decomposing before it can react with more iodide ion increases and the first term in Eq. (13) becomes insignificant.

A number of catalysts have been proposed for the Dushman reaction (10). Eggert found that sulfite reacted much faster than thiosulfate with iodine. He was unable to show whether the true catalyst was actually thiosulfate or sulfur held in a collodial suspension. He proposed Eq. (20) as a possible mechanism.

$$4IO_3^- + 3S_2O_3^= + 3H_2O \longrightarrow 4I^- + 6SO_4^= + 6H^+ \qquad (20)$$

$$IO_3^- + 5I^- + 6H^+ \longrightarrow 3I_2 + 3H_2O$$

$$3I_2 + 6S_2O_3^= \longrightarrow 3S_4O_6^= + 6I^-$$

Roman-Levinson devised a classification scheme based on the relative amounts of sulfite and thiosulfate in the solution (20). He lists three types of Dushman reactions. The Dushman S reaction contains only sulfite ions in solution. The Dushman T reaction utilizes only thiosulfate as the reducing agent. If amounts of both thiosulfate and sulfite are present, the reaction is called a Dushman S-T reaction. The Dushman S-T reaction predominates at low concentrations of thiosulfate. As the concentration of thiosulfate increases in relation to the concentration of sulfite, the reaction time decreases until a minimum is reached. At this point the concentrations of sulfite and thiosulfate are nearly equal. From this point any additional thiosulfate causes the Dushman T reaction to predominate and the reaction time to increase.

The study of the third reaction has been more difficult due to the high velocity of the reaction. Analytical work has shown that the reaction proceeds quantitatively to sulfuric acid. There is no separation of sulfur (22). Thiel and Meyer suggested participation by hydroxide ion in the reaction on the basis of the twenty-fold increase in reaction velocity from pH one to pH two.

G. Bunau and M. Eigen using spectroscopic techniques were able to measure the rate constant in highly acidic solutions (24). At pH values less than one the principle mechanism is believed to be Eq. (21). Table IV shows the rate constant at various pH values. The two columns containing

$$SO_2 + H_2O \underset{K_5}{\overset{K_6}{\rightleftarrows}} H_2SO_3 \xrightarrow[K_9]{+ I_2 + H_2O} H_2SO_4 + HI \qquad (21)$$

Table IV - Rate Constant for the Iodine-Sulfite Reaction at Various pH Values

Initial I_2 and $SO_3^=$ Concentration	H^+ Concentration	K_9K_6/K_5
5.45×10^{-3}	0.1	3.0×10^5
5.45×10^{-3}	1.0	2.5×10^5
5.45×10^{-3}	1.5	1.2×10^5
5.45×10^{-3}	2.0	6.2×10^4

concentration terms have units of moles/liter. The rate constant has time units of seconds. An examination of the values in Table IV confirms the work of Thiel and Meyers, i.e., there is a decrease in velocity as the hydrogen ion concentration increases. Bunau and Eigen also derived

Eq. (22) from which the amount of iodine present at any given time, t, can be calculated. C_S is the amount of sulfite initially present and C_I is the initial iodine concentration. If the initial iodine and sulfite concentrations are equal and t is greater than $(K_9K_6/K_5)C_I$ then the concentration of the remaining iodine, x(t), at time t is independent of the initial concentrations and approaches the limiting value shown by Eq. (23).

$$x(t) = \frac{(C_S - C_I)}{(C_S/C_I)\exp((K_9K_6/K_5)(C_S-C_I)t) - 1} \qquad (22)$$

$$x(t) \longrightarrow K_5/K_9K_6t \qquad (23)$$

A number of alternative reducing agents have been used in place of sulfite ions. The principal disadvantage of a sulfite solution is its instability due to air oxidation and the loss of sulfur dioxide (22). Sulfite substitutes include ferrocyanide, thiosulfate, arsenite and hydroxylamine (8). Eggert has classified the reducing agents used in the Landolt reaction into three groups (12). Reducing agents in Type I are sulfite and thiosulfate. This group is characterized by complete utilization of all available reducing agent at the time of the endpoint. Ferrocyanide and arsenite are members of the Type II reducing agent group. With this group of reducing agents, the rate of Eq. (2) becomes greater than the rate of Eq. (3) as the reaction progresses. At the first appearance of the blue color signifying the endpoint of the reaction some of the reducing agent remains. Eq. (24) describes the mechanism of the Landolt reaction employing ferrocyanide as the reducing agent. The mechanism for the Landolt reaction using arsenite

$$IO_3^- + 6Fe(CN)_6^{-4} + 6H^+ \longrightarrow I^- + 6Fe(CN)_6^{-3} + 3H_2O \quad (24)$$

$$IO_3^- + 5I^- + 6H^+ \longrightarrow 3I_2 + 3H_2O$$

$$I_2 + 2Fe(CN)_6^{-4} \longrightarrow 2I^- + 2Fe(CN)_6^{-3}$$

as the reducing agent is shown in Eq. (25). It should be noted that in each case the products of each reaction remain the same as those in the reaction using sulfite as the reducing agent.

$$3AsO_3^{-3} + IO_3^- \longrightarrow 3AsO_4^{-3} + I^- \quad (25)$$

$$IO_3^- + 5I^- + 6H^+ \longrightarrow 3I_2 + 3H_2O$$

$$I_2 + AsO_3^{-3} + H_2O \longrightarrow 2I^- + AsO_4^{-3} + 2H^+$$

The Type III Landolt reaction is a special type since the Landolt effect is absent. Eq. (2) is faster than Eq. (1) and (3). Iodine is produced on mixing. Hydroxylamine is an example of a reducing agent for a Type III reaction.

$$10NH_3OH^+ + 4IO_3^- \longrightarrow 2I_2 + 5N_2O + 17H_2O + 6H^+ \quad (26)$$

$$IO_3^- + 5I^- + 6H^+ \longrightarrow 3I_2 + 3H_2O$$

$$2I_2 + 2NH_3OH^+ \longrightarrow N_2O + H_2O + 4I^- + 6H^+$$

A number of catalysts for the Landolt reaction have been reported. The principal ones are the halogens (30). The order of increase in the velocity of the catalyzed reaction is

$$I^- > Br^- > Cl^-$$

Skrabal and Rieder reported that the velocity of the reaction employing a halogen as a catalyst can be determined from Eq. (28). The rate constants for the reaction have been

$$\begin{aligned} -d[IO_3^-]/dt = {} & K_1[IO_3^-][H^+][SO_3^{=}] + K_2[IO_3^-][H^+]^2[I^-]^2 \\ & K_3[IO_3^-][H^+]^2[I^-][Br^-] + K_4[IO_3^-][H^+]^2[I^-][Cl^-] \\ & K_5[IO_3^-][H^+]^2[Br^-]^2 + K_6[IO_3^-][H^+]^2[Br^-][Cl^-] \\ & K_7[IO_3^-][H^+]^2[Cl^-]^2 \end{aligned} \qquad (28)$$

determined and are $K_1 = 10^3$, $K_2 = 5 \times 10^8$, $K_3 = 10^8$, $K_4 = 10^6$, $K_5 = 110$, $K_6 = 100$, and $K_7 = 10$. Eq. (29) represents the overall kinetics of the reaction where X and Y are either the same or different halogens.

$$-d[IO_3^-]/dt = K[IO_3^-][H^+]^2[X][Y] \qquad (29)$$

L-ascorbic acid with either sulfite or arsenite as the reducing agent has been reported as a catalyst for the Landolt reaction (24). The effect is a reduction in the reaction time. The mechanism of the L-ascorbic acid catalyzed reaction is shown in Eq. (30). The summation of the individual steps of Eq. (30) is Eq. (31) which is the

$$HIO_3 + 3C_6H_8O_6 \longrightarrow HI + 3C_6H_6O_6 + 3H_2O \qquad (30)$$

$$HIO_3 + 5HI \longrightarrow 3I_2 + 3H_2O$$

$$2I_2 + 3H_2SO_3 + 2H_2O \longrightarrow 4HI + 2H_2SO_4$$

$$3C_6H_6O_6 + 3H_2SO_3 + 3H_2O \longrightarrow 3C_6H_8O_6 + 3H_2SO_4$$

same as the summation of Eqs. (1), (2) and (3). Other

$$2HIO_3 + 5H_2SO_3 \longrightarrow I_2 + 5H_2SO_4 + H_2O \qquad (31)$$

reported catalysts include α,α'-dioxoadipic acid, pyrocathechol, triose reductone, and hydroxy comenic acid (14).

The latest work on the Landolt reaction has been done by J. Bognar who examined a hydrazine, bromate, bromide reaction (4). He also has done work in the area of trace analysis using the Landolt reaction (3).

Introduction

The intent of this study was an investigation of a number of aspects of the Landolt reaction. The results of these investigations have been divided into three sections.

1. A Comparison of the Reaction Time of the Landolt Reaction in Different Solvents.
2. The Effect of Buffer Systems of Varying Values of pH on the Rate of the Landolt Reaction.
3. An Examination of the Rate Expressions for the Three Steps of the Landolt Reaction Through the Use of a Computer Simulation.

The original purpose of this study was an investigation of the effect of different solvents on the rate of the Landolt reaction. Problems concerning the reproducibility of the reaction times and the instability of the sulfite solution necessitated an early abandonment of this investigation. Although incomplete in certain respects, the results which were obtained were interesting and have been included. Four solvents, ethylene glycol, water, a 20% 1,4-dioxane - 80% water solution and a 30% 1,4-dioxane - 70% water solution, were used in the first section. The reaction times at various concentrations were determined experimentally and compared. Differences were noted and attempts were made to explain any anomalies.

The problem of obtaining reproducible values for the reaction time was also studied. The hydrogen ion concentration since it controls the relative amounts of sulfurous acid, bisulfite and sulfite in solution was considered the most crucial factor. A citrate-citric acid buffer system was employed to determine if this was the case. A comparison of the average percent uncertainties in the reaction times for the buffered and the unbuffered system was made. Results showed the buffered system to have reaction times with lower percent uncertainties. A system which prevented the instability of the sulfite solution was also discovered. The apparatus is discussed in the Experimental section.

Finally, the potentiometric curves of the hydrogen and iodide concentrations were examined. A computer simulation was written using the rate expressions for Eqs. (1), (2) and (3) found in the literature and the experimental data from the hydrogen ion curve. The rate constants were adjusted in order to obtain results consistent with those found experimentally, A comparison was made between the literature values for the rate constants and those found to give results which best fit the experimental data for both the buffered and the unbuffered solutions.

In conclusion suggestions were made for further work. Two appendices have also been included. The first deals with standardization procedures which have been found to be useful. The second appendix lists the computer programs and sample data used in the computer simulation.

Experimental

A Corning Model 12 Research pH meter coupled with a Sargent Model SRL recorder was used in this work. Two electrodes were used. The hydrogen ion concentration was determined using a Corning Combination hydrogen ion electrode. The iodide concentration was measured using a saturated calomel reference electrode and a silver wire.

The potassium iodate solution was made from Mallinckrodt analytical reagent grade primary standard potassium iodate. The assay value was 99.95% potassium iodate. Depending on its use the approximate concentration of the potassium iodate solution was 0.02 M. The sulfuric acid solution was made from Mallinckrodt analytical reagent grade sulfuric acid. The assay value was 95.0 - 98.0% sulfuric acid. The necessary volume of the reagent was pipetted into a volumetric flask and diluted to the proper volume. The actual concentration of the sulfuric acid solution depended on its use. A listing of the concentrations is given in Table VIII on page 33.

The sodium sulfite solution was made using Baker's Analyzed reagent grade sodium sulfite assay 99.95 - 100.05% sodium sulfite. The approximate concentration of the solution was 0.02 M. The distilled water used in making the sodium sulfite solution was boiled first to remove the dissolved oxygen and then stored under a nitrogen atmosphere until it was used. Table VIII on page 33 contains the various sulfite solution concentrations which were used.

Special care was necessary in the storage of the sulfite solution. The concentration of a sulfite solution decreases due to air oxidation to sulfate and due to loss of sulfur dioxide (16), (22). If the solution is basic as is the case of a sodium sulfite solution, air oxidation to sulfate occurs at an appreciable rate. Loss of sulfur dioxide occurs in an acidic solution; however, at a much slower rate. To prevent this decrease in sulfite concentration while the solution is stored, oxygen must be excluded.

Table V gives an indication as to the rate of oxidation of the sulfite solution. The table consists of twelve trials. The trials are grouped in pairs having the same initial volumes of reactants and are listed in chronological order. Those appearing at the top of the table were run first and those trials at the bottom of the table were run last. The time differential between the time the sulfite solution was made and the time the last trial was run is three hours. The sulfite solution used in the trials was made just prior to the time at which the trials were run. The concentration of the sulfite solution was 0.02508 ± .00001 M. For each pair of trials the second trial is always faster than the first trial.

Another indication of the rate of air oxidation of the sulfite solution is shown by Table VI on page 23. A new sulfite solution was made having a concentration of 0.02508

Table V - Reaction Times Showing Decomposition of Sodium Sulfite Solution

Volumes of Reactants				Reaction Time
KIO_3	Na_2SO_3	H_2SO_4	H_2O	
9.958 ± .008	9.95 ± .01	14.89 ± .02	0.00	220.0
9.958 ± .008	9.95 ± .01	14.89 ± .02	0.00	211.8
9.958 ± .008	9.95 ± .01	14.29 ± .02	0.59 ± .01	289.1
9.958 ± .008	9.95 ± .01	14.29 ± .02	0.59 ± .01	288.9
9.958 ± .008	9.95 ± .01	13.70 ± .02	1.18 ± .01	341.7
9.958 ± .008	9.95 ± .01	13.70 ± .02	1.18 ± .01	333.7
9.958 ± .008	9.95 ± .01	13.11 ± .02	1.78 ± .01	430.3
9.958 ± .008	9.95 ± .01	13.11 ± .02	1.78 ± .01	392.9
9.958 ± .008	9.95 ± .01	12.51 ± .02	2.37 ± .01	491.8
9.958 ± .008	9.95 ± .01	12.51 ± .02	2.37 ± .01	464.0
9.958 ± .008	9.95 ± .01	11.92 ± .02	2.96 ± .01	550.3
9.958 ± .008	9.95 ± .01	11.92 ± .02	2.96 ± .01	513.5

Table VI - Reaction Times Showing
Decomposition of Sodium Sulfite Solution

Volumes of Reactants				Reaction Time
KIO_3	Na_2SO_3	H_2SO_4	H_2O	
9.958 ± .008	9.95 ± .01	11.92 ± .02	2.96 ± .01	758.5
9.958 ± .008	9.95 ± .01	12.51 ± .02	2.37 ± .01	625.8
9.958 ± .008	9.95 ± .01	13.11 ± .02	1.78 ± .01	511.6
9.958 ± .008	9.95 ± .01	13.70 ± .02	1.18 ± .01	397.7
9.958 ± .008	9.95 ± .01	14.29 ± .02	0.59 ± .01	289.6
9.958 ± .008	9.95 ± .01	14.89 ± .02	0.00	194.2

± .00001 M. The other reactants had the same concentrations as those used in the trials listed in Table V. The trials contained in Table VI are listed chronologically. The difference between Table V and Table VI is the order in which the trials of each set of reactants were run. In Table V the shortest reactions were run first and in Table VI the longest reactions were run first.

The time of the reaction is directly proportional to the sulfite concentration. Table V shows that the reaction time is decreasing between each pair of reactions. Therefore the sulfite concentration is decreasing. The same observation can be made by comparing the reaction times of the same trials in Table VI. The trial with the longest reaction time in Table VI is much longer than its counterpart in Table V.

To eliminate the air oxidation of the sulfite solution a dry box was tried initially. The amount of pipetting required and the limited space in the dry box made this an impractical solution. Thorten and Chapman described a simple apparatus for storing and utilizing air sensitive materials (34). Their apparatus is shown in Figure I. A is a nitrogen tank. The solution is stored in B. C is a buret with a three-way stopcock. The operation is simple and works well for titrations; however, the use of a buret is not conducive to making repeated precise additions.

Figure II on page 26 shows the apparatus, a modified version of the one shown in Figure I, which was used to

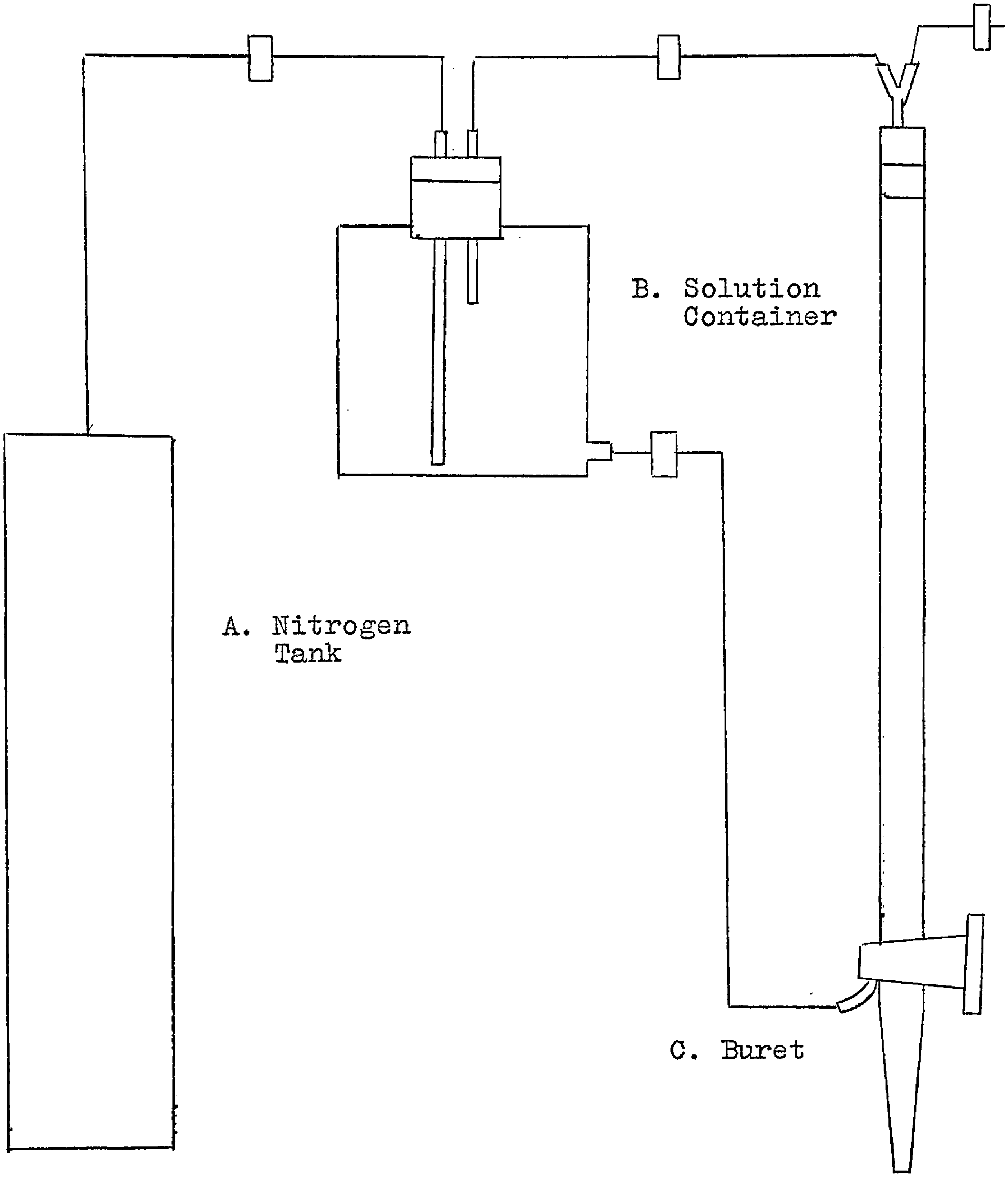


Figure I -
Thorten and Chapman Apparatus for
Storing Air Sensitive Materials

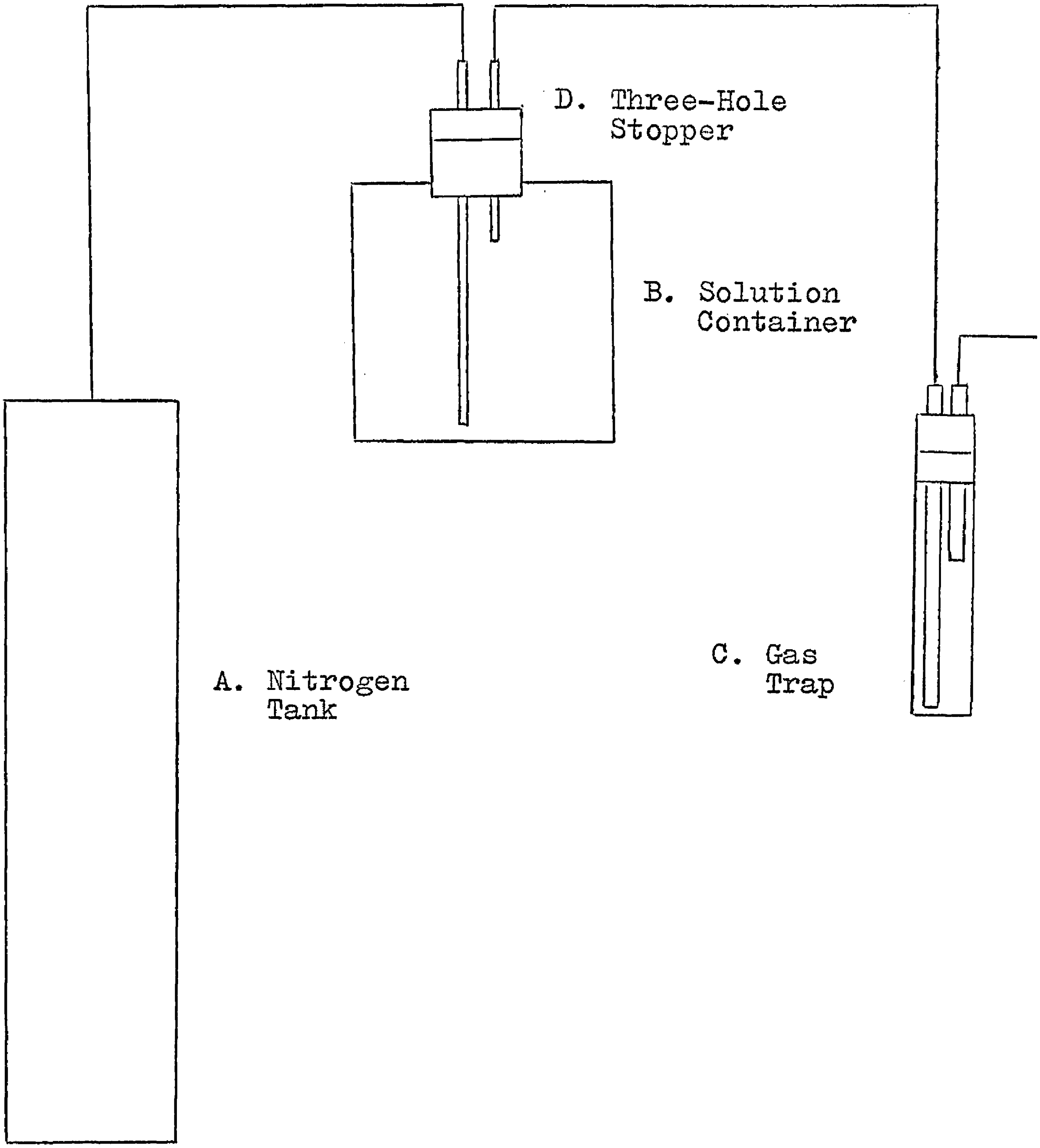


Figure II -
Modified Thorten and Chapman Apparatus
for Storing Air Sensitive Materials

preserve the sulfite solution. A is a tank of nitrogen. The solution container is B. A trap, C, is used to slow the loss of nitrogen. D is a three-hole stopper used in place of the two-hole stopper of Figure I. The third hole is enlarged enough to allow the insertion of a pipet. When not in use a cork stopper is inserted into the third hole and the system is sealed. The remaining two holes serve as the gas inlet and outlet sites.

In order to test the effectiveness of the apparatus a standardization procedure was developed for determining the concentration of the sulfite solution. The procedure is outlined in Appendix I. The results are shown in Table VII. The concentration of the sulfite solution did not change within the limits of experimental error during the tested period. The effectiveness of the apparatus can be verified by comparing the results in Table VII with previous results. On April 4, 1974, a sulfite solution was made having a concentration of 0.0200 ± .0001 M. The

Table VII - Concentration of Sulfite Solution at Various Dates

Date	Concentration of $SO_3^=$
May 2, 1974	0.0201 ± .0003 M.
May 9, 1974	0.0201 ± .0002 M.
May 24, 1974	0.0200 ± .0001 M.
June 14, 1974	0.0200 ± .0006 M.

same solution was again measured on April 25, 1974 and found to have a concentration of 0.0019 ± .0002 M. The solution was contained in a stoppered bottle during this time. The only difference between that solution and the one listed in Table VII was the absence of an inert atmosphere above the solution.

The starch solution was made using Mallinckrodt analytical reagent grade soluble starch. A mixture of 0.50 g. of starch and 25 ml. of water was added to 500 ml. of boiling distilled water. Approximately 1 g. of boric acid was added as a preservative.

In addition to water two other solvents were used. Baker Co. Baker grade 1,4-dioxane was used as well as ethylene glycol from the Fisher Scientific Co. The 20% dioxane and 80% water solution was made using weight percents. The same procedure was used for the 30% dioxane and 70% water solution. The ethylene glycol was distilled in order to remove any water and dissolved oxygen. However, because of the poor solubility of potassium iodate in ethylene glycol, it was necessary to add 5% water by volume.

A citrate-citric acid and an acetate-acetic acid buffer were also used during the study. The citrate-citric acid buffer was made using 10.51 ± .01 g. of Calbiochem analytical reagent grade citric acid assay 99.5% and 22.50 ± .01 g. of Baker's Analyzed reagent grade sodium acetate dihydrate assay 99.6%. The pH of the citrate-citric acid buffer was adjusted to the proper pH by adding either Baker's Analyzed reagent grade nitric acid assay 90.% or Baker's Analyzed reagent grade sodium hydroxide. The acetate-acetic acid buffer was made by adding 20.6185 ± .0004 g. of Baker's purified anhydrous sodium acetate to 14.3 ml. of Baker's U.S.P. grade glacial acetic acid. This mixture was then diluted to 250 ml. with distilled water.

A standard procedure was established for each trial. The combination hydrogen ion electrode was calibrated using Coleman certified buffer tablets having pH values of 2.00 ± .02, 3.00 ± .02, 5.00 ± .02 and 6.00 ± .02 at a temperature of 25° C. The silver wire and saturated calomel electrodes were calibrated using iodide solutions. The iodide solutions were made by taking one to one hundred serial dilutions of a 0.1003 ± .0003 M. potassium iodide solution made from Mallinckrodt analytical reagent grade potassium iodide. The iodide solution was standardized using the procedure outlined in Appendix I. A coating of silver iodide must be plated onto the silver wire since it is actually a silver-silver iodide electrode.

All solutions were added to a 100 ml. beaker using pipets which had been previously calibrated. The solution was stirred using a magnetic stirring plate. The same order of addition of the various solvents was followed consistently. The solvent was added first followed by the starch solution. The iodate solution was added next followed by the sulfuric acid solution. The volumes which were used of each reactant are listed in the various tables in the Results and Discussion section. At this point both the pH meter and recorder were started. The sulfite solution was then added from a pipet to initiate the reaction. The stopwatch was started when the solution in the beaker and the sulfite solution came in contact. The time of the reaction was measured between the time of the first addition of the sulfite solution and the first appearance of the iodine-starch complex. Occassionally, instead of using starch as an indicator the appearance of yellow triiodide signified the formation of excess iodine and the endpoint of the reaction.

The recorder response is proportional to the millivolt reading between the silver - silver iodide and saturated calomel electrodes. The millivolt response is proportional to the $\log(1/[I^-])$. In all of the Figures of recorder plotted values of millivolts vs. time the iodide concentration is also shown for illustrative purposes even though it would be more correct to label the axis $\log(1/[I^-])$. Throughout the thesis these Figures are refered to as iodide concentration vs. time in order to facilitate their discussion and comparison with other Figures.

Results and Discussion

A Comparison of the Reaction Time of the Landolt Reaction in Different Solvents

Four different solvents were used in this section. They were water, a solution of 20% 1,4-dioxane and 80% water, a solution of 30% 1,4-dioxane and 70% water and ethylene glycol. The primary requirement for a solvent was the ability to dissolve sulfuric acid, potassium iodate, sodium sulfite and soluble starch. The results for the system using ethylene glycol as a solvent is discussed first. The results are then shown for the Landolt reaction run in water and the water and dioxane solutions.

Because of the nature of the results of the ethylene glycol system, they are discussed first. Many factors were found which influenced the length of the reaction time of the Landolt reaction in ethylene glycol. The age of the solutions was very important. The potassium iodate solution was not stable which was indicated by a yellowing of the solution. This may have been due to the reduction of iodate to iodine and iodide which in turn formed triiodide ion. Air oxidation of the sodium sulfite also caused instability in that solution. The length of time between additions was critical. Because some of the iodate was reduced to iodide, addition of sulfuric acid

Table VIII - Reactant Concentrations[a]

Solutions	Solvents			
	80% Water 20% Dioxane	70% Water 30% Dioxane	Ethylene Glycol	Water
Potassium Iodate	.02000±.00002	.02005±.00002	.02003±.00002	.02000±.00001
Sodium Sulfite	.01991±.00002	.01996±.00002	.02000±.00002	.0200 ±.0001[c]
Sulfuric[b] Acid	0.99 ± 0.03	0.99 ± 0.03	0.097 ± .003	.0198 ± .0006[c]
Starch	0.25 g/250 ml	0.25 g/250 ml	not used	0.25 g/250 ml

a.) All concentrations are expressed in moles/liter unless otherwise stated.

b.) Concentration of sulfuric acid is expressed in terms of normality.

c.) Solution was standardized using the procedures outlined in Appendix I.

to the solvent and iodate solution initiated the Dushman reaction. The first reaction was bypassed. This made it necessary to add the sulfite and iodate solutions simultaneously.

The viscosity of ethylene glycol caused a number of problems. The stirring rate became very critical and had to be constant throughout the work. Addition of the sulfite solution from a pipet was very slow. If addition was too slow the endpoint was seen almost immediately indicating that the sulfite was being consummed faster than it was being added to the solution. These factors made consistent results impossible. Table IX is included as an example of the degree of variation in the reaction time. On the basis of the data in Table IX no further work was done using ethylene glycol as a solvent.

1,4-Dioxane is a polar molecule. Solutions containing as much as 50% dioxane and 50% water by weight dissolve enough potassium iodate to make a 0.02 M. solution (25). The concentrations of the individual reactants for the dioxane-water solvents are listed in Table VIII. Table X on page 36 contains the volumes of each reactant in milliliters along with the reaction time in seconds for the 20% dioxane - 80% water solvent system. Table XI, page 37, shows the total solution volume in milliliters and the concentrations of each reactant after mixing in moles/liter. The average reaction time in seconds is also listed. In the same manner the results for the 30% dioxane and 70% water

Table IX - Volumes of Reactants with Ethylene Glycol as Solvent

Volumes used of -				Reaction Time
KIO_3	Na_2SO_3	H_2SO_4	Solvent	
9.958 ± .008	9.95 ± .01	3.50 ± .02	0.00	286.7
9.958 ± .008	9.95 ± .01	3.50 ± .02	0.00	538.2
9.958 ± .008	9.95 ± .01	3.50 ± .02	0.00	294.6
9.958 ± .008	9.95 ± .01	3.50 ± .02	0.00	451.0
9.958 ± .008	9.95 ± .01	3.50 ± .02	0.00	398.1
9.958 ± .008	9.95 ± .01	3.50 ± .02	0.00	496.1
9.958 ± .008	9.95 ± .01	3.50 ± .02	0.00	69.8
9.958 ± .008	9.95 ± .01	3.50 ± .02	0.00	969.5

Table X - Volumes of Reactants using
20% Dioxane-80% Water as Solvent[c]

Set of Reactant Volumes	Volumes Used of KIO_3	 Na_2SO_3	 H^+	 Solvent	 Starch	Average Reaction Time
1	9.958±.008	9.95±.01	0.200±.001	9.94±.01	4.969±.005	107.± 5.[b]
2	9.958±.008	9.95±.01	0.200±.001	19.88±.02	4.969±.005	171.± 3.[b]
3	9.958±.008	9.95±.01	0.200±.001	29.82±.03	4.969±.005	234.± 4.[a]
4	19.92 ±.02	9.95±.01	0.200±.001	19.88±.02	4.969±.005	110.± 2.[a]
5	9.958±.008	19.90±.02	0.200±.001	19.88±.02	4.969±.005	368.±18.[a]
6	9.958±.008	9.95±.01	0.400±.002	19.88±.02	4.969±.005	54.± 2.[a]

a.) Average value for two trials.

b.) Average value for four trials.

c.) Results taken from laboratory notebook, pages 1-2.

Table XI - Concentrations of Reactants using 20% Dioxane-80% Water as Solvent[c]

Set of Reactant Volumes	Total Reaction Volume	KIO_3 x10^3	Na_2SO_3 x10^3	H^+ x10^3	Average Reaction Time
1	35.02±.02	5.69±.02	5.66±.02	5.7±.2	107.± 5.[b]
2	44.96±.04	4.43±.01	4.41±.01	4.4±.1	171.± 3.[b]
3	54.89±.05	3.63±.01	3.61±.01	3.6±.1	234.± 4.[a]
4	54.92±.05	7.25±.02	3.61±.01	3.6±.1	110.± 2.[a]
5	54.91±.05	3.63±.01	7.22±.02	3.6±.1	368.±18.[a]
6	45.16±.04	4.41±.01	4.38±.01	8.8±.2	54.± 2.[a]

a.) Average value for two trials.

b.) Average value for four trials.

c.) Results taken from laboratory notebook, pages 1-2.

solvent system are shown in Table XII and Table XIII which is on page 40. The values for the system using water as a solvent are shown in Table XIV on page 41 and in Table XV on page 42.

A consistent relationship was exhibited between the six sets of volumes of reactants for each of the three solvents. The one exception is the fifth set of volumes in which the sulfite concentration is doubled for the 30% dioxane - 70% water solvent system. When the volume used of each solvent was increased and the volume of the reactants was held constant, the reaction time increased. The addition of more sulfuric acid, as shown by the sixth set of reactant volumes, caused a decrease in the reaction time in the case of each solvent. The reaction time also decreased when the volume of iodate used was doubled. In the case in which water was the solvent and in the case of the solvent consisting of 20% dioxane - 80% water, the reaction time increased when the sulfite concentration increased. However for the 30% dioxane - 70% water solvent, increasing the sulfite concentration caused a decrease in the reaction time.

Table XVI on page 43 contains the average reaction time in seconds of each of the three solvents for the six different sets of volumes of reactants. The concentration values are the average molar concentrations of each reactant after mixing for the three solvents. The uncertainty in the average concentration reflects the maximum uncer-

Table XII - Volumes of Reactants using 30% Dioxane-70% Water as Solvent[c]

Set of Reactant Volumes	Volumes Used of					Average Reaction Time
	KIO_3	Na_2SO_3	H^+	Solvent	Starch	
1	9.958±.008	9.95±.01	0.200±.001	9.94±.01	4.969±.005	225.± 5.[a]
2	9.958±.008	9.95±.01	0.200±.001	19.88±.02	4.969±.005	234.±20.[b]
3	9.958±.008	9.95±.01	0.200±.001	29.82±.03	4.969±.005	356.±35.[b]
4	19.92 ±.02	9.95±.01	0.200±.001	19.88±.02	4.969±.005	141.± 7.[b]
5	9.958±.008	19.90±.02	0.200±.001	19.88±.02	4.969±.005	186.± 6.[a]

a.) Average value for two trials.

b.) Average value for three trials.

c.) Results are taken from laboratory notebook, pages 3-4.

Table XIII - Concentrations of Reactants using
30% Dioxane-70% Water as Solvent[c]

Set of Reactant Volumes	Total Reaction Volume	KIO_3 x10^3	Na_2SO_3 x10^3	H^+ x10^3	Average Reaction Time
1	35.02±.03	5.70±.02	5.67±.02	5.7±.2	225.± 5.[a]
2	44.96±.04	4.44±.01	4.42±.01	4.4±.1	234.±20.[b]
3	54.89±.05	3.64±.01	3.62±.01	3.6±.1	356.±35.[b]
4	54.92±.05	7.27±.02	3.62±.01	3.6±.1	131.± 7.[b]
5	54.91±.05	3.64±.01	7.23±.02	3.6±.1	186.± 6.[a]

a.) Average value of two trials.
b.) Average value of three trials.
c.) Results are taken from laboratory notebook, page 3-4.

Table XIV - Volumes of Reactants using
Water as Solvent[b]

Set of Reactant Volumes	Volumes Used of KIO_3	Na_2SO_3	H^+	Solvent	Starch	Average Reaction Time
1	9.958±.008	9.95±.01	9.94±.01	0.00	4.969±.005	60.4± .2[a]
2	9.958±.008	9.95±.01	9.94±.01	9.956±.004	4.969±.005	130. ± 4.[a]
3	9.958±.008	9.95±.01	9.94±.01	19.912±.008	4.969±.005	214.0± 0.1[a]
4	19.92± .02	9.95±.01	9.94±.01	9.956±.008	4.969±.005	87. ± 2.[a]
5	9.958±.02	9.95±.01	19.88±.02	9.956±.008	4.969±.005	40.2± 0.2[a]
6	9.958±.02	19.90±.02	9.94±.01	9.956±.008	4.969±.005	2774. ±22.[a]

a.) Average value of two trials.

b.) Results are taken from laboratory notebook, page 59.

Table XV - Concentrations of Reactants using Water as Solvent[b]

Set of Reactant Volumes	Total Reaction Volume	KIO_3 x10^3	Na_2SO_3 x10^3	H^+ x10^3	Average Reaction Time
1	34.82±.04	5.72±.02	5.72±.02	5.7±.2	60.4± 0.2[a]
2	44.77±.04	4.45±.02	4.45±.02	4.4±.1	130. ± 4.[a]
3	54.73±.05	3.64±.02	3.64±.02	3.6±.1	214.0± 0.1[a]
4	54.74±.05	7.28±.04	3.64±.02	3.6±.1	87. ± 2.[a]
5	54.71±.05	3.64±.02	3.64±.02	7.2±.2	40.2± 0.2[a]
6	54.72±.05	3.64±.02	7.27±.04	3.6±.1	2774. ±22.[a]

a.) Average value of two trials.

b.) Results are taken from laboratory notebook, page 59.

Table XVI - Comparison of Average Times of Reaction of Various Solvent Systems

Set of Reactant Concentrations	Concentrations of $(x10^3)$					
	KIO_3	Na_2SO_3	H^+	100% Water	20% Dioxane 80% Water	30% Dioxane 70% Water
1	5.70±.04	5.68±.06	5.7 ± .2	60.4± 0.2	107. ± 5.	225. ± 5.
2	4.44±.03	4.43±.04	4.4 ± .1	130. ± 4.	171. ± 3.	234. ±20.
3	3.64±.02	3.62±.04	3.6 ± .1	214.0± 0.1	234. ± 4.	356. ±35.
4	7.27±.05	3.62±.04	3.6 ± .1	87. ± 2.	110. ± 2.	141. ± 7.
5	3.64±.02[a]	3.64±.02[a]	7.2 ± .2[a]	40.2± 0.2	54. ± 2.	b
6	3.64±.02	7.24±.07	3.6 ± .1	2774. ±22.	368. ±18.	186. ± 6.

a.) Concentrations only of solutions with water as solvent.

b.) Value for the reaction time is not available.

tainty necessary to include the uncertainty in each of the three concentration values used to determine the average concentration. For the first five sets of reactant volumes the average reaction time increases in the order

30% dioxane-70% water > 20% dioxane-80% water > water

The order is reversed when the sulfite concentration is doubled and becomes

water > 20% dioxane-80% water > 30% dioxane-70% water

The Effect of Buffer Systems of Varying Values of pH on the Rate of the Landolt Reaction

The reaction was run in a citrate-citric acid buffer system. The system was chosen because a number of its dissociation constants are within the range of the pH values investigated. No allowance was made for the ionic strength of the buffered solution which changed as the pH of the buffer was adjusted. The results are shown in Table XVII. The volumes are in milliliters. The concentrations of reactants are listed in Table VIII in the column for the water solvent system. The reaction time is the average time of the reaction in seconds. The average was determined on the basis of three trials for each set of reactant volumes except in the case of the first set of reactant volumes which was determined from only two trials. The uncertainty is the standard deviation from the mean reaction time.

The pH of the buffer is in pH units. The uncertainty associated with the value reflects the uncertainty in the buffers used to calibrate the pH meter. The pH values listed in Table XVII are actually the initial pH values before the iodate and sulfite solutions were added. Because such a small amount of buffer was added, the pH of the solution did not remain constant throughout the

Table XVII - Reaction Times in Buffer Solutions of Varying pH Values

Volumes of -				pH of Buffer	Average Reaction Time
Starch	KIO_3	Na_2SO_3	Buffer		
4.969 ± .004	9.958 ± .008	9.95 ± .01	9.94 ± .01	2.25 ± .02	12.70± 0.01
4.969 ± .004	9.958 ± .008	9.95 ± .01	9.94 ± .01	2.50 ± .02	19.0 ± 0.2
4.969 ± .004	9.958 ± .008	9.95 ± .01	9.94 ± .01	2.75 ± .02	28.2 ± 0.2
4.969 ± .004	9.958 ± .008	9.95 ± .01	9.94 ± .01	3.00 ± .02	38.3 ± 0.2
4.969 ± .004	9.958 ± .008	9.95 ± .01	9.94 ± .01	3.25 ± .02	54.5 ± 0.1
4.969 ± .004	9.958 ± .008	9.95 ± .01	9.94 ± .01	3.50 ± .02	76.1 ± 1.4
4.969 ± .004	9.958 ± .008	9.95 ± .01	9.94 ± .01	3.75 ± .02	106.1 ± 0.6
4.969 ± .004	9.958 ± .008	9.95 ± .01	9.94 ± .01	4.00 ± .02	152.3 ± 0.4
4.969 ± .004	9.958 ± .008	9.95 ± .01	9.94 ± .01	4.25 ± .02	212. ± 1.
4.969 ± .004	9.958 ± .008	9.95 ± .01	9.94 ± .01	4.50 ± .02	308. ± 1.
4.969 ± .004	9.958 ± .008	9.95 ± .01	9.94 ± .01	4.90 ± .02	513. ± 4.
4.969 ± .004	9.958 ± .008	9.95 ± .01	9.94 ± .01	5.02 ± .02	663. ±19.

reaction. Table XVIII lists the values for the maximum and minimum pH values which were observed for each buffered system.

Figure III on page 49 is a recorder plot of the pH versus time for the Landolt reaction in a citrate-citric acid buffer. Figure IV on page 50 is a recorder plot for the iodide concentration versus time of the same reaction. The initial pH of this buffer solution was 4.25 ± .02 pH units. The expanded pH scale was used to accentuate the change in pH. The reason the system was not buffered adequately enough to prevent this change in pH was two-fold. An increased amount of buffer caused the reaction time to increase and produced a more gradual appearance of the endpoint as denoted by the blue color of the iodine-starch complex. This was a particular disadvantage at higher values of pH. The weakly buffered system did maintain a constant initial pH which was considered more important than a constant pH value throughout the reaction.

The range of pH values which were studied was limited to between 2.25 and 5.00 pH units. At pH values lower than 2.25 the length of the reaction is less than the time required to drain the pipet. Values greater than 5.00 could not be used because the endpoint was no longer distinct. Instead, it appeared very gradually, The end-point could not be detected potentiometrically because the change in hydrogen and iodide ion concentrations at the endpoint was too small.

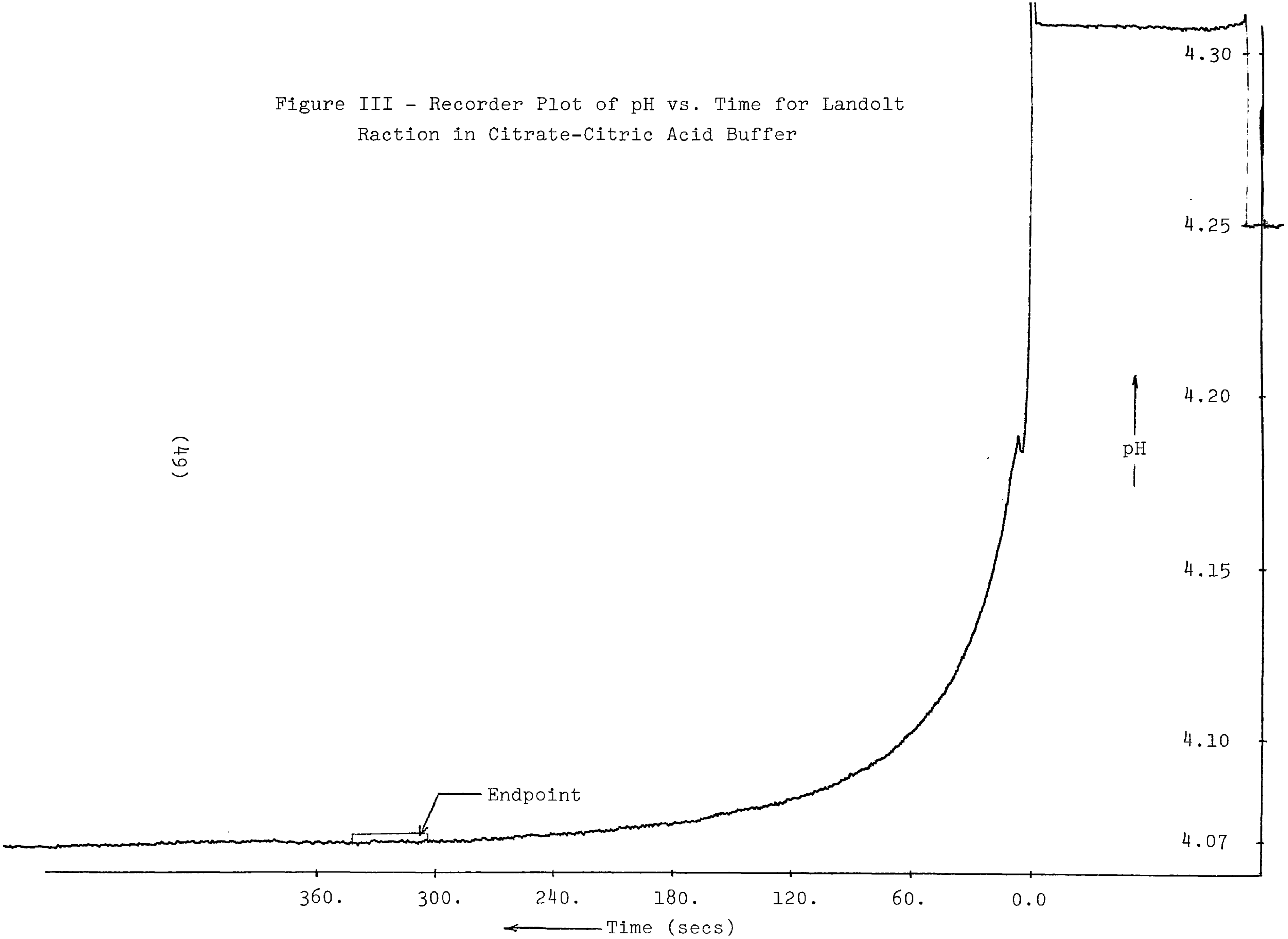
Table XVIII - Maximum and Minimum pH During the Landolt Reaction in a Citrate-Citric Acid Buffer

pH of Buffer	Maximum pH	Minimum pH
2.25 ± .02	2.45 ± .02[a]	2.18 ± .02[a]
2.50 ± .02	2.65 ± .02[b]	2.32 ± .02[b]
2.75 ± .02	2.86 ± .02[b]	2.55 ± .02[b]
3.00 ± .02	3.14 ± .02[b]	2.79 ± .02[b]
3.25 ± .02	3.33 ± .02[b]	3.04 ± .02[b]
3.50 ± .02	3.60 ± .02[b]	3.20 ± .02[b]
3.75 ± .02	3.81 ± .02[b]	3.49 ± .02[b]
4.00 ± .02		
4.25 ± .02	4.33 ± .04[b]	4.04 ± .03[b]
4.50 ± .02	4.60 ± .02[b]	4.14 ± .02[b]
4.90 ± .02		
5.02 ± .02	5.10 ± .02	4.78 ± .02[b]

a.) Average value determined from two trials.

b.) Average value determined from three trials.

Figure III - Recorder Plot of pH vs. Time for Landolt Raction in Citrate-Citric Acid Buffer



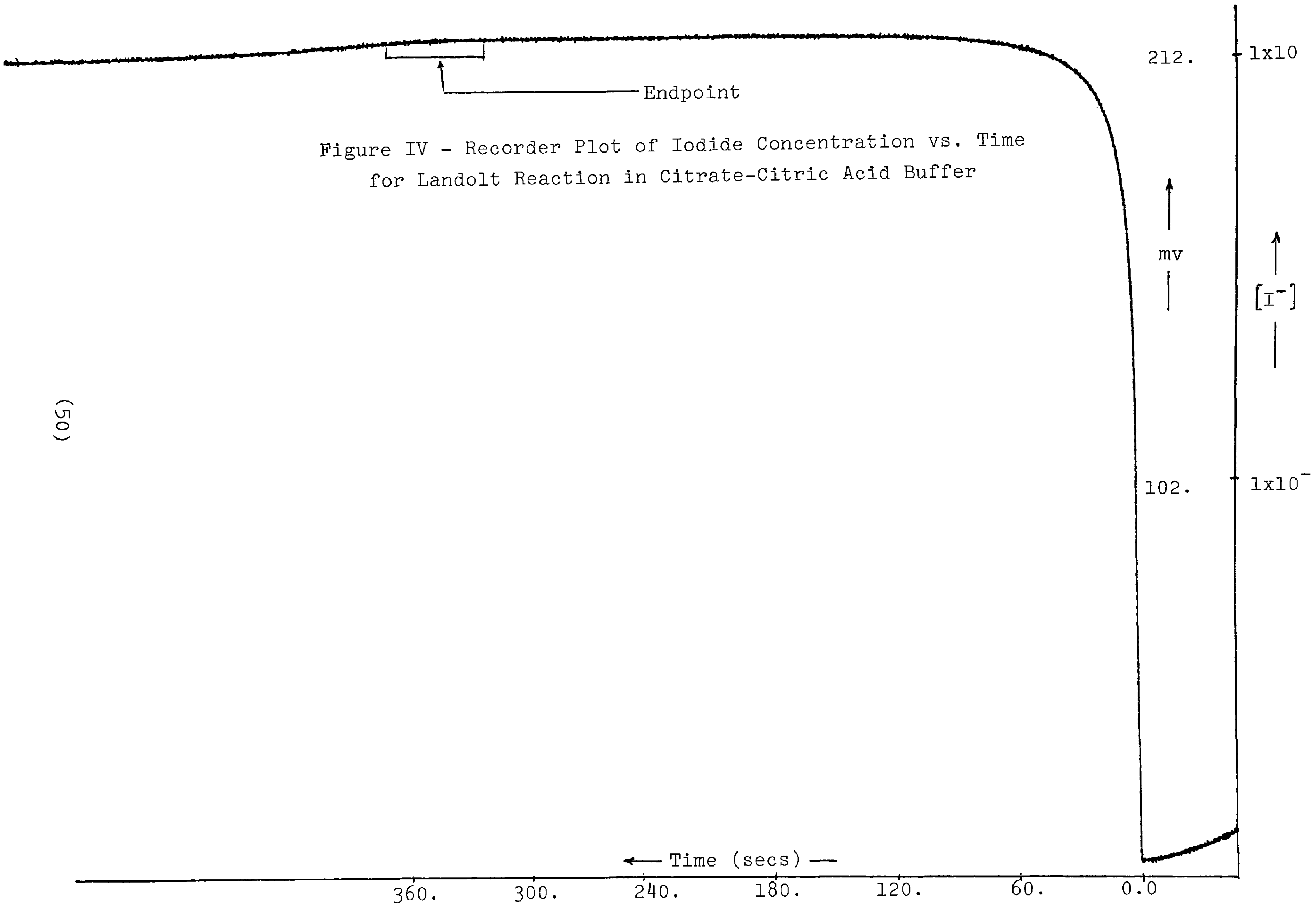


Figure IV - Recorder Plot of Iodide Concentration vs. Time for Landolt Reaction in Citrate-Citric Acid Buffer

Figure V shows a plot of Log t versus pH. The values plotted on the graph were taken from Table XVII on page 46. The graph is linear with the exception of the reaction times of the buffer systems having pH values greater than 4.75 ± .02 and less than 2.50 ± .02. The slope of the line is 0.59 ± .03. The y-intercept determined graphically is -0.17 ± .01. The equation for the line is Eq. (32).

$$\log t = 0.59\text{pH} + (-.17) \tag{32}$$

Taking the antilog of both sides of Eq. (32) gives Eq. (33).

$$t = .67(1/[H^+]^{.59}) \tag{33}$$

Table XVIIIa on page 53 is a comparison between the percent uncertainties in six sets of reactant volumes for an unbuffered system and in six sets of reactant volumes for a buffered system. The values for the unbuffered solutions were taken from Table XIV on page 41. The results were chosen because they represented the last set of reactions which were run in an unbuffered system. The first six sets of concentrations from Table XVII on page 46 were used to represent the buffered system. The average percent uncertainty for the unbuffered solutions 1.2 ± 1.0 % and the percent uncertainty for the buffered solution is 0.71 ± .56 %.

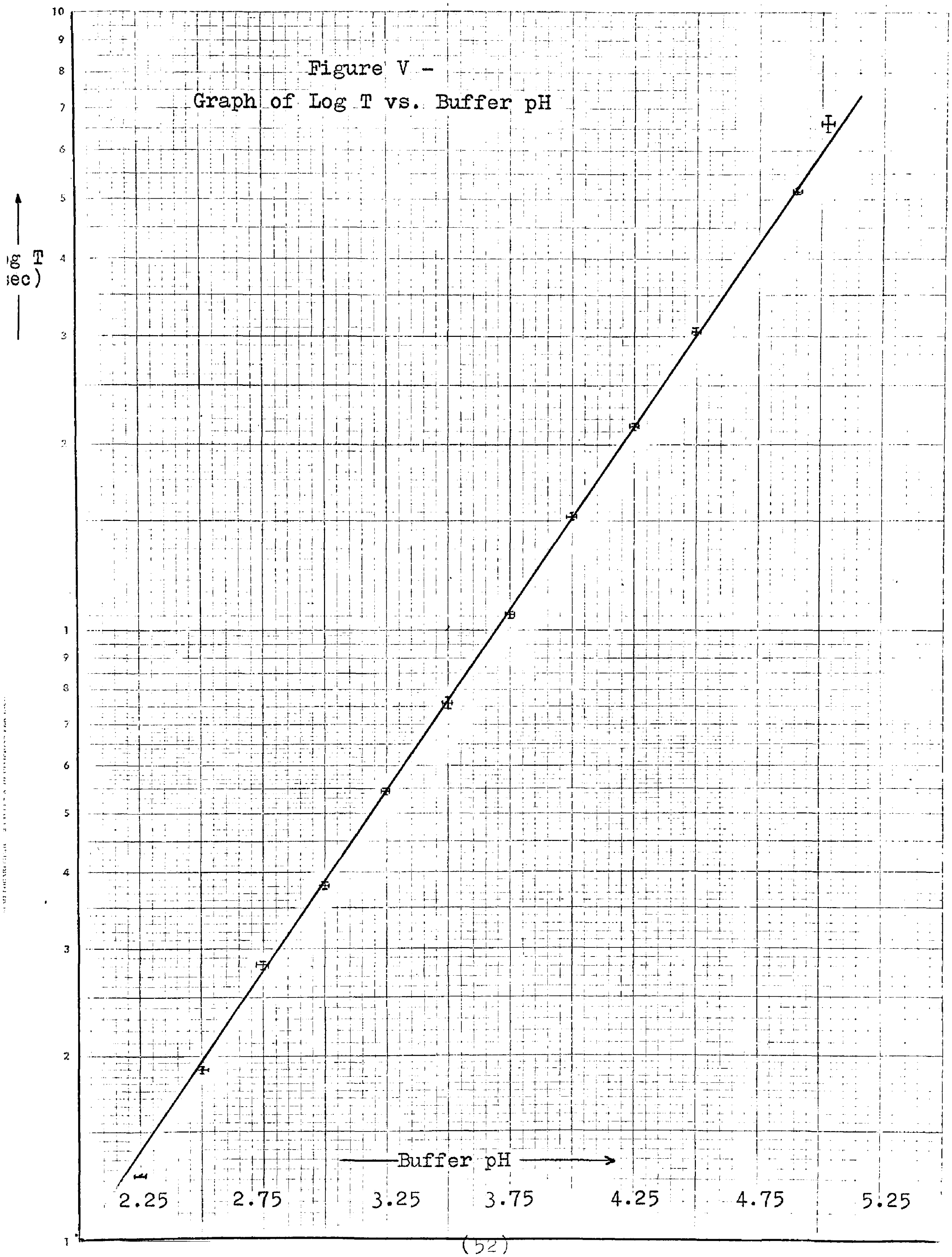


Figure V -

Graph of Log T vs. Buffer pH

Table XVIIIa - Comparison of Percent Uncertainty between Buffered and Unbuffered Systems

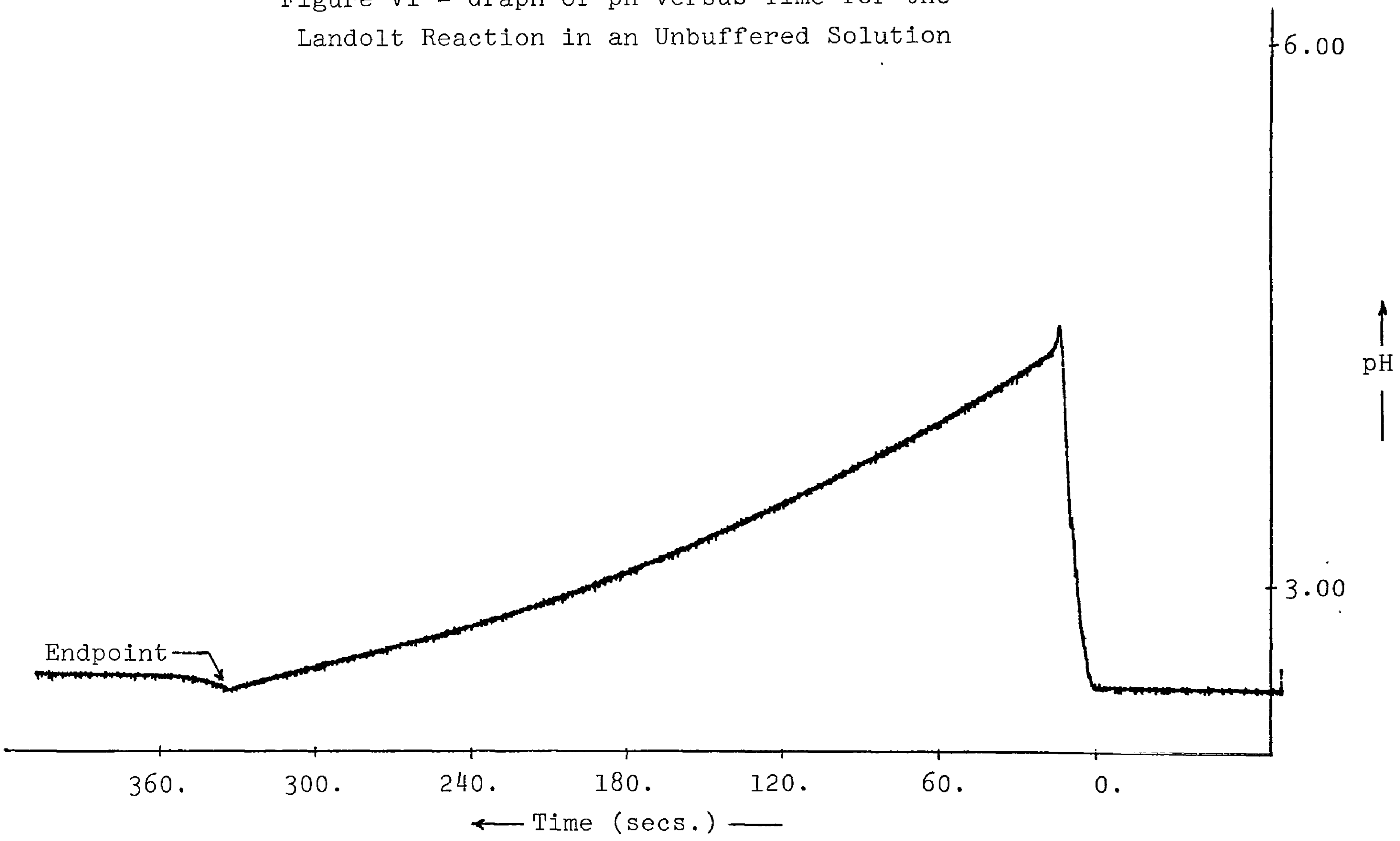
Unbuffered System		Buffered System	
Reaction Time (sec)	Percent Uncertainty	Reaction Time (sec)	Percent Uncertainty
60.4± 0.2	0.33%	12.70±.01	0.079%
130. ± 4.	3.1 %	19.0 ±.2	1.0 %
214.0± 0.1	0.047%	28.2 ±.2	0.71 %
87. ± 2.	2.3 %	38.3 ±.2	0.52 %
40.2± 0.2	0.50%	54.5 ±.1	0.18 %
2774. ±22.	0.80%	76.1 ±1.4	1.8 %

An Examination of the Rate Expressions for the Three Steps of the Landolt Reaction Through the Use of a Computer Simulation

This section is subdivided into two parts. The first part deals with the Landolt reaction in unbuffered solutions. The experimental results are presented first in the form of recorder drawn graphs of iodide concentration versus time and pH versus time. In order to verify the rate constants for Eq.(11) and Eq.(13) found in the literature, a computer simulation was used to produce a plot of the iodide concentration versus time. In the second part the same procedure is used for the buffered system.

Figure VI shows a graph which represents the pH of the solution at any time during the Landolt reaction. The pH value is in pH units and the time is in seconds. The curve is for a solution consisting of 9.958 ± .008 ml. of a 0.0200 ± .0001 m/l potassium iodate solution, 9.95 ± .01 ml. of a 0.02000 ± .00001 m/l sodium sulfite solution, 9.94 ± .01 ml. of a 0.0198 ± .0006 normal sulfuric acid solution, 29.85 ± .02 ml. of water and 4.969 ± .005 ml. of a starch solution. The concentrations of the solutions as well as the volumes of those solutions used in this section are the same as those just mentioned unless otherwise stated. Figure VII represents a plot of pH versus

Figure VI - Graph of pH versus Time for the Landolt Reaction in an Unbuffered Solution



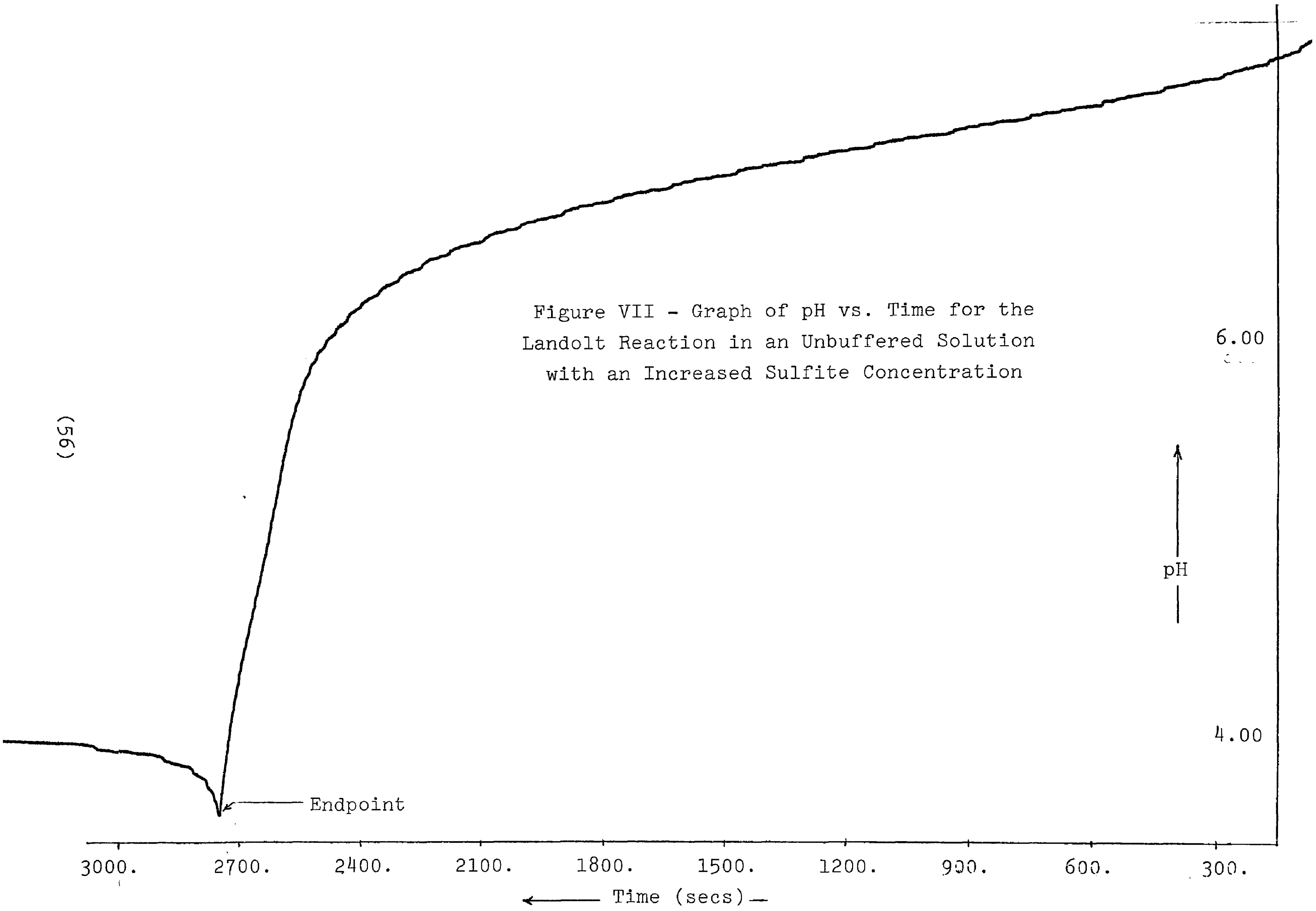


Figure VII - Graph of pH vs. Time for the Landolt Reaction in an Unbuffered Solution with an Increased Sulfite Concentration time for a reaction consisting of 9.958 ± .008 ml. of a 0.0200 ± .0001 m/l potassium iodate solution, 9.94 ± .01 ml. of a 0.0198 ± .0006 normal sulfuric acid solution, 19.90 ± .02 ml. of a 0.02000 ± .00001 m/l sodium sulfite solution, 9.95 ± .01 ml. of water and 4.969 ± .005 ml. of a starch solution. Figure VIII represents the plot of iodide concentration versus time for the Landolt reaction. The solution used is the same as the solution used to produce Figure VI.

In order to check the validity of the rate expressions found in the literature for Eqs. (1), (2) and (3) a computer simulation was written. A copy of the computer program is included in Appendix II. The program incorporated the rate expressions for each of the three reactions making up the Landolt reaction. The rate expressions which were used are Eqs. (11), (13) and (23) for Eqs. (1), (2) and (3) respectively. A subroutine calculates the concentrations of bisulfite, sulfite, and iodate for the given pH value and total sulfite and iodate concentrations. The dissociation constants used in the subrountine are listed in Table XIX on page 59. The data consisted of the pH values taken from Figure VI on page 55. In addition, the experimentally determined iodide concentrations represented in Figure VIII were introduced in order to compare the calculated iodide concentration with the experimental iodide concentration. The same initial concen-

Figure VIII - Graph of Iodide Concentration vs. Time for the Landolt Reaction in an Unbuffered Solution

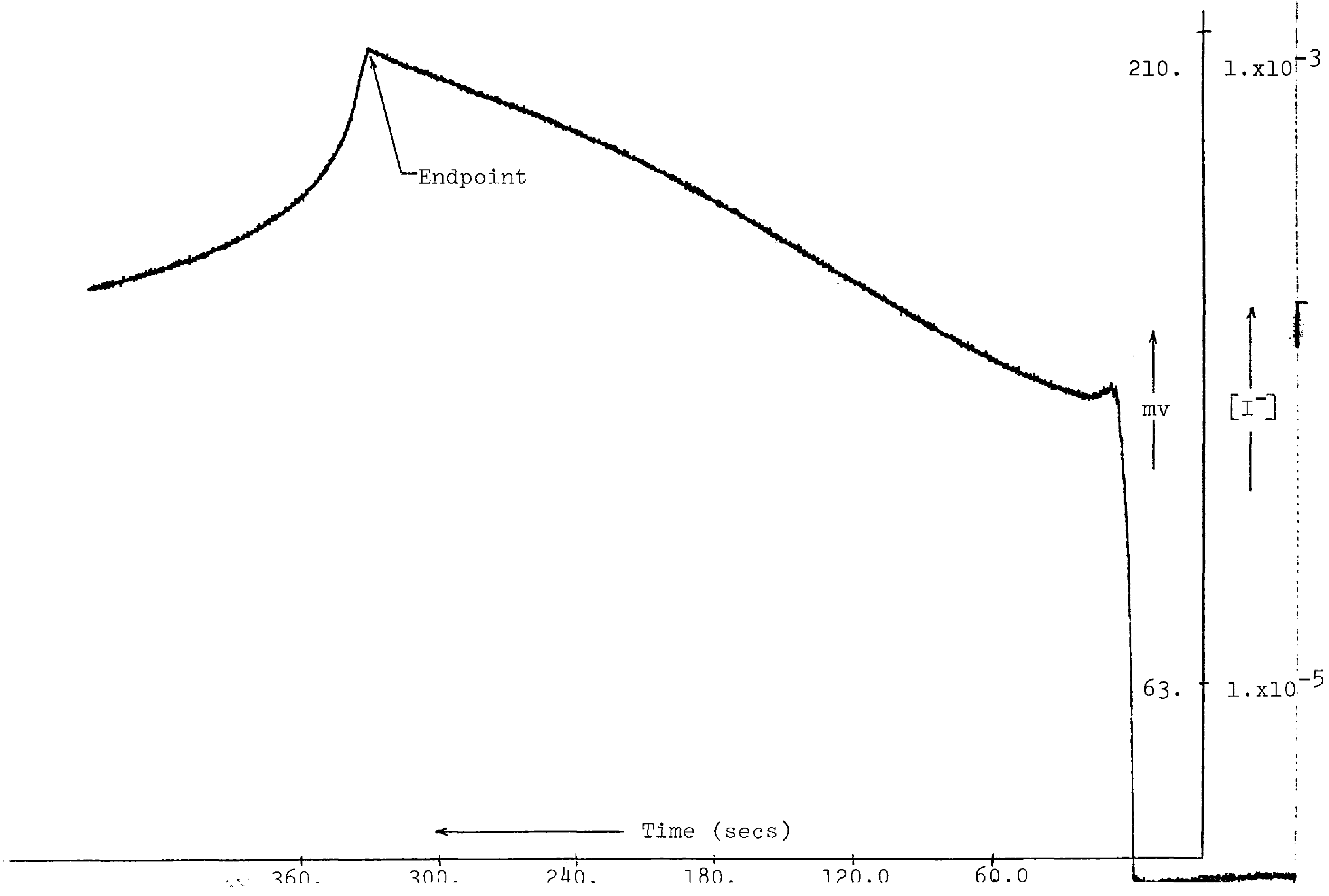


Table XIX - Dissociation Constants Used in Computer Program

Reactant	First Dissociation Constant	Second Dissociation Constant
HIO_3	1.7×10^{-1} (19)	
H_2SO_4		1.00×10^{-2} (15)
H_2SO_3	1.72×10^{-2} (32)	6.31×10^{-8} (32)

trations of the reactants that were used to produce Figures VI on page 55 and VIII on page 58 were used in the computer simulation.

A total of four rate constants are necessary in the program. Two rate constant, RC1 and RC2, are used in Eq. (11), the rate expression for Eq. (1). Two rate constants, RC3 and RC4, are used in Eq. (13), the rate expression for Eq. (2). The rate expression for Eq. (3) is an approximation due to its high velocity compared with the velocities of Eq. (1) and Eq. (2) and does not include a rate constant. Since it is a curve fitting program, provision has been made to vary these four rate constants.

The first output is the value for each of the four rate constants. These are followed by a table containing the solution pH, the time of the reaction, the iodide concentration after the first reaction, Eq. (1), the change in iodide concentration which results from reaction two, Eq. (2), the change in iodide concentration which results from the third reaction, Eq. (3), the total iodide concentration in the solution at time t and the experimental iodide concentration at the same time, t. Each line in the table corresponds to an increase in the reaction time of six seconds. This increment of time was chosen because it corresponds to one square of chart paper when the recorder is set at medium scan speed.

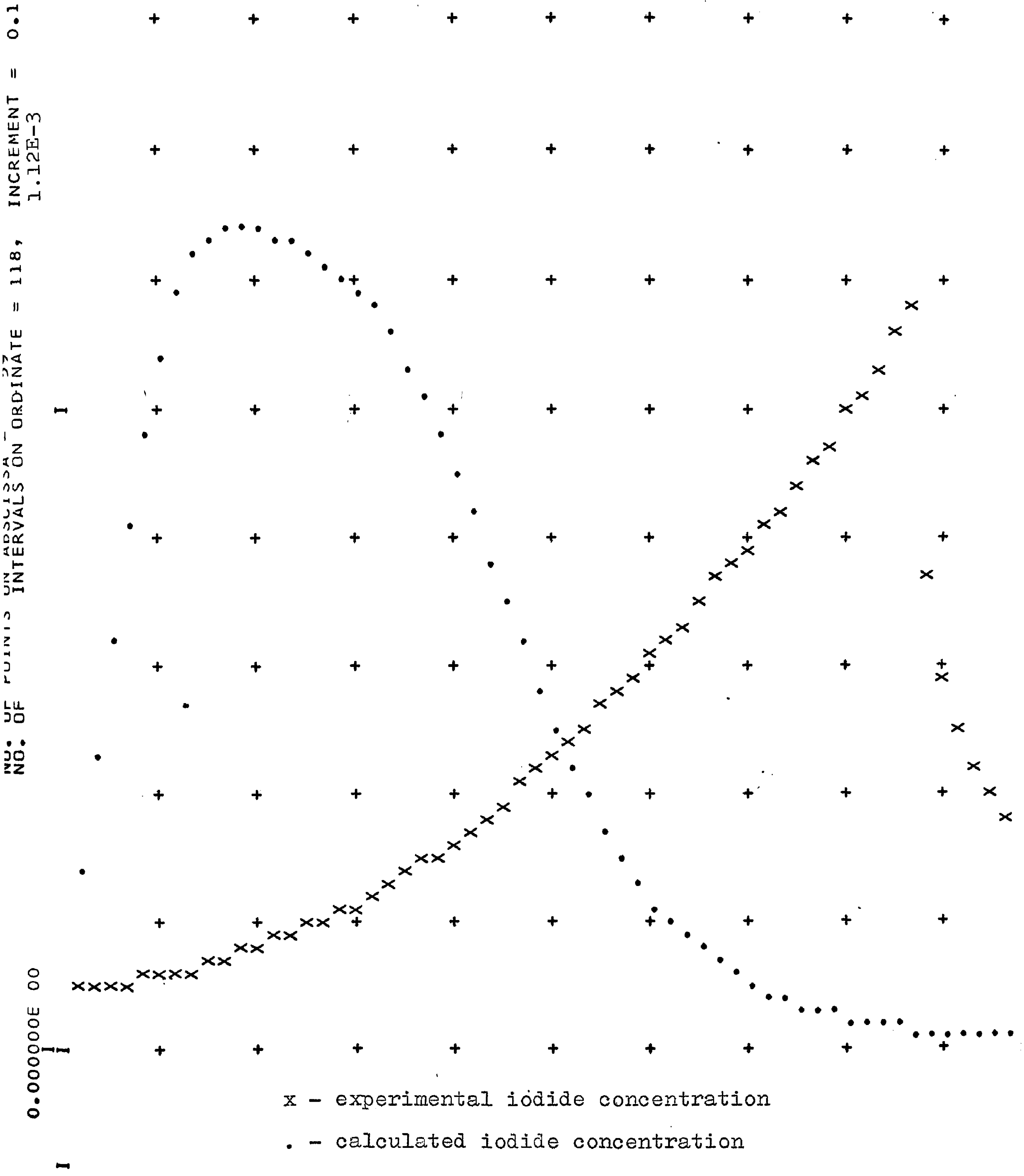
The experimental and calculated iodide concentrations were then plotted. The ordinate is the iodide concentration and the abscissa is the time. Each line on the abscissa represents a time change of six seconds. The experimental iodide concentration is represented by "X"'s and the calculated iodide concentration is shown by "."'s . Whenever the two curves intersect only one symbol, the symbol for the experimental iodide concentration, is printed. This format is followed in all of the computer printed tables and graphs which follow.

Table XX contains the results of the Landolt reaction using the same initial reactant concentrations as those used in producing Figure VIII on page 58. The rate expressions are Eqs. (11), (13) and (23). The time units on the rate constants have been converted from minutes to seconds. The calculations contained in Table XX are plotted in Figure IX on page 62 along with the data from Figure VIII which is on page 58.

Table XX - Results for Computer Simulation of Landolt Reaction Using Literature Values for Rate Constants

```
RC1 =       0.8830E 04      RC2 =       0.1120E 16
RC3 =       0.1270E 09      RC4 =       0.8110E 09
     PH           T(I)          CONI1         CONI2         CONI3       CONI(I)        EXPI
 0.4306E 01  0.1800E 02  0.1021E-03-0.1156E-08-0.2764E-06  0.1018E-03  0.7502E-04
 0.4256E 01  0.2400E 02  0.2256E-03-0.8499E-08  0.6575E-07  0.2256E-03  0.7720E-04
 0.4198E 01  0.3000E 02  0.3656E-03-0.3325E-07  0.7694E-07  0.3656E-03  0.8019E-04
 0.4140E 01  0.3600E 02  0.5112E-03-0.9370E-07  0.1389E-06  0.5113E-03  0.8252E-04
 0.4083E 01  0.4200E 02  0.6508E-03-0.2142E-06  0.2769E-06  0.6509E-03  0.8572E-04
 0.4025E 01  0.4800E 02  0.7741E-03-0.4224E-06  0.5223E-06  0.7742E-03  0.8905E-04
 0.3975E 01  0.5400E 02  0.8717E-03-0.7162E-06  0.8718E-06  0.8719E-03  0.9339E-04
 0.3934E 01  0.6000E 02  0.9410E-03-0.1076E-05  0.1301E-05  0.9412E-03  0.9888E-04
 0.3884E 01  0.6600E 02  0.9863E-03-0.1585E-05  0.1911E-05  0.9866E-03  0.1037E-03
 0.3851E 01  0.7200E 02  0.1011E-02-0.2075E-05  0.2498E-05  0.1011E-02  0.1088E-03
 0.3769E 01  0.7800E 02  0.1023E-02-0.3330E-05  0.4002E-05  0.1024E-02  0.1152E-03
 0.3744E 01  0.8400E 02  0.1026E-02-0.4018E-05  0.4827E-05  0.1027E-02  0.1219E-03
 0.3694E 01  0.9000E 02  0.1027E-02-0.5391E-05  0.0000E 00  0.1022E-02  0.1291E-03
 0.3661E 01  0.9600E 02  0.1022E-02-0.6596E-05  0.0000E 00  0.1015E-02  0.1367E-03
 0.3620E 01  0.1020E 03  0.1015E-02-0.8332E-05  0.0000E 00  0.1007E-02  0.1447E-03
 0.3579E 01  0.1080E 03  0.1007E-02-0.1045E-04  0.0000E 00  0.9963E-03  0.1532E-03
 0.3529E 01  0.1140E 03  0.9963E-03-0.1353E-04  0.0000E 00  0.9828E-03  0.1638E-03
 0.3488E 01  0.1200E 03  0.9828E-03-0.1669E-04  0.0000E 00  0.9661E-03  0.1751E-03
 0.3455E 01  0.1260E 03  0.9661E-03-0.1964E-04  0.0000E 00  0.9464E-03  0.1836E-03
 0.3413E 01  0.1320E 03  0.9464E-03-0.2379E-04  0.0000E 00  0.9226E-03  0.1944E-03
 0.3355E 01  0.1380E 03  0.9226E-03-0.3071E-04  0.0000E 00  0.8919E-03  0.2078E-03
 0.3314E 01  0.1440E 03  0.8919E-03-0.3604E-04  0.0000E 00  0.8559E-03  0.2221E-03
 0.3289E 01  0.1500E 03  0.8559E-03-0.3854E-04  0.0000E 00  0.8173E-03  0.2330E-03
 0.3240E 01  0.1560E 03  0.8173E-03-0.4568E-04  0.0000E 00  0.7717E-03  0.2467E-03
 0.3207E 01  0.1620E 03  0.7717E-03-0.4893E-04  0.0000E 00  0.7227E-03  0.2612E-03
 0.3165E 01  0.1680E 03  0.7227E-03-0.5349E-04  0.0000E 00  0.6692E-03  0.2765E-03
 0.3124E 01  0.1740E 03  0.6692E-03-0.5706E-04  0.0000E 00  0.6122E-03  0.2928E-03
 0.3099E 01  0.1800E 03  0.6122E-03-0.5497E-04  0.0000E 00  0.5572E-03  0.3100E-03
 0.3074E 01  0.1860E 03  0.5572E-03-0.5239E-04  0.0000E 00  0.5048E-03  0.3314E-03
 0.3041E 01  0.1920E 03  0.5048E-03-0.5134E-04  0.0000E 00  0.4535E-03  0.3508E-03
 0.3008E 01  0.1980E 03  0.4535E-03-0.4942E-04  0.0000E 00  0.4041E-03  0.3680E-03
 0.2967E 01  0.2040E 03  0.4041E-03-0.4858E-04  0.0000E 00  0.3555E-03  0.3859E-03
 0.2942E 01  0.2100E 03  0.3555E-03-0.4312E-04  0.0000E 00  0.3124E-03  0.4047E-03
 0.2909E 01  0.2160E 03  0.3124E-03-0.3964E-04  0.0000E 00  0.2727E-03  0.4285E-03
 0.2893E 01  0.2220E 03  0.2727E-03-0.3334E-04  0.0000E 00  0.2394E-03  0.4537E-03
 0.2860E 01  0.2280E 03  0.2394E-03-0.3057E-04  0.0000E 00  0.2088E-03  0.4713E-03
 0.2843E 01  0.2340E 03  0.2088E-03-0.2566E-04  0.0000E 00  0.1832E-03  0.4896E-03
 0.2802E 01  0.2400E 03  0.1832E-03-0.2439E-04  0.0000E 00  0.1588E-03  0.5086E-03
 0.2777E 01  0.2460E 03  0.1588E-03-0.2098E-04  0.0000E 00  0.1378E-03  0.5334E-03
 0.2760E 01  0.2520E 03  0.1378E-03-0.1741E-04  0.0000E 00  0.1204E-03  0.5594E-03
 0.2744E 01  0.2580E 03  0.1204E-03-0.1464E-04  0.0000E 00  0.1057E-03  0.5867E-03
 0.2711E 01  0.2640E 03  0.1057E-03-0.1342E-04  0.0000E 00  0.9233E-04  0.6037E-03
 0.2686E 01  0.2700E 03  0.9233E-04-0.1170E-04  0.0000E 00  0.8063E-04  0.6271E-03
 0.2678E 01  0.2760E 03  0.8063E-04-0.9454E-05  0.0000E 00  0.7117E-04  0.6515E-03
 0.2653E 01  0.2820E 03  0.7117E-04-0.8419E-05  0.0000E 00  0.6275E-04  0.6768E-03
 0.2612E 01  0.2880E 03  0.6275E-04-0.8064E-05  0.0000E 00  0.5469E-04  0.7031E-03
 0.2595E 01  0.2940E 03  0.5469E-04-0.6735E-05  0.0000E 00  0.4795E-04  0.7373E-03
 0.2579E 01  0.3000E 03  0.4795E-04-0.5692E-05  0.0000E 00  0.4226E-04  0.7587E-03
 0.2554E 01  0.3060E 03  0.4226E-04-0.5045E-05  0.0000E 00  0.3722E-04  0.7957E-03
 0.2529E 01  0.3120E 03  0.3722E-04-0.4463E-05  0.0000E 00  0.3275E-04  0.8188E-03
 0.2504E 01  0.3180E 03  0.3275E-04-0.3942E-05  0.0000E 00  0.2881E-04  0.8506E-03
 0.2488E 01  0.3240E 03  0.2881E-04-0.3349E-05  0.0000E 00  0.2546E-04  0.8920E-03
 0.2463E 01  0.3300E 03  0.2546E-04-0.2981E-05  0.0000E 00  0.2248E-04  0.9267E-03
 0.2479E 01  0.3360E 03  0.2248E-04-0.2193E-05  0.0000E 00  0.2029E-04  0.5980E-03
 0.2496E 01  0.3420E 03  0.2029E-04-0.1685E-05  0.0000E 00  0.1860E-04  0.4580E-03
 0.2521E 01  0.3480E 03  0.1860E-04-0.1287E-05  0.0000E 00  0.1732E-04  0.3933E-03
 0.2529E 01  0.3540E 03  0.1732E-04-0.1092E-05  0.0000E 00  0.1623E-04  0.3442E-03
 0.2529E 01  0.3600E 03  0.1623E-04-0.9742E-06  0.0000E 00  0.1525E-04  0.3130E-03
 0.2529E 01  0.3660E 03  0.1525E-04-0.8747E-06  0.0000E 00  0.1438E-04  0.2900E-03
```

Figure IX - Plot of Results from Computer Simulation of Landolt Reaction Using Literature Values for Rate Constants



The four rate constants were then varied until the shape of the calculated iodide curve approached that of the experimental curve. The best approximation is shown in Table XXI and Figure X on pages 64 and 65 respectively. Instead of determining the uncertainty associated with each rate constant, the range of values over which suitable results may be obtained is given. The range of each rate constant was determined by varying each rate constant individually while holding constant the remaining three rate constants and examining the effect of the variation on the graph of the iodide concentration.

Table XXII on page 66 and Figure XI on page 67 show the result of varying the first rate constant in the rate expression for Eq. (1). The time of the reaction is six seconds shorter than the experimentally determined results. On this basis the first rate constant of Eq. (1) has a value of 7. and can approximate the experimental curve within a range of 6. to 8. This same procedure was used for the second rate constant of Eq. (11). The results are listed in Table XXIII on page 68 and in Figure XII on page 69. The value of the second rate constant of Eq. (11) is $1. \times 10^{15}$ within the range of $5. \times 10^{14}$ to $5. \times 10^{15}$. The units on both the first and second rate constants are $l^2 moles^{-2} sec^{-1}$ and $l^4 moles^{-4} sec^{-1}$ respectively.

The value for the first rate constant in Eq. (13) is $1. \times 10^7$ and approximates the experimental curve within the range of $9. \times 10^6$ to $2. \times 10^7$. The rate constant has

Table XXII - Determination of the Upper Limit on Range of First Rate Constant of Eq. (11)

```
RC1 =        0.7000E 01     RC2 =        0.1120E 16
RC3 =        0.1000E 08     RC4 =        0.2000E 07
    PH          T(I)          CONI1         CONI2          CONI3        CONI(I)        EXPI
 0.4306E 01 0.1800E 02 0.3169E-05-0.9065E-13-0.2778E-06 0.2891E-05 0.7502E-04
 0.4256E 01 0.2400E 02 0.6834E-05-0.6614E-12 0.5556E-07 0.6890E-05 0.7720E-04
 0.4198E 01 0.3000E 02 0.1160E-04-0.2978E-11 0.3704E-07 0.1163E-04 0.8019E-04
 0.4140E 01 0.3600E 02 0.1708E-04-0.9825E-11 0.2647E-07 0.1711E-04 0.8252E-04
 0.4083E 01 0.4200E 02 0.2329E-04-0.2718E-10 0.1987E-07 0.2331E-04 0.8572E-04
 0.4025E 01 0.4800E 02 0.3020E-04-0.6694E-10 0.1551E-07 0.3021E-04 0.8905E-04
 0.3975E 01 0.5400E 02 0.3778E-04-0.1459E-09 0.1252E-07 0.3779E-04 0.9339E-04
 0.3934E 01 0.6000E 02 0.4601E-04-0.2871E-09 0.1045E-07 0.4602E-04 0.9888E-04
 0.3884E 01 0.6600E 02 0.5486E-04-0.5580E-09 0.9087E-08 0.5487E-04 0.1037E-03
 0.3851E 01 0.7200E 02 0.6429E-04-0.9636E-09 0.8279E-08 0.6430E-04 0.1088E-03
 0.3769E 01 0.7800E 02 0.7434E-04-0.2023E-08 0.8533E-08 0.7435E-04 0.1152E-03
 0.3744E 01 0.8400E 02 0.8491E-04-0.3158E-08 0.9081E-08 0.8491E-04 0.1219E-03
 0.3694E 01 0.9000E 02 0.9599E-04-0.5389E-08 0.1110E-07 0.9600E-04 0.1291E-03
 0.3661E 01 0.9600E 02 0.1075E-03-0.8335E-08 0.1409E-07 0.1075E-03 0.1367E-03
 0.3620E 01 0.1020E 03 0.1195E-03-0.1314E-07 0.1939E-07 0.1195E-03 0.1447E-03
 0.3579E 01 0.1080E 03 0.1320E-03-0.2035E-07 0.2767E-07 0.1320E-03 0.1532E-03
 0.3529E 01 0.1140E 03 0.1448E-03-0.3227E-07 0.4165E-07 0.1448E-03 0.1638E-03
 0.3488E 01 0.1200E 03 0.1581E-03-0.4860E-07 0.6096E-07 0.1581E-03 0.1751E-03
 0.3455E 01 0.1260E 03 0.1716E-03-0.6957E-07 0.8588E-07 0.1716E-03 0.1836E-03
 0.3413E 01 0.1320E 03 0.1856E-03-0.1023E-06 0.1250E-06 0.1856E-03 0.1944E-03
 0.3355E 01 0.1380E 03 0.1999E-03-0.1609E-06 0.1951E-06 0.1999E-03 0.2078E-03
 0.3314E 01 0.1440E 03 0.2146E-03-0.2324E-06 0.2807E-06 0.2146E-03 0.2221E-03
 0.3289E 01 0.1500E 03 0.2295E-03-0.3082E-06 0.3715E-06 0.2296E-03 0.2330E-03
 0.3240E 01 0.1560E 03 0.2448E-03-0.4549E-06 0.5474E-06 0.2449E-03 0.2467E-03
 0.3207E 01 0.1620E 03 0.2604E-03-0.6178E-06 0.7428E-06 0.2605E-03 0.2612E-03
 0.3165E 01 0.1680E 03 0.2763E-03-0.8661E-06 0.1041E-05 0.2764E-03 0.2765E-03
 0.3124E 01 0.1740E 03 0.2925E-03-0.1207E-05 0.1450E-05 0.2927E-03 0.2928E-03
 0.3099E 01 0.1800E 03 0.3089E-03-0.1551E-05 0.1862E-05 0.3092E-03 0.3100E-03
 0.3074E 01 0.1860E 03 0.3255E-03-0.1980E-05 0.2377E-05 0.3259E-03 0.3314E-03
 0.3041E 01 0.1920E 03 0.3424E-03-0.2613E-05 0.3137E-05 0.3429E-03 0.3508E-03
 0.3008E 01 0.1980E 03 0.3596E-03-0.3435E-05 0.4122E-05 0.3603E-03 0.3680E-03
 0.2967E 01 0.2040E 03 0.3773E-03-0.4674E-05 0.5609E-05 0.3782E-03 0.3859F-03
 0.2942E 01 0.2100E 03 0.3952E-03-0.5872E-05 0.7047E-05 0.3964E-03 0.4047E-03
 0.2909E 01 0.2160E 03 0.4136E-03-0.7639E-05 0.9167E-05 0.4151E-03 0.4285E-03
 0.2893E 01 0.2220E 03 0.4321E-03-0.9175E-05 0.1101E-04 0.4340E-03 0.4537E-03
 0.2860E 01 0.2280E 03 0.4511E-03-0.1186E-04 0.1423E-04 0.4535E-03 0.4713E-03
 0.2843E 01 0.2340E 03 0.4704E-03-0.1416E-04 0.1699E-04 0.4733E-03 0.4896E-03
 0.2802E 01 0.2400E 03 0.4904E-03-0.1892E-04 0.2271E-04 0.4942E-03 0.5086E-03
 0.2777E 01 0.2460E 03 0.5113E-03-0.2341E-04 0.2809E-04 0.5159E-03 0.5334E-03
 0.2760E 01 0.2520E 03 0.5326E-03-0.2783E-04 0.3339E-04 0.5382E-03 0.5594E-03
 0.2744E 01 0.2580E 03 0.5545E-03-0.3300E-04 0.3960E-04 0.5611E-03 0.5867E-03
 0.2711E 01 0.2640E 03 0.5773E-03-0.4218E-04 0.5061E-04 0.5857E-03 0.6037E-03
 0.2686E 01 0.2700E 03 0.6015E-03-0.5193E-04 0.6231E-04 0.6119E-03 0.6271E-03
 0.2678E 01 0.2760E 03 0.6268E-03-0.5923E-04 0.7107E-04 0.6387E-03 0.6515E-03
 0.2653E 01 0.2820E 03 0.6530E-03-0.7276E-04 0.8731E-04 0.6676E-03 0.6768E-03
 0.2612E 01 0.2880E 03 0.6816E-03-0.9660E-04 0.1159E-03 0.7009E-03 0.7031E-03
 0.2595E 01 0.2940E 03 0.7138E-03-0.1150E-03 0.1380E-03 0.7368E-03 0.7373E-03
 0.2579E 01 0.3000E 03 0.7484E-03-0.1371E-03 0.1645E-03 0.7758E-03 0.7587E-03
 0.2554E 01 0.3060E 03 0.7861E-03-0.1699E-03 0.2038E-03 0.8201E-03 0.7957E-03
 0.2529E 01 0.3120E 03 0.8287E-03-0.2115E-03 0.2538E-03 0.8710E-03 0.8188E-03
 0.2504E 01 0.3180E 03 0.8775E-03-0.2647E-03 0.3176E-03 0.9305E-03 0.8506E-03
 0.2488E 01 0.3240E 03 0.9345E-03-0.3211E-03 0.3854E-03 0.9987E-03 0.8920E-03
 0.2463E 01 0.3300E 03 0.9999E-03-0.4064E-03 0.4877E-03 0.1081E-02 0.9267E-03
 0.2479E 01 0.3360E 03 0.1081E-02-0.4310E-03 0.0000E 00 0.6502E-03 0.5980E-03
 0.2496E 01 0.3420E 03 0.6502E-03-0.1407E-03 0.0000E 00 0.5094E-03 0.4580E-03
 0.2521E 01 0.3480E 03 0.5094E-03-0.7733E-04 0.0000E 00 0.4321E-03 0.3933E-03
 0.2529E 01 0.3540E 03 0.4321E-03-0.5404E-04 0.0000E 00 0.3781E-03 0.3442E-03
 0.2529E 01 0.3600E 03 0.3781E-03-0.4181E-04 0.0000E 00 0.3362E-03 0.3130E-03
 0.2529E 01 0.3660E 03 0.3362E-03-0.3347E-04 0.0000E 00 0.3028E-03 0.2900E-03
```

Figure X - Plot of Results from Computer Simulation of Landolt Reaction Using Adjusted Values for Rate Constants

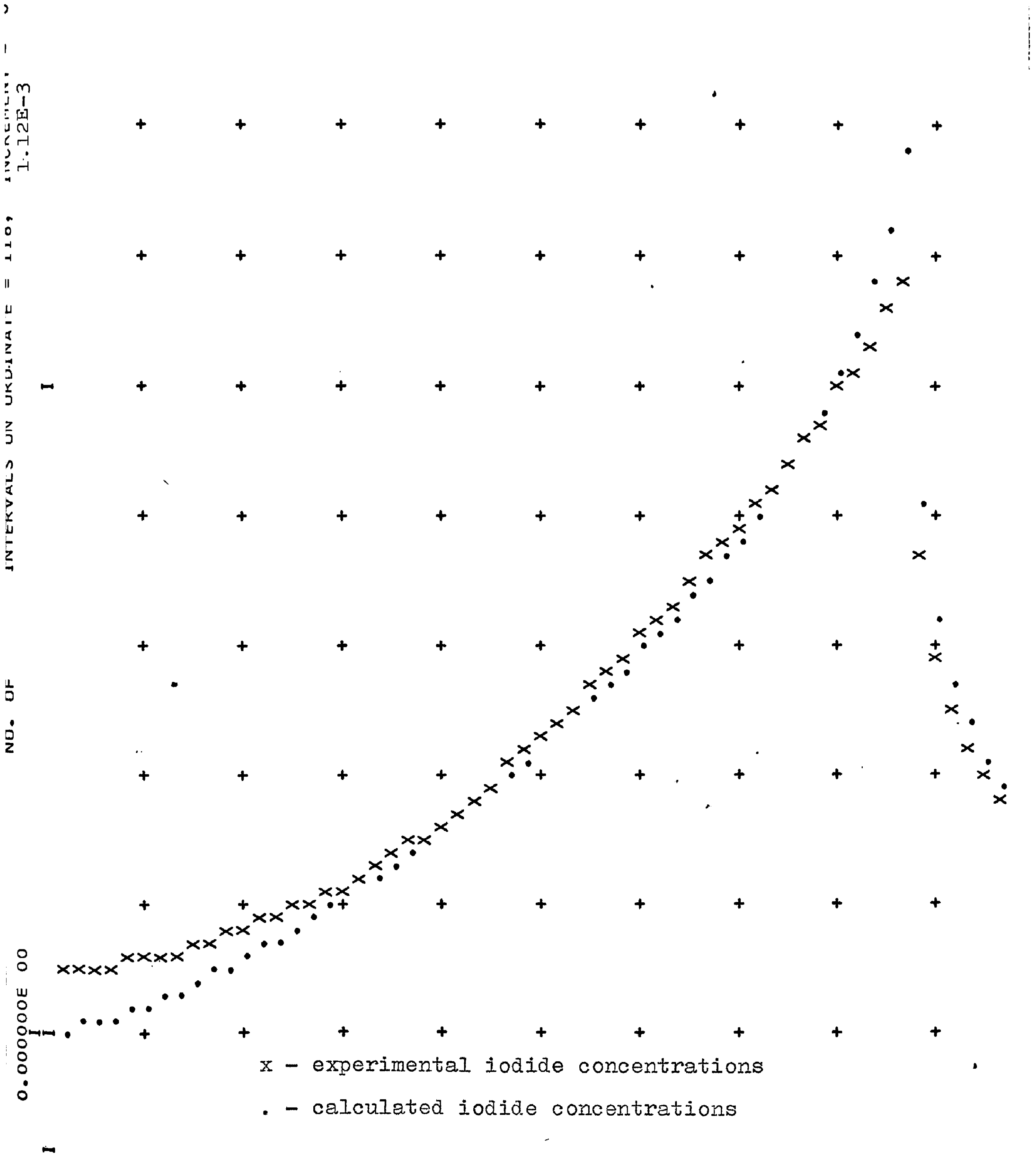


Table XXI - Results for Computer Simulation of Landolt Reaction Using Adjusted Rate Constants

```
RC1 =        0.8000E 01      RC2 =        0.1120E 16
RC3 =        0.1000E 08      RC4 =        0.2000E 07
    PH           T(I)          CONI1          CONI2          CONI3        CONI(I)         EXPI
 0.4306E 01  0.1800E 02  0.3180E-05-0.9130E-13-0.2778E-06  0.2902E-05  0.7502E-04
 0.4256E 01  0.2400E 02  0.6861E-05-0.6666E-12  0.5556E-07  0.6917E-05  0.7720E-04
 0.4198E 01  0.3000E 02  0.1164E-04-0.3002E-11  0.3704E-07  0.1168E-04  0.8019E-04
 0.4140E 01  0.3600E 02  0.1716E-04-0.9911E-11  0.2647E-07  0.1719E-04  0.8252E-04
 0.4083E 01  0.4200E 02  0.2340E-04-0.2744E-10  0.1987E-07  0.2342E-04  0.8572E-04
 0.4025E 01  0.4800E 02  0.3035E-04-0.6763E-10  0.1551E-07  0.3037E-04  0.8905E-04
 0.3975E 01  0.5400E 02  0.3799E-04-0.1475E-09  0.1252E-07  0.3800E-04  0.9339E-04
 0.3934E 01  0.6000E 02  0.4628E-04-0.2905E-09  0.1045E-07  0.4629E-04  0.9888E-04
 0.3884E 01  0.6600E 02  0.5521E-04-0.5651E-09  0.9096E-08  0.5522E-04  0.1037E-03
 0.3851E 01  0.7200E 02  0.6473E-04-0.9768E-09  0.8295E-08  0.6474E-04  0.1088E-03
 0.3769E 01  0.7800E 02  0.7490E-04-0.2053E-08  0.8569E-08  0.7490E-04  0.1152E-03
 0.3744E 01  0.8400E 02  0.8558E-04-0.3208E-08  0.9141E-08  0.8559E-04  0.1219E-03
 0.3694E 01  0.9000E 02  0.9681E-04-0.5481E-08  0.1121E-07  0.9682E-04  0.1291E-03
 0.3661E 01  0.9600E 02  0.1085E-03-0.8486E-08  0.1427E-07  0.1085E-03  0.1367E-03
 0.3620E 01  0.1020E 03  0.1207E-03-0.1339E-07  0.1970E-07  0.1207E-03  0.1447E-03
 0.3579E 01  0.1080E 03  0.1333E-03-0.2076E-07  0.2817E-07  0.1333E-03  0.1532E-03
 0.3529E 01  0.1140E 03  0.1464E-03-0.3297E-07  0.4249E-07  0.1464E-03  0.1638E-03
 0.3488E 01  0.1200E 03  0.1599E-03-0.4971E-07  0.6230E-07  0.1599E-03  0.1751E-03
 0.3455E 01  0.1260E 03  0.1738E-03-0.7126E-07  0.8792E-07  0.1738E-03  0.1836E-03
 0.3413E 01  0.1320E 03  0.1880E-03-0.1049E-06  0.1281E-06  0.1880E-03  0.1944E-03
 0.3355E 01  0.1380E 03  0.2027E-03-0.1653E-06  0.2004E-06  0.2028E-03  0.2078E-03
 0.3314E 01  0.1440E 03  0.2178E-03-0.2391E-06  0.2888E-06  0.2179E-03  0.2221E-03
 0.3289E 01  0.1500E 03  0.2332E-03-0.3176E-06  0.3828E-06  0.2332E-03  0.2330E-03
 0.3240E 01  0.1560E 03  0.2489E-03-0.4696E-06  0.5651E-06  0.2490E-03  0.2467E-03
 0.3207E 01  0.1620E 03  0.2650E-03-0.6388E-06  0.7681E-06  0.2651E-03  0.2612E-03
 0.3165E 01  0.1680E 03  0.2814E-03-0.8971E-06  0.1078E-05  0.2816E-03  0.2765E-03
 0.3124E 01  0.1740E 03  0.2983E-03-0.1253E-05  0.1505E-05  0.2985E-03  0.2928E-03
 0.3099E 01  0.1800E 03  0.3153E-03-0.1612E-05  0.1935E-05  0.3157E-03  0.3100E-03
 0.3074E 01  0.1860E 03  0.3326E-03-0.2061E-05  0.2474E-05  0.3330E-03  0.3314E-03
 0.3041E 01  0.1920E 03  0.3501E-03-0.2725E-05  0.3271E-05  0.3507E-03  0.3508E-03
 0.3008E 01  0.1980E 03  0.3681E-03-0.3587E-05  0.4305E-05  0.3688E-03  0.3680E-03
 0.2967E 01  0.2040E 03  0.3865E-03-0.4889E-05  0.5867E-05  0.3875E-03  0.3859E-03
 0.2942E 01  0.2100E 03  0.4053E-03-0.6151E-05  0.7382E-05  0.4065E-03  0.4047E-03
 0.2909E 01  0.2160E 03  0.4245E-03-0.8013E-05  0.9617E-05  0.4261E-03  0.4285E-03
 0.2893E 01  0.2220E 03  0.4439E-03-0.9638E-05  0.1157E-04  0.4458E-03  0.4537E-03
 0.2860E 01  0.2280E 03  0.4637E-03-0.1247E-04  0.1497E-04  0.4662E-03  0.4713E-03
 0.2843E 01  0.2340E 03  0.4840E-03-0.1491E-04  0.1789E-04  0.4869E-03  0.4896E-03
 0.2802E 01  0.2400E 03  0.5049E-03-0.1994E-04  0.2393E-04  0.5089E-03  0.5086E-03
 0.2777E 01  0.2460E 03  0.5268E-03-0.2470E-04  0.2964E-04  0.5317E-03  0.5334E-03
 0.2760E 01  0.2520E 03  0.5491E-03-0.2938E-04  0.3526E-04  0.5550E-03  0.5594E-03
 0.2744E 01  0.2580E 03  0.5720E-03-0.3487E-04  0.4185E-04  0.5789E-03  0.5867E-03
 0.2711E 01  0.2640E 03  0.5958E-03-0.4459E-04  0.5351E-04  0.6047E-03  0.6037E-03
 0.2686E 01  0.2700E 03  0.6211E-03-0.5493E-04  0.6591E-04  0.6321E-03  0.6271E-03
 0.2678E 01  0.2760E 03  0.6475E-03-0.6267E-04  0.7520E-04  0.6600E-03  0.6515E-03
 0.2653E 01  0.2820E 03  0.6748E-03-0.7700E-04  0.9240E-04  0.6902E-03  0.6768E-03
 0.2612E 01  0.2880E 03  0.7046E-03-0.1022E-03  0.1227E-03  0.7250E-03  0.7031E-03
 0.2595E 01  0.2940E 03  0.7381E-03-0.1217E-03  0.1461E-03  0.7624E-03  0.7373E-03
 0.2579E 01  0.3000E 03  0.7740E-03-0.1450E-03  0.1740E-03  0.8030E-03  0.7587E-03
 0.2554E 01  0.3060E 03  0.8130E-03-0.1796E-03  0.2155E-03  0.8490E-03  0.7957E-03
 0.2529E 01  0.3120E 03  0.8571E-03-0.2234E-03  0.2680E-03  0.9018E-03  0.8188E-03
 0.2504E 01  0.3180E 03  0.9076E-03-0.2793E-03  0.3351E-03  0.9634E-03  0.8506E-03
 0.2488E 01  0.3240E 03  0.9663E-03-0.3383E-03  0.4060E-03  0.1034E-02  0.8920E-03
 0.2463E 01  0.3300E 03  0.1034E-02-0.4275E-03  0.0000E 00  0.6065E-03  0.9267E-03
 0.2479E 01  0.3360E 03  0.6065E-03-0.1330E-03  0.0000E 00  0.4735E-03  0.5980E-03
 0.2496E 01  0.3420E 03  0.4735E-03-0.7547E-04  0.0000E 00  0.3980E-03  0.4580E-03
 0.2521E 01  0.3480E 03  0.3980E-03-0.4807E-04  0.0000E 00  0.3499E-03  0.3933E-03
 0.2529E 01  0.3540E 03  0.3499E-03-0.3621E-04  0.0000E 00  0.3137E-03  0.3442E-03
 0.2529E 01  0.3600E 03  0.3137E-03-0.2947E-04  0.0000E 00  0.2843E-03  0.3130E-03
 0.2529E 01  0.3660E 03  0.2843E-03-0.2452E-04  0.0000E 00  0.2598E-03  0.2900E-03
```

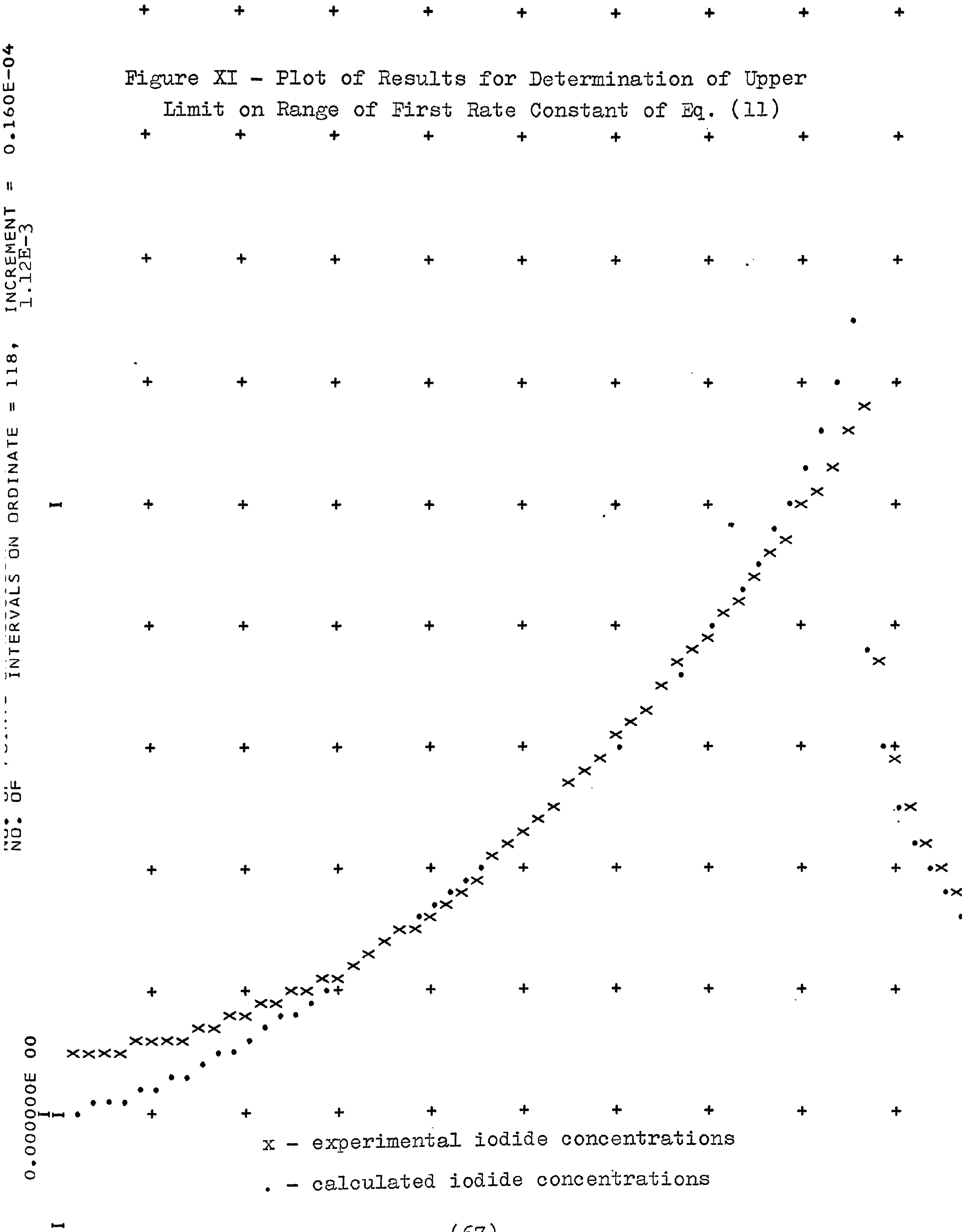


Figure XI - Plot of Results for Determination of Upper Limit on Range of First Rate Constant of Eq. (11)

Table XXIII - Determination of the Upper Limit on Range of Second Rate Constant of Eq. (11)

```
RC1 =        0.7000E 01        RC2 =        0.5000E 16
RC3 =        0.1000E 08        RC4 =        0.2000E 07
     PH            T(I)            CONI1           CONI2          CONI3         CONI(I)         EXPI
 0.4306E 01 0.1800E 02 0.1387E-04-0.1732E-11-0.2778E-06 0.1360E-04 0.7502E-04
 0.4256E 01 0.2400E 02 0.3041E-04-0.1299E-10 0.5557E-07 0.3046E-04 0.7720E-04
 0.4198E 01 0.3000E 02 0.4987E-04-0.5438E-10 0.3710E-07 0.4990E-04 0.8019E-04
 0.4140E 01 0.3600E 02 0.7154E-04-0.1692E-09 0.2666E-07 0.7157E-04 0.8252E-04
 0.4083E 01 0.4200E 02 0.9505E-04-0.4421E-09 0.2037E-07 0.9507E-04 0.8572E-04
 0.4025E 01 0.4800E 02 0.1200E-03-0.1026E-08 0.1666E-07 0.1200E-03 0.8905E-04
 0.3975E 01 0.5400E 02 0.1461E-03-0.2104E-08 0.1487E-07 0.1461E-03 0.9339E-04
 0.3934E 01 0.6000E 02 0.1729E-03-0.3887E-08 0.1476E-07 0.1729E-03 0.9888E-04
 0.3884E 01 0.6600E 02 0.2002E-03-0.7073E-08 0.1691E-07 0.2002E-03 0.1037E-03
 0.3851E 01 0.7200E 02 0.2277E-03-0.1143E-07 0.2084E-07 0.2277E-03 0.1088E-03
 0.3769E 01 0.7800E 02 0.2551E-03-0.2238E-07 0.3296E-07 0.2551E-03 0.1152E-03
 0.3744E 01 0.8400E 02 0.2822E-03-0.3259E-07 0.4440E-07 0.2822E-03 0.1219E-03
 0.3694E 01 0.9000E 02 0.3090E-03-0.5186E-07 0.6686E-07 0.3090E-03 0.1291E-03
 0.3661E 01 0.9600E 02 0.3352E-03-0.7479E-07 0.9383E-07 0.3352E-03 0.1367E-03
 0.3620E 01 0.1020E 03 0.3608E-03-0.1099E-06 0.1355E-06 0.3608E-03 0.1447E-03
 0.3579E 01 0.1080E 03 0.3857E-03-0.1589E-06 0.1939E-06 0.3857E-03 0.1532E-03
 0.3529E 01 0.1140E 03 0.4099E-03-0.2352E-06 0.2851E-06 0.4099E-03 0.1638E-03
 0.3488E 01 0.1200E 03 0.4333E-03-0.3307E-06 0.3995E-06 0.4333E-03 0.1751E-03
 0.3455E 01 0.1260E 03 0.4558E-03-0.4428E-06 0.5337E-06 0.4559E-03 0.1836E-03
 0.3413E 01 0.1320E 03 0.4777E-03-0.6096E-06 0.7337E-06 0.4778E-03 0.1944E-03
 0.3355E 01 0.1380E 03 0.4987E-03-0.8975E-06 0.1079E-05 0.4989E-03 0.2078E-03
 0.3314E 01 0.1440E 03 0.5191E-03-0.1215E-05 0.1460E-05 0.5193E-03 0.2221E-03
 0.3289E 01 0.1500E 03 0.5387E-03-0.1514E-05 0.1818E-05 0.5390E-03 0.2330E-03
 0.3240E 01 0.1560E 03 0.5576E-03-0.2100E-05 0.2521E-05 0.5580E-03 0.2467E-03
 0.3207E 01 0.1620E 03 0.5759E-03-0.2684E-05 0.3223E-05 0.5765E-03 0.2612E-03
 0.3165E 01 0.1680E 03 0.5937E-03-0.3547E-05 0.4258E-05 0.5944E-03 0.2765E-03
 0.3124E 01 0.1740E 03 0.6109E-03-0.4666E-05 0.5600E-05 0.6119E-03 0.2928E-03
 0.3099E 01 0.1800E 03 0.6277E-03-0.5665E-05 0.6799E-05 0.6288E-03 0.3100E-03
 0.3074E 01 0.1860E 03 0.6440E-03-0.6852E-05 0.8223E-05 0.6454E-03 0.3314E-03
 0.3041E 01 0.1920E 03 0.6599E-03-0.8579E-05 0.1030E-04 0.6616E-03 0.3508E-03
 0.3008E 01 0.1980E 03 0.6755E-03-0.1071E-04 0.1286E-04 0.6777E-03 0.3680E-03
 0.2967E 01 0.2040E 03 0.6910E-03-0.1386E-04 0.1663E-04 0.6938E-03 0.3859E-03
 0.2942E 01 0.2100E 03 0.7065E-03-0.1659E-04 0.1991E-04 0.7098E-03 0.4047E-03
 0.2909E 01 0.2160E 03 0.7220E-03-0.2059E-04 0.2471E-04 0.7261E-03 0.4285E-03
 0.2893E 01 0.2220E 03 0.7375E-03-0.2365E-04 0.2838E-04 0.7423E-03 0.4537E-03
 0.2860E 01 0.2280E 03 0.7531E-03-0.2925E-04 0.3510E-04 0.7590E-03 0.4713E-03
 0.2843E 01 0.2340E 03 0.7691E-03-0.3352E-04 0.4022E-04 0.7758E-03 0.4896E-03
 0.2802E 01 0.2400E 03 0.7853E-03-0.4299E-04 0.5159E-04 0.7939E-03 0.5086E-03
 0.2777E 01 0.2460E 03 0.8028E-03-0.5116E-04 0.6140E-04 0.8130E-03 0.5334E-03
 0.2760E 01 0.2520E 03 0.8210E-03-0.5862E-04 0.7035E-04 0.8327E-03 0.5594E-03
 0.2744E 01 0.2580E 03 0.8398E-03-0.6715E-04 0.8058E-04 0.8532E-03 0.5867E-03
 0.2711E 01 0.2640E 03 0.8596E-03-0.8297E-04 0.9956E-04 0.8762E-03 0.6037E-03
 0.2686E 01 0.2700E 03 0.8816E-03-0.9894E-04 0.1187E-03 0.9014E-03 0.6271E-03
 0.2678E 01 0.2760E 03 0.9057E-03-0.1096E-03 0.1315E-03 0.9276E-03 0.6515E-03
 0.2653E 01 0.2820E 03 0.9310E-03-0.1309E-03 0.1571E-03 0.9572E-03 0.6768E-03
 0.2612E 01 0.2880E 03 0.9595E-03-0.1692E-03 0.2031E-03 0.9933E-03 0.7031E-03
 0.2595E 01 0.2940E 03 0.9944E-03-0.1967E-03 0.2361E-03 0.1034E-02 0.7373E-03
 0.2579E 01 0.3000E 03 0.1034E-02-0.2295E-03 0.0000E 00 0.8043E-03 0.7587E-03
 0.2554E 01 0.3060E 03 0.8043E-03-0.1551E-03 0.0000E 00 0.6492E-03 0.7957E-03
 0.2529E 01 0.3120E 03 0.6492E-03-0.1135E-03 0.0000E 00 0.5357E-03 0.8188E-03
 0.2504E 01 0.3180E 03 0.5357E-03-0.8717E-04 0.0000E 00 0.4485E-03 0.8506E-03
 0.2488E 01 0.3240E 03 0.4485E-03-0.6652E-04 0.0000E 00 0.3820E-03 0.8920E-03
 0.2463E 01 0.3300E 03 0.3820E-03-0.5463E-04 0.0000E 00 0.3273E-03 0.9267E-03
 0.2479E 01 0.3360E 03 0.3273E-03-0.3766E-04 0.0000E 00 0.2897E-03 0.5980E-03
 0.2496E 01 0.3420E 03 0.2897E-03-0.2772E-04 0.0000E 00 0.2620E-03 0.4580E-03
 0.2521E 01 0.3480E 03 0.2620E-03-0.2053E-04 0.0000E 00 0.2414E-03 0.3933E-03
 0.2529E 01 0.3540E 03 0.2414E-03-0.1704E-04 0.0000E 00 0.2244E-03 0.3442E-03
 0.2529E 01 0.3600E 03 0.2244E-03-0.1494E-04 0.0000E 00 0.2095E-03 0.3130E-03
 0.2529E 01 0.3660E 03 0.2095E-03-0.1321E-04 0.0000E 00 0.1963E-03 0.2900E-03
```

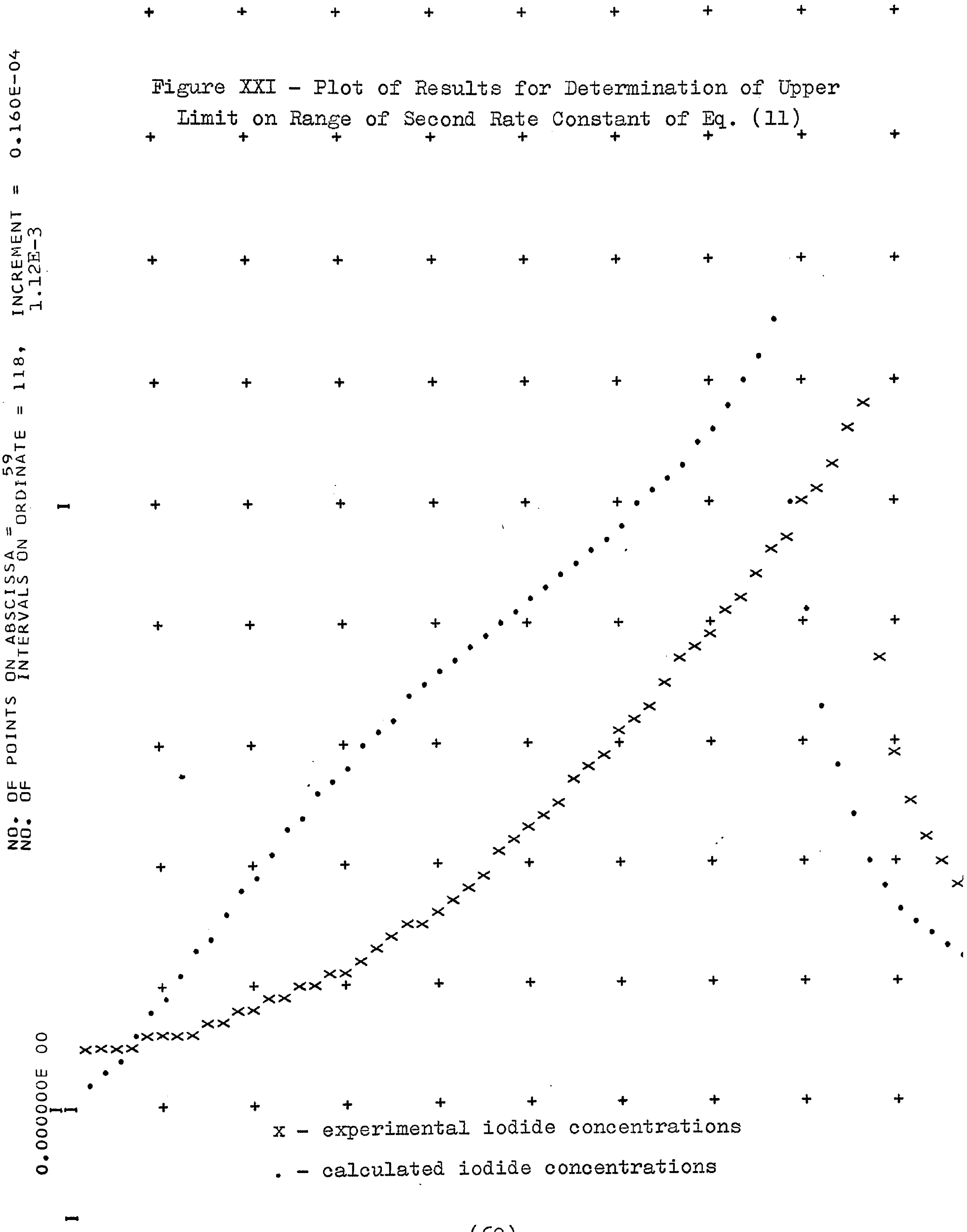


Figure XXI - Plot of Results for Determination of Upper Limit on Range of Second Rate Constant of Eq. (11)

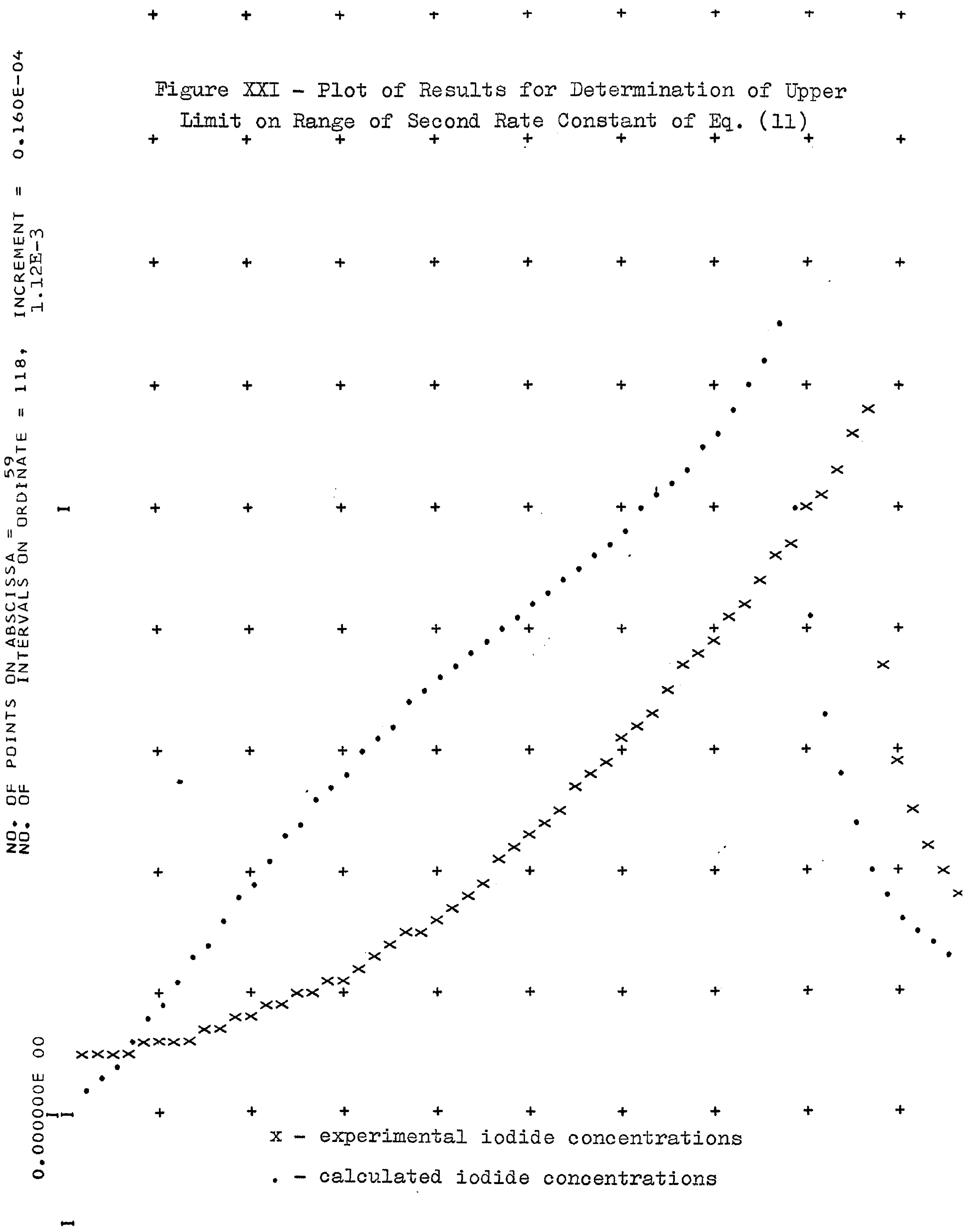


Figure XXI - Plot of Results for Determination of Upper Limit on Range of Second Rate Constant of Eq. (11)

units of l^4moles^{-4}sec^{-1}. Moving near the upper limit of the range of the rate constant causes the reaction time for the calculated iodide curve to be too short when compared to the experimental value. These results are shown in Table XXIV on page 71 and in Figure XIII on page 72. The second rate constant of Eq. (13) is not important in the reaction. This can be seen by examining Table XXV on page 73 and Figure XIV on page 74. There is no difference between the values in Table XXII on page 66 when the rate constant has a value of 2.00 x 10^6 and the values in Table XXV where the rate constant has a value of zero for both the total iodide concentration or the change in iodide concentration which results from the second reaction.

Figure XV on page 75 is a recorder plot of the iodide concentration versus time for a solution consisting of 9.958 ± .008 ml. of a 0.02000 ± .00001 m/l potassium iodate solution, 9.95 ± .01 ml. of a 0.0200 ± .0001 m/l sodium sulfite solution, 19.88 ± .02 ml. of a 1.000 ± .005 m/l sodium acetate - 1.000 ± .005 m/l acetic acid buffer and 4.969 ± .005 ml. of a starch solution. There is a point of inflection in the curve which is considered the endpoint in the reaction. The change in iodide concentration; however, is so small that the visual endpoint is undectable until much later. Both the recorder and the visual endpoint locations are indicated in Figure XV.

Table XXIV - Determination of the Upper Limit on Range of First Rate Constant of Eq. (13)

```
RC1 =         0.7000E 01       RC2 =         0.1120E 16
RC3 =         0.2000E 08       RC4 =         0.2000E 07
    PH            T(I)             CONI1         CONI2          CONI3          CONI(I)           EXPI
 0.4306E 01  0.1800E 02  0.3169E-05-0.1813E-12-0.2778E-06  0.2891E-05  0.7502E-04
 0.4256E 01  0.2400E 02  0.6834E-05-0.1323E-11  0.5556E-07  0.6890E-05  0.7720E-04
 0.4198E 01  0.3000E 02  0.1160E-04-0.5955E-11  0.3704E-07  0.1163E-04  0.8019E-04
 0.4140E 01  0.3600E 02  0.1708E-04-0.1965E-10  0.2648E-07  0.1711E-04  0.8252E-04
 0.4083E 01  0.4200E 02  0.2329E-04-0.5436E-10  0.1991E-07  0.2331E-04  0.8572E-04
 0.4025E 01  0.4800E 02  0.3020E-04-0.1339E-09  0.1559E-07  0.3021E-04  0.8905E-04
 0.3975E 01  0.5400E 02  0.3778E-04-0.2918E-09  0.1270E-07  0.3779E-04  0.9339E-04
 0.3934E 01  0.6000E 02  0.4601E-04-0.5742E-09  0.1079E-07  0.4602E-04  0.9888E-04
 0.3884E 01  0.6600E 02  0.5486E-04-0.1116E-08  0.9757E-08  0.5487E-04  0.1037E-03
 0.3851E 01  0.7200E 02  0.6429E-04-0.1927E-08  0.9435E-08  0.6430E-04  0.1088E-03
 0.3769E 01  0.7800E 02  0.7434E-04-0.4047E-08  0.1096E-07  0.7435E-04  0.1152E-03
 0.3744E 01  0.8400E 02  0.8491E-04-0.6316E-08  0.1287E-07  0.8491E-04  0.1219E-03
 0.3694E 01  0.9000E 02  0.9599E-04-0.1078E-07  0.1756E-07  0.9600E-04  0.1291E-03
 0.3661E 01  0.9600E 02  0.1075E-03-0.1667E-07  0.2409E-07  0.1075E-03  0.1367E-03
 0.3620E 01  0.1020E 03  0.1195E-03-0.2627E-07  0.3516E-07  0.1195E-03  0.1447E-03
 0.3579E 01  0.1080E 03  0.1320E-03-0.4071E-07  0.5210E-07  0.1320E-03  0.1532E-03
 0.3529E 01  0.1140E 03  0.1448E-03-0.6455E-07  0.8038E-07  0.1448E-03  0.1638E-03
 0.3488E 01  0.1200E 03  0.1581E-03-0.9721E-07  0.1193E-06  0.1581E-03  0.1751E-03
 0.3455E 01  0.1260E 03  0.1717E-03-0.1392E-06  0.1694E-06  0.1717E-03  0.1836E-03
 0.3413E 01  0.1320E 03  0.1856E-03-0.2047E-06  0.2478E-06  0.1856E-03  0.1944E-03
 0.3355E 01  0.1380E 03  0.2000E-03-0.3220E-06  0.3884E-06  0.2000E-03  0.2078E-03
 0.3314E 01  0.1440E 03  0.2147E-03-0.4651E-06  0.5599E-06  0.2148E-03  0.2221E-03
 0.3289E 01  0.1500E 03  0.2296E-03-0.6170E-06  0.7421E-06  0.2298E-03  0.2330E-03
 0.3240E 01  0.1560E 03  0.2450E-03-0.9110E-06  0.1095E-05  0.2452E-03  0.2467E-03
 0.3207E 01  0.1620E 03  0.2606E-03-0.1238E-05  0.1487E-05  0.2609E-03  0.2612E-03
 0.3165E 01  0.1680E 03  0.2766E-03-0.1737E-05  0.2085E-05  0.2770E-03  0.2765E-03
 0.3124E 01  0.1740E 03  0.2930E-03-0.2423E-05  0.2909E-05  0.2935E-03  0.2928E-03
 0.3099E 01  0.1800E 03  0.3097E-03-0.3115E-05  0.3739E-05  0.3103E-03  0.3100E-03
 0.3074E 01  0.1860E 03  0.3265E-03-0.3982E-05  0.4780E-05  0.3273E-03  0.3314E-03
 0.3041E 01  0.1920E 03  0.3438E-03-0.5265E-05  0.6319E-05  0.3448E-03  0.3508E-03
 0.3008E 01  0.1980E 03  0.3614E-03-0.6933E-05  0.8321E-05  0.3628E-03  0.3680E-03
 0.2967E 01  0.2040E 03  0.3797E-03-0.9457E-05  0.1135E-04  0.3815E-03  0.3859E-03
 0.2942E 01  0.2100E 03  0.3984E-03-0.1192E-04  0.1430E-04  0.4008E-03  0.4047E-03
 0.2909E 01  0.2160E 03  0.4178E-03-0.1556E-04  0.1868E-04  0.4209E-03  0.4285E-03
 0.2893E 01  0.2220E 03  0.4376E-03-0.1878E-04  0.2254E-04  0.4414E-03  0.4537E-03
 0.2860E 01  0.2280E 03  0.4582E-03-0.2440E-04  0.2928E-04  0.4631E-03  0.4713E-03
 0.2843E 01  0.2340E 03  0.4795E-03-0.2933E-04  0.3520E-04  0.4854E-03  0.4896E-03
 0.2802E 01  0.2400E 03  0.5020E-03-0.3947E-04  0.4737E-04  0.5099E-03  0.5086E-03
 0.2777E 01  0.2460E 03  0.5262E-03-0.4930E-04  0.5916E-04  0.5360E-03  0.5334E-03
 0.2760E 01  0.2520E 03  0.5517E-03-0.5926E-04  0.7112E-04  0.5636E-03  0.5594E-03
 0.2744E 01  0.2580E 03  0.5786E-03-0.7118E-04  0.8542E-04  0.5928E-03  0.5867E-03
 0.2711E 01  0.2640E 03  0.6074E-03-0.9227E-04  0.1107E-03  0.6259E-03  0.6037E-03
 0.2686E 01  0.2700E 03  0.6397E-03-0.1156E-03  0.1388E-03  0.6628E-03  0.6271E-03
 0.2678E 01  0.2760E 03  0.6752E-03-0.1347E-03  0.1617E-03  0.7022E-03  0.6515E-03
 0.2653E 01  0.2820E 03  0.7135E-03-0.1694E-03  0.2032E-03  0.7473E-03  0.6768E-03
 0.2612E 01  0.2880E 03  0.7574E-03-0.2310E-03  0.2772E-03  0.8036E-03  0.7031E-03
 0.2595E 01  0.2940E 03  0.8116E-03-0.2851E-03  0.3421E-03  0.8686E-03  0.7373E-03
 0.2579E 01  0.3000E 03  0.8742E-03-0.3538E-03  0.4246E-03  0.9449E-03  0.7587E-03
 0.2554E 01  0.3060E 03  0.9478E-03-0.4590E-03  0.5509E-03  0.1040E-02  0.7957E-03
 0.2529E 01  0.3120E 03  0.1040E-02-0.6033E-03  0.0000E 00  0.4363E-03  0.8188E-03
 0.2504E 01  0.3180E 03  0.4363E-03-0.1141E-03  0.0000E 00  0.3222E-03  0.8506E-03
 0.2488E 01  0.3240E 03  0.3222E-03-0.6753E-04  0.0000E 00  0.2547E-03  0.8920E-03
 0.2463E 01  0.3300E 03  0.2547E-03-0.4776E-04  0.0000E 00  0.2070E-03  0.9267E-03
 0.2479E 01  0.3360E 03  0.2070E-03-0.2961E-04  0.0000E 00  0.1773E-03  0.5980E-03
 0.2496E 01  0.3420E 03  0.1773E-03-0.2045E-04  0.0000E 00  0.1569E-03  0.4580E-03
 0.2521E 01  0.3480E 03  0.1569E-03-0.1451E-04  0.0000E 00  0.1424E-03  0.3933E-03
 0.2529E 01  0.3540E 03  0.1424E-03-0.1168E-04  0.0000E 00  0.1307E-03  0.3442E-03
 0.2529E 01  0.3600E 03  0.1307E-03-0.9997E-05  0.0000E 00  0.1207E-03  0.3130E-03
 0.2529E 01  0.3660E 03  0.1207E-03-0.8656E-05  0.0000E 00  0.1120E-03  0.2900E-03
```

Figure XIII - Plot of Results for Determination of Upper Limit on Range of First Rate Constant of Eq. (13)

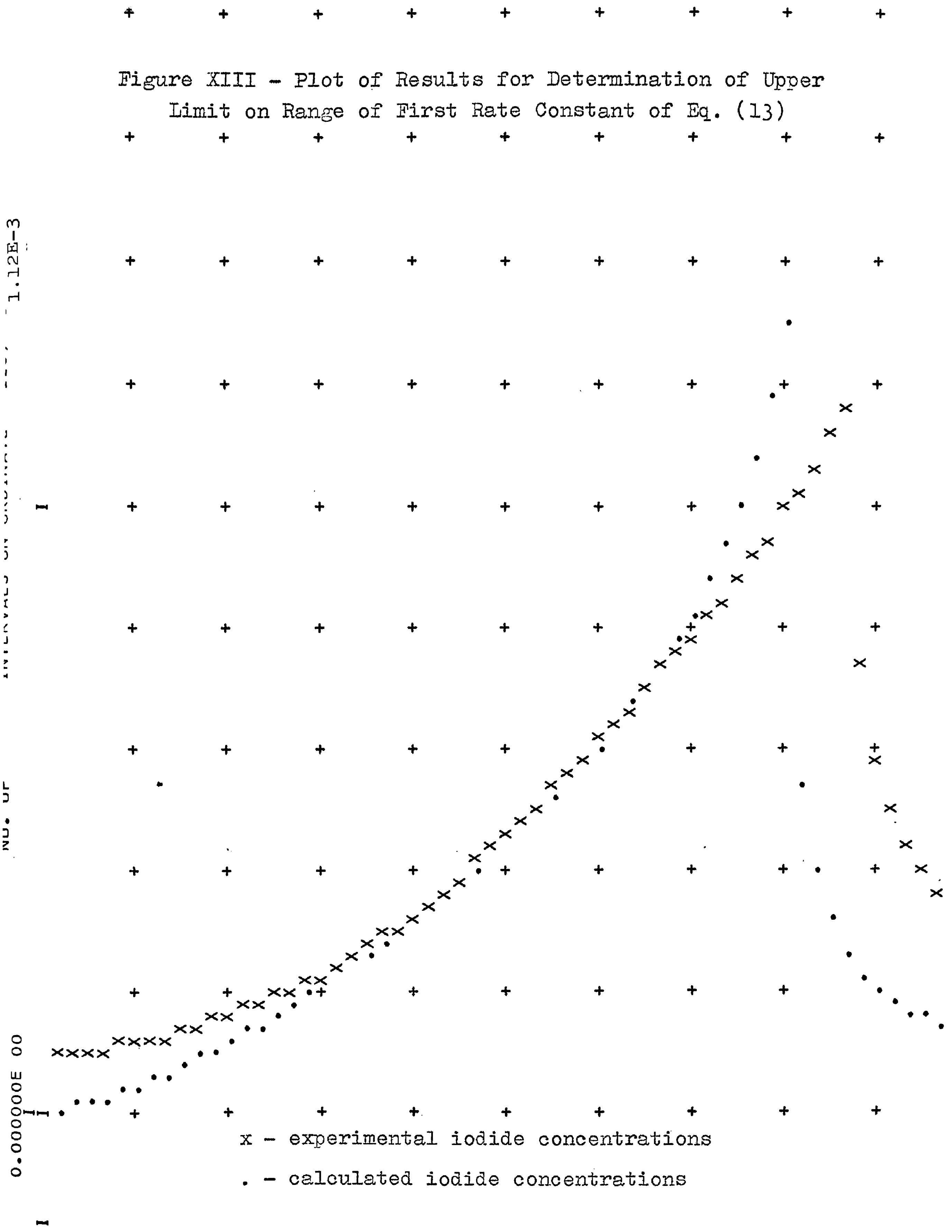


Table XXV - Determination of the Lower Limit on Range of Second Rate Constant of Eq. (13)

```
RC1 =        0.7000E 01      RC2 =        0.1120E 16
RC3 =        0.1000E 08      RC4 =        0.0000E 00
     PH           T(I)           CONI1         CONI2        CONI3       CONI(I)        EXPI
 0.4306E 01  0.1800E 02  0.3169E-05-0.9065E-13-0.2778E-06  0.2891E-05  0.7502E-04
 0.4256E 01  0.2400E 02  0.6834E-05-0.6614E-12  0.5556E-07  0.6890E-05  0.7720E-04
 0.4198E 01  0.3000E 02  0.1160E-04-0.2978E-11  0.3704E-07  0.1163E-04  0.8019E-04
 0.4140E 01  0.3600E 02  0.1708E-04-0.9825E-11  0.2647E-07  0.1711E-04  0.8252E-04
 0.4083E 01  0.4200E 02  0.2329E-04-0.2718E-10  0.1987E-07  0.2331E-04  0.8572E-04
 0.4025E 01  0.4800E 02  0.3020E-04-0.6694E-10  0.1551E-07  0.3021E-04  0.8905E-04
 0.3975E 01  0.5400E 02  0.3778E-04-0.1459E-09  0.1252E-07  0.3779E-04  0.9339E-04
 0.3934E 01  0.6000E 02  0.4601E-04-0.2871E-09  0.1045E-07  0.4602E-04  0.9888E-04
 0.3884E 01  0.6600E 02  0.5486E-04-0.5580E-09  0.9087E-08  0.5487E-04  0.1037E-03
 0.3851E 01  0.7200E 02  0.6429E-04-0.9636E-09  0.8279E-08  0.6430E-04  0.1088E-03
 0.3769E 01  0.7800E 02  0.7434E-04-0.2023E-08  0.8533E-08  0.7435E-04  0.1152E-03
 0.3744E 01  0.8400E 02  0.8491E-04-0.3158E-08  0.9081E-08  0.8491E-04  0.1219E-03
 0.3694E 01  0.9000E 02  0.9599E-04-0.5389E-08  0.1110E-07  0.9600E-04  0.1291E-03
 0.3661E 01  0.9600E 02  0.1075E-03-0.8335E-08  0.1409E-07  0.1075E-03  0.1367E-03
 0.3620E 01  0.1020E 03  0.1195E-03-0.1314E-07  0.1939E-07  0.1195E-03  0.1447E-03
 0.3579E 01  0.1080E 03  0.1320E-03-0.2035E-07  0.2767E-07  0.1320E-03  0.1532E-03
 0.3529E 01  0.1140E 03  0.1448E-03-0.3227E-07  0.4165E-07  0.1448E-03  0.1638E-03
 0.3488E 01  0.1200E 03  0.1581E-03-0.4860E-07  0.6096E-07  0.1581E-03  0.1751E-03
 0.3455E 01  0.1260E 03  0.1716E-03-0.6957E-07  0.8588E-07  0.1716E-03  0.1836E-03
 0.3413E 01  0.1320E 03  0.1856E-03-0.1023E-06  0.1250E-06  0.1856E-03  0.1944E-03
 0.3355E 01  0.1380E 03  0.1999E-03-0.1609E-06  0.1951E-06  0.1999E-03  0.2078E-03
 0.3314E 01  0.1440E 03  0.2146E-03-0.2324E-06  0.2807E-06  0.2146E-03  0.2221E-03
 0.3289E 01  0.1500E 03  0.2295E-03-0.3082E-06  0.3715E-06  0.2296E-03  0.2330E-03
 0.3240E 01  0.1560E 03  0.2448E-03-0.4549E-06  0.5474E-06  0.2449E-03  0.2467E-03
 0.3207E 01  0.1620E 03  0.2604E-03-0.6178E-06  0.7428E-06  0.2605E-03  0.2612E-03
 0.3165E 01  0.1680E 03  0.2763E-03-0.8661E-06  0.1041E-05  0.2764E-03  0.2765E-03
 0.3124E 01  0.1740E 03  0.2925E-03-0.1207E-05  0.1450E-05  0.2927E-03  0.2928E-03
 0.3099E 01  0.1800E 03  0.3089E-03-0.1551E-05  0.1862E-05  0.3092E-03  0.3100E-03
 0.3074E 01  0.1860E 03  0.3255E-03-0.1980E-05  0.2377E-05  0.3259E-03  0.3314E-03
 0.3041E 01  0.1920E 03  0.3424E-03-0.2613E-05  0.3137E-05  0.3429E-03  0.3508E-03
 0.3008E 01  0.1980E 03  0.3596E-03-0.3435E-05  0.4122E-05  0.3603E-03  0.3680E-03
 0.2967E 01  0.2040E 03  0.3773E-03-0.4674E-05  0.5609E-05  0.3782E-03  0.3859E-03
 0.2942E 01  0.2100E 03  0.3952E-03-0.5872E-05  0.7047E-05  0.3964E-03  0.4047E-03
 0.2909E 01  0.2160E 03  0.4136E-03-0.7639E-05  0.9167E-05  0.4151E-03  0.4285E-03
 0.2893E 01  0.2220E 03  0.4321E-03-0.9175E-05  0.1101E-04  0.4340E-03  0.4537E-03
 0.2860E 01  0.2280E 03  0.4511E-03-0.1186E-04  0.1423E-04  0.4535E-03  0.4713E-03
 0.2843E 01  0.2340E 03  0.4704E-03-0.1416E-04  0.1699E-04  0.4733E-03  0.4896E-03
 0.2802E 01  0.2400E 03  0.4904E-03-0.1892E-04  0.2271E-04  0.4942E-03  0.5086E-03
 0.2777E 01  0.2460E 03  0.5113E-03-0.2341E-04  0.2809E-04  0.5159E-03  0.5334E-03
 0.2760E 01  0.2520E 03  0.5326E-03-0.2783E-04  0.3339E-04  0.5382E-03  0.5594E-03
 0.2744E 01  0.2580E 03  0.5545E-03-0.3300E-04  0.3960E-04  0.5611E-03  0.5867E-03
 0.2711E 01  0.2640E 03  0.5773E-03-0.4218E-04  0.5061E-04  0.5857E-03  0.6037E-03
 0.2686E 01  0.2700E 03  0.6015E-03-0.5193E-04  0.6231E-04  0.6119E-03  0.6271E-03
 0.2678E 01  0.2760E 03  0.6268E-03-0.5923E-04  0.7107E-04  0.6387E-03  0.6515E-03
 0.2653E 01  0.2820E 03  0.6530E-03-0.7276E-04  0.8731E-04  0.6676E-03  0.6768E-03
 0.2612E 01  0.2880E 03  0.6816E-03-0.9660E-04  0.1159E-03  0.7009E-03  0.7031E-03
 0.2595E 01  0.2940E 03  0.7138E-03-0.1150E-03  0.1380E-03  0.7368E-03  0.7373E-03
 0.2579E 01  0.3000E 03  0.7484E-03-0.1371E-03  0.1645E-03  0.7758E-03  0.7587E-03
 0.2554E 01  0.3060E 03  0.7861E-03-0.1699E-03  0.2038E-03  0.8201E-03  0.7957E-03
 0.2529E 01  0.3120E 03  0.8287E-03-0.2115E-03  0.2538E-03  0.8710E-03  0.8188E-03
 0.2504E 01  0.3180E 03  0.8775E-03-0.2647E-03  0.3176E-03  0.9305E-03  0.8506E-03
 0.2488E 01  0.3240E 03  0.9345E-03-0.3211E-03  0.3854E-03  0.9987E-03  0.8920E-03
 0.2463E 01  0.3300E 03  0.9999E-03-0.4064E-03  0.4877E-03  0.1081E-02  0.9267E-03
 0.2479E 01  0.3360E 03  0.1081E-02-0.4310E-03  0.0000E 00  0.6502E-03  0.5980E-03
 0.2496E 01  0.3420E 03  0.6502E-03-0.1407E-03  0.0000E 00  0.5094E-03  0.4580E-03
 0.2521E 01  0.3480E 03  0.5094E-03-0.7733E-04  0.0000E 00  0.4321E-03  0.3933E-03
 0.2529E 01  0.3540E 03  0.4321E-03-0.5404E-04  0.0000E 00  0.3781E-03  0.3442E-03
 0.2529E 01  0.3600E 03  0.3781E-03-0.4181E-04  0.0000E 00  0.3362E-03  0.3130E-03
 0.2529E 01  0.3660E 03  0.3362E-03-0.3347E-04  0.0000E 00  0.3028E-03  0.2900E-03
```

Figure XIV - Plot of Results for Determination of the Lower Limit on Range of Second Rate Constant of Eq. (13)

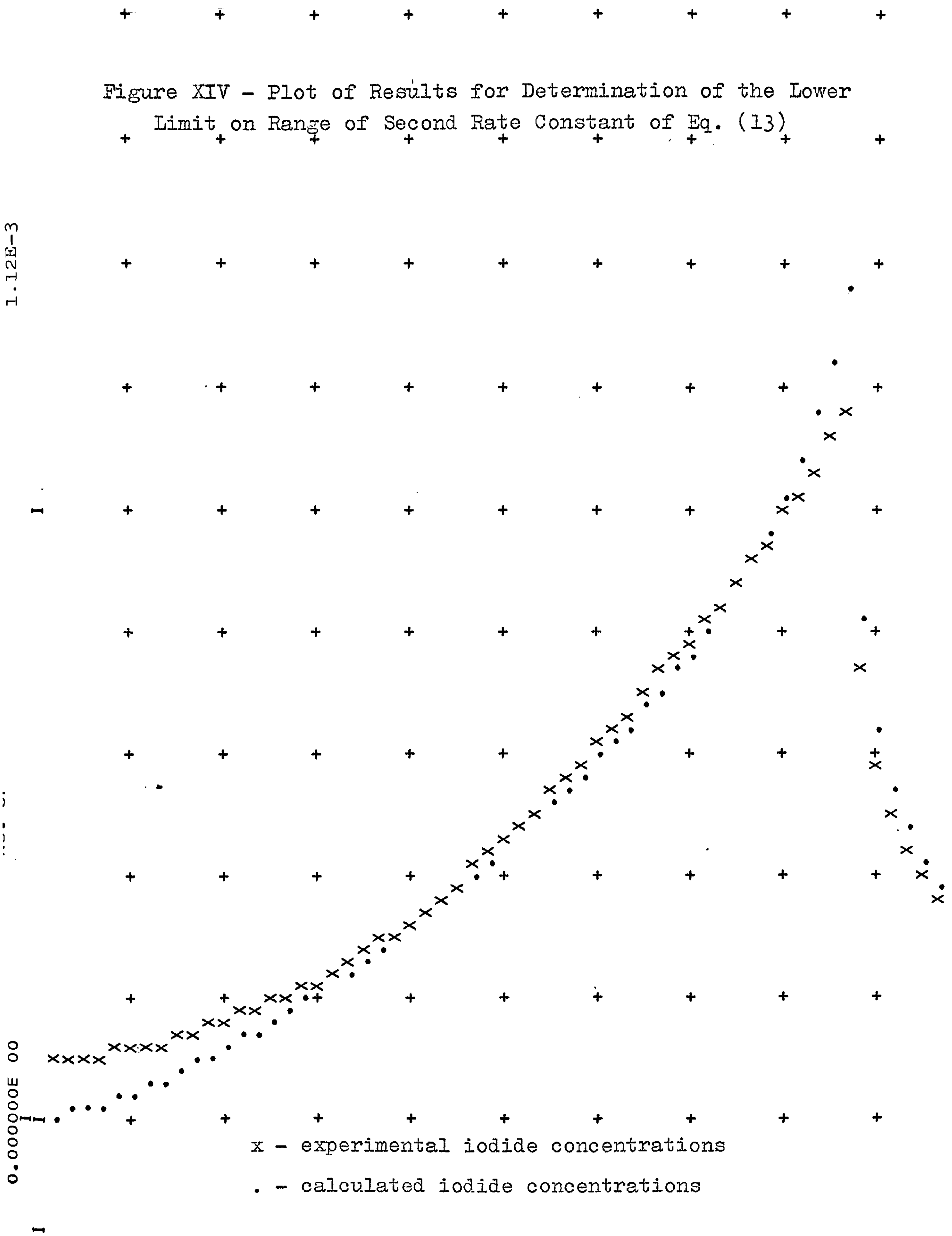
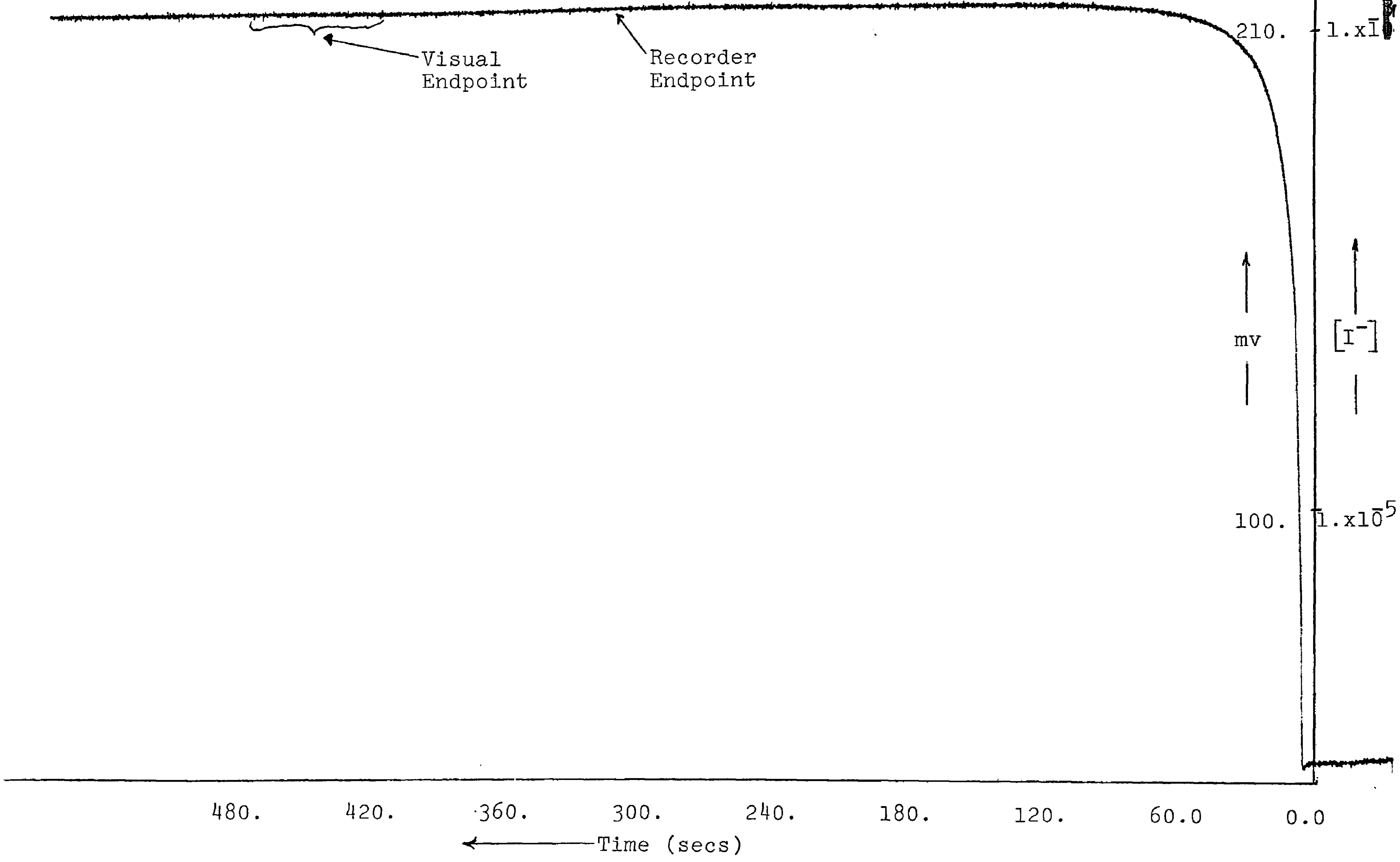


Figure XV - Recorder Plot of Iodide Concentration vs. Time for the Landolt Reaction in an Acetate-Acetic Acid Buffer



The computer simulation used for the unbuffered solution was slightly modified, in order to check the literature values for the rate constants used in Eq. (11) and Eq. (12) for the Landolt reaction in a buffered solution. The changes as well as a listing of the program are included in Appendix II. The same format as that used for the unbuffered solution was used for all of the tables and figures for the buffered solutions. Table XXVI shows the results using the literature values for the rate constants. A better comparison can be made by examining Figure XVI on page 78 where the calculated iodide concentrations and the experimental iodide concentrations are plotted together. The rate constants were then adjusted in an attempt to bring the two curves in closer agreement. The result of the closest approximation is shown in Table XXVII on page 79 and in Figure XVII on page 80.

Table XXVI - Results for Computer Simulation of Landolt Reaction Using Literature Values for Rate Constants in a Buffered Solution

```
RC1 =        0.8830E 04        RC2 =         0.1120E 16
RC3 =        0.8810E 09        RC4 =         0.2830E 09
    PH             T(I)              CONI1              CONI2           CONI3          CONI(I)          EXPI
 0.4740E 01  0.0000E 00  0.2123E-04-0.1743E-10-0.1111E-05  0.2012E-04  0.1604E-03
 0.4740E 01  0.6000E 01  0.6171E-04-0.2918E-09  0.5559E-06  0.6227E-04  0.4372E-03
 0.4740E 01  0.1200E 02  0.1221E-03-0.1690E-08  0.1872E-06  0.1223E-03  0.6612E-03
 0.4740E 01  0.1800E 02  0.1974E-03-0.5784E-08  0.9953E-07  0.1975E-03  0.7980E-03
 0.4740E 01  0.2400E 02  0.2841E-03-0.1467E-07  0.7316E-07  0.2841E-03  0.9046E-03
 0.4740E 01  0.3000E 02  0.3784E-03-0.3054E-07  0.7368E-07  0.3785E-03  0.1013E-02
 0.4740E 01  0.3600E 02  0.4768E-03-0.5519E-07  0.9268E-07  0.4768E-03  0.1078E-02
 0.4740E 01  0.4200E 02  0.5760E-03-0.8974E-07  0.1275E-06  0.5760E-03  0.1119E-02
 0.4740E 01  0.4800E 02  0.6733E-03-0.1345E-06  0.1768E-06  0.6733E-03  0.1162E-02
 0.4740E 01  0.5400E 02  0.7666E-03-0.1889E-06  0.2390E-06  0.7666E-03  0.1192E-02
 0.4740E 01  0.6000E 02  0.8545E-03-0.2520E-06  0.3125E-06  0.8546E-03  0.1207E-02
 0.4740E 01  0.6600E 02  0.9360E-03-0.3224E-06  0.3953E-06  0.9361E-03  0.1222E-02
 0.4740E 01  0.7200E 02  0.1011E-02-0.3984E-06  0.4852E-06  0.1011E-02  0.1237E-02
 0.4740E 01  0.7800E 02  0.1078E-02-0.4787E-06  0.5805E-06  0.1078E-02  0.1253E-02
 0.4740E 01  0.8400E 02  0.1138E-02-0.5616E-06  0.6793E-06  0.1139E-02  0.1269E-02
 0.4740E 01  0.9000E 02  0.1192E-02-0.6461E-06  0.7799E-06  0.1192E-02  0.1269E-02
 0.4740E 01  0.9600E 02  0.1239E-02-0.7309E-06  0.8812E-06  0.1239E-02  0.1269E-02
 0.4740E 01  0.1020E 03  0.1280E-02-0.8153E-06  0.9820E-06  0.1280E-02  0.1269E-02
 0.4740E 01  0.1080E 03  0.1315E-02-0.8986E-06  0.1082E-05  0.1315E-02  0.1269E-02
 0.4740E 01  0.1140E 03  0.1345E-02-0.9802E-06  0.1179E-05  0.1346E-02  0.1269E-02
 0.4740E 01  0.1200E 03  0.1371E-02-0.1060E-05  0.1275E-05  0.1371E-02  0.1269E-02
 0.4740E 01  0.1260E 03  0.1392E-02-0.1138E-05  0.1368E-05  0.1393E-02  0.1269E-02
 0.4740E 01  0.1320E 03  0.1410E-02-0.1213E-05  0.1458E-05  0.1411E-02  0.1269E-02
 0.4740E 01  0.1380E 03  0.1425E-02-0.1286E-05  0.1545E-05  0.1426E-02  0.1269E-02
 0.4740E 01  0.1440E 03  0.1437E-02-0.1357E-05  0.1630E-05  0.1438E-02  0.1269E-02
 0.4740E 01  0.1500E 03  0.1447E-02-0.1426E-05  0.1713E-05  0.1447E-02  0.1269E-02
 0.4740E 01  0.1560E 03  0.1455E-02-0.1493E-05  0.1793E-05  0.1455E-02  0.1269E-02
 0.4740E 01  0.1620E 03  0.1461E-02-0.1558E-05  0.1872E-05  0.1462E-02  0.1269E-02
 0.4740E 01  0.1680E 03  0.1466E-02-0.1622E-05  0.1948E-05  0.1466E-02  0.1269E-02
 0.4740E 01  0.1740E 03  0.1470E-02-0.1685E-05  0.2023E-05  0.1470E-02  0.1269E-02
 0.4740E 01  0.1800E 03  0.1473E-02-0.1746E-05  0.2096E-05  0.1473E-02  0.1269E-02
 0.4740E 01  0.1860E 03  0.1475E-02-0.1806E-05  0.2169E-05  0.1475E-02  0.1269E-02
 0.4740E 01  0.1920E 03  0.1477E-02-0.1866E-05  0.2240E-05  0.1477E-02  0.1269E-02
 0.4740E 01  0.1980E 03  0.1478E-02-0.1925E-05  0.2311E-05  0.1478E-02  0.1269E-02
 0.4740E 01  0.2040E 03  0.1479E-02-0.1983E-05  0.2381E-05  0.1479E-02  0.1269E-02
 0.4740E 01  0.2100E 03  0.1479E-02-0.2041E-05  0.2450E-05  0.1480E-02  0.1269E-02
 0.4740E 01  0.2160E 03  0.1480E-02-0.2099E-05  0.2520E-05  0.1480E-02  0.1269E-02
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 0.4740E 01  0.2340E 03  0.1476E-02-0.2256E-05  0.0000E 00  0.1474E-02  0.1269E-02
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 0.4740E 01  0.2880E 03  0.1454E-02-0.2678E-05  0.0000E 00  0.1451E-02  0.1253E-02
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 0.4740E 01  0.3000E 03  0.1449E-02-0.2765E-05  0.0000E 00  0.1446E-02  0.1237E-02
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 0.4740E 01  0.3480E 03  0.1425E-02-0.3092E-05  0.0000E 00  0.1422E-02  0.1207E-02
```

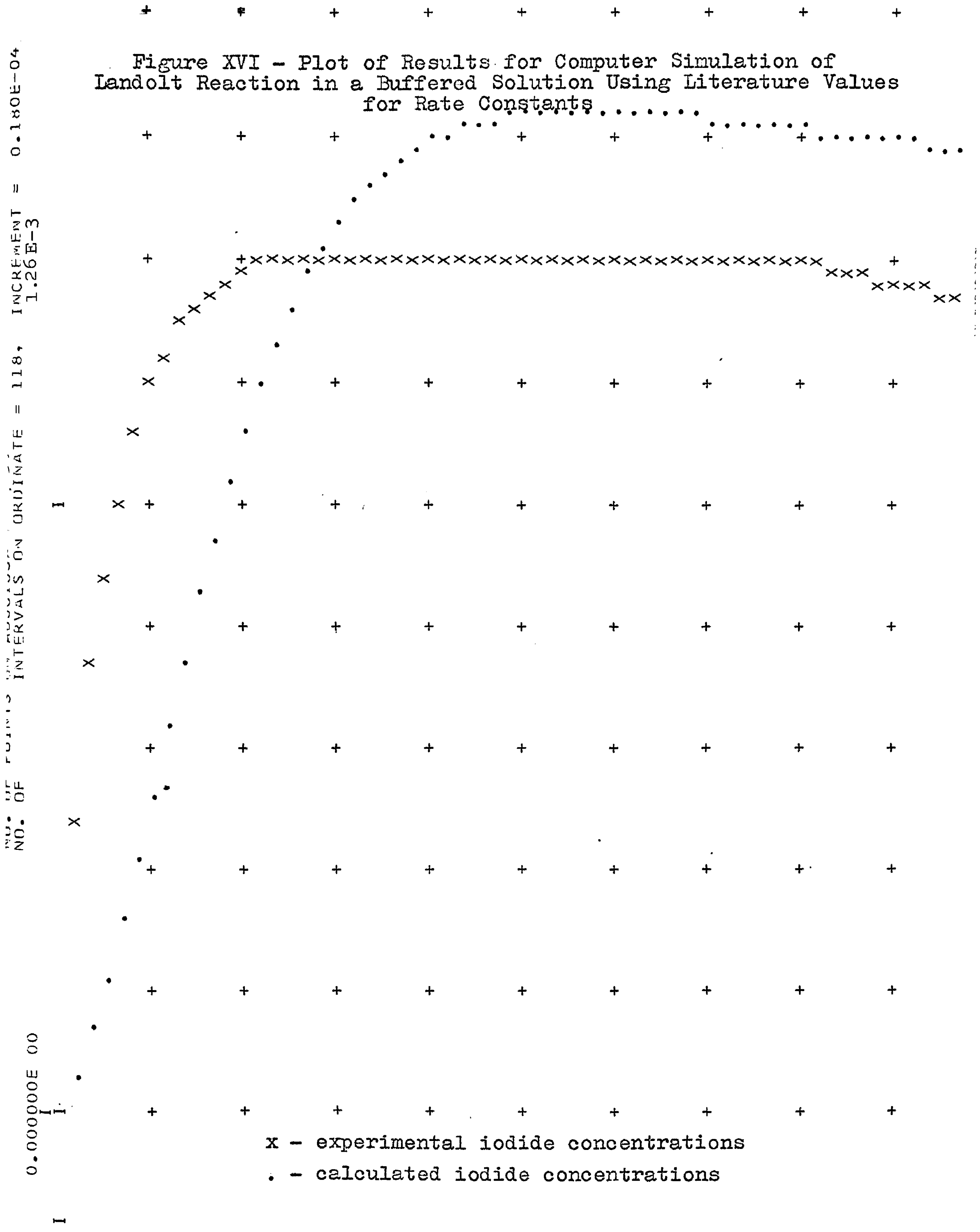

Figure XVI - Plot of Results for Computer Simulation of Landolt Reaction in a Buffered Solution Using Literature Values for Rate Constants

Table XXVII - Results for Computer Simulation of Landolt Reaction Using Adjusted Rate Constants in a Buffered Solution

```
RC1 =         0.3000E 04       RC2 =           0.4000E 17
RC3 =         0.8810E 09       RC4 =           0.2830E 09
    PH             T(I)          CONI1            CONI2           CONI3          CONI(I)          EXPI
 0.4740E  01  0.0000E  00  0.8904E-04-0.3019E-09-0.1111E-05  0.8793E-04  0.1604E-03
 0.4740E  01  0.6000E  01  0.2428E-03-0.4330E-08  0.5608E-06  0.2434E-03  0.4372E-03
 0.4740E  01  0.1200E  02  0.4220E-03-0.1878E-07  0.2077E-06  0.4222E-03  0.6612E-03
 0.4740E  01  0.1800E  02  0.5915E-03-0.4712E-07  0.1491E-06  0.5916E-03  0.7980E-03
 0.4740E  01  0.2400E  02  0.7372E-03-0.8805E-07  0.1612E-06  0.7373E-03  0.9046E-03
 0.4740E  01  0.3000E  02  0.8575E-03-0.1383E-06  0.2030E-06  0.8575E-03  0.1013E-02
 0.4740E  01  0.3600E  02  0.9553E-03-0.1948E-06  0.2602E-06  0.9554E-03  0.1078E-02
 0.4740E  01  0.4200E  02  0.1035E-02-0.2553E-06  0.3262E-06  0.1035E-02  0.1119E-02
 0.4740E  01  0.4800E  02  0.1100E-02-0.3182E-06  0.3972E-06  0.1100E-02  0.1162E-02
 0.4740E  01  0.5400E  02  0.1153E-02-0.3825E-06  0.4714E-06  0.1153E-02  0.1192E-02
 0.4740E  01  0.6000E  02  0.1198E-02-0.4476E-06  0.5473E-06  0.1198E-02  0.1207E-02
 0.4740E  01  0.6600E  02  0.1235E-02-0.5132E-06  0.6242E-06  0.1235E-02  0.1222E-02
 0.4740E  01  0.7200E  02  0.1266E-02-0.5788E-06  0.7017E-06  0.1266E-02  0.1237E-02
 0.4740E  01  0.7800E  02  0.1293E-02-0.6444E-06  0.7794E-06  0.1293E-02  0.1253E-02
 0.4740E  01  0.8400E  02  0.1316E-02-0.7098E-06  0.8570E-06  0.1316E-02  0.1269E-02
 0.4740E  01  0.9000E  02  0.1335E-02-0.7750E-06  0.9346E-06  0.1335E-02  0.1269E-02
 0.4740E  01  0.9600E  02  0.1352E-02-0.8399E-06  0.1012E-05  0.1352E-02  0.1269E-02
 0.4740E  01  0.1020E  03  0.1367E-02-0.9045E-06  0.1089E-05  0.1367E-02  0.1269E-02
 0.4740E  01  0.1080E  03  0.1380E-02-0.9688E-06  0.1166E-05  0.1380E-02  0.1269E-02
 0.4740E  01  0.1140E  03  0.1391E-02-0.1033E-05  0.1242E-05  0.1391E-02  0.1269E-02
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 0.4740E  01  0.1560E  03  0.1442E-02-0.1472E-05  0.1768E-05  0.1442E-02  0.1269E-02
 0.4740E  01  0.1620E  03  0.1446E-02-0.1534E-05  0.1842E-05  0.1446E-02  0.1269E-02
 0.4740E  01  0.1680E  03  0.1450E-02-0.1595E-05  0.1916E-05  0.1450E-02  0.1269E-02
 0.4740E  01  0.1740E  03  0.1454E-02-0.1657E-05  0.1989E-05  0.1454E-02  0.1269E-02
 0.4740E  01  0.1800E  03  0.1457E-02-0.1718E-05  0.2062E-05  0.1457E-02  0.1269E-02
 0.4740E  01  0.1860E  03  0.1460E-02-0.1778E-05  0.2135E-05  0.1460E-02  0.1269E-02
 0.4740E  01  0.1920E  03  0.1462E-02-0.1839E-05  0.2208E-05  0.1463E-02  0.1269E-02
 0.4740E  01  0.1980E  03  0.1465E-02-0.1899E-05  0.2280E-05  0.1465E-02  0.1269E-02
 0.4740E  01  0.2040E  03  0.1467E-02-0.1959E-05  0.2352E-05  0.1467E-02  0.1269E-02
 0.4740E  01  0.2100E  03  0.1469E-02-0.2019E-05  0.2424E-05  0.1469E-02  0.1269E-02
 0.4740E  01  0.2160E  03  0.1470E-02-0.2079E-05  0.2495E-05  0.1471E-02  0.1269E-02
 0.4740E  01  0.2220E  03  0.1472E-02-0.2138E-05  0.2567E-05  0.1472E-02  0.1269E-02
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 0.4740E  01  0.2580E  03  0.1478E-02-0.2492E-05  0.2990E-05  0.1479E-02  0.1269E-02
 0.4740E  01  0.2640E  03  0.1479E-02-0.2550E-05  0.3061E-05  0.1479E-02  0.1269E-02
 0.4740E  01  0.2700E  03  0.1479E-02-0.2608E-05  0.3130E-05  0.1480E-02  0.1269E-02
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 0.4740E  01  0.2880E  03  0.1478E-02-0.2771E-05  0.0000E  00  0.1475E-02  0.1253E-02
 0.4740E  01  0.2940E  03  0.1475E-02-0.2816E-05  0.0000E  00  0.1472E-02  0.1253E-02
 0.4740E  01  0.3000E  03  0.1472E-02-0.2861E-05  0.0000E  00  0.1469E-02  0.1237E-02
 0.4740E  01  0.3060E  03  0.1469E-02-0.2905E-05  0.0000E  00  0.1466E-02  0.1237E-02
 0.4740E  01  0.3120E  03  0.1466E-02-0.2949E-05  0.0000E  00  0.1463E-02  0.1237E-02
 0.4740E  01  0.3180E  03  0.1463E-02-0.2992E-05  0.0000E  00  0.1460E-02  0.1222E-02
 0.4740E  01  0.3240E  03  0.1460E-02-0.3034E-05  0.0000E  00  0.1457E-02  0.1222E-02
 0.4740E  01  0.3300E  03  0.1457E-02-0.3076E-05  0.0000E  00  0.1454E-02  0.1222E-02
 0.4740E  01  0.3360E  03  0.1454E-02-0.3117E-05  0.0000E  00  0.1451E-02  0.1222E-02
 0.4740E  01  0.3420E  03  0.1451E-02-0.3157E-05  0.0000E  00  0.1448E-02  0.1207E-02
 0.4740E  01  0.3480E  03  0.1448E-02-0.3197E-05  0.0000E  00  0.1445E-02  0.1207E-02
```
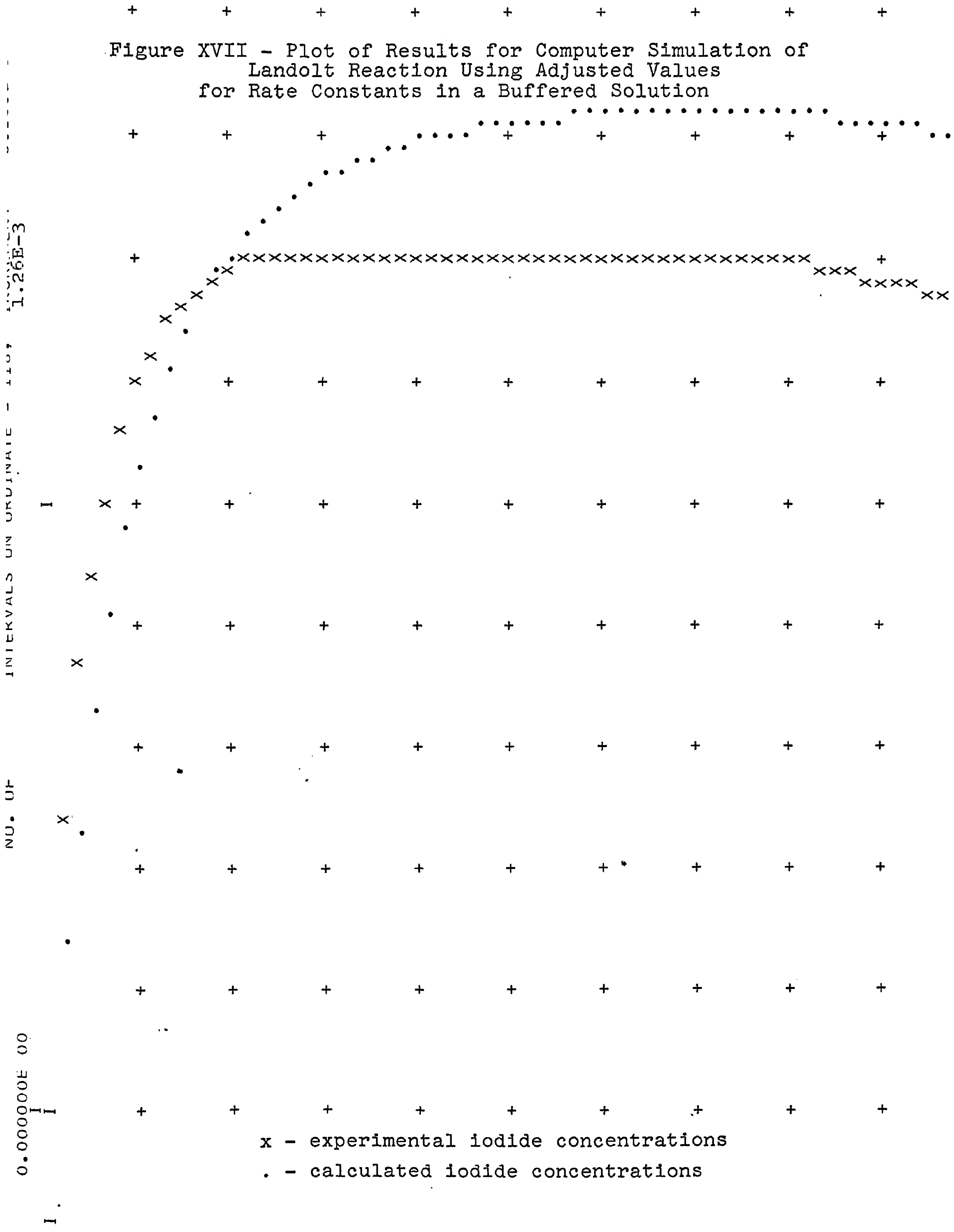

Figure XVII - Plot of Results for Computer Simulation of Landolt Reaction Using Adjusted Values for Rate Constants in a Buffered Solution



Conclusions and Suggestions for Further Study

The addition of increased amounts of solvent decreases the concentrations of the reactants and increases the length of the reaction. This dilution effect is reflected in the results of all three solvents which were examined. Skrabal has reported that the reaction time is directly proportional to the sulfite concentration, inversely proportional to the square of the hydrogen ion concentration, inversely proportional to the iodate concentration and inversely proportional to the square of the iodide concentration (29). The experimental results did not directly support this relationship possible because iodide was not included as one of the reactants. The results did follow the proportionality in general for every set of reactant volumes except the case in which the sulfite concentration was increased for the 30% dioxane-70% water solvent system.

Increasing the amount of iodate present decreased the time of the reaction. Iodate is a reactant in both Eq. (1) and Eq. (2) and it is expected that an increase in its concentration would decrease the time of the reaction. All three solvent systems show this result. The experimental results also show that increasing the concentration of hydrogen ion decreases the time of the reaction. There is a two-fold effect resulting from an increase in the hydrogen ion concentration. First, the amount of sulfurous acid in the solution is increased. Because sulfurous acid is a better reducing agent than either bisulfite or sulfite, the rate of Eq. (1) and Eq. (3) is increased. An increase in the rate of Eq. (1) and Eq. (3) decreases the time of the reaction. Second, the rate of Eq. (2) is dependent on the pH of the solution. The lower the pH the faster the rate of Eq. (2) and the shorter the reaction time. Again this trend is reflected by all three solvent systems.

There are two competing effects which must be considered in determining whether an increase in the sulfite concentration will increase the time of the reaction. In Eq. (1) and Eq. (3) sulfite is the reducing agent and any increase in its concentration will decrease the time of the reaction. However, the endpoint of the reaction is signified by the appearance of the iodine-starch complex which of course means that iodine must be present. Iodine cannot accumulate in the system until all of the sulfite is consummed. If any sulfite is present, the iodine produced in Eq. (2) is reduced to iodide by Eq. (3). An increase in the amount of sulfite present initially would then increase the time of the reaction. The two effects, an increase of the rate of Eq. (1) and (3) and an increase in the length of time until the iodine-starch complex forms, must both be considered. When water is used as a solvent, the second effect predominates and the time of the reaction increases with an increase in the sulfite concentration. The same effect is present when the solvent is 20% dioxane-80% water; however, the effect is less pronounced. For the 30% dioxane-70% water solvent system the effect is absent and there is a decrease in the reaction time when the sulfite concentration is increased indicating that the first effect predominates.

The major difference between dioxane and water is the difference in polarity. Water is the more polar molecule. As the percentage of dioxane increases in the solvent, the polarity of the solvent decreases. This has a direct effect on the degree of dissociation of each reactant. Because of this change the rate of the overall reaction decreases. For the same set of reactant volumes the reaction times would be expected to be in the order of

water > 20% dioxane-80% water > 30% dioxane-70% water

This is the case in every instance except the set of reactant volumes in which the sulfite concentration is doubled. In this case the time of the reaction is reversed and has the order of

30% dioxane-70% water > 20% dioxane-80% water > water

This trend can be explained by the change in the dissociation of sulfurous acid. As was previously mentioned sulfurous acid is a better reducing agent than the other sulfite species. In the less polar solvents the amount of sulfurous acid present would be greater than in the more polar solvents. As a result the rate of Eq. (1) and Eq. (3) would increase. On the basis of the experimental results this increase in the rates of Eq. (1) and Eq. (3) is enough to offset the effects of a decrease in solvent polarity. This accounts for the above order for the reaction times of the case when the sulfite concentration is increased.

The rate of the Landolt reaction decreases as the hydrogen ion concentration increases (33). The greater the hydrogen ion concentration the greater the concentration of sulfurous acid in relation to the bisulfite and sulfite concentrations. This in turn influences the rate of Eq. (1) and Eq. (3). Skrabal and Zahorka and Thiel and Meyer found that in general the rate of the reaction depends on the inverse square of the hydrogen ion concentration (31),(33).

There is a linear relationship between the time of the reaction and the pH of the buffer for buffer systems having pH values between 2.50 and 4.75 pH units. The relationship may extend further; however, there are experimental limitations which in themselves cause deviations from linearity outside this range of pH values. For buffer systems at pH values less than pH 2.50 the average reaction time was too short. This probably resulted because the time of addition of the sulfite solution using a pipet was approximately 10 - 12 seconds which is very close to the length of the reaction. At pH values greater than 4.75 pH units the average reaction time was too long.

The rate of the Dushman reaction is a function of the solution pH. At high pH values the rate becomes very slow. The endpoint of the reaction denoted by the appearance of iodine is also dependent on the Dushman reaction, the only reaction which produces iodine. If the rate of the Dushman reaction is very slow, the production of iodine will be very slow and the endpoint will be denoted by a very gradual bluing of the solution. This makes the initial appearance of the iodine-starch complex very hard to detect. Although the reaction might be completed in terms of all of the sulfite being consummed, the visual endpoint does not occur until much later. The relationship may be a linear one over a wider range of pH values; but, according to the visual endpoint this is not the case outside the range of 2.50 - 4.75 pH units. The endpoint was also undectable using either the hydrogen ion or iodide electrodes due to the small change in hydrogen and iodide ion at the endpoint.

It is not possible to derive Eq. (32) solely on the basis of Eq. (11) and Eq. (13), the rate expressions for the first and second reactions of the Landolt reaction. It was found that the curve in Figure V on page 52 pertains only to the Landolt reaction having reactants of the concentrations shown in Table VIII on page 33 under the column for the water solvent system and using reactant volumes listed in Table XVII on page 46. Any change in these initial conditions produces reaction times which do not correspond to points on the curve. This in effect implies that the initial reactant concentrations or some intermediate concentration of reactants and products including those at the endpoint of the reaction must have a bearing on Eq. (32).

The experimental results indicate that the time of the reaction is inversely proportional to the hydrogen ion concentration to the 0.59 power. This does not necessarily contradict previous results (31), (33), since these results were for a system in an acetate-acetic acid buffer with a pH of 4.74. No previous attempt has been made to determine the relationship between reaction time and hydrogen ion concentration at different pH values. Before a derivation of Eq. (32) can be considered on the basis of Eq. (11) and Eq. (13) these rate expressions must be determined for a number of buffer systems of varying pH values.

The results of the comparison of the percent uncertainties between the buffered and the unbuffered systems indicate that the buffered system has the lower percent uncertainty. This may not be conclusive due to the high uncertainty in the mean percent uncertainty for both systems. Before any meaningful conclusions can be drawn, a greater sample is needed in order to reduce the high uncertainty. In addition, the mean reaction times of both the buffered and the unbuffered systems should have approximately the same values.

Figure VI on page 55 can be divided into two sections. In section one there is a very rapid change in pH corresponding to an increase in the hydrogen ion concentration. The second section, the portion of the graph after the endpoint, corresponds to an increase in pH and a decrease in hydrogen ion concentration. By way of a comparison, Figure VII on page 56 can be divided into three parts. The first part is a slow decrease in pH. Section two is a more rapid decrease in pH. After the endpoint, section three shows an increase in pH.

The difference between Figure VI and Figure VII is due to a different amount of sulfite being used. The solution from which Figure VI was made has less sulfite. Because there is a smaller concentration of sulfite, the pH of the reaction solution is less than 4.5 pH units. At pH values in this range, Eqs. (1), (2) and (3) operate and the rate of hydrogen ion production is very fast. The reaction from which Figure VII was taken has a higher concentration of sulfite ion. As a result the pH of the solution after addition of sulfite is approximately 6.5 pH units. The Dushman reaction proceeds very slowly at pH values this high The increase in hydrogen ion is due only to the first reaction, Eq. (1). Because of this the slope of the first section of the curve is less than the second section. As the hydrogen ion concentration continues to increase, the rate of reaction two, Eq. (2), increases and the slope of the curve increases. This may seem like a contradiction since reaction two consumes hydrogen ions; however, the sum of reactions two and three is a net increase of hydrogen ion which is produced since the rate of reaction three is very high. The third section of the curve in both Figures VI and VII is essentially the same. Reaction two alone continues after the endpoint since all of the sulfite has been consumed. As reaction two continues after the endpoint hydrogen ion is consumed and the pH begins to increase.

In Figure VIII on page 58, the initial rise in the curve is due to an initial increase in the iodide concentration from 0. to 7.5 x 10^{-5} m/l. This is followed by a steady increase in iodide concentration followed by a rapid increase in iodide concentration and after the endpoint there is a sharp decrease in the iodide concentration. The iodide curve is very similar to the hydrogen ion curve. This is expected since the same reactions which produce iodide produce hydrogen ion and the same reactions which use iodide use hydrogen ion. Initially, reaction one predominates producing iodide at a slow rate. As the pH of the solution becomes more acidic, reaction two increases in velocity. Reaction two and three combined give a net increase in iodide. The rate of formation of iodide ion increases. At the endpoint both reactions one and three stop because all of the sulfite has been oxidized to sulfate. Reaction two which does not depend on sulfite ion continues using iodide ion and producing iodine. The iodine which is produced reacts to form the iodine-starch complex indicating the end of the reaction. The iodide continues to be consumed by the second reaction reducing the iodide to low enough values so as to essentially cause the reaction to stop.

Eqs. (11) and (13) were derived for a reaction having a pH within the range of pH 4 to pH 13 (31). The results from Table XX page 61 tend to agree with Skrabal's results. The rate constants found in Eq. (11) and Eq. (13) do not adequately describe a system having a pH below four. For solutions of this acidity the rate constants are too large. According to the computer simulation the reaction is expected to end after 84 seconds. In reality the reaction time is between 330 and 336 seconds. In order to obtain better agreement between the graph of the experimental results and the graph of the calculated results the rate constants were adjusted to the values listed in Table XXI on page 64. Figure X on page 65 shows a close correlation between the graphs of the calculated iodide concentrations and the experimental iodide concentrations.

There are two areas in which differences remained between the graphs of the calculated iodide concentrations and the experimental iodide concentrations. At the beginning of the reaction there is not a very close agreement between the two curves. There are two possible explanations for the higher experimental results. The silver - silver iodide electrode may not be very responsive for iodide concentrations in the area of 10^{-5} m/l. The other possibility is the possible interference of sulfate ions. At the beginning of the reaction there is a much greater concentration of sulfate ions than iodide ions. In fact, this difference is on the order of 2 x 10^{-3} to 1 x 10^{-6}. If there was any problem concerning the selectivity of the electrode it would have been most evident at this point.

There is also a discrepancy between the two curves in Figure X on page 65 near the endpoint. Difference between the two curves at the endpoint is 1.5 x 10^{-4} m/l. The response of the electrode may once again be at fault. If the electrode response is too slow, by the time the electrode begins to respond to the increase in iodide the iodide concentration in the solution may already be decreasing and the actual height of the peak may be missed.

The range of the rate constant values was not very great except in the instance of the second rate constant of Eq. (13). The terms in that part of the rate expression involve iodide and iodine concentrations. Initially, the iodide concentration was zero in the case of this study. Much of the previous work involved iodide as one of the reactants in which case the initial iodide concentration would be much higher. Throughout the reaction until after the endpoint the iodine concentration is also very low due to the high velocity of reaction three, Eq. (3). The combination of a low iodide and iodine concentration make the second term small in comparison with the first term in Eq. (13). The only point at which the term might become significant is near the endpoint when the iodide concentration is large or after the endpoint when the iodine concentration is large. There was no change in the calculated iodide concentrations at either of these points by making the second term zero. This indicated that the second term was not significant in the case in which iodide was not initially present as a reactant.

Figure XV on page 75 shows the graph of the iodide concentration in a buffered solution. The curve shows an initial rapid rise in the iodide concentration followed by a leveling off. At the endpoint there is a gradual decline in the iodide curve. A comparison between the curve for the reaction in an unbuffered solution, Figure VIII on page 58, and the curve for the reaction in a buffered solution shows that the curves are considerably different. There are two differences chemically between the two systems. In the buffered case there is no sulfate present. There is also a constant available source of hydrogen ion in the buffered solution.

The initial rise in the iodide curve for the buffered solution must be due to reaction one, Eq. (1). Reaction two, Eq. (2), has a very slow rate at pH values as high as pH 4.74. This is evident by the very gradual change in iodide concentration after the endpoint. Reaction three, Eq. (3), is linked directly to reaction two since it depends on the iodine produced in reaction two. This leaves only reaction one to produce the large initial increase in iodide ion. If there is any degree of reversibility in reaction one, then elimination of the sulfuric acid, which is part of the original formulation in the unbuffered reaction, would cause reaction one in the buffered case to be shifted in favor of the products, of which sulfate ion is one. The constant availibility of hydrogen ions favors the formation of sulfurous acid and bisulfite over the weaker reducing agent sulfite. These two trends could account for the initial iodide increase.

After the initial increase, the iodide concentration remains constant until the endpoint of the reaction. This is due to a decrease in the rate of the first reaction. The rate of the first reaction decreases as the sulfite concentration decreases. Most of the sulfite is used initially to produce the large initial increase in iodide. The rate of the second reaction increases because of the increase in the iodide concentration; but, the increase is so small in comparison to the total iodide concentration that the iodide concentration remains constant.

After the endpoint, there is a decrease in the iodide concentration. At this point in the reaction there is a great deal of similarity between the buffered and the unbuffered reactions. In both cases the sulfite concentration becomes zero and reactions one and three stop. Only reaction two continues which uses up iodide and produces iodine. This results in the recorder showing a decrease in the iodide concentration. This decrease in iodide concentration is more gradual in the buffered solution because the solution pH is so high.

There are three major differences between Figure XV on page 75 and the recorder plot of the iodide concentration which is shown in Figure XVI on page 78. The first difference is in the shape of the initial rise of the curve. In the computer plot the initial increase in iodide concentration is more gradual. There is also a difference in the iodide concentrations when the two plots level off. For the experimental graph the concentration is 1.3×10^{-3} m/l and for the calculated graph the value is 1.5×10^{-3} m/l. The final difference is the time of reaction. The calculated reaction time is less than the experimental reaction time.

The initial difference between the two graphs was eliminated by increasing the second rate constant of Eq. (11) from 1.12×10^{15} to 4.00×10^{17} $l^4 moles^{-4} sec^{-1}$. The reaction time for the simulated reaction was also changed by decreasing the value of the first constant from 8.8×10^3 to 3.0×10^3 $l^2 moles^{-2} sec^{-1}$. These adjustments are not unreasonable since Eq. (11) was derived for solutions having pH values between pH 4 - 13 and the system used to produce Figure XVI on page 78 has a solution pH of 4.74 ± .02 pH units which is on the lower limit of this range of pH values. The result of these adjustments is shown in Figure XVII on page 80.

There remained a difference in the concentrations between the computer simulation and the experimental graph.

The shape of the two curves is the same; however, it was not possible to match the shapes of the two curves and bring the concentration values into agreement. A possible explanation may lie with the experimental values. The value of the experimental iodide concentrations depends on the standard iodide solutions as well as the electrode response. Although the difference on the graph appears to be very large, it corresponds to a difference of about one square on the chart paper. Assuming an amount of uncertainty in the recorder plotted value, it is possible that the experimental iodide values should be more in line with the theoretical values.

It is hoped that this study will suggest new areas of investigation of the Landolt reaction. The change in dependence of the reaction time as the solvent polarity is decreased is such an area. In particular, the relationship between the time of the reaction and the sulfite concentration as the solvent polarity decreases is interesting.

The relationship of the solution pH to the time of the reaction although represented by a linear relationship cannot be explained on the basis of the two rate expressions. The possiblity of similar relationships exisiting between the reaction time and the other reactants could be explored and may aid in understanding the relationship between the reaction time and the solution pH. The determination of the rate constants for the rate expressions of reactions one and two for solutions of various pH values appears to be a necessary requirement for an accurate explanation of the relationship. The effects of changing the concentrations of the initial reactants on this relationship is also worth examining.

The computer simulation can be a valuable aid in studying these relationships. There are some modifications which could enhance its potential use. Many mechanisms have been proposed to explain reactions one, two and three. The inclusion of these might aid in making the program even more realistic in terms of simulating the actual reaction conditions.

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Appendix I

Methods of Standardizing Sulfite and Iodide Solutions

Standardization of a Sodium Sulfite Solution

The method of standardizing a sulfite solution has long been open to discussion (16),(17),(18),(22). The primary cause for this discussion is the oxidation of sulfite to sulfate and the loss of sulfur dioxide. Both result in the experimentally determined value of the sulfite concentration to be lower than the expected value.

The general procedure uses an oxidizing agent to oxidize the sulfite to sulfate. Hendrixson reports that the oxidation of sulfite using dichromate, bromate, and permanganate ions is incomplete due to the possible formation of dithionate ion (17). However, he does state that iodate may be successfully used. Unfortunately, there is still some loss of sulfite due to air oxidation during the titration.

Another possible reducing agent is iodine (22). Iodine has the added advantage of allowing the use of a starch indicator to determine the endpoint of the reaction.
The sulfite solution can be stored under an inert atmosphere and added using a buret (34). An even easier method involves adding an aliquot of the sulfite solution to an excess of iodine and titrating the remaining iodine with a reducing agent which is not sensitive to air oxidation

such as sodium thiosulfate. This is the procedure which was used.

The iodine solution used to titrate the sulfite solution must in turn be standardized against a primary standard. Arsenious oxide was chosen as the primary standard. When arsenious oxide is dissolved in water it forms arsenious acid as is shown by the reaction

$$As_2O_3 + 3H_2O \longrightarrow 2H_3AsO_3$$

Arsenious acid reacts with iodine to produce iodide ions as is shown.

$$H_3AsO_3 + I_2 + H_2O \longrightarrow H_3AsO_4 + 2I^- + 2H^+$$

The endpoint of the reaction can be noted using a starch indicator.

A sample of iodine was sublimed. To a 250 ml. beaker 12.7 g. of the sublimed iodine was added along with 40. g. of potassium iodide. The potassium iodide must be free from iodate in order to prevent loss of iodide ion through Eq. (2). To check for the presence of iodate add approximately one gram of iodide to 20 ml. of water, one ml. of 6N sulfuric acid and 2 ml. of starch solution. If a blue color develops within 30 seconds, iodate is present. Dissolve the iodine and potassium iodide in 25 ml. of water and transfer the solution to a 1000 ml. volumetric flask. Since the solution will be standardized it is not necessary to add exactly one liter of water. As an added precaution the solution should be kept in a brown bottle and stored away from light. The bottle should also be tightly stoppered to reduce the air oxidation of iodide (27).

The arsenious oxide solution is made by carefully weighing about 1.25 g. of arsenious oxide into a beaker. Since arsenious oxide is nonhygroscopic, drying is unnecessary. To this add a solution made by dissolving three g. of sodium hydroxide dissolved in 10 ml. of water. Swirl the solution until the arsenious oxide dissolves. Add 50 ml. of water, two drops of phenolphthalein indicator and enough dilute hydrochloric acid to cause the pink color to disappear. At this point a slight excess of hydrochloric acid should be added; the entire solution is transfered quantitatively to a 250 ml. volumetric flask and diluted to the mark.

To standardize the iodine solution transfer by pipet 10 ml. of the arsenious oxide solution to a 100 ml. beaker. Sodium bicarbonate is added to neutralize the excess acid. When the effervesence has stopped add approximately a 3 g. excess of sodium bicarbonate to act as a buffer during the titration. Add 5 ml. of starch indicator and some water if desired. Titrate with iodine until the first appearance of a blue color. Approximately 10 ml. of the iodine solution will be required.

Thiosulfate was used as the other reducing agent to titrate the excess iodine. Thiosulfate is not air oxidized;

but, the water should be boiled before the solution is made to kill any sulfur fixing bacteria. Sodium carbonate is usually added as a preservative. Iodine oxidizes thiosulfate according to

$$I_2 + 2S_2O_3^{=} \longrightarrow 2I^{-} + S_4O_6^{=}$$

Once again starch is used as the indicator.

The thiosulfate solution was made by dissolving 25. g. of $Na_2S_2O_3 \cdot 5H_2O$ in 1000 ml. of water. For a preservative 0.2 g. of sodium carbonate was added. 10 ml. of the standardized iodine solution was pipetted into a 100 ml. beaker and diluted with water. This solution was titrated with thiosulfate added from a buret. When the solution color had become light yellow, 5 ml. of starch solution was added and the titration continued until the disappearance of the blue color.

Knowing the molarity of both the thiosulfate and iodine solutions it is possible to determine the molarity of the sulfite solution. From a pipet 10 ml. of the iodine solution was added to a 100 ml. beaker. To the same beaker 10 ml. of the sulfite solution was added. The remaining iodine was then titrated using the thiosulfate solution.

The calculations involved in determining the molarity of the sulfite solution are not complicated. The following is a sample calculation.

Sample Calculation of the Molarity of the Sulfite Solution

Moles of iodine used:	
molarity of iodine solution	$.0483 \pm .0001$ M
volume of iodine used	$9.958 \pm .008$ ml.
moles of iodine used	$(4.810 \pm .014) \times 10^{-4}$ m.
Moles of thiosulfate used:	
molarity of thiosulfate solution	$.0558 \pm .0001$ M
volume of thiosulfate used	$10.10 \pm .01$ ml.
moles of thiosulfate used	$(5.63 \pm .02) \times 10^{-4}$ m.
moles of iodine remaining after reacting with thiosulfate	$(1.99 \pm .03) \times 10^{-4}$ m.
Molarity of sulfite solution:	
moles of sulfite used	$(1.99 \pm .03) \times 10^{-4}$ m.
volume of sulfite used	$9.95 \pm .01$ ml.
molarity of sulfite solution	$.0200 \pm .0003$ M

Standardization of a Potassium Iodide Solution

Iodide can be determined using iodate in a strongly acidic solution. The acid used must be hydrochloric acid. Starch can not be used as the indicator since the iodine-starch complex does not form in highly acidic solutions. Instead chloroform or carbon tetrachloride is used. In the presence of iodine both chloroform and carbon tetrachloride are colored violet. The reduction of iodate in an acidic medium proceeds through the following steps:

$$IO_3^- + 6H^+ + 6e^- \longrightarrow I^- + 3H_2O$$

$$IO_3^- + 5I^- + 6H^+ \longrightarrow 3I_2 + 3H_2O$$

$$IO_3^- + 2I_2 + 6H^+ \longrightarrow 5I^+ + 3H_2O$$

The overall reaction is

$$IO_3^- + 6H^+ + 4e^- \longrightarrow I^+ + 3H_2O$$

The particular reaction for the determination of iodide using hydrochloric acid is

$$IO_3^- + 6H^+ + 3Cl^- + 2I^- \longrightarrow 3ICl + 3H_2O$$

Pipet 10 ml. of an approximately 1.00×10^{-1} molar potassium iodide solution into a stoppered bottle. A small volumetric flask with a glass stopper works best. The vessel must be inverted during the reaction to note the color of the organic layer. The stopper must be glass because iodine attacks rubber and cork stoppers. Add 25 ml. of concentrated hydrochloric acid and 10 ml. of chloroform to the potassium iodide solution. The iodate solution is added from a buret. The same solution which was used for the Landolt reaction, a 0.02 M. potassium iodate solution, can be used for the titration. The titration requires about 25 ml. of the iodate solution. As the reaction continues iodine is produced until all of the iodide is used up. From this point on the iodine is oxidized by the iodate and the solution color becomes yellow. The yellow color is due to the formation of iodine monochloride. The remaining iodine is in the organic layer and can be seen more clearly by inverting the flask.

The titration is continued by adding more iodate dropwise. After each drop the reaction flask should be stoppered and shaken vigorously. The endpoint is reached when the organic layer becomes clear. The concentration of the iodide solution can be determined from the concentration and volumes used of the iodate solution and the stoichiometry of the reaction.

Appendix II

Computer Programs

The computer program used to simulate the Landolt reaction is an attempt to duplicate the experimental situation as closely as possible. There are essentially three parts to the program corresponding to the three reactions which comprise the Landolt reaction. What follows is a brief description of the program along with an explanation of the symbols used in the program.

NUM is the number of data cards containing the solution pH values and the number of experimental iodide concentration values which are read in. It also is the number of iterations in the DO loop which calculates the theoretical iodide concentrations from the rate expressions. The iodide values, CHARTI(I), are read in as the number of squares on the chart paper. These are translated into the experimental iodide concentration, EXPI(I). In the same way the chart value for each pH value, PH(I), are read in as ANUM(K). The four rate constants, RC1, RC2, RC3 and RC4 are the last data which are used. The initial reactant concentrations are then specified. CONI(I) is the initial iodide concentration. C102(I) is the initial sulfite concentration and is also the sulfite concentration remaining after the third reaction. C122(I) and CI2 have the same significance for the iodate and iodine concentrations respectively.

The computer then enters a DO loop. The number of iterations of the DO loop is controlled by the value of NUM. The value for the hydrogen ion concentration, CH(I), is calculated from PH(I). The time of the reaction, DT(I), is determined by increasing the initial time, T(I), by six seconds. The subroutine ALPHA is then called and calculates the bisulfite concentration, CHSO3, the sulfite concentration, CSO3, and the iodate concentration, CIO3. AK12, AK10 and AK20 are the dissociation constants for iodic acid and the first and second dissociation constants for sulfurous acid respectively.

