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Part I Chemical kinetics of the oxidation of
manganese to permanganate by periodate Part II
Solubility, activity coefficients and activity product
of manganese (II) iodate

Anson Mack Hayes
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**Part I CHEMICAL KINETICS OF THE OXIDATION OF MANGANESE TO
PERMANGANATE BY PERIODATE**

**Part II SOLUBILITY, ACTIVITY COEFFICIENTS AND ACTIVITY
PRODUCT OF MANGANESE (II) IODATE**

by

Anson Mack Hayes

**A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY**

Major Subject: Physical Chemistry

Approved:

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76 A. ACKNOWLEDGMENTS

75 IV. SUMMARY

68 III. DISCUSSION AND RESULTS

66 E. Procedure

66 D. Apparatus

66 C. Preparation of Solutions

65 B. Analyses

65 A. Materials

65 II. EXPERIMENTAL

64 I. INTRODUCTION

PRODUCT OF MANGANESE (II) IODATE

Part II SOLUBILITY, ACTIVITY COEFFICIENTS AND ACTIVITY

63 IV. SUMMARY

60 D. Suggested Experiments

58 C. Analytical Significance

46 B. Manganese (II)

43 A. Manganese (III)

43 III. DISCUSSION AND RESULTS

35 E. Appendix

12 D. Method

9 C. Analyses

8 B. Apparatus

7 A. Materials

7 II. EXPERIMENTAL

1 I. INTRODUCTION

TO PERMANGANATE BY PERIODATE

Part I CHEMICAL KINETICS OF THE OXIDATION OF MANGANESE

Page

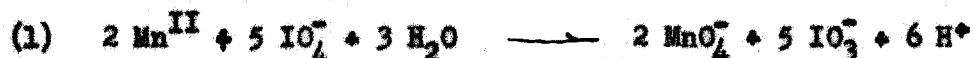
TABLE OF CONTENTS

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Part I CHEMICAL KINETICS OF THE OXIDATION OF MANGANESE TO
PERMANGANATE BY PERIODATE

I. INTRODUCTION

One of the more common analytical procedures in the determination of manganese by oxidizing it to permanganate ion and subsequently determining it by colorimetric or titrimetric methods. The oxidizing agents available for this oxidation include sodium bismuthate, potassium periodate or periodic acid and ammonium persulfate with silver as a catalyst. The chemical kinetics of the periodate oxidation and some allied phenomena is the subject of this work. In ionic form this reaction can be given as



where manganese (II)* is oxidized to permanganate by metaperiodate.

The periodate oxidation of manganese as an analytical method for the colorimetric estimation of manganese was first proposed by

*The confusion in the names of ions corresponding to the various oxidation states of manganese can be avoided by use of the Stock system of nomenclature. Frequently the predominant ionic species in aqueous solution of some of the intermediate states are not known and the assumption of a more descriptive name would not be justified. The use of the term permanganate instead of manganate (VII) has been retained because of long established usage. The use of this system is in accord with the Report of the Committee for the Reform of Inorganic Nomenclature of the International Union of Chemistry, 1940. This has been indicated by W. P. Janissen, H. Basset, A. Darniens, F. Fichter and H. Remy in J. Am. Chem. Soc., 63, 889 (1941).

Willard and Greathouse¹ who included the following comments concerning this reaction in their article:

1. "The periodate method is free from all the faults of the other methods and yields results of a high degree of accuracy."
2. "Solutions of manganese (II) salts oxidized by periodate have exactly the same color as aqueous solutions of pure potassium permanganate."
3. Nitric, sulfuric or phosphoric acids used separately and in varying concentrations were satisfactory as long as sufficient acid was present to prevent precipitation of the manganese.
4. The only effect of varying the periodate concentration was the rate at which the oxidation proceeds. Only a slight excess of periodate was needed for the complete oxidation of the manganese.
5. "A remarkable feature of the solutions oxidized is the great stability when a slight excess is present." Such a solution stored for three months in a stoppered flask showed no change whatever, when compared with a similar solution freshly oxidized. This made it possible to leave the standard solution in the colorimeter, renewing it only occasionally instead of preparing a fresh solution each time as is necessary when persulfate is used.
6. The common metals did not interfere in this method except in so far as they themselves imparted a color to the solution.

¹H. H. Willard and L. Greathouse, J. Am. Chem. Soc., 39, 2366 (1917).

Richards² showed that for very small amounts of manganese, such as those used in biological work, too great an acid concentration could exist; and he reported a maximum allowable concentration. Willard and Thompson³ modified the method by precipitation of the excess periodate with mercury followed by filtration, so that the determination could be completed volumetrically by titrating with a standard reducing agent.

None of the work mentioned concerned itself with the chemical kinetics of the reaction except for qualitative statements about the rate. An article by Strickland and Spieer⁴ has appeared since this work was initiated which deals with the kinetics of this reaction.

The following was included in the summary of this article:

1. It was found possible to describe the reaction with equations representing a first order autocatalytic reaction.
2. Velocity constants were evaluated for the reaction upon this basis.
3. The reaction was found to have a minimum reaction rate with respect to acid concentration at approximately 1.5 molar hydrogen ion concentration.
4. It was deduced that manganese (II) was oxidized only slowly by the periodate ion unless a catalyst was present and that this catalyst was manganese (IV).

²M. B. Richards, *Analyst*, **55**, 554 (1930).

³H. H. Willard and J. Thompson, *Ind. Eng. Chem. Anal. Ed.*, **3**, 398 (1931).

⁴J. D. Strickland and G. Spieer, *Analytica Chemica Acta*, **3** 517 (1949).

5. Recommendations were made in regard to analytical applications of this reaction. These authors reported little concerning the reaction at low acidity, nor did they make any proposals concerning the mechanism of the reaction at low acidity.

The experimental work by Strickland and Spicer appeared to be very satisfactory. A colorimetric method was used to follow the formation of the permanganate. All of the reactions reported by them were performed in the temperature range 60° to 100°. These authors did not perform any experiments with varying periodate or manganese concentrations. The variables investigated were acidity, temperature, effect of small amounts of manganese (IV) oxide and ionic strength. The mechanism suggested in their article was deduced from a consideration of thermodynamic potentials and involved a rapid equilibrium between periodate, iodate, manganese (IV) and permanganate. That such an equilibrium does not exist is readily demonstrated by the very slow reduction of permanganate with iodic acid. Detectable color changes occur only after several days.

No information concerning the ions present in aqueous solutions of paraperiodic acid was available when the above work was published. This subject has been treated by Crouthamel and co-workers^{5,6} and

⁵C. E. Crouthamel, H. V. Meek, D. S. Martin and C. V. Banks, J. Am. Chem. Soc., 3031 (1949).

⁶C. E. Crouthamel, A. M. Hayes and D. S. Martin, Accepted for publication J. Am. Chem. Soc.

these results make possible a more specific assignment of the actual periodate species involved in the oxidation. Paraperiodic acid was found to be a polybasic acid with apparent ionization constants at 25° of

$$K_1 = 2.30 \times 10^{-2}$$

$$K_2 = 4.35 \times 10^{-9}$$

$$K_3 = 1 \times 10^{-15}$$

for the first three dissociations of the acid. Evidence was presented indicating that the univalent ion of periodic acid in aqueous solution existed in two different equilibrium forms, the paraperiodate and the metaperiodate ions; and from spectrophotometric work the constant for the equilibrium



was evaluated as 40 at 25°. The heat of reaction for the dehydration process was evaluated as approximately ten kilocalories in the temperature range between 0° and 100°. This results in the heat of ionization being abnormally high. If the actual oxidizing species were the metaperiodate ion, the contribution of the heat of ionization to the activation energy would account for the abnormal temperature coefficients observed in some periodate oxidations.⁷

From the variations of reaction rate with pH in the oxidation of glycols with periodate observed by Price⁸ it can be concluded that

⁷Y. Duke, *J. Am. Chem. Soc.*, **69**, 3054 (1947).

⁸C. C. Price and H. Kroll, *J. Am. Chem. Soc.*, **60**, 2726 (1938).

the metaperiodate ion, IO_4^- , is the species involved in that oxidation.

Although only one article was found concerned with the kinetics of the oxidation of manganese (II) to permanganate, various authors^{9, 10, 11, 12, 13, 14, 15} have reported on the reaction between manganese (II) and permanganate. The most comprehensive and best work appears to be that of Tomkins¹⁵ in which he showed that the autocatalysis observed is caused by a surface phenomena afforded by the manganese (IV) oxide. He proposed that manganese (III) is probably the initial reaction product. The initial production of manganese (III) has been postulated by some of the other authors. During the oxidation of manganese (II) by periodate both permanganate and manganese (II) are present; hence, the contribution of this reaction must be considered. This reaction has become known as the Guyard reaction.

⁹H. Basset and I. Sanderson, J. Chem. Soc., 207 (1936).

¹⁰H. F. Launer and A. M. Yost, J. Am. Chem. Soc., 56, 2571 (1934).

¹¹M. J. A. Muller and E. Peytrail, Bull soc chim, 5, 1457 (1935).

¹²M. J. Polissar, J. Chem. Ed., 13, 40 (1936).

¹³J. M. G. Barredo and S. Sennet, Naturwissenschaften, 31, 550 (1943).

¹⁴M. J. Polissar, J. Phys. Chem., 39, 1057 (1935).

¹⁵F. C. Tomkins, Trans Faraday Soc., 36, 131 (1935).

II. EXPERIMENTAL

A. Materials

Electrolytic manganese of a purity of better than 99.99% was used as a primary standard for this element. A standard solution of manganese (II) was prepared by dissolving 6.248 grams of the metal in perchloric acid, by evaporating off as much excess acid as possible and by diluting this solution to volume in a clean calibrated 1 liter volumetric flask.

Potassium acid iodate prepared by the G. F. Smith Chemical Co., Columbus, Ohio, of a purity of 99.99% was used as a primary standard for iodate and also in acidimetry.

Periodic acid of a purity of better than 99.99% prepared by the G. F. Smith Chemical Co., Columbus, Ohio, was used throughout as a source of periodate.

Iodic acid of a purity of better than 99.9% prepared by the G. F. Smith Chemical Co., Columbus, Ohio, was used in the kinetics work.

Potassium permanganate, perchloric acid, sodium thiosulfate pentahydrate and potassium iodate prepared by the General Chemical Division, Allied Chemical and Dye Co., New York, N. Y., were used. These chemicals were of a quality to meet A. C. S. Standards as were all other chemicals used.

The water used throughout these experiments was prepared by

distilling from alkaline potassium permanganate water from the laboratory distilled water supply. The conductance of this water was less than 10^{-6} mhos cm^{-1} .

B. Apparatus

All spectrophotometric measurements were made using a Cary Recording Spectrophotometer manufactured by the Applied Physics Co., Pasadena, California. The optical system is of quartz enabling the operator to work in any spectral region between 2050 Å and 7500 Å with light which could be considered essentially monochromatic. The light beam is split by the optical system, half passing through the blank cell and the other half through the sample cell after which the light falls upon photocells. The electrical signals from the photocells are amplified electronically in a differential amplifier, and the differential signal is impressed across a logarithmically wound resistor where the signal is measured by a Brown recording potentiometer. This makes possible the presentation of the light-absorbing characteristