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REACTIONS OF CHLORINE DIOXIDE AND OTHER
OXY-CHLORO COMPOUNDS WITH ORGANIC COMPOUNDS

Third Annual Progress Report on

Kinetics and Mechanisms of the Reaction Between
Chlorite and Hypochlorous Acid in Aqueous Solution

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PREFACE

In recent years chlorine dioxide has been found useful for a variety of purposes including the bleaching of flour, textiles and grease and as a water treatment reagent.

Elemental chlorine has been found to be the most useful of disinfecting chemicals for water or waste water; however there are some disadvantages to its use. Its initial hydrolysis product, hypochlorous acid, dissociates to yield the relatively poor disinfectant, hypochlorite ion. Also the hypochlorous acid reacts readily with some amino type compounds commonly found in water to form a chlorine-amine system which is a poorer disinfectant than hypochlorous acid. Despite the dissociation or formation of chlorine-amine compounds, chlorine remains the disinfectant of choice in most instances. However, when "phenols" are present the chlorine reacts with the "phenols" to form chlorophenols which are odorous; in fact so odorous the water may be unpalatable. It has been observed repeatedly that chlorine dioxide seems to destroy, in many cases, the chlorophenols reducing or eliminating that odor problem.

Chlorine dioxide is a rather unstable gas at ordinary conditions and is quite soluble in water. It may be prepared in a number of ways; for water works practice, the generation is usually by means of mixing aqueous solutions of chlorine and sodium chlorite. This paper is a report of the study of the reaction between hypochlorous acid and chlorite ion which, under the condition of the experiments, yielded chlorine dioxide, chlorate and chloride. It was found possible to use the ultra-violet range of the spectrophotometer to trace the course of the reaction. Other means were also used to measure the various species of chlorine present. The experimental work made possible the determination of the reaction kinetics under a variety of conditions, the activation energies

and also a reasonable deduction of the reaction mechanism.

The work was conducted by Dr. Marvin L. Granstrom, Dr. Bernard H. Israel, Dr. W. Brewster Snow and Miss M. E. Lynch in the Sanitary Engineering Laboratories of the Department of Civil Engineering, Rutgers University, New Brunswick, New Jersey. The work was supported in part by research grants NSF G9707 and Army Chemical Center Grant DAC41-18-1081G26.

New Brunswick, New Jersey

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CHAPTER I

INTRODUCTION

Chlorine dioxide as used in water works practice is generated at the place of use by mixing aqueous solutions of hypochlorous acid and sodium chlorite in a reaction vessel termed a generator. Little is known of the reaction in terms of kinetics, yield, or mechanisms. It is the purpose of this research to seek this information.

Within a pH range of 3.5 to 5.5 almost all of the chlorine present is in the form of hypochlorous acid and the chlorite in the form of the ion⁽¹⁾. Thus the reaction may be indicated by Equation 1.



It was necessary to determine the values of g, h, p, q and r. Under certain conditions the reaction is sufficiently slow to allow tracing of absorbancies due to hypochlorous acid, chlorite and chlorine dioxide with time using the ultra-violet range of the spectrophotometer. Calculation of concentration of these three molecular species at various times was then possible. Tracing the concentration with time of chlorate or chloride was not possible; however, concentration of these two latter species could be measured at the completion of a run. It was found that the relative values of g, h, p, q, and r remained constant during the course of a single run, but did change with experimental conditions.

Also with the concentration-time information on hypochlorous acid, chlorite and chlorine dioxide it became possible to establish kinetic equations. The reaction rate is described by Equation (2).

$$\frac{d[\text{ClO}_2]}{dt} = k_{\text{app}} [\text{HOCl}]^m [\text{ClO}_2^-]^n \quad (2)$$

The k_{app} , the apparant reaction velocity coefficient, is affected by pH and by buffer concentration; the effect of each on the k_{app} was determined. Furthermore each of the several components of k_{app} were

affected by temperature so activation energies were determined. Since the stoichiometry of Equation (1) was reasonably well supported by measurement and the need of oxidation-reduction balance apparent, it became possible to suggest a certain reaction mechanism.

The experimental procedures, methods and results of data analysis, the proposed mechanisms and reaction thermodynamics are described in detail in the succeeding chapters of this report.

CHAPTER 2

EXPERIMENTAL PROCEDURES

In this section is included a discussion of the reagents, equipment used, the analytical procedures and the actual conduct of the experiments.

A. Reagents

1. Organic Free Distilled Water (O.F.D.)

The preparation of water suitable as a solvent for any of the oxychloro species was one of the most troublesome problems. The procedure adopted involved the redistillation of regular distilled water from acid permanganate (1% conc. H_2SO_4 and 1% KMnO_4), the permanganate being effective in removing volatile amines. The distillate traveled through a long vertical column containing glass beads and wrapped with asbestos. It was necessary to use a heating tape near the top of the column in order to break the continuous film of water from the distillation flask; otherwise, there was creeping of the permanganate and the distillate would contain about 10^{-5}M of the oxidizing agent.

2. Hypochlorous Acid (HOCl)

Hypochlorous acid was prepared according to the method of Zimmerman and Strong (2) by saturating water with chlorine gas, neutralizing to a pH of about 5 with sodium hydroxide, and distilling under reduced pressure at a temperature of $<15^\circ\text{C}$, using a cold finger submerged in an acetone - dry ice trap. The first distillate was rejected and the succeeding ones were collected. Silver sulfate was added to the distillate to precipitate the remaining chloride ions, the mixture was shaken overnight, and the solution was redistilled, the first distillate again being rejected. Previous experience has demonstrated the need for rejecting the first distillate in each distillation. This procedure yielded a distillate which gave a

negative test for chloride ions when silver nitrate was added and also a negative test for sulfate ions when barium chloride was added. A solution of about 0.05M hypochlorous acid resulted when this procedure was used for its preparation, the concentration being determined iodometrically using thiosulfate with starch as the indicator.

3. Chlorine Dioxide (ClO_2)

Chlorine dioxide was prepared according to a method of Granstrom and Lee⁽¹⁾ by dissolving 4 grams of sodium chlorite in 50 ml distilled water in the reaction vessel - to this was added a solution of 2 grams of potassium persulfate in 100 ml distilled water. High purity nitrogen gas (Linde) was used to sweep out the chlorine dioxide formed; this $\text{N}_2 - \text{ClO}_2$ gas mixture was passed through a dry sodium chlorite column to remove any traces of hypochlorous acid which may have been formed; next, the gases were passed into a trap to remove any sodium chlorite dust which may have been carried over and finally the chlorine dioxide was collected in cool O.F.D. water. The temperature of the receiving solution was kept from 0-10°C, by immersing the container in a beaker of crushed ice; this increases the solubility of chlorine dioxide. A solution concentration which ranged from 2 to $10 \times 10^{-3} \text{M}$, could be prepared thus, the resulting concentration being determined iodometrically at a pH of 1 to 1.5.

4. Sodium Chlorite Solutions

The most important concern in the preparation of sodium chlorite solutions was the purity of the salt. Finally the solutions were prepared from an analytical grade material which, on iodometric analysis, was 98.2% pure. Sodium chlorite salt (analytical grade) apparently deteriorates more rapidly than anticipated⁽³⁾. The

salt on our shelf yielded about 85% chlorite whereas two years ago the salt was about 98% chlorite. Attempts to recrystallize the sodium chlorite using the method of Weiner ⁽⁴⁾ were somewhat disappointing; apparently we could increase yield to only about 92%. However, a fresh sample of sodium chlorite (98+%) was obtained from the Olin Mathieson Co. A private communication from Dr. Max Metzger of that company provided us with procedures for further repurification which we did not believe necessary. See Appendix A for procedures.

5. Buffer System

It was decided to use a phosphate buffer system--some of the organic systems which are appropriate in this pH range especially acetic acid--acetate may react with the oxychloro compounds present. It is not likely that this phosphate system would be thus affected. Also some previous experience showed that at a molal concentration of 0.1 or more the phosphate buffer system would hold the pH constant under the experimental conditions anticipated in this research.

It was decided to hold the ionic strength of the reaction at 0.3 using molal concentrations throughout. This necessitated evaluation of the ionic strength of the buffer systems as described below:

1) In the concentration region of interest, i.e.

0.1-0.3 molal, the pH of a KH_2PO_4 solution is about 4.1.

Thus to obtain pH of 5 it would be necessary to add K_2HPO_4 .

The relative amounts of H_2PO_4^- and HPO_4^{2-} at a pH of 5 may be calculated thus:



$$K_2 = \frac{[\text{H}^+][\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} = 7.5 \times 10^{-8} \quad (4)$$

or at a pH of 5,

$$\frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} = \frac{K_2}{[\text{H}^+]} = \frac{7.5 \times 10^{-8}}{1 \times 10^{-5}} = 7.5 \times 10^{-3}$$

or about 99.25% of the total system is in the form of H_2PO_4^- .

Since the salt KH_2PO_4 dissociates, $\text{KH}_2\text{PO}_4 \rightleftharpoons \text{K}^+ + \text{H}_2\text{PO}_4^-$, into two monovalent ions, the ionic strength is equal to the concentration. Thus, at a pH of 5 the ionic strength of an $\text{H}_2\text{PO}_4^- - \text{HPO}_4^{2-}$ system can be considered to be equal to the concentration of the KH_2PO_4 salt.

2) Similarly to obtain a pH of say 4, H_3PO_4 would be added to the KH_2PO_4 salt.

The relative concentrations of the acid and the salt could be calculated as follows:



$$K_1 = \frac{[\text{H}_2\text{PO}_4^-][\text{H}^+]}{[\text{H}_3\text{PO}_4]} = 1.1 \times 10^{-2} \quad (6)$$

or at a pH of 4,

$$\frac{[\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]} = \frac{K_1}{[\text{H}^+]} = \frac{1.1 \times 10^{-2}}{1 \times 10^{-4}} = 1.1 \times 10^2$$

or the salt concentration is 100 times the acid concentration.

Thus the ionic strength of the $\text{H}_3\text{PO}_4 - \text{KH}_2\text{PO}_4$ system could be considered equal to the concentration of the KH_2PO_4 salt.

To prepare the buffer systems to be used, either H_3PO_4 or K_2HPO_4 solution was added to the KH_2PO_4 solution. At each of the reaction pH's (4.2, 4.5 or 5.0) three different buffer concentrations would be used in the reaction runs, namely 0.1, 0.2 and 0.3 molal. Since the buffer concentration affects the pH, nine different concentrated buffers were prepared in sets

of three: each of the sets having a nominal pH. Thus, for a given pH the appropriate concentrated buffer would upon dilution yield that pH value. At a different dilution of that concentrated buffer the final pH would be different. To avoid this, the pH of the concentrated buffer was adjusted slightly.

All other chemicals used were reagent or analytical reagent grade except those as described previously in this section.

B. Equipment - The equipment in this research included:

1. Cary Recording Spectrophotometer Model 11S with a hydrogen discharge lamp. Matched pairs of 1.00 and 10.00 cm silica cells with ground glass stoppers were used; cell corrections were made when necessary.
2. Beckman, Model G, pH meter
3. Fisher, Type S Potentiometer with silver-silver chloride and calomel electrodes. The calomel electrode was physically connected to the solution under analysis by a potassium nitrate-agar U tube salt bridge.
4. Precision Scientific Co. constant temperature water bath (circulating system) was used when the reaction temperature was above ambient. The water was circulated using a Fisher Circulating Pump, Model B-1. When reaction temperature was less than ambient the contents of the water bath were cooled by circulating cold water through the coils. This outside cold water was itself cooled by submerged coils which were in effect the remote coils of a refrigerator.

The additional apparatus used in conjunction with the procedures in this report, outside of the apparatus described, were, for the most part, of the simple laboratory equipment type.

C. Measurements

1. Spectral Calibration of Hypochlorous Acid, Chlorite and Chlorine Dioxide

Previous experience indicated that very accurate values of molar absorptivity were needed to trace the reactions of the research. Also previous experience revealed the extreme difficulty of obtaining replicability of these values. However, now it appears that a satisfactory system has been established. The spectra of hypochlorous acid, chlorite and chlorine dioxide are shown in Appendix B.

a. Collection of Calibration Data

The reagents and buffers were prepared as described in Section A and concentration determinations of the oxychloro species were done using the iodometric technique with thiosulfate and starch indicator. The pH values used were approximately 4 for hypochlorous acid and 1.0 to 1.5 for chlorite and chlorine dioxide. Spectra were taken using a Cary Recording Spectrophotometer Model 11S. Because of the relative instability of these oxychloro compounds, it was necessary to determine concentration by titration simultaneously with the spectrum tracing. This was repeated numerous times with each species under a variety of the typical conditions which will be used for the kinetic runs. That is, pH 4.2 to 5.0, buffer concentration 0.1 to 0.3 molal, and ionic strength up to 0.3 molal using sodium sulfate.

b. Analysis of the Data

As anticipated the wave lengths of maximum absorbancy were 235, 260, and 357 m μ for hypochlorous acid, chlorite ion and chlorine dioxide respectively. At 238 m μ the spectrum of chlorite is in a valley, whereas at 235 m μ the spectrum is rising steeply. On the other hand the spectrum of hypochlorous acid is reasonably flat in the region of 230-240 m μ . Therefore, the wave lengths

selected for absorptivity value determinations were 238, 260 and 357 mμ. The values obtained for each of the oxychloro species at each of the three wave lengths are shown in Table 1.

TABLE 1

Molar Absorptivities of HOCl, ClO₂⁻ and ClC₂

Wave Length mμ	Chlorine Dioxide	Chlorite Ion	Hypochlorous Acid
238	140	66	102
260	45	155	44
357	1242	4.4	1.7

c. Experimental Difficulties

Stock solutions of chlorine dioxide proved to be somewhat unstable and were always prepared on the day of use and stored at refrigerator temperature when not in use. The instability of chlorine dioxide appears to derive from its volatility at an air-water interface. Dilutions in stoppered Cary cells showed no evidence of light-activated decomposition in the spectrophotometer with time. Therefore, the precautions taken bear only on the calibration runs and will not affect the absorbancy readings on chlorine dioxide being produced by reaction with the Cary cell.

d. Analysis of Calibration Data

Using this simultaneous titration - absorbancy tracing procedure, it was determined that solutions of chlorine dioxide follow Beer's law up to a concentration of 14×10^{-4} molar. There was some indication that at higher concentrations the absorbancy tends to fall below this linear relationship. This was not investigated since concentrations of chlorine dioxide higher than this value were not generated in this research.

In the final determination of this adherence to Beer's law, only replicated data at each of five concentrations was used. Thereby the reproducibility of both absorbancy and titrated molarity could be expressed. Finally, a least squares fit of the replicate data was calculated as follows:

$$A = 0.0043 + 1236 C$$

where A is the recorded absorbancy at 357 mμ and C is the molar concentration of chlorine dioxide. This linear relationship passes through the cross at each concentration formed by lines extending horizontally and vertically one standard deviation from the mean absorbancy - mean molar concentration.

Since this relationship nearly approaches but does not exactly pass through the origin, it was felt that further refinement was not warranted but that a mean value of 1242 could be considered. Once the experimental difficulties were resolved it was possible using replicate dilutions of a single concentration to obtain molar absorptivity values with average deviations of $\pm 2\%$.

2. Measurements of Chloride and Chlorate

Use of potentiometry was made in analysis of the forms of chlorine in the system at the completion of a run. The equipment included a Type S Fisher Potentiometer, a calomel electrode vessel, and a silver-silver chloride electrode. The calomel electrode vessel consisted of an agar salt bridge and a saturated mercury calomel electrode. The agar salt bridge⁽⁵⁾ consists of a narrow U-shaped tube filled with a gel of saturated potassium nitrate in agar. This gel is prepared by heating 30 gm. potassium nitrate, 3 gm. agar and 100 ml. of distilled water gently, until all has gone into solution and the solution is clear. Analysis was carried

out by immersing the silver-silver chloride electrode and one end of the salt bridge in a beaker containing the solution of chloride to be titrated and titrating with silver nitrate. The normality of the silver nitrate was previously determined using this potentiometric titration with a chloride solution as a primary standard.

Two types of reductions were carried out on the system at the completion of a run and the reduced solutions were titrated potentiometrically for chloride.

1. The chloride formed as a product of the reaction was determined by the reduction with hydroxylamine sulfate.⁽¹⁾ The following procedure was used: Equal amounts of each half sample were mixed and allowed to react for the same length of time that the reaction had been traced in the spectrophotometer run. Twenty-five ml. of hydroxylamine sulfate solution (0.1M) was added and the resulting solution titrated potentiometrically with a silver nitrate solution of known concentration. The calculations and discussion of these data are described in Section F of Chapter 3.
2. Amalgamated zinc in a Jones reductor column served as the reducing agent to reduce the chlorate in the system to chloride.⁽⁶⁾ The amalgamated zinc for use in the reductor column is prepared as follows:⁽⁷⁾ Add 300 ml. of a 2% mercuric nitrate solution and 1.5 ml. of concentrated nitric acid to 300 gm. of pure 20 mesh zinc in a beaker. Stir the mixture thoroughly for 5 to 10 minutes, then decant the solution from the zinc and wash 2 or 3 times by decantation. Fill the reductor tube with water, then add the zinc slowly until the column is completely packed. Wash with 500 ml. of distilled water,

using gentle suction.

The following procedure⁽⁶⁾ was used for analysis of the mixture for total amount of chlorine present in all forms at the end of the reaction. Equal amounts of each half sample were mixed and allowed to react for the same length of time the reaction was followed in the spectrophotometer. Fifty ml. of 4N sulfuric acid and 7.5 ml. of 0.1 M sodium molybdate were added to this and the solution passed through the Jones reductor column. The column, reaction beaker and filter flask were washed three times with small portions of distilled water and these washings added to the filtrate. The Mo^{+++} , making the solution green, was oxidized to $\text{MoO}_4^{=}$ (colorless) by dropwise addition of 0.1N potassium permanganate solution. The pH of the solution, which was initially around 0.3, was then adjusted to 1.5 with solid dibasic potassium phosphate.

The solution was titrated potentiometrically with silver nitrate. The calculations and discussion of these data are described in Section F of Chapter 3.

D. Temperature Control

Because reaction kinetics are usually temperature dependent it was necessary, in the course of these experiments, to maintain constant reaction temperatures. For this purpose the following equipment and techniques were used.

1. Laboratory

All spectrophotometric observations were made in an air conditioned laboratory. The ambient temperature was about 22°C and the variation during a day was less than 1°C.

2. Reaction Solutions

All solutions used in the reaction were brought to reaction temperature by placing in a water bath kept at that temperature. The nominal temperatures used in these experiments were 12.5°C, 23.1°C and 30.3°C.

3. Cell Chamber

The cell chamber of the spectrophotometer has included within its wall, coils through which water from the water bath can be circulated. The liquid contents of the cells were usually 1°C warmer than the temperature of the circulating water.

4. Water Bath System

Temperature control of the circulating water was maintained by use of a water bath equipped with a mercury column thermostat and heating coils. An integral pump circulated the contents of this bath through the spectrophotometer. When the reaction temperature was less than ambient the contents of this water bath were cooled by pumping cold water through coils submerged in the bath. The source of cold water was a tank into which was submerged the coils of a refrigerator.

The temperature range of the water circulating external to this system, i.e. through the spectrophotometer, was less than 0.5°C after equilibrium was established.

The temperature recorded for a given run was the average of the temperature at the beginning and at the end of the run. The temperature at the beginning of the run was taken of the reaction solution at the time of mixing. The temperature at the end of a run was taken by inserting a thermometer into the contents of the cell.

- E. Making A Run to Trace The Concentrations of Hypochlorous Acid, Chlorite and Chlorine Dioxide - The step by step procedure used in the collection of the spectrophotometric data is shown as follows:

1. Separate stock solutions of hypochlorous acid and chlorite were prepared and the concentrations determined iodometrically.
2. Aliquots of these stock solutions were taken to prepare each half sample and the buffer or buffer electrolyte was added.
3. The concentration of each half-sample was determined spectrophotometrically.
4. Equal volumes of the two solutions were mixed intimately at time zero.
5. A portion of the mixture was pipetted into the cuvette (either 1 cm. or 10 cm.) which was then put into the instrument. The blank cell contained all of the mixture components except the reactants.
6. The drive mechanism of the instrument was turned on after the reaction cell was in place, and the time of the reaction was noted. Because the scan speed of the instrument is known, the time at any point on the tracing can be determined. A tracing of the absorbancy at a given wave length vs. time or absorbancy vs. wave length was obtained for each run. It was decided to repeat the experiment at each of the three wave lengths, 357, 260, and 238 mμ in order to trace the reactions. This procedure was followed in Runs 8, 14, 19, 20, 24, 25, 27-31, 43-66, 84-92, these runs were designated A, B, and C respectively.

However, experience showed that when the reaction is reasonably slow, i.e. time of completion > 15 minutes, it would be possible to collect enough readings for each of the three wave lengths by scanning repeatedly from

220 to 380 mμ. This was accomplished by reversing the direction of the drive mechanism when either the 220 or 380 mμ wave length was reached. The times were noted on the tracing, and it was observed that a scan from 380 to 220 mμ could be taken every 40 seconds, or faster, if desired. This procedure was followed in Runs 3 and 4 and these runs were designated as M runs. Nevertheless, this procedure was discontinued after Run 4 in favor of the A, B, C Runs because of the lengthy procedure necessary to calculate the component concentrations. The computational techniques used to convert the spectrophotometric tracings to concentrations of hypochlorous acid, chlorite and chlorine dioxide are shown in Section A of Chapter 3.

F. Check on the Reaction Between Chlorine Dioxide with Hypochlorous Acid or Chlorite

In addition to the actual kinetic runs, several parallel runs were made by taking separate mixtures of each component and chlorine dioxide. These were prepared in order to check if any reaction took place between them. These dual reaction studies were done on solutions of chlorine dioxide and chlorite and of hypochlorous acid and chlorine dioxide. The results obtained from these studies indicated that any reaction between each reactant and the product is very slow and therefore, negligible in comparison with the rate of reaction of chlorite and hypochlorous acid. This is in agreement with the work of Ellis et al.⁽⁸⁾ who found that the reaction of hypochlorous acid and chlorine dioxide is very slow and therefore, would not contribute significantly to the overall reaction of hypochlorous acid and chlorite.

G. Experimental Difficulties

There were several experimental difficulties with which there was concern. As described above in Section C.c. of this chapter the volatility of chlorine dioxide is high - this gave some difficulty in the determination of the molar absorptivity. However, by simultaneous titration and spectrophotometric observation, replicity was noted.

The rate of the reaction which is described by Equation 1, is pH dependent - this necessitated the use of a buffer system. The buffer system affected the reaction rate; consequently buffer concentration became another variable to be considered tripling the number of runs necessary.

As will be shown in Chapter 3, computation for the concentration values of hypochlorous acid, chlorite and chlorine dioxide necessitates the solution of three simultaneous equations. The molar absorptivity values shown in Table 1 are coefficients in these equations. The very similarity of absorptivity values of the three components at the 238 and the 260 mμ wave lengths results in computational difficulties. A slight error in the value of molar absorptivity or of the observed absorbancy is magnified considerably in final values obtained of the concentration hypochlorous acid, chlorite and chlorine dioxide. The manners of adjustments of the data are described in Chapter 3.

CHAPTER 3

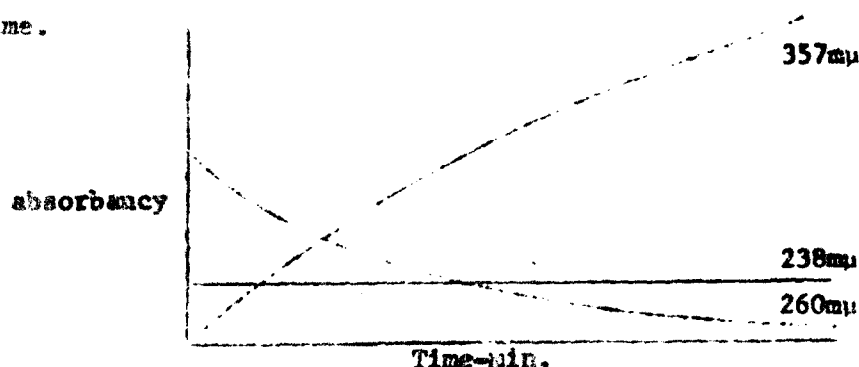
ANALYSIS OF DATA

During the course of the experimentation for this research, some 100 kinetic runs were made. In addition, measurements for chloride and chlorate formation on all but the first 23 runs were made. Unfortunately the data from all the runs were not usable

A. Conversion of Spectrophotometric Data to Concentration Values for Hypochlorous Acid, Chlorite and Chlorine Dioxide

From the tracings obtained on the spectrophotometer charts during the course of a reaction, absorbancy data at designated times at 238, 260, and 357 m μ were picked off of the tracings and tabulated. Cell correction values were applied and the final values of absorbancy at each of the three wave lengths were plotted against time.

A smooth curve was drawn through the points. A typical run might yield a set of curves such as shown in Figure 1. From these curves, absorbancy values at each of the three wave lengths could be selected at any time.



FIGURE

Absorbancy Values vs. Time, at Wave Length Indicated

It has been shown that the total absorbancy at any wave length is due to the sum of the absorbancy of the various species in solution. Thus, the following equations may be written:

$$A_{238} = \epsilon_{238-ClO_2} [ClO_2] + \epsilon_{238-ClO_2^-} [ClO_2^-] + \epsilon_{238-HOCl} [HOCl] \quad (7)$$

$$A_{260} = \epsilon_{260-ClO_2} [ClO_2] + \epsilon_{260-ClO_2^-} [ClO_2^-] + \epsilon_{260-HOCl} [HOCl] \quad (8)$$

$$A_{357} = \epsilon_{357-ClO_2} [ClO_2] + \epsilon_{357-ClO_2^-} [ClO_2^-] + \epsilon_{357-HOCl} [HOCl] \quad (9)$$

in which

A = absorbancy

ϵ = molar absorptivity

[] = molar concentration

the subscripts refer to the wave length and species indicated. The values of the molar absorptivity, as shown in Section C, Chapter 2, were substituted into the above equations. Thus, the values of the "A's" and the "epsilon's" were known allowing the solution of the above equations for the values of [HOCl], [ClO₂⁻], and [ClO₂]. These concentration values were then plotted as shown in Figure 2.

An inventory of the various runs used in the calculations is shown in Table 2. As explained below in Section C of this chapter, the results of some of the runs made were so erratic that it was not possible to include them in the calculations. It may be noted that the variables considered were temperature, pH and buffer concentration.

D. Determination of the Apparent Reaction Velocity Coefficients

Solution of Equation 2

$$\frac{d[ClO_2]}{dt} = k_{app} [HOCl]^m [ClO_2]^n \quad (2)$$

requires evaluation for k_{app} , m and n. The value of the left hand side of Equation 2 at any time t can be determined by taking tangents to the curve of

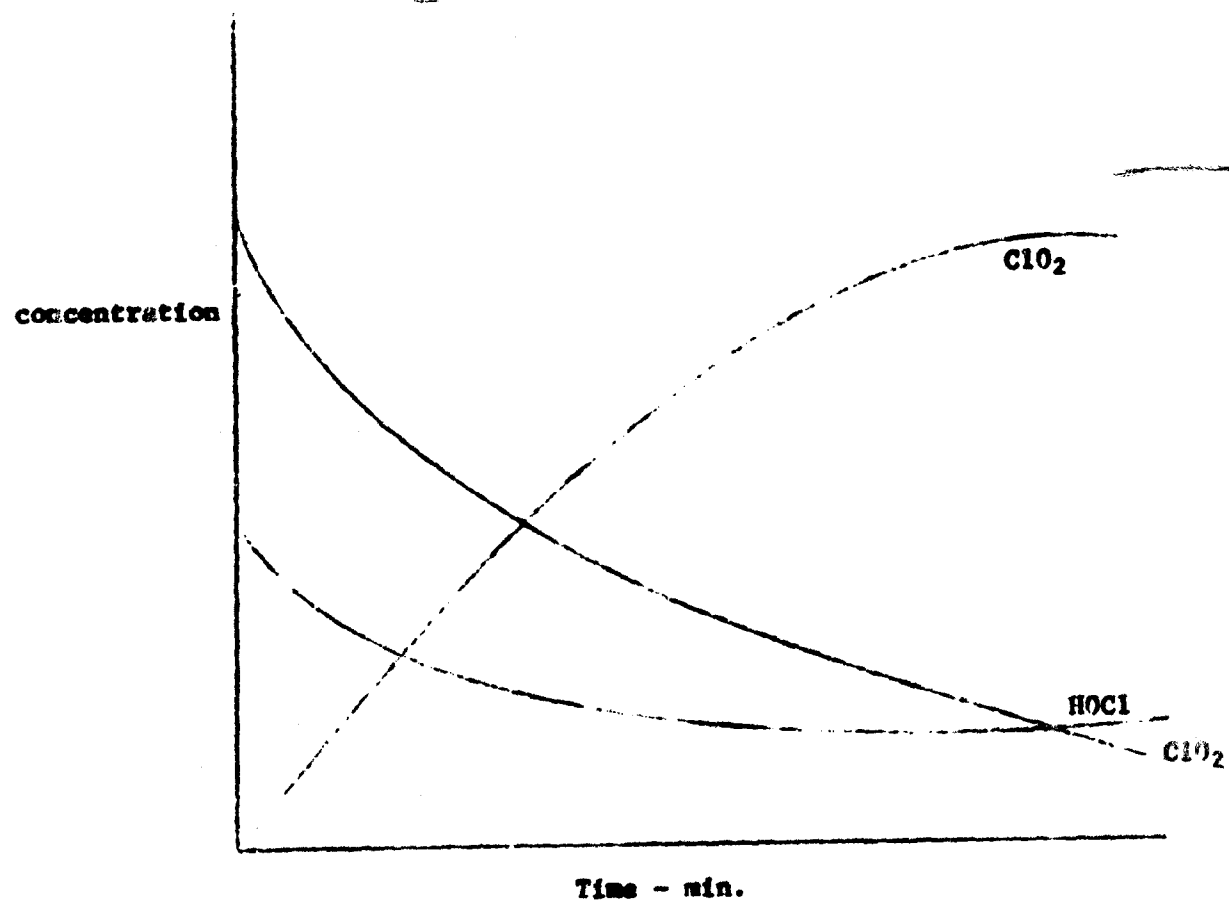


FIGURE 2

Calculated Values of ClO_2 , ClO_2^- and HOCl Versus Time

TABLE 2

Experimental Conditions and Value of Apparent Reaction Velocity
Coefficient k_{app} for Kinetic Runs

Ionic Strength Constant at 0.3M

Run No.	Initial [HCO ₂] M ⁻¹	Initial [ClO ₂] M ⁻¹	pH	Buffer molal	Temp. °C	k_{app} l mole ⁻¹ min. ⁻¹
21	4.77	8.77	4.36	0.1	21.6	290
22	4.41	8.37	4.35	0.1	21.3	230
23	4.41	8.37	4.35	0.1	21.3	260
24	9.71	9.87	4.32	0.2	21.7	540
25	4.85	10.06	4.43	0.3	22.8	458
26	4.95	14.50	4.51	0.1	25.2	365
27	4.90	14.52	4.54	0.1	23.6	265
28	9.41	9.77	4.25	0.1	22.2	495
29	9.22	10.03	4.21	0.2	22.0	610
30	10.34	10.45	5.01	0.1	22.9	157
31	10.34	10.29	4.91	0.2	23.1	218
32	12.65	10.29	5.01	0.3	24.2	150
33	9.85	10.19	5.02	0.3	25.8	188
34	9.71	10.10	4.24	0.3	25.4	1085
35	9.85	9.90	5.02	0.1	30.7	181
36	9.17	10.10	5.00	0.1	30.5	207
37	9.90	10.23	5.00	0.1	30.7	190
38	9.56	10.23	4.99	0.1	30.8	182
39	9.36	9.94	4.87	0.2	30.2	285
40	9.46	9.77	5.00	0.2	30.2	277
41	9.70	9.90	5.00	0.2	30.0	225
42	8.97	10.06	5.00	0.3	30.9	214
43	10.25	10.10	5.04	0.3	31.0	264
44	9.51	9.68	4.21	0.1	30.9	513
45	9.75	9.71	4.25	0.2	30.9	770
46	9.66	9.94	4.19	0.2	30.6	980
47	10.34	10.13	4.19	0.3	30.8	1150
48	9.95	9.97	4.19	0.3	30.6	1230
49	9.51	10.03	4.51	0.1	30.8	345
50	10.29	10.19	4.51	0.1	31.0	335
51	10.39	9.74	4.51	0.2	30.6	480
52	9.85	9.65	4.48	0.3	31.5	540
53	10.34	9.94	4.49	0.3	30.3	540
54	9.75	10.10	4.23	0.2	13.5	600
55	9.61	10.23	4.28	0.3	13.7	540
56	9.56	10.10	4.22	0.1	12.0	340
57	9.75	10.00	4.51	0.3	11.5	365
58	9.80	10.32	4.52	0.2	12.4	305
59	9.75	10.32	4.53	0.1	12.5	190
60	9.41	9.94	5.02	0.3	12.2	168
61	9.36	9.94	4.99	0.2	12.2	159
62	10.64	10.00	4.98	0.1	12.6	143

$[ClO_2]$ versus time. At the same instant of time, the value of hypochlorous acid and chlorite concentrations can be taken from the same figure. It was assumed, in the initial calculation, that m and n are unity. This assumption is borne out if, during the course of a single run, the value of k remains constant. This was found to be true; that is, the rate equation may be written:

$$\frac{d[ClO_2]}{dt} = k_{app} [HOCl] [ClO_2] \quad (2a)$$

The values of k_{app} thus determined are shown in Table 2.

4. Adjustments on the Data

In certain runs the values of k_{app} obtained from solution of equation (2a) at several points in time were not reasonably constant and showed no definite trend. For these same runs it was noted that the intercept obtained by back extrapolation to zero time of the concentration-time curves as illustrated by Figure 2 did not match the zero time value obtained by independent observation. As described in Section E of Chapter II, zero-time values of concentration of hypochlorous acid and chlorite were obtained by independent spectrophotometric readings on separate samples of each of the two reactants. These separate samples were designated as half-samples. The two separate samples which became, upon mixing, the reaction solution were equal in volume; so dividing the spectrophotometric reading obtained by two and using the molar absorptivity values as shown in Table 1, it was possible to compute the zero-time concentration values of hypochlorous acid and of chlorite. Where the zero-time values were not coincident the adjustments were made as follows:

1. If the two points did not coincide the whole absorbancy-time curve was moved vertically to allow it to pass through the half-

sample zero-time value. Since the absorbancies due to hypochlorous acid and chlorite at 357 $m\mu$ are so small no adjustment of the absorbancy-time curve at that wave length was necessary.

2. The new values of absorbancies at 238 and at 260 $m\mu$ thus obtained were used to recalculate the concentration values for hypochlorous acid and chlorite. The inconsistencies noted above, notably the variations in the k_{app} values, were eliminated in most instances.

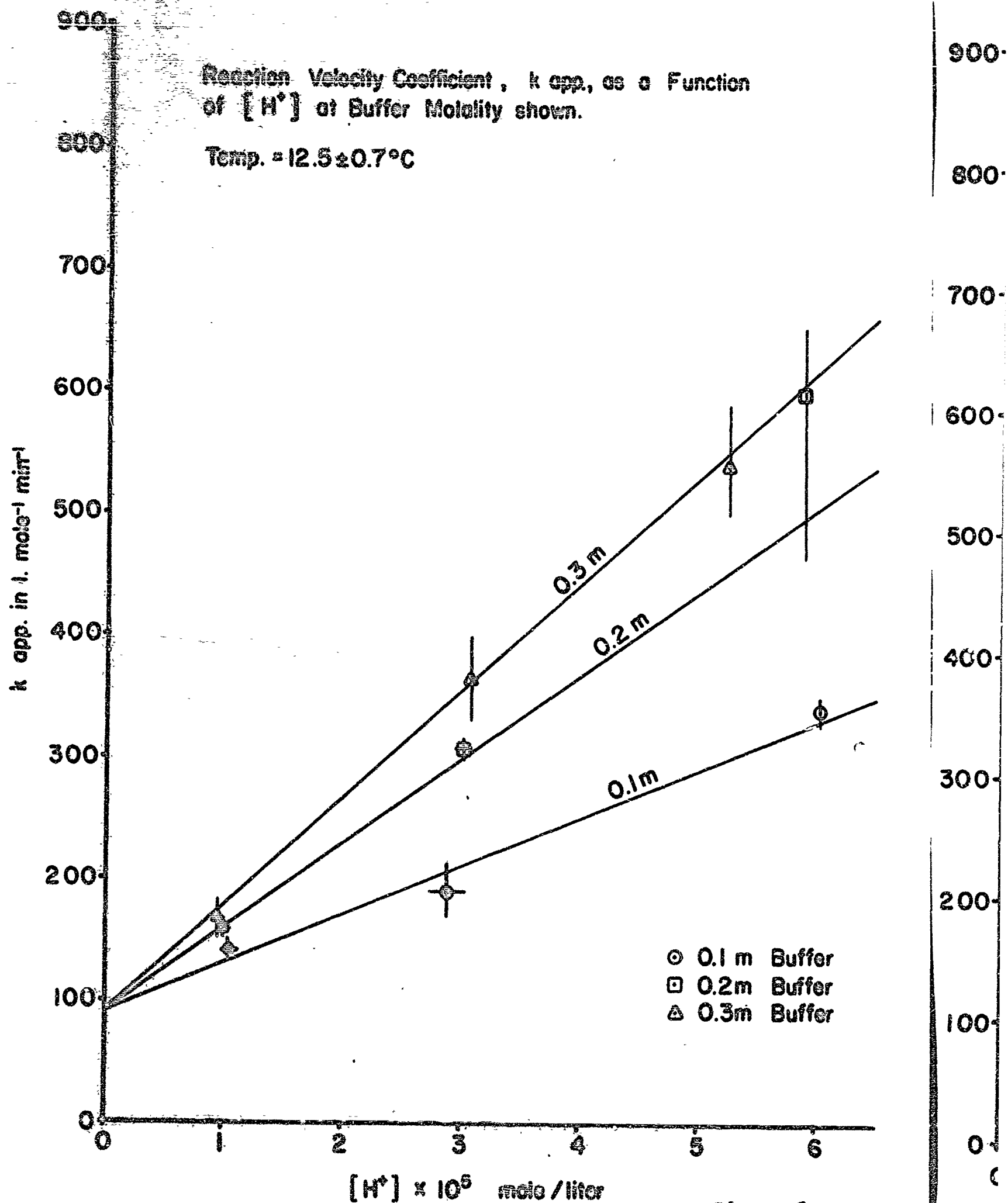
D. Evaluation of the Components of Apparent Reaction Velocity Coefficient

It is apparent that the values of k_{app} obtained are influenced by pH, buffer molality and temperature. Evaluation of these several variables is discussed in this section. The values of k_{app} taken from Table 2 are plotted against hydrogen ion activity on Figures 3, 4, and 5. Figure 3 is for the values at 12.5°C, Figure 4 for 23.1°C and Figure 5 for 30.3°C. On each of the figures the values of k_{app} versus (H^+) values are plotted separately for the different buffer molalities. Because the computed value of k_{app} was not always constant for a single run despite the adjustment described in Section C above, the range of values are indicated by a vertical line on the plot. Straight lines were drawn by eye through the plotted points or lines. The slopes of these straight lines were designated as S_1 and are shown in Table 3.

TABLE 3

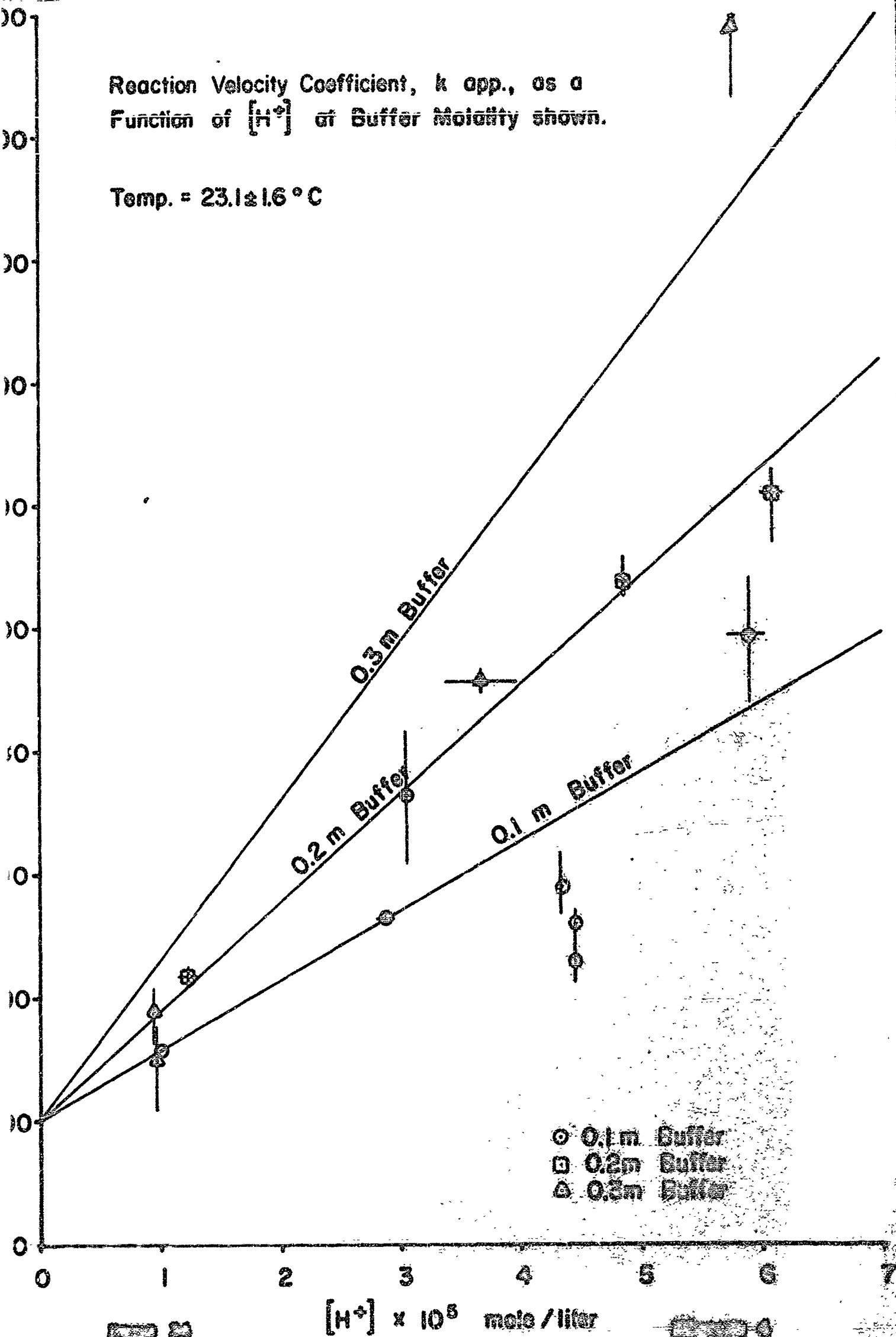
Values of Slope (S_1) versus (H^+) at Buffer Molality and Temperature Indicated. Dimensions of S_1 are $l^2 \text{ mole}^{-2} \text{ min.}^{-1}$

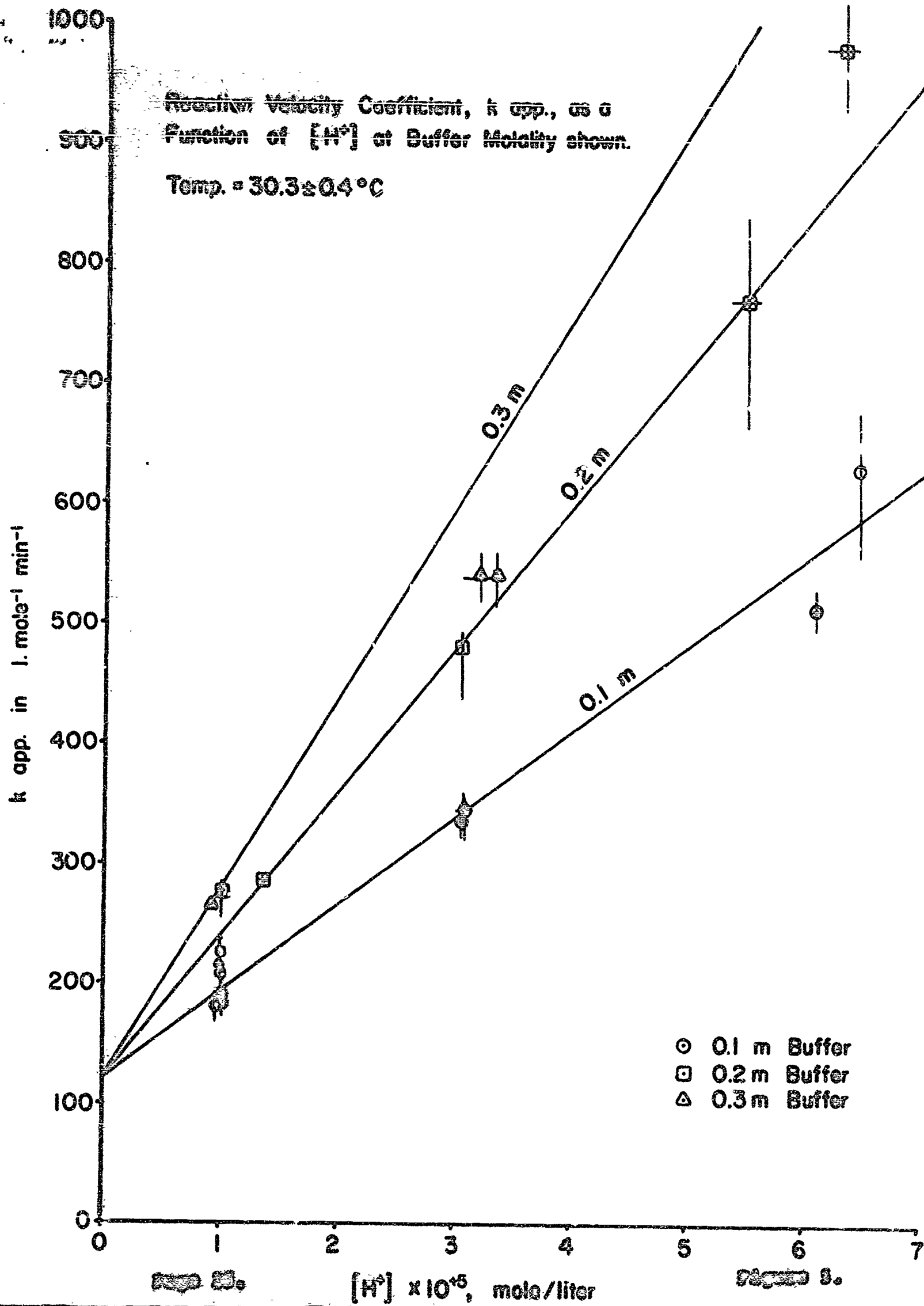
Temperature °C	Buffer Molality			Intercept value of k_{app} at $(H^+) = 0$
	0.1	0.2	0.3	
12.5	$4.0 \times 10^{+6}$	$6.9 \times 10^{+6}$	$8.8 \times 10^{+6}$	90
23.1	$5.7 \times 10^{+6}$	$8.8 \times 10^{+6}$	$12.9 \times 10^{+6}$	100
30.3	$7.2 \times 10^{+6}$	$11.9 \times 10^{+6}$	$15.8 \times 10^{+6}$	120



Reaction Velocity Coefficient, $k_{app.}$, as a
Function of $[H^+]$ at Buffer Molarity shown.

Temp. = $23.1 \pm 1.6^\circ C$





The finite values of the intercepts, and the increase in k_{app} values with hydrogen ion activity and with buffer molality on Figures 3 to 5, suggests that the reaction rate is general acid catalyzed - the three acids being water, hydrogen ion and buffer. The form of the equation, for each temperature, suggested by the plot on Figures 3 to 5 is:

$$k_{app} = k_w + k_H + [H+] + S_2 [H+] [B] \quad (10)$$

In which

k_w - that portion of the reaction velocity coefficient due to the presence of water multiplied by the molar concentration of water in the reaction. The concentration of water is assumed constant.

k_H - that portion of the reaction velocity coefficient due to the presence of hydrogen ion at buffer molality equal to zero.

S_2 - that portion of the reaction velocity coefficient due to the buffer molality and to hydrogen ion at some value of buffer molality greater than zero.

[B] - Buffer molality

1. Effect of Water on Reaction Rate

At each of the three temperatures used in this research, the intercept values of k_{app} at $[H+] = 0$ are independent of buffer molality. Therefore, the values of k_w are 90, 100, and 120 $\text{l mole}^{-1} \text{min}^{-1}$ at the temperatures of 12.5, 23.1 and 30.3°C, respectively.

2. Effect of Hydrogen Ion Activity and Buffer Molality on Reaction Rate

It may be seen from Figures 3 to 5 that the reaction rate increases linearly with the hydrogen ion activity. Also the rate is increased with buffer molality. To evaluate the effect of each of these two acids the following procedure was used:

The slope values of the lines on Figures 3 to 5, designated as S_1 were plotted versus buffer molality on Figure 6.

The intercept values at buffer molality equal zero are designated as k_{H^+} and the slopes of the lines as S_2 .

The values obtained are given in Table 4.

TABLE 4

Values of Constants to be Used in Solution of Equation (10)
for k_{app} at Temperature Noted.

Temp °C	k_w $\text{l mole}^{-1} \text{ min}^{-1}$	k_{H^+} $\text{l}^2 \text{ mole}^{-2} \text{ min}^{-1}$ $\times 10^{-6}$	S_2 $\text{l}^3 \text{ mole}^{-3} \text{ min}^{-1}$ $\times 10^{-6}$
12.5	90	1.75	24.2
23.1	100	2.1	35.2
30.3	120	3.1	42.9

3. Example of Use of Equation (10)

Let Temp = 30°C, Buffer Molality = 0.3, $[H^+] = 5 \times 10^{-5}$

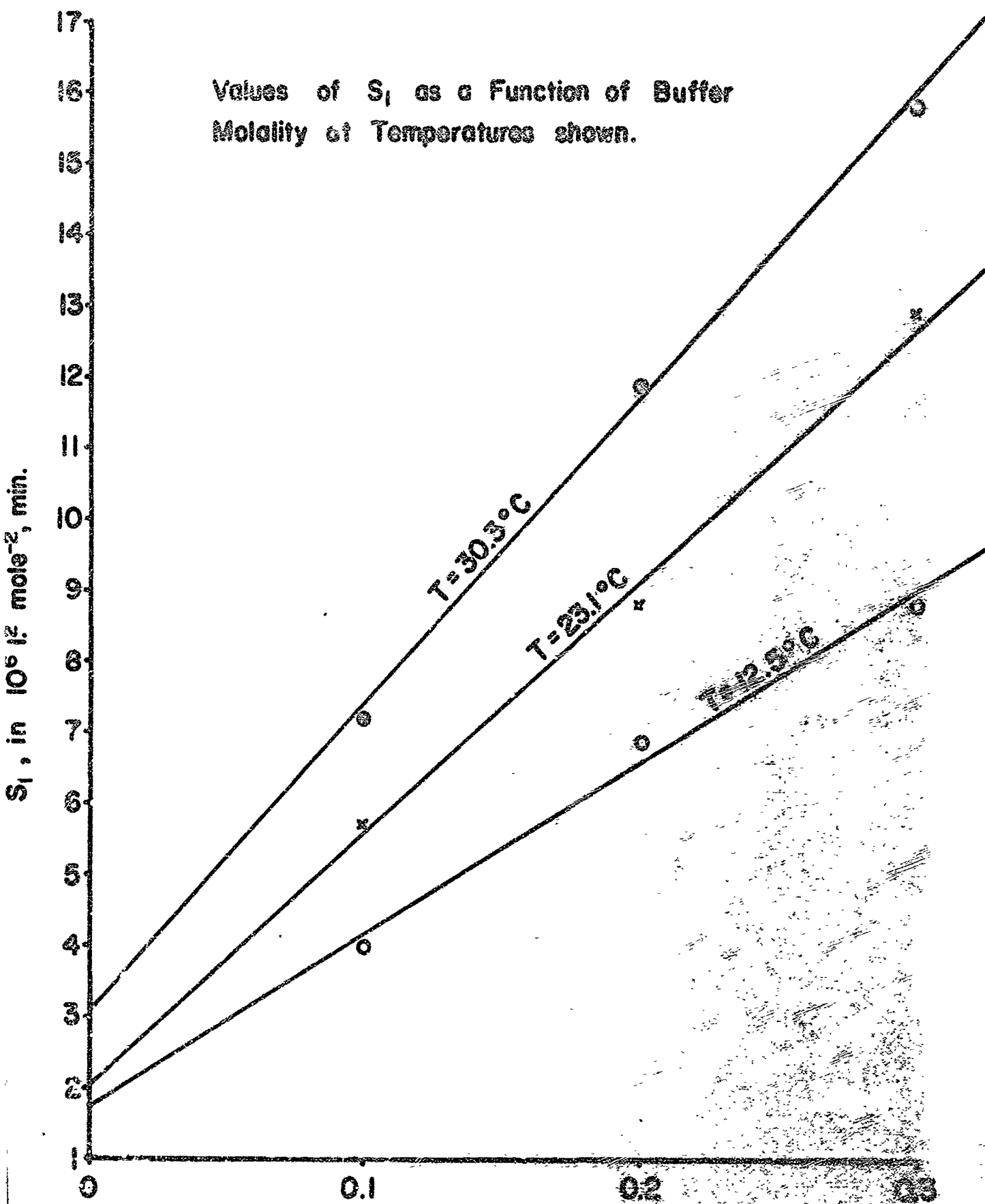
$$k_{app} = k_w + k_{H^+} [H^+] + S_2 [B] [H^+] \quad (10)$$

Selection of the values of coefficients from Table 4 and

substituting values of variables into Equation (10) yield:

$$\begin{aligned} k_{app} &= 120 + [3.1 \times 10^6] \times [5 \times 10^{-5}] + [42.9 \times 10^6] \times [5 \times 10^{-5}] \times [0.3] \\ &= 120 + 155 + 645 \\ &= 920 \end{aligned}$$

S_1 , in $10^6 \text{ l}^2 \text{ mole}^{-2} \text{ min}^{-1}$



From Figure 5 the values obtained for these conditions is 920 also.

E. Determination of Activation Energies

It is noted from Figures 3 to 6 that the reaction rate is increased with temperature within the range used in this research, i.e. 12-30°C. The data collected makes possible the computation of activation energies of each of the three components, k_w , k_{H+} and S_2 . Information on the activation energies not only aids in the analysis of the thermodynamics of the reaction but also makes possible computation of the values of k_{app} at experimental conditions other than those used in the research. To compute the activation energies the Arrhenius Equation was used - Equation (11).

$$k = Ae^{-E/RT} \quad (11)$$

$$\ln k = \ln A - E/RT \quad (11a)$$

in which

A = coefficient - "frequency factor"

E = activation energy - calories

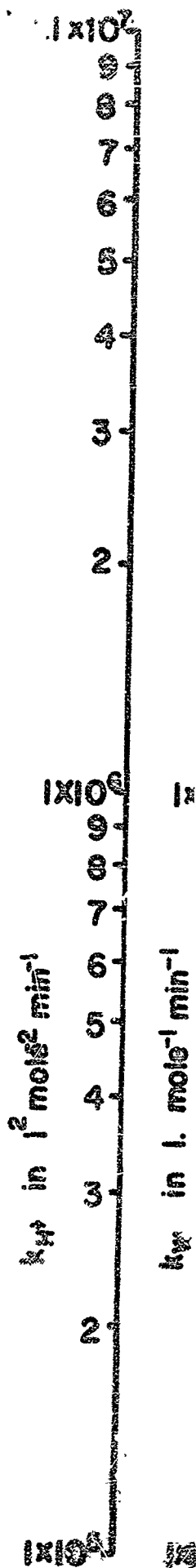
R = gas constant - 1.987 calories deg⁻¹ mole⁻¹

T = absolute temperature - °Kelvin

k = reaction velocity coefficient

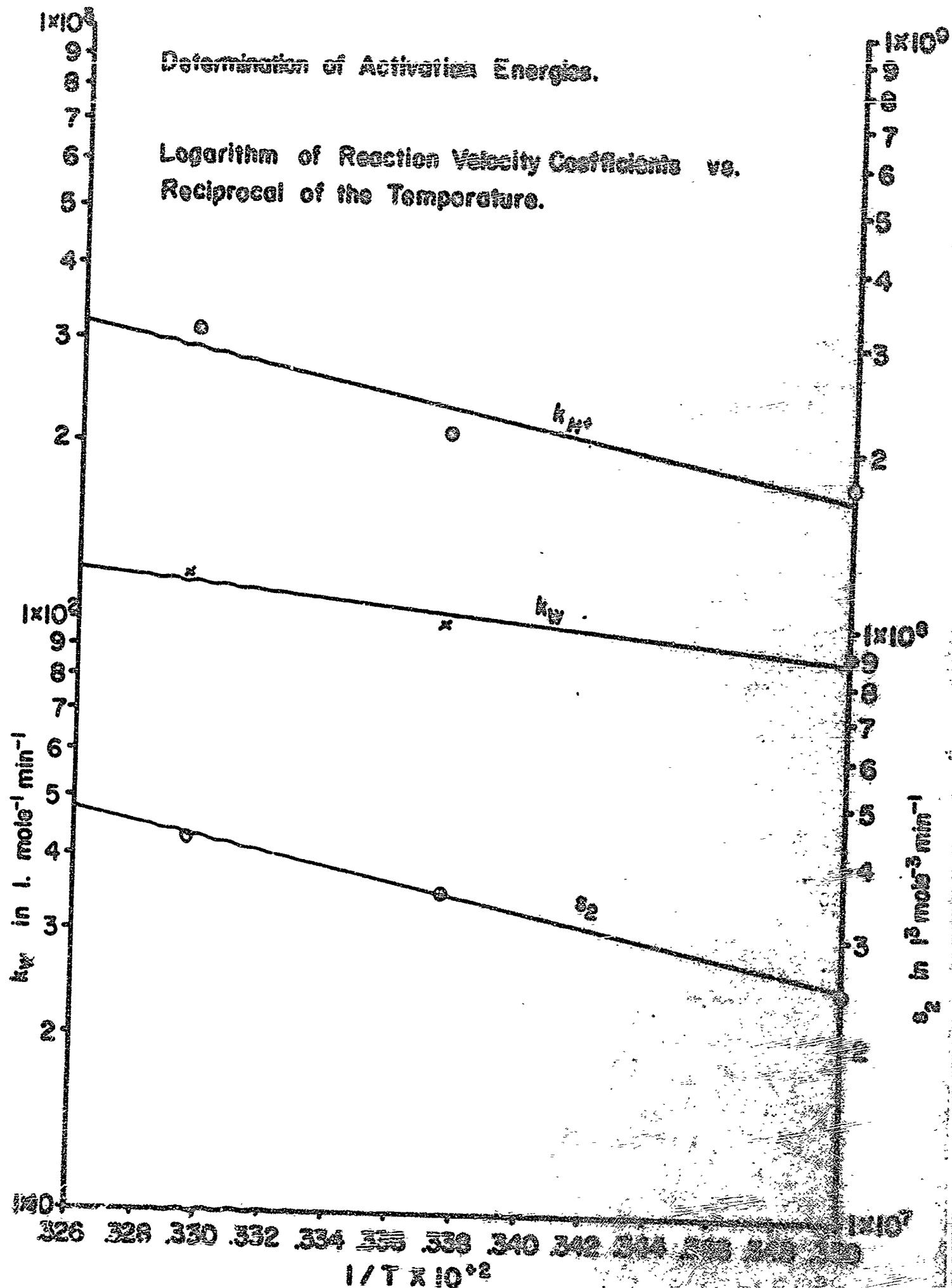
A straight line defined by plotting $\ln k$ against $1/T$ would yield a straight line with a slope equal to E/R and an intercept equal to $\ln A$.

The values of k_w , k_{H+} and S_2 , taken from Table 4 are plotted against the reciprocal of the absolute temperatures on Figure 7. The value of the Arrhenius Equation constants obtained are shown in Table 5.



Determination of Activation Energies.

Logarithm of Reaction Velocity Coefficients vs. Reciprocal of the Temperature.



Reciprocal of Absolute Temperature, $^{\circ}K^{-1} \times 10^3$

TABLE 5

Values of A and E for the Various Components of k_{app} .

Component	A $\mu\text{mole}^{-1}\text{min}^{-1}$	E Calories/mole
k_w	9.2×10^3	2.64×10^3
k_{H^+}	2.15×10^{10}	5.4×10^3
S_2	3.9×10^{11}	5.5×10^3

Substituting the values shown in Table 5 into Equation (10) yields Equation (12)

$$k_{app} = 9.2 \times 10^3 e^{-2640/RT} + 2.15 \times 10^{10} [H^+] e^{-5400/RT} + 3.9 \times 10^{11} [H^+] [B] e^{-5500/RT} \quad (12)$$

To test the validity of Equation 5 the computed values for k_{app} are compared with observed values as shown in Table 6.

TABLE 6

Comparison of Computed and Observed Values of k_{app} for Runs Indicated

Run No.	$k_{app}, \mu\text{mole}^{-1}\text{min}^{-1}$	
	Observed	Computed by Eq. (12)
44r.	260	362
5	540	533
30	188	248
56	770	784
65	540	671

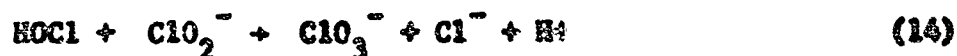
The results compare within 15 percent lending validity to Equation 12.

F. Chlorine and Electron Balances

If it is assumed, as shown in Equation 1



that only chlorine dioxide, chloride and chlorate are formed by the reaction between hypochlorous acid and chlorite within the range of the experimental conditions used, then three balanced equations can be suggested. These are Equations (13), (14), and (15):



To test the validity of assuming that Equations (13), (14), and (15), are reasonable paths for Equation 1 a comparison was made of the values of chloride and chlorate calculated and the values measured.

1. Calculations for Values of Chloride and Chlorate Formed Using Assumed Equations

As described in Section A of this Chapter the concentrations of hypochlorous acid and of chlorite were calculated at the beginning and also at the end of the runs. Furthermore, the concentration of chlorine dioxide at the end of a run was calculated. Thus, knowing the amount of hypochlorous acid and chlorite consumed in the reaction and the amount of chlorine dioxide formed, by use of Equations (13), (14), and (15) the amounts of chloride and chlorate formed could be readily calculated. For example, if seven units of chlorite and five units of hypochlorous acid were used to form four units of chlorine dioxide by use of Equation (13), four units of chlorite and two units of hypochlorous acid would be consumed and two units of chloride formed. The remaining three units each of hypochlorous

acid and chlorite could be consumed by Equation (14) to form three units of chloride and chlorate. And in the cases where the relative amount of chlorite consumed was greater, the use of Equation (15) might be necessary.

2. Calculations for Chloride and Chlorate Using Experimental Data

As described in Section C of Chapter 2, at the end of each run, after Run 25, all of the oxidizing form of chlorine except chlorate was reduced to chloride using hydroxylamine sulfate titrated potentiometrically with silver nitrate. The total amount of chlorine in the form of hypochlorous acid, chlorite and chlorine dioxide, as determined spectrophotometrically, was subtracted from the value of total chloride determined potentiometrically to yield the value of chloride formed in the reaction. Also, in a separate operation, total reduction of all forms of oxidizing chlorine to chloride, was accomplished on the Jones reductor. The resulting solution was titrated potentiometrically. The difference in total chloride found in the two potentiometric titrations was considered to be the chlorate formed.

Unfortunately, the laboratory technique seemed to have some shortcomings. Chlorine dioxide escapes rapidly from aqueous solution even more rapidly than does hypochlorous acid. Thus, in the process of passing the solution through the Jones reductor column some chlorine dioxide and possibly some hypochlorous acid, if present, was lost into the atmosphere. The amount was small - normally more than 95% of the initial chlorine was accounted for in the effluent of the Jones reductor. However, since the total chlorate was determined by small difference calculations as described above the percentage error in chlorate

concentration might be considerable. Because the Jones reductor step was the one most subject to error, it was assumed that the chlorate formed was simply the difference between the initial total chlorine and the value found by the potentiometric titration of the hydroxylamine sulfate reduction products. That is, since it was shown that the effluent from the Jones reductor accounted for 95% plus of the initial chlorine present, the data obtained from the reductor was not used.

3. Comparison of Concentration Values of Chloride and Chlorate Obtained by Computational and Experimental Methods.

A comparison of the values of chloride and chlorate obtained by calculations using Equations (13), (14), (15), and obtained by adjusted experimental procedures are shown in Table 7. It may be noted from Table 7 that the values of chloride based on observation are usually very slightly higher than those obtained by calculations. No concrete explanation for this discrepancy in chloride concentrations is offered; however, it is suggested that both the hypochlorous acid and chlorite solutions when several days old might have decomposed to form chlorides. A 5% or less decomposition of each of the two reactants would account for the majority of the excess chloride found by the experimental method. The values of chlorate found by the two methods are different by the same amount as the chloride values but in opposite manner. This is necessary because in both methods 100% chlorine balance was assumed.

4. Yields of Chlorine Dioxide and of Chlorate from Chlorite Consumed.

Taube and Dodgen (9) showed by use of radioactive tracers that the majority of the chlorite consumed was transformed into chlorine dioxide and chlorate. This is consistent with Equations (13), (14), and (15) - only the last one allows a yield of chloride from chlorite alone

TABLE 7

Comparison of Chloride and Chlorate Values

Found by Computation and by Experiment

Run No.	Total initial chlorine moles / l	<u>Chloride</u>		<u>Chlorate</u>	
		Calc. moles / l	Exper. moles / l	Calc. moles / l	Exper. moles / l
25	19.25	5.40	5.23	3.22	3.38
27	20.79	6.35	5.16	5.06	6.31
28	20.63	7.31	7.43	5.24	5.08
29	23.94	6.87	8.28	5.44	4.07
30	20.04	6.70	8.15	5.73	4.28
31	19.81	5.79	6.33	3.89	3.35
43	19.75	6.00	7.43	4.39	2.97
44	19.27	5.06	6.42	4.55	4.18
45	20.13	6.32	6.95	4.98	4.34
46	19.79	5.89	6.67	4.78	4.10
47	19.30	5.63	7.21	4.39	2.80
48	19.23	6.35	9.53	5.35	2.17
49	19.60	6.28	8.12	5.21	3.38
51	19.03	6.32	9.56	5.22	1.97
52	20.35	6.66	9.07	5.98	3.57
53	19.19	5.03	5.37	3.17	2.73
56	19.46	6.07	6.15	3.63	3.53
58	19.60	5.87	8.04	3.87	1.69
59	20.47	5.58	7.20	3.91	2.28
60	19.92	5.36	7.62	3.27	2.01
61	19.54	6.09	6.68	3.78	3.15
62	20.43	5.24	6.56	3.76	2.43
63	20.03	5.97	6.22	4.03	3.77
65	19.50	5.66	6.83	4.25	3.07
66	20.28	5.78	6.51	4.21	3.50
84	19.85	6.06	7.03	2.94	1.96
85	19.83	4.16	2.11	1.88	3.94
86	19.66	4.64	5.12	3.71	3.14
87	19.75	5.44	5.45	3.15	2.14
88	20.12	5.97	4.93	3.10	3.76
89	20.07	4.99	4.94	2.48	2.43
90	19.35	5.46	6.40	3.93	2.99
91	19.30	5.07	6.56	3.31	1.88
92	20.64	6.19	6.33	3.94	3.01

and the amount is small. The experimental results from this research support these findings. The ratios of chlorine dioxide produced to chlorite consumed and chlorate produced to chlorite consumed are shown in Table 8. The values of the chlorate produced are taken from the calculations using Equations (13), (14), and (15).

During the course of a single run the ratio of chlorine dioxide produced to chlorite consumed remained constant. It was assumed that the relative proportions of chlorate and chloride produced also remained constant.

From Table 8 it appears that the yield of chlorine dioxide is enhanced by a decrease in pH and reduced by an increase in temperature and buffer molality. Figures 8, 9, and 10 are plots of the ratio of chlorine dioxide formed to chlorite consumed at the buffer molality and temperature shown. The data, though somewhat scattered, showed a definite trend and this is fairly well approximated by the straight lines drawn by eye in Figs. 8-10. The slopes of the straight lines and the intercepts at zero hydrogen ion activity are shown in Table 9.

TABLE 9

Slope and Intercept Values of Plots of $[\text{ClO}_2]$ formed

/ $[\text{ClO}_2^-]$ consumed at Buffer Molality and Temperatures Shown

Buffer Molality	Temperature °C					
	12.5		23.1		30.2	
	Slope x 10 ⁵	Intercept	Slope x 10 ⁵	Intercept	Slope x 10 ⁵	Intercept
0.1	.05	.51	.03	.48	.03	.41
0.2	.05	.47	.03	.44	.03	.37
0.3	.05	.44	.03	.41	.03	.33

The intercept values, that is, the chlorine dioxide-chlorite ratio at zero hydrogen ion activity taken from Table 9, are plotted for each of the three temperatures on Figure 11. The slope and intercept values are shown on Table 10.

TABLE 8

Ratios of Chlorine Dioxide Produced to Chlorite Consumed
and Chlorate Produced to Chlorite Consumed

¹ Run No.	² Temp. °C	³ pH	⁴ Buffer Molality	⁵ $\frac{[\text{ClO}_2]}{[\text{ClO}_2^-]}$	⁶ $\frac{[\text{ClO}_3^-]}{[\text{ClO}_2^-]}$	^{5 & 6}
3M	21.0	4.36	0.1	0.51	0.40	0.91
4M	21.3	4.35	0.1	0.54	0.34	.88
4Mr	21.3	4.35	0.1	0.56	0.34	.90
8	21.7	4.32	0.2	0.56	0.39	.95
14	22.8	4.43	0.3	.59	.31	.90
19	25.2	4.51	0.1	.63	0.27	.90
20	23.6	4.54	0.1	.66	.25	.91
24	22.2	4.25	0.1	.53	.39	.92
25	22.0	4.21	0.2	.60	.36	.96
27	22.9	5.01	0.1	.42	.50	.92
28	23.1	4.91	0.2	.47	.60	1.07
29	24.2	5.01	0.3	.37	.61	.98
30	25.8	5.02	0.3	.34	.60	.94
31	25.4	4.24	0.3	.54	.39	.93
43	30.7	5.02	.1	.45	.50	.95
44	30.5	5.00	.1	.45	.48	.93
45	30.7	5.00	.1	.42	.52	.94
46	30.8	4.99	.1	.41	.50	.91
47	30.2	4.87	.2	.44	.48	.92
48	30.2	5.00	.2	.36	.57	.93
49	30.0	5.00	.2	.37	.57	.94
51	30.9	5.00	0.3	0.36	.60	0.96
52	31.0	5.04	0.3	.31	.60	.91
53	30.9	4.21	0.1	.57	.37	.94
56	30.9	4.25	0.2	.58	.42	1.00
58	30.6	4.19	0.2	.54	.40	.94
59	30.8	4.19	0.3	.52	.39	.91
60	30.6	4.19	0.3	.52	.34	.86
61	30.8	4.51	0.1	.56	.41	.97
62	31.0	4.51	0.1	.51	.40	.91
63	30.6	4.51	0.2	.51	.46	.97
65	31.5	4.48	0.3	.45	.47	.92
66	30.3	4.49	0.3	.47	.46	.93
84	13.5	4.23	.2	.68	.30	.98
85	13.7	4.28	.3	.70	.21	.91
86	12.0	4.22	0.1	.59	.32	.91
87	11.5	4.51	0.3	.60	.35	.95
88	12.4	4.52	.2	.68	.37	.95
89	12.5	4.53	.1	.67	.31	.98
90	12.2	5.02	0.3	.48	.46	.94
91	12.2	4.99	.2	.54	.40	.94
92	12.6	4.98	.1	.55	.48	1.03

Fig. 23.

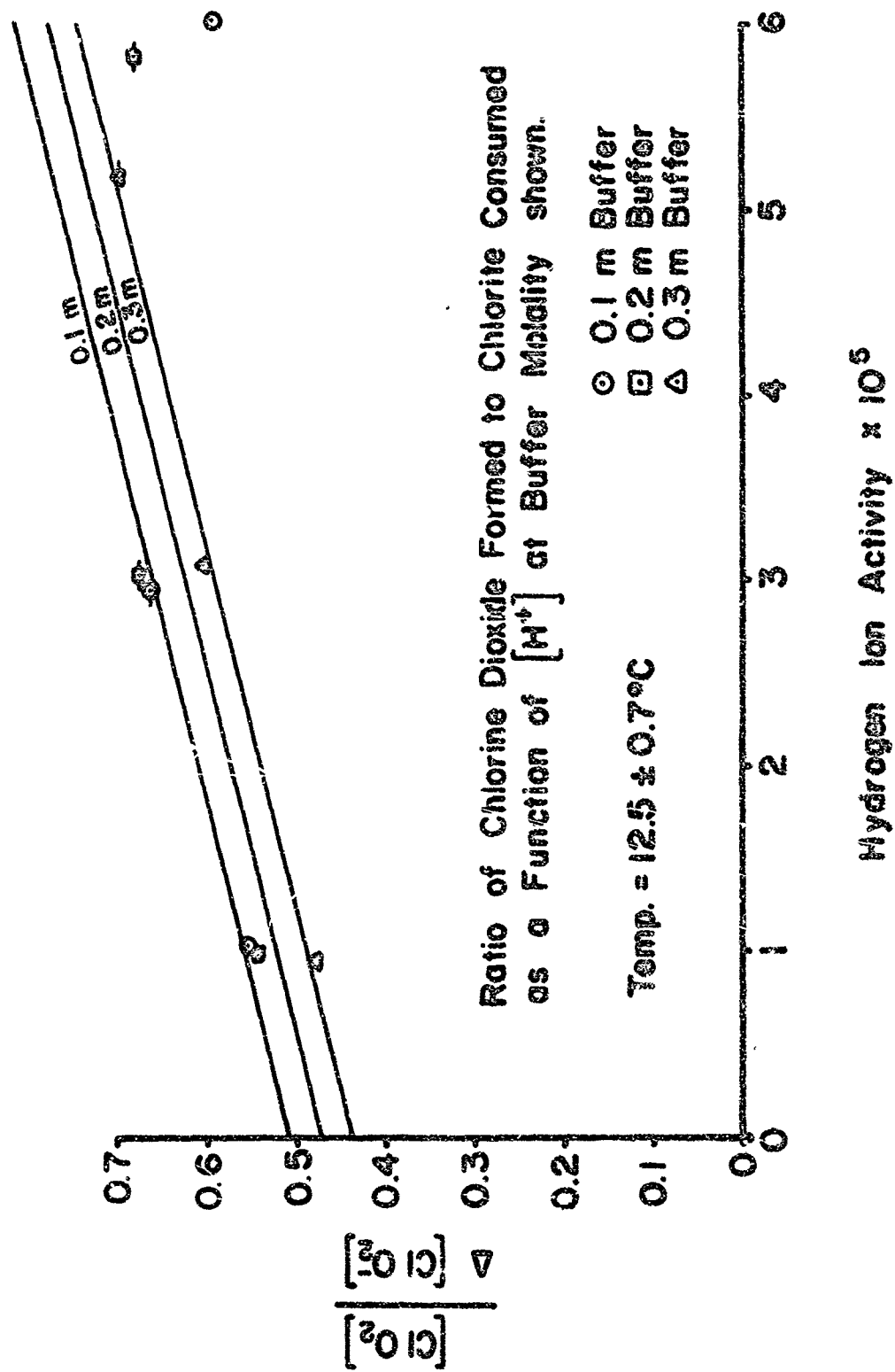
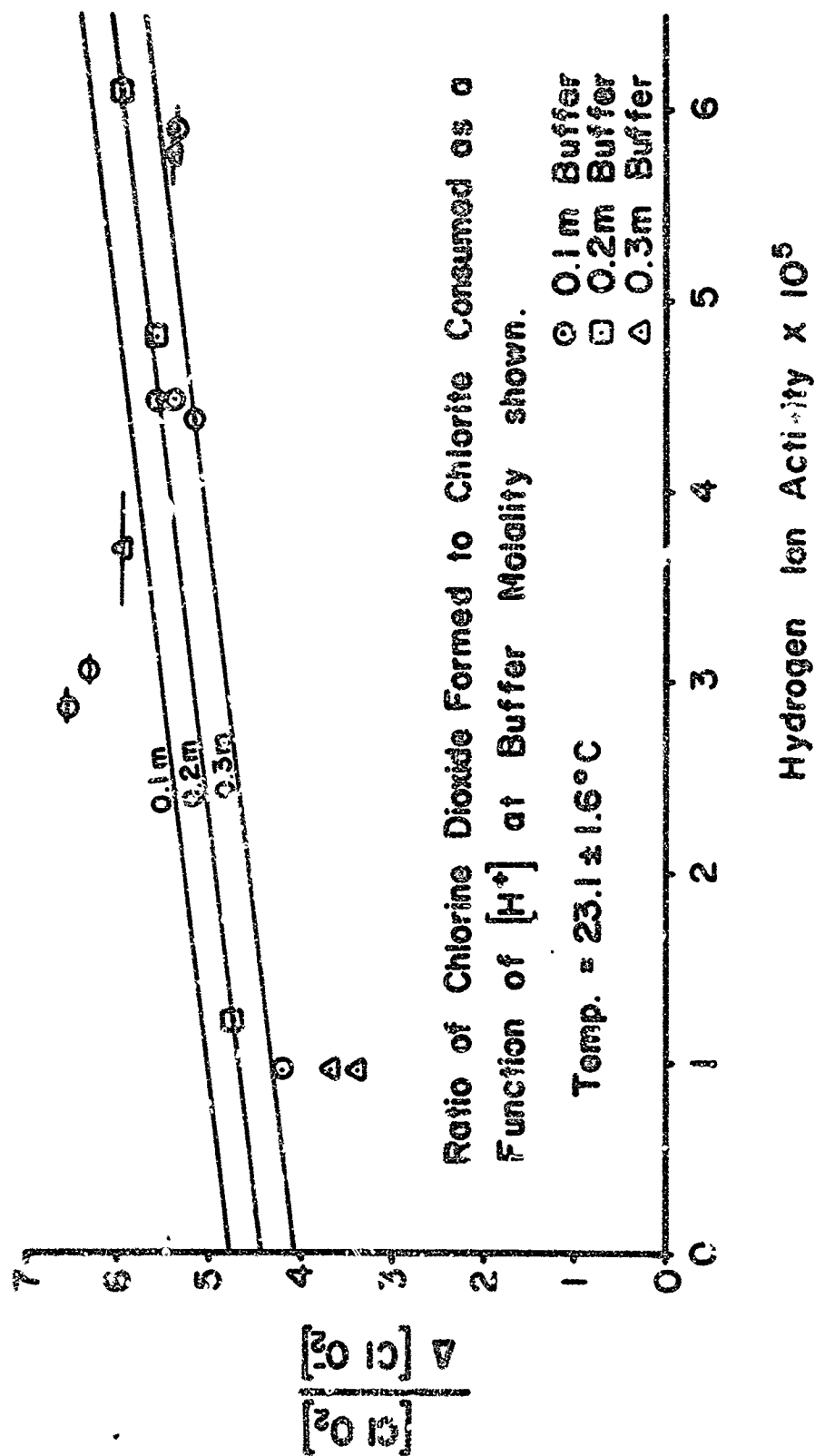
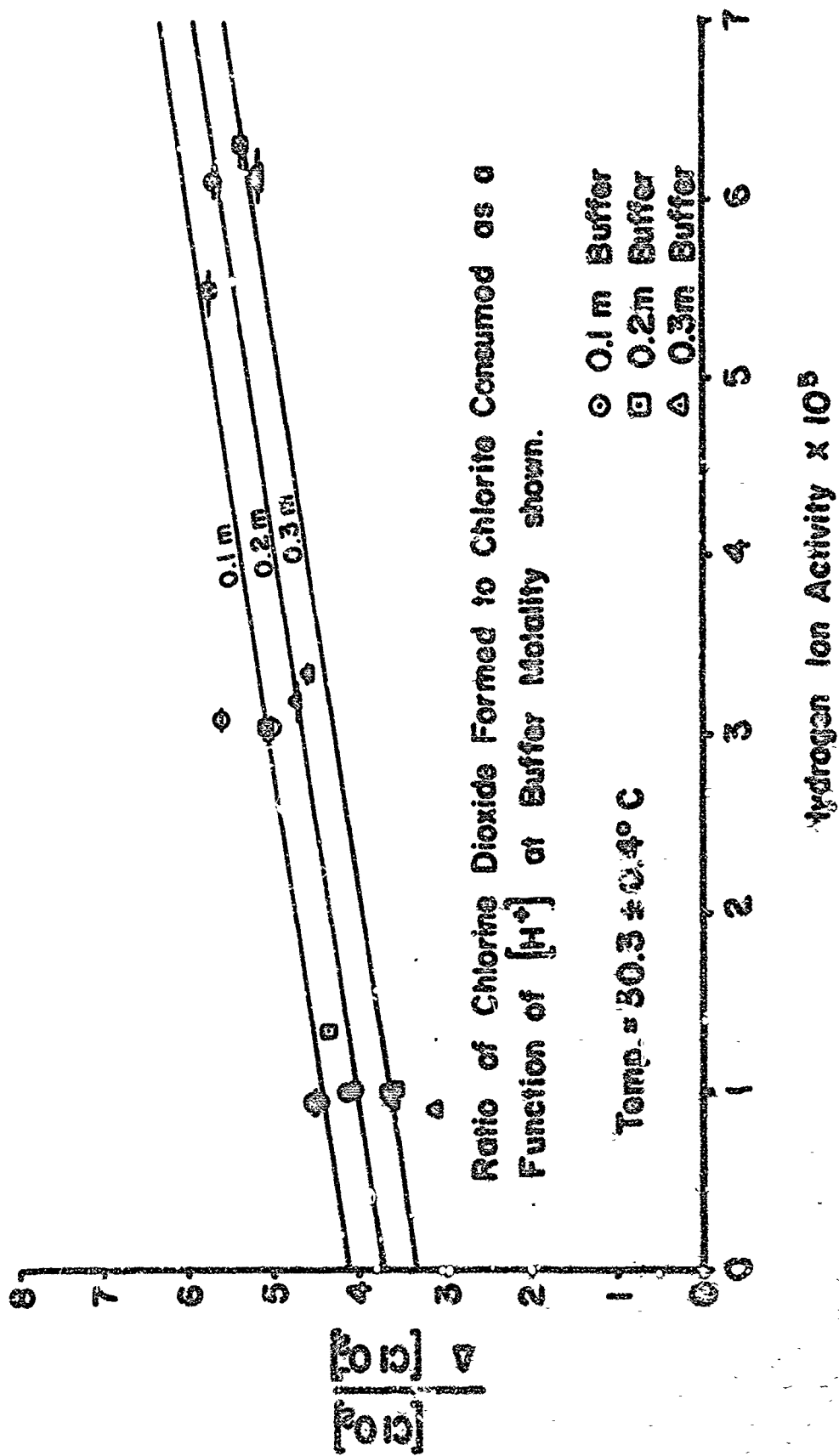


Fig. 24.





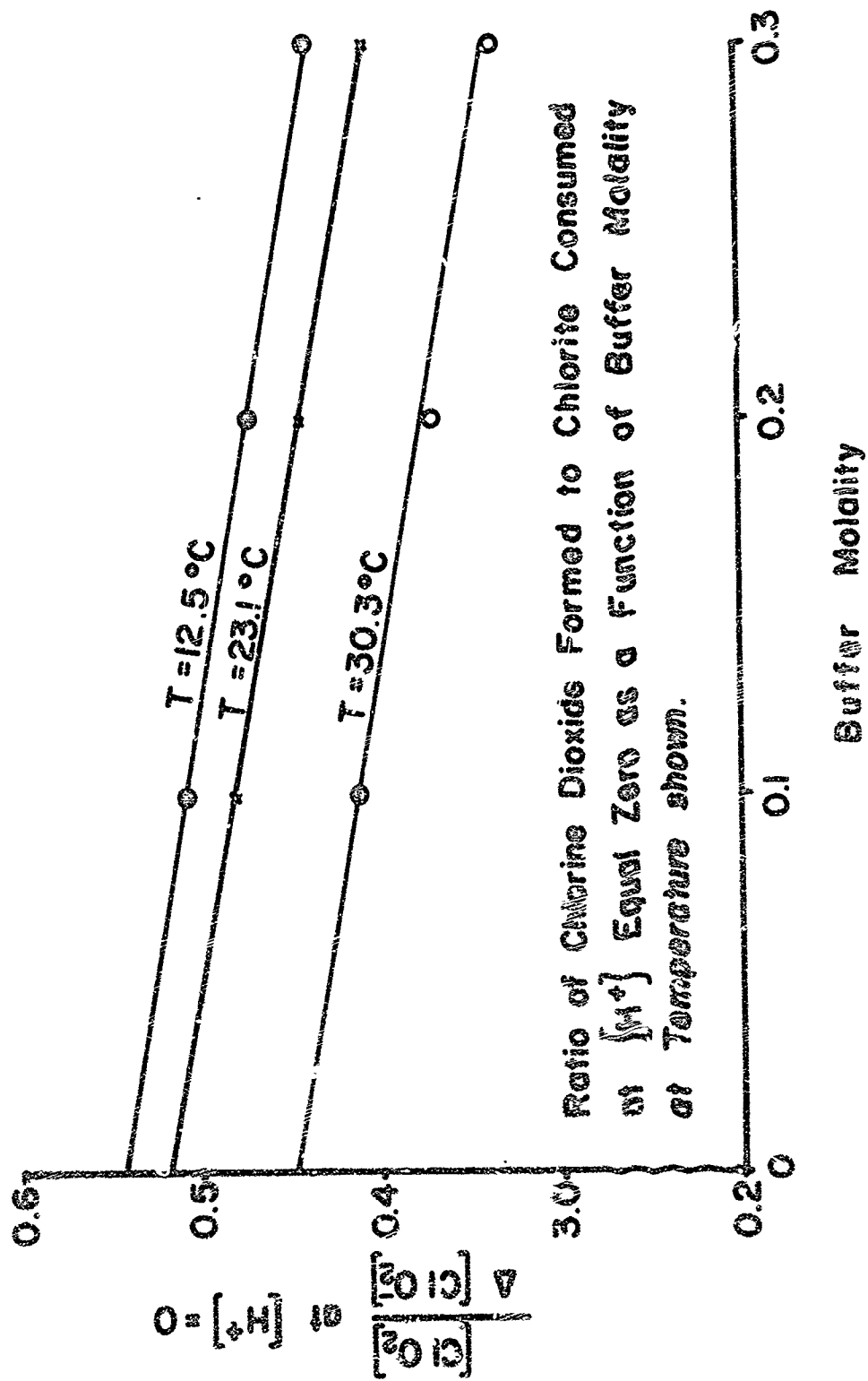


TABLE 10

Slope and Intercept Values of $[\text{ClO}_2]$ formed /
 $[\text{ClO}_2^-]$ consumed at $[\text{H}^+] = 0$ as a Function of
 Buffer Molality at Temperature Shown

Temperature °C	Slope	Intercept
12.5	0.37	0.54
23.1	.37	.52
30.3	.37	.45

These analyses allow writing Equations (16), (17), and (18).

at 12.5°C:

$$\frac{[\text{ClO}_2] \text{ formed}}{[\text{ClO}_2^-] \text{ consumed}} = 0.54 - 0.37 [\text{B}] + 0.05 \times 10^5 [\text{H}^+] \quad (16)$$

at 23.1°C:

$$\frac{[\text{ClO}_2] \text{ formed}}{[\text{ClO}_2^-] \text{ consumed}} = 0.52 - 0.37 [\text{B}] + 0.03 \times 10^5 [\text{H}^+] \quad (17)$$

at 30.3°C:

$$\frac{[\text{ClO}_2] \text{ formed}}{[\text{ClO}_2^-] \text{ consumed}} = 0.45 - 0.37 [\text{B}] + 0.03 \times 10^5 [\text{H}^+] \quad (18)$$

H. Summary of Chapter

By kinetic analysis of concentration values of hypochlorous acid, chlorite and chlorine dioxide changing with time during the course of the reaction it was possible to write Equations (2a) and (12)

$$\frac{d[\text{ClO}_2]}{dt} = k_{\text{app}} [\text{HOCl}] [\text{ClO}_2^-] \quad (2a)$$

$$k_{app} = 9.2 \times 10^3 e^{-2640/RT} + 2.15 \times 10^{10} [H+] e^{-5400/RT} \\ + 3.9 \times 10^{11} [H+] [B] e^{-5500/RT} \quad (12)$$

The equations are applicable between pH values of about 4 and 5 and between temperatures of about 10 to 35°C with a phosphate buffer system; these were the experimental conditions under which this research was conducted. The yield of chlorine dioxide from chlorite consumed varied, within the experimental conditions described, from about 35 to 65%.

It was observed that the majority of the chlorite consumed was oxidized to chlorine dioxide or chlorate whereas the hypochlorous acid consumed was reduced to chloride.

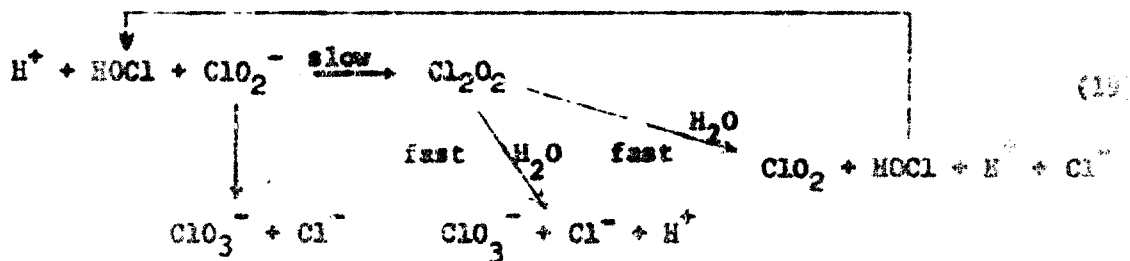
CHAPTER 4

MECHANISM OF THE REACTION

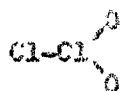
The kinetic analysis of this research as described in Chapter 3 reveals that the rate of the overall reaction in which chlorine dioxide is formed from hypochlorous acid and chlorite is first order with respect to the two reactants under the range of experimental conditions used. The rate equation may therefore be written:

$$\frac{d[\text{ClO}_2]}{dt} = k_{\text{app}} [\text{HOCl}] [\text{ClO}_2^-] \quad (2a)$$

Furthermore, this research reveals that the ratio of hypochlorous acid to chlorite consumed during the course of a single reaction is constant and always less than unity but the value of the ratio shifts with experimental conditions. Also the relative proportion of the reaction products (i.e. chlorine dioxide, chloride and chlorate) shifts with experimental conditions. A mechanism is suggested as shown in Equation (19).



This mechanism is in agreement with the proposal by Taube and Dodgen⁽⁹⁾. They suggested that the intermediate Cl_2O_2 have the structural form.



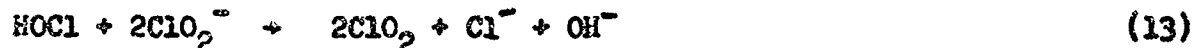
to account for the observation that chlorine atoms remain distinct according to their origin, i.e. from the hypochlorous acid and the chlorite. The distinction was demonstrated using radioactive chlorine in the hypochlorous acid molecule.

As shown in Section G. of Chapter 3 the proportion following each of the two paths shifts with experimental conditions. Within the range of the experimental conditions of this research, the yield of chlorine dioxide formed to chlorite consumed varied from a ratio 0.35 to 0.65. To make the chlorine balance (Section F Chapter 3) it is necessary to suggest the disproportionation of chlorite to form chlorate and chloride as shown in Equation (15) and suggested schematically in Equation (19). Since this reaction does not take place spontaneously it is hypothesized that either the activated intermediate or the hypochlorous acid catalyzes the reaction.

CHAPTER 5

SOME THERMODYNAMIC CONSIDERATIONS

To check the spontaneity of the chemical reaction proposed in Equations (13), (14), and (15),



the concept of change in free energy is employed. The values of F° , the energy of formation of the ion or molecule at unit activity, for the appropriate reagents, are listed in Table 11.

TABLE 11

Values of Free Energy at Unit Activity (F°)⁽¹⁰⁾

<u>Compound or Ion</u>	<u>$F^\circ \times 10^{-3}$</u>
H^+	+0.00
OH^-	-37.595
Cl^-	-31.350
ClO_3^-	-0.62
ClO_2^-	+2.740
HOCl	-19.110
ClO_2	+29.49

The change in free energy during the course of reaction is described by Equation (20).

$$\Delta F = \sum F_{\text{products}} - \sum F_{\text{reactants}} \quad (20)$$

The free energy of each of the constituents is related to its free energy at unit activity (F°) by Equation (21):

$$F = F^\circ + RT \ln a \quad (21)$$

in which

F° = free energy of formation of the ion or molecule at unit activity

R = gas constant = 1.987 calories deg⁻¹ mole⁻¹

T = temperature in degrees Kelvin

a = activity of the ion or molecule

For a reaction such as the one described by Equation (19), Equation (21) may be written:

$$\Delta F = \Delta F^{\circ} + RT \ln \frac{a^2 \text{ClO}_2 \times a_{\text{Cl}^-} \times a_{\text{OH}^-}}{a_{\text{HOCl}} \times a^2 \text{ClO}_2^-} \quad (22)$$

It may be noted that the expression within the parentheses is the equilibrium constant (K) of Equation (13). Equation (22) may be written:

$$\Delta F = \Delta F^{\circ} + RT \ln K \quad (23)$$

At equilibrium ΔF equals zero. Therefore, Equation (23) may be written:

$$\ln K = \frac{-\Delta F^{\circ}}{RT} \quad (24)$$

$$\begin{aligned} \Delta F^{\circ} &= 2F^{\circ} \text{ClO}_2 + F^{\circ} \text{Cl}^- + F^{\circ} \text{OH}^- - F^{\circ} \text{HOCl} - 2F^{\circ} \text{ClO}_2^- \\ &= 3.665 \times 10^3 \\ &= 3665 \end{aligned}$$

At 27°C:

$$\log K = \frac{-3665}{2.303 \times 1.987 \times 300}$$

$$\begin{aligned} \log K &= -2.6697 \\ \text{Therefore, } K &= 2.14 \times 10^{-3} \end{aligned}$$

Substituting the value for K obtained above yields Equation (25).

$$K = \frac{a^2 \text{ClO}_2 \times a_{\text{Cl}^-} \times a_{\text{OH}^-}}{a_{\text{HOCl}} \times a^2 \text{ClO}_2^-} \quad (25)$$

$$K = 2.14 \times 10^{-3}$$

At a pH of 5, at 25°C, $a_{\text{OH}^-} = (\text{OH}^-) = 1 \times 10^{-9}$. Substituting this into

Equation (21) yields Equation (26):

$$K' = \frac{2.14 \times 10^{-3}}{1 \times 10^{-9}} = 2.14 \times 10^6$$

$$K' = \frac{a^2 \text{ClO}_2 \times a_{\text{Cl}^-}}{a^2 \text{ClO}_2^- \times a_{\text{HOCl}}} \quad (26)$$

This shows that at this pH value the reaction shown by Equation (13) has its equilibrium far to the right.

Similarly, for Equation (14):

$$\Delta F^\circ = F^\circ_{\text{ClO}_3^-} + F^\circ_{\text{Cl}^-} + F^\circ_{\text{H}^+} - F^\circ_{\text{HOCl}} - F^\circ_{\text{ClO}_2^-}$$

$$\Delta F^\circ = -15,600$$

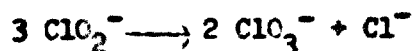
At 27°C:

$$\log K = \frac{15,600}{2.303 \times 1.987 \times 300}$$

$$\log K = 11.36$$

Again it is evident that the reaction, at equilibrium, is far to the right.

This is equally true for the reaction shown by Equation (15). The logarithm of the equilibrium constant, i.e. log K, is about 30.



$$\Delta F^\circ = \sum F^\circ_{\text{products}} - \sum F^\circ_{\text{reactants}}$$

$$\Delta F^\circ = 2F^\circ_{\text{ClO}_3^-} + F^\circ_{\text{Cl}^-} - 3F^\circ_{\text{ClO}_2^-}$$

$$\Delta F^\circ = (2)(-0.62) - 31.350 - (3)(2.74)$$

$$\Delta F^\circ = -RT \ln K$$

$$-40.81 = -1.987 \times 300 \ln K$$

$$\ln K = 70$$

Therefore, log K = 30

CHAPTER 6

SUMMARY

The reaction, the formation of chlorine dioxide from hypochlorous acid and chlorite in aqueous solutions, which was studied in the present research is shown in Equation (1):



Since chlorine dioxide, chlorite and hypochlorous acid have different absorption peaks in the ultra-violet range, the spectrophotometer was used as the method of analysis for this study.

Kinetic analysis of the concentration values of hypochlorous acid, chlorine dioxide and chlorite changing with time during the course of the reaction given by Equation (1) reveals that the rate of the overall reaction is first order with respect to the two reactants under the range of experimental conditions used. The rate equation may therefore be written:

$$\frac{d[\text{ClO}_2]}{dt} = k_{\text{app}} [\text{HOCl}] [\text{ClO}_2^-] \quad (2a)$$

By assuming that the apparent rate constant is the sum of the rate constants due to the three individual acid species existing in solution, i.e. water, buffer and hydrogen ion, it was possible to write equation (12):

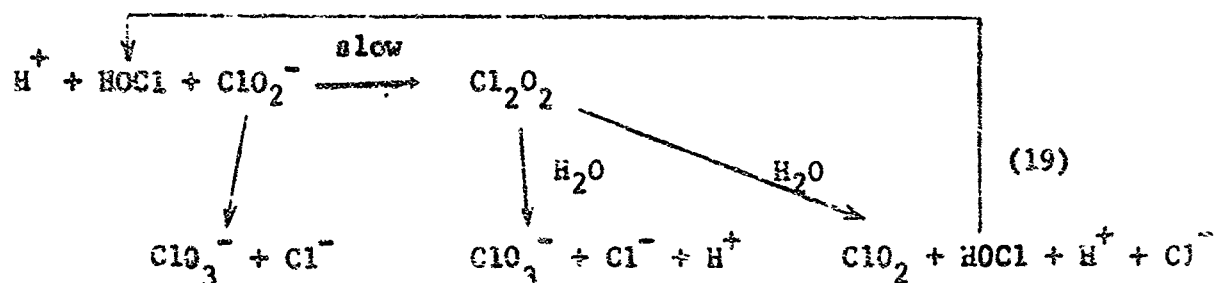
$$k_{\text{app}} = 9.2 \times 10^3 e^{\frac{-2640}{RT}} + 2.15 \times 10^{10} [\text{H}^+] e^{\frac{-5400}{RT}} + 3.9 \times 10^{11} [\text{H}^+] [\text{B}] e^{\frac{-5500}{RT}} \quad (12)$$

The latter two equations are applicable within certain experimental conditions as determined from data collected for the hundred different trials performed in this research. The pH must be controlled at 4 to 5 with a given buffer molality and solution temperature may be varied from 10 to 35°C.

The yield of chlorine dioxide from chlorite varied from 35 to 65% within the experimental conditions described.

It was observed that the majority of the chlorite consumed was oxidized to chlorine dioxide or chlorate whereas the hypochlorous acid consumed was reduced to chloride.

A mechanism is suggested, as shown by Equation (19), in which Cl_2O_2 is the activated intermediate complex.



This mechanism suggests that the formation of the intermediate is the slow rate determining step.

BIBLIOGRAPHY

1. Granström, I. L. and Lee, G. F., Jour. Am. Water Works Assoc., 50, 1453 (1958).
2. Zimmerman, G. and Strong, F. C., J. Amer. Chem. Soc., 79, 2063 (1957).
3. Taylor, M. C., White, J. F., Vincent, G. P. and Cunningham, G. L., Ind. Engr. Chem., 32, 899 (1940).
4. Weiner, R., Zeit. Elect. Chem., 52, 234 (1948).
5. Kolthoff, I. M. and Laitinen, H. A., "pH and Electro Titrations", Second ed., J. Wiley and Sons, Inc., N. Y., 1944, p. 85.
6. Haight, G. P., Jr., Anal. Chem., 25, 642 (1953).
7. Kolthoff, I. M. and Sandell, E. B., "Textbook of Quantitative Analysis", 3rd. ed., The Macmillan Company, N. Y., 1959, p. 569.
8. Flis, I. E., Mishchenko, K. P., and Salnis, K. Yu., Journal Applied Chem. of U.S.S.R., 32, 295 (1959).
9. Taube, H. and Dodgen, H., J. Amer. Chem. Soc., 71, 3330 (1949).
10. Latimer, W. M., "Oxidation Potentials", Second ed., Prentice - Hall Inc., N. Y., 1952, Appendix II.

APPENDIX A

The Purification of Sodium Chlorite

1. The simplest procedure is to prepare a saturated water solution at 43-45°C, filter and cool to about 10°C. The crystals, which are $\text{NaClO}_2 \cdot 3\text{H}_2\text{O}$, are separated from the mother-liquor, placed in a crystallizing dish and dried in a vacuum oven at 50°C and 2-5 mm of mercury. In drying the material forms a solid mass. It should be ground in a mortar and redried for several hours at 60-65°C. The material should analyze above 99.5% and maybe 99.8% if the starting material is in the 99% range.
2. Washing and dehydration using methyl-alcohol: The crystals of $\text{NaClO}_2 \cdot 3\text{H}_2\text{O}$ obtained in the above procedure are washed first with 60% methyl-alcohol to remove the mother-liquor without precipitating chloride. This is followed by a light wash with absolute methyl-alcohol. The crystals are then taken from the filter and added to several volumes of absolute methyl-alcohol and stirred to complete the conversion to the anhydrous salt. The crystals are filtered, washed with more pure alcohol and dried in a vacuum oven first at room temperature and finally at 50°C. The methyl-alcohol should contain a small amount of NaOH (1 gm. per liter approx.) to prevent decomposition of the chlorite. The chlorite should not be exposed to the air more than necessary. Pure crystals can be grown in fairly large size from either a 60 or 80% methyl-alcohol solution by slow cooling.