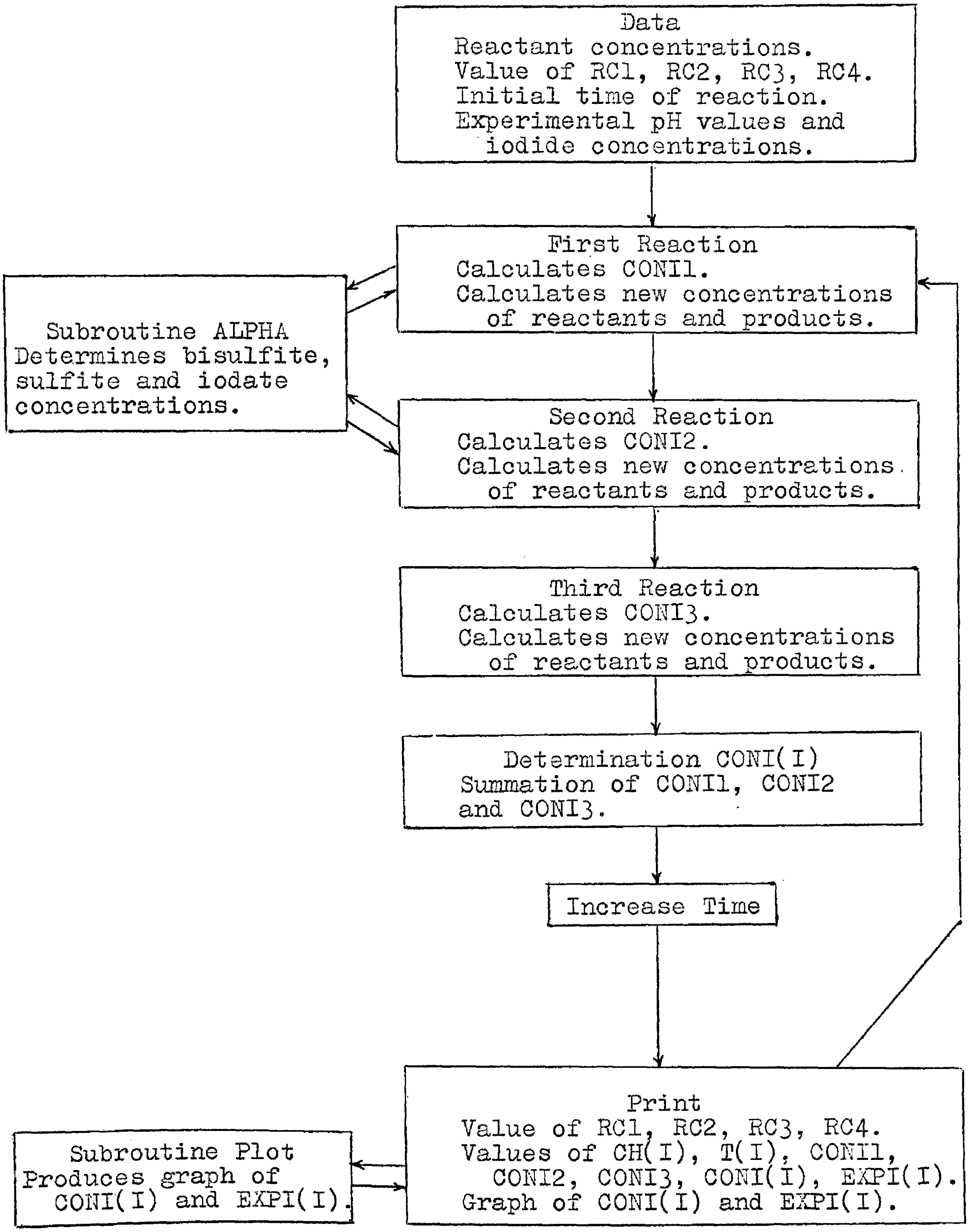
After these values are determined the computer returns and calculates the change in iodide concentration, CONI1, as a result of the first rate expression. Following the calculation, the total remaining sulfite, C10(I), iodate, C12(I), and iodide, CONI1, concentrations are determined on the basis of the stoichiometry of the first reaction. This procedure is repeated for the second reaction. CI21 is the iodine concentration remaining after the second reaction; C121 is the iodate concentration remaining after the second reaction; and the change in iodide concentration as a result of the second reaction is CONI2.

The change in the iodide concentration as a result of the third reaction is CONI3. Again all of the concentrations of reactants and products are determined on the basis of the stoichiometry of the reaction. The total iodide concentration, CONI(I), is the sum of CONI1, CONI2, and CONI3. The amount of triiodide, CI3, is also calculated and the total iodide concentration adjusted accordingly. The values for CH(I), T(I), CONI1, CONI2, CONI3, CONI(I) and EXPI(I) are printed out and the program returns to the beginning of the DO loop.

When the program exits from the DO loop the plotting subroutine is called. NB is the total number of points to be plotted; YMAX is the maximum value on the ordinate; YMIN is the minimum value on the ordinate and NGR is the number of graphs to be printed. In each case the calculated iodide concentrations and the experimental iodide concentrations are graphed together. The program returns again if a new set of rate constants is provided and repeats the entire program. Execution time for one set of rate constants is approximately four seconds. A summary of the program follows in semi-flow chart format in Figure XVIII.

The computer program for the Landolt reaction in a buffered solution is on page 119. The program is essentially the same as the program for the Landolt reaction in an unbuffered solution. The DO loop used to read in the experimental pH values is removed since the pH solution is constant. This is established by assigning a value to PH(I) of 4.74. The second rate expression must be modified slightly. The second term containing the hydrogen ion concentration to the second power must be changed to the hydrogen ion concentration to the 1.9 power.

Figure XVIII - Diagramatic Representation of Computer Simulation



```
$JOB HOI,'PETER A. BEHNKE       ',PAGES=30,TIME=150
      DIMENSION PH(300),CH(300),C10(300),C101(300),C102(300)
      DIMENSION C121(300),C122(300),CI2(300),CI21(300),CI22(300),
     1CIO3(300),CIO31(300),DT(300),CONI(300),Z(300),X(300),
     1CHSO3(300),C12(300),CHSO31(300),CSO3(300),CSO31(300),
     1Y(300),T(300),ANUM(300),EXPI(300),CHARTI(300)
      NUM = 59
      DO 8 I = 1,NUM
      READ(5,7) CHARTI(I)
    7 FORMAT(F5.2)
      RECVAL = ((65.4 - CHARTI(I))/49.1)*1.47
      VALMV = (.12/1.47)*RECVAL
      EXPI(I) = 10.**((VALMV-((.0591)*(-3.0)))/(-.0591))
    8 CONTINUE
      DO 20 K = 1,NUM
      READ(5,10) ANUM(K)
   10 FORMAT(F5.2)
   20 CONTINUE
      DO 150 J=1,10
      READ(5,6) RC1,RC2,RC3,RC4
    6 FORMAT(4E15.6)
      CONI(1) = 0.0
      C102(1) = 3.08E-3
      C122(1) = 3.08E-3
      CI2(1) = 0.00
      T(1) = 18.0
      WRITE(6,2)RC1,RC2
    2 FORMAT('1','RC1 = ',E15.4,5X,'RC2 = ',E15.4)
      WRITE(6,3) RC3,RC4
    3 FORMAT(' ','RC3 = ',E15.4,5X,'RC4 = ',E15.4)
      WRITE(6,11)
   11 FORMAT(' ',5X,'PH',8X,'T(I)',7X,'CONI1',7X,'CONI2',6X,
     1'CONI3',5X,'CONI(I)',5X,'EXPI')
      DO 100 I = 1,NUM
      PH(I) = ((ANUM(I) - 36.2)/12.1) + 3.0
      CH(I) = 10.**(-PH(I))
      DT(I) = T(I) + 6.0
C
C
C     SUBROUTINE DETERMINING CONCENTRATIONS FROM ALPHA FORMULAS.
      CALL ALPHA (CH(I),C102(I),C122(I),CSO3(I),CHSO3(I),CIO3(I))
C
C     EQUATION FOR IODIDE PRODUCED IN FIRST REACTION.
C     IO3  +  3 SO3   =   I  +  3 SO4
C     REFERENCE  SKRABAL, A. AND A. ZAHORKA,Z. EL. CH.,33,63(1927)
C
      CONI1 = DT(I)*((RC1    *CH(I)*CHSO3(I)*CIO3(I))+(RC2    *
     1CH(I)*CH(I)*CSO3(I)*CSO3(I)*CIO3(I)))
      C12(I) = C122(I) -CONI1
      C10(I) = C102(I) - 3.*CONI1
      CONI1 = CONI1 + CONI(I)
C
C
C     SUBROUTINE RECALLED TO DETERMINE NEW CONCENTRATIONS.
      CALL ALPHA  (CH(I),C10(I),C12(I),CSO31(I),CHSO31(I),CIO31(I))
C
C     EQUATION FOR IODIDE USED IN SECOND REACTION.
C     IO3  +  5 I  +  6 H   =    3 H2O  +  3 I2
C     REFERENCE  SKRABAL, A. AND A. ZAHORKA,Z.EL.CH.,33,42(1927)
C
      CONI2 = (DT(I)*(-5.0))*((RC3    *CIO31(I)*(CH(I)**2.0)*CO
     1NI1**2.0) + (RC4     *CIO31(I)*(CH(I)**2.0)*(CONI1**2.0)*
     1CI2(I))/710.)
      CI21(I) = CI2(I) - 0.60*CONI2
      C121(I) = C12(I) + 0.2*CONI2
      C101(I) = C10(I)
C
C
C     EQUATION FOR IODIDE PRODUCED IN THIRD REACTION.
C     H2O  +  I2  +  SO3   =   2H  +  2I  +  SO4
C     REFERENCE  BUNAU, G.V. AND M. EIGEN, Z. PHYSK. CH.,7,113(1956)
C
      IF(C101(I).EQ.0.0) GO TO 75
      IF(C101(I).LT.0.0) GO TO 75
   80 X(I) = 1.00/((3.0E5)*DT(I))
   90 CONTINUE
      CONI3 = 2.0*(CI21(I) - X(I))
      CI2(I+1) = X(I)
      C102(I+1) = C101(I) -0.5*CONI3
      C122(I+1) = C121(I)
```

```
      CI3 = 0.00
      GO TO 85
   75 CI2(I+1) = CI21(I)
      C102(I+1) = 0.0
      C122(I+1) = C121(I)
      CONI3 = 0.00
C
C
C     CONI(I) IS AMOUNT OF IODIDE PRODUCED IN REACTIONS ONE,
C     TWO AND THREE.
   85 CONI(I) = CONI1 + CONI2 + CONI3
      IF(CONI(I).LT.0.00) GO TO 86
      GO TO 87
   86 CONI(I) = 0.00
   87 CI3 = CONI(I) * CI2(I+1)/710.
      CONI(I)= CONI(I) - CI3
      CI2(I+1) = CI2(I+1) - CI3
      T(I+1) = T(I) + 6.0
      WRITE(6,12) PH(I),T(I),CONI1,CONI2,CONI3,CONI(I),EXPI(I)
   12 FORMAT(' ',7E11.4)
      CONI(I+1) = CONI(I)
      IF(C102(I+1).LT.0.0) GO TO 95
      GO TO 951
   95 C102(I+1) = 0.0
  951 IF(C122(I+1).LT.0.0) GO TO 96
      GO TO 961
   96 C122(I+1) = 0.00
  961 IF(CI2(I+1) .LT.0.0) GO TO 97
      GO TO 100
   97 CI2(I+1) = 0.00
  100 CONTINUE
      DO 200 I=1,NUM
      Y(I) = CONI(I)
  200 Y(I+NUM) = EXPI(I)
      NB = NUM*2.0
      YMAX = 1.60E-3
      YMIN = 0.00
      NWRITE = 6
      NGR = 2
      CALL PLOT ( Y,NB,YMIN,YMAX,NWRITE,NGR)
  150 CONTINUE
      DO 175 I = 1,NUM
  175 Y(I) = EXPI(I)
      NB = NUM
      NGR = 1
      CALL PLOT ( Y,NB,YMIN,YMAX,NWRITE,NGR)
      DO 300 I=1,NUM
  300 Y(I) = PH(I)
      NB = NUM
      YMAX = 7.00
       YMIN = 2.00
      NWRITE = 6
      NGR = 1
      CALL PLOT ( Y,NB,YMIN,YMAX,NWRITE,NGR)
      STOP
      END


      SUBROUTINE ALPHA (CONH,C10,C12,CS03,CHS03,CI03)
      AK12 = 1.70E-1
      AK10 = 1.70E-2
      AK20 = 6.3E-8
      ALP22 = 1.0/(1.00 + (AK12/CONH))
      ALP12 = ALP22*AK12/CONH
      ALP30 = 1.00/(1.00+(AK10/CONH)+(AK10*AK20/CONH**2.0))
      ALP20 = ALP30*AK10/CONH
      ALP10 = ALP30*AK10*AK20/CONH**2.0
      CHS03 = ALP20*C10
      CS03 = ALP10*C10
      CI03 = ALP12 * C12
      RETURN
      END


      SUBROUTINE PLOT (Y,NDIM,YMIN,YMAX,NWRITE,NGR)
      DIMENSION Y(NDIM),A(119),NZ(10),CHAR(10)
      CHARACTER BLANK,PLUS,CHAR,A
      DATA BLANK,PLUS,CHAR(1),CHAR(2),CHAR(3),CHAR(4),CHAR(5),
     1CHAR(6),CHAR(7),CHAR(8),CHAR(9),CHAR(10)
     1/' ','+','.','X','C','D','E','F','G','I','J','K'/
```

```
      YMN=YMIN - 9.*DELTA
      DO 10 I=1,119
   10 A(I)=BLANK
      IF(YMAX-YMIN) 11,11,15
   11 WRITE(NWRITE,29)
      RETURN
   15 WRITE(NWRITE,9) NPTS,DELTA
      WRITE(NWRITE,19) YMNT,YMXT
      DO 60 I=2,NPTS
      IF (MOD(I,6)-1) 24,17,24
   17 DO 20 J=10,119,10
   20 A(J)=PLUS
   24 DO 30 J=1,NGR
      N=(Y(I+(J-1)*NPTS)-YMN)/DELTA+1.5
      IF (N.LT.1) N=1
      IF (N.GT.119) N=119
      NZ(J)=N
   30 A(N) = CHAR(J)
      WRITE(NWRITE,39) (A(J),J=1,119)
      DO 40 J=1,NGR
      N=NZ(J)
   40 A(N)=BLANK
      IF (MOD(I,6)-1) 60,38,60
   38 DO 50 J=10,119,10
   50 A(J)=BLANK
   60 CONTINUE
    9 FORMAT('1'31X,'NO. OF POINTS ON ABSCISSA = 'I5/32X,'NO. OF
     1INTERVALS ON ORDINATE = 118,  INCREMENT = 'E10.3)
   19 FORMAT(' 'E16.6,E101.6/10X,'I'99X,'I'/' I',8X,'I',2(49X,'I'),
     18X,'I')
   29 FORMAT (' YMAX AND YMIN SPECIFIED INCORECTLY')
   39 FORMAT(' '119A1)
      RETURN
      END

$ENTRY
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$JOB H01,'PETER A. BEHNKE       ',PAGES=30,TIME=150
      DIMENSION PH(300),CH(300),C10(300),C101(300),C102(300)
      DIMENSION C121(300),C122(300),CI2(300),CI21(300),CI22(300),
     1CI03(300),CI031(300),DT(300),CONI(300),Z(300),X(300),
     1CHS03(300),C12(300),CHS031(300),CS03(300),CS031(300),
     1Y(300),T(300),ANUM(300),EXPI(300),CHARTI(300)
      NUM = 59
      DO 8 I = 1,NUM
      READ(5,7) CHARTI(I)
    7 FORMAT(F5.2)
      RECVAL = ((76.6 - CHARTI(I))/37.3)*1.10
      VALMV = (.12/1.10)*RECVAL
      EXPI(I) = 10.**((VALMV-((.0591)*(-3.0)))/(-.0591))
    8 CONTINUE
      DO 150 J=1,10
      READ(5,6) RC1,RC2,RC3,RC4
    6 FORMAT(4E15.6)
      CONI(1) = 0.0
      C122(1) = 4.44E-3
      C102(1) = 4.44E-3
      CI2(1) = 0.00
      T(1) = 0.0
      WRITE(6,2)RC1,RC2
    2 FORMAT('1','RC1 = ',E15.4,5X,'RC2 = ',E15.4)
      WRITE(6,3) RC3,RC4
    3 FORMAT(' ','RC3 = ',E15.4,5X,'RC4 = ',E15.4)
      WRITE(6,11)
   11 FORMAT(' ',5X,'PH',8X,'T(I)',7X,'CONI1',7X,'CONI2',6X,
     1'CONI3',5X,'CONI(I)',5X,'EXPI')
      DO 100 I = 1,NUM
      PH(I) = 4.74
      CH(I) = 10.**(-PH(I))
      DT(I) = T(I) + 6.0
C
C
C     SUBROUTINE DETERMINING CONCENTRATIONS FROM ALPHA FORMULAS.
      CALL ALPHA (CH(I),C102(I),C122(I),CS03(I),CHS03(I),CI03(I))
C
C     EQUATION FOR IODIDE PRODUCED IN FIRST REACTION.
C     I03  +  3 S03   =    I  +  3 S04
C     REFERENCE  SKRABAL, A. AND A. ZAHORKA,Z. EL. CH.,33,63(1927)
C
      CONI1 = DT(I)*((RC1    *CH(I)*CHS03(I)*CI03(I))+(RC2    *
     1CH(I)*CH(I)*CS03(I)*CS03(I)*CI03(I)))
      C12(I) = C122(I) -CONI1
      C10(I) = C102(I) - 3.*CONI1
      CONI1 = CONI1 + CONI(I)
C
C
C     SUBROUTINE RECALLED TO DETERMINE NEW CONCENTRATIONS.
      CALL ALPHA  (CH(I),C10(I),C12(I),CS031(I),CHS031(I),CI031(I))
C
C     EQUATION FOR IODIDE USED IN SECOND REACTION.
C     I03  +  5 I  +  6 H   =    3 H2O  +  3 I2
C     REFERENCE  SKRABAL, A. AND A. ZAHORKA,Z.EL.CH.,33,42(1927)
C
      CONI2 = (DT(I)*(-5.0))*((RC3   *CI031(I)*(CH(I)**2.0)*CO
     1NI1**2.0) + (RC4     *CI031(I)*(CH(I)**1.9)*(CONI1**2.0)*
     1CI2(I))/710.)
      CI21(I) = CI2(I) - 0.60*CONI2
      C121(I) = C12(I) + 0.2*CONI2
      C101(I) = C10(I)
C
C
C     EQUATION FOR IODIDE PRODUCED IN THIRD REACTION.
C     H2O  +  I2  +  S03   =    2H  +  2I  +  S04
C     REFERENCE  BUNAU, G.V. AND M. EIGEN, Z. PHYSK. CH.,7,113(1956
C
      IF(C101(I).EQ.0.0) GO TO 75
      IF(C101(I).LT.0.0) GO TO 75
   80 X(I) = 1.00/((3.0E5)*DT(I))
   90 CONTINUE
      CONI3 = 2.0*(C121(I) - X(I))
      CI2(I+1) = X(I)
      C102(I+1) = C101(I) -0.5*CONI3
      C122(I+1) = C121(I)
      CI3 = 0.00
      GO TO 85
   75 CI2(I+1) = C121(I)
      C102(I+1) = 0.0
```

```
$JOB HOI,'PETER BEHNKE        '
      WRITE(6,2)
    2 FORMAT(' ','PROGRAM FOR DETERMINING CONCENTRATIONS OF')
      WRITE(6,3)
    3 FORMAT(' ','STANDARD SOLUTIONS - I2,SO3, AND S2O3.')
C
C
C     INFORMATION FOR PRIMARY STANDARD ARSENIOUS OXIDE
C
C     CSTDA=CONCENTRATION OF ARSENIOUS  OXIDE, DSTDA=DEVIATION
C     OF CSTDA, VSTDA=VOLUME OF ARSENIOUS OXIDE USED AND DVSTDA
C     IS THE DEVIATION OF VSTDA.
C
      CSTDA = 2.526E-2
      DSTDA = 1.00E-5
      VSTDA = 9.956E-3
      DVSTDA = 4.00E-6
      STDMA = CSTDA*VSTDA
      DSTDMA = STDMA*((DVSTDA/VSTDA)+(DSTDA/CSTDA))
C
C
C     CALCULATION OF THE CONCENTRATION OF THE IODINE
C
C     AVOLI2=AVERAGE VOLUME OF I2 USED, DAVI2=DEVIATION OF AVOLI2,
C     AMOLI2=MOLES OF I2, DMOLI2=DEVIATION IN AMOLI2, CSTDI2=
C     CONCENTRATION OF I2 SOLUTION, DSTDI2=DEVIATION IN CSTDI2
C
      READ(5,11) VOL1I2,VOL2I2,VOL3I2
   11 FORMAT(3E15.4)
      AVOLI2 = (VOL1I2 + VOL2I2+ VOL3I2)/3.0
      DAVI2 = SQRT((ABS(VOL1I2 - AVOLI2)**2.0 + ABS(VOL2I2-AVO
     1LI2)**2.0+ ABS(VOL3I2-AVOLI2)**2.0)/3.0)
      AMOLI2 = 2.0*STDMA
      DMOLI2 = 2.0*DSTDMA
      CSTDI2 = AMOLI2/AVOLI2
      DSTDI2 = CSTDI2*((DMOLI2/AMOLI2)+(DAVI2/AVOLI2))
      WRITE(6,13) CSTDI2
   13 FORMAT(' ','CONCENTRATION OF I2 SOLUTION = ',E15.4)
      WRITE(6,14) DSTDI2
   14 FORMAT(' ','DEVIATION = ',E15.4)
C
C
C     CALCULATION OF THE CONCENTRATION OF THE THIOSULFATE STANDARD
C
C     AVS2O3=AVERAGE VOLUME OF S2O3,DVS2O3=DEVIATION IN THAT VOLUME
C     AMOLI2 AND DMOLI2 ARE AS PREVIOUSLY DEFINED, AMS2O3=MOLES
C     OF S2O3, DMS2O3=DEVIATION IN AMS2O3, CS2O3=CONCENTRATION
C     OF S2O3, AND DS2O3=DEVIATION OF CS2O3.
C
      READ(5,15) VOLI2,DVOLI2,VS2O31,VS2O32,VS2O33
   15 FORMAT(5E10.4)
      AVS2O3 = ( VS2O31 + VS2O32 + VS2O33)/3.0
      DVS2O3 = SQRT((ABS(VS2O31-AVS2O3)**2.0+ABS(VS2O32-AVS2O3
     1)**2.0 + ABS(VS2O33-AVS2O3)**2.0)/3.0)
      AMOLI2 = CSTDI2 * VOLI2
      DMOLI2 = AMOLI2 * ((DVOLI2/VOLI2) + (DSTDI2/CSTDI2))
      AMS2O3 = 2.0 * AMOLI2
      DMS2O3 = 2.0 * DMOLI2
      CS2O3 = AMS2O3/AVS2O3
      DS2O3 = CS2O3 * ((DMS2O3/AMS2O3) + (DVS2O3/AVS2O3))
      WRITE(6,16) CS2O3
   16 FORMAT(' ','CONCENTRATION S2O3 SOLUTION = ',1X,E15.4)
      WRITE(6,17) DS2O3
   17 FORMAT(' ','DEVIATION = ',E15.4)
C
C
C     CALCULATION OF THE CONCENTRATION OF THE SULFITE SOLUTION.
C
C     AMOLI2, DMOLI2, AVS2O3, AND DVS2O3 ARE AS PREVIOUSLY DEFINED
C     AMS2O3 AND DMS2O3 ARE AS PREVIOUSLY DEFINED, AMSO3=MOLES
C     OF SO3, DMSO3=DEVIATION IN AMSO3, CSO3=CONCENTRATION OF
C     SO3 AND DSO3=DEVIATION IN CSO3.
C
      READ(5,20) VOLI2,DVOLI2,VOLSO3,DVSO3,VS2O31,VS2O32,VS2O33
   20 FORMAT(7E10.4)
      AMOLI2 = CSTDI2 * VOLI2
      DMOLI2 = AMOLI2*((DVOLI2/VOLI2) + (DSTDI2/CSTDI2))
      AVS2O3 = ( VS2O31 + VS2O32 + VS2O33)/3.0
      DVS2O3 = SQRT((ABS(VS2O31-AVS2O3)**2.0+ABS(VS2O32-AVS2O3
```

```
      C122(I+1) = C121(I)
      CONI3 = 0.00
C
C
C     CONI(I) IS AMOUNT OF IODIDE PRODUCED IN REACTIONS ONE,
C     TWO AND THREE.
   85 CONI(I) = CONI1 + CONI2 + CONI3
      IF(CONI(I).LT.0.00) GO TO 86
      GO TO 87
   86 CONI(I) = 0.00
   87 CI3 = CONI(I) * CI2(I+1)/710.
      CONI(I)= CONI(I) - CI3
      CI2(I+1) = CI2(I+1) - CI3
      T(I+1) = T(I) + 6.0
      WRITE(6,12) PH(I),T(I),CONI1,CONI2,CONI3,CONI(I),EXPI(I)
   12 FORMAT(' ',7E11.4)
      CONI(I+1) = CONI(I)
      IF(C102(I+1).LT.0.0) GO TO 95
      GO TO 951
   95 C102(I+1) = 0.0
  951 IF(C122(I+1).LT.0.0) GO TO 96
      GO TO 961
   96 C122(I+1) = 0.00
  961 IF(CI2(I+1) .LT.0.0) GO TO 97
      GO TO 100
   97 CI2(I+1) = 0.00
  100 CONTINUE
      DO 200 I=1,NUM
      Y(I) = CONI(I)
  200 Y(I+NUM) = EXPI(I)
      NB = NUM*2.0
      YMAX = 1.800E-3
      YMIN = 0.00
      NWRITE = 6
      NGR = 2
      CALL PLOT ( Y,NB,YMIN,YMAX,NWRITE,NGR)
  150 CONTINUE
      DO 175 I = 1,NUM
  175 Y(I) = EXPI(I)
      NB = NUM
      NGR = 1
      CALL PLOT ( Y,NB,YMIN,YMAX,NWRITE,NGR)
      DO 300 I=1,NUM
  300 Y(I) = PH(I)
      NB = NUM
      YMAX = 7.00
       YMIN = 2.00
      NWRITE = 6
      NGR = 1
      CALL PLOT ( Y,NB,YMIN,YMAX,NWRITE,NGR)
      STOP
      END

      SUBROUTINE ALPHA (CONH,C10,C12,CSO3,CHSO3,CIO3)
      AK12 = 1.70E-1
      AK10 = 1.70E-2
      AK20 = 6.3E-8
      ALP22 = 1.0/(1.00 + (AK12/CONH))
      ALP12 = ALP22*AK12/CONH
      ALP30 = 1.00/(1.00+(AK10/CONH)+(AK10*AK20/CONH**2.0))
      ALP20 = ALP30*AK10/CONH
      ALP10 = ALP30*AK10*AK20/CONH**2.0
      CHSO3 = ALP20*C10
      CSO3 = ALP10*C10
      CIO3 = ALP12 * C12
      RETURN
      END

      SUBROUTINE PLOT (Y,NDIM,YMIN,YMAX,NWRITE,NGR)
      DIMENSION Y(NDIM),A(119),NZ(10),CHAR(10)
      CHARACTER BLANK,PLUS,CHAR,A
      DATA BLANK,PLUS,CHAR(1),CHAR(2),CHAR(3),CHAR(4),CHAR(5),
     1CHAR(6),CHAR(7),CHAR(8),CHAR(9),CHAR(10)
     1/' ','+','.','X','C','D','E','F','G','I','J','K'/
      NPTS = NDIM/NGR
      YMNT=YMIN
      YMXT=YMAX
      DELTA=(YMAX-YMIN)/100.
```

```
      NPTS = NDIM/NGR
      YMNT=YMIN
      YMXT=YMAX
      DELTA=(YMAX-YMIN)/100.
      YMN=YMIN - 9.*DELTA
      DO 10 I=1,119
   10 A(I)=BLANK
      IF(YMAX-YMIN) 11,11,15
   11 WRITE(NWRITE,29)
      RETURN
   15 WRITE(NWRITE,9) NPTS,DELTA
      WRITE(NWRITE,19) YMNT,YMXT
      DO 60 I=2,NPTS
      IF (MOD(I,6)-1) 24,17,24
   17 DO 20 J=10,119,10
   20 A(J)=PLUS
   24 DO 30 J=1,NGR
      N=(Y(I+(J-1)*NPTS)-YMN)/DELTA+1.5
      IF (N.LT.1) N=1
      IF (N.GT.119) N=119
      NZ(J)=N
   30 A(N) = CHAR(J)
      WRITE(NWRITE,39) (A(J),J=1,119)
      DO 40 J=1,NGR
      N=NZ(J)
   40 A(N)=BLANK
      IF (MOD(I,6)-1) 60,38,60
   38 DO 50 J=10,119,10
   50 A(J)=BLANK
   60 CONTINUE
    9 FORMAT('1'31X,'NO. OF POINTS ON ABSCISSA = 'I5/32X,'NO. OF
     1INTERVALS ON ORDINATE = 118,  INCREMENT = 'E10.3)
   19 FORMAT(' 'E16.6,E101.6/10X,'I'99X,'I'/' I',8X,'I',2(49X,'I'),
     18X,'I')
   29 FORMAT (' YMAX AND YMIN SPECIFIED INCORECTLY')
   39 FORMAT(' '119A1)
      RETURN
      END

$ENTRY
```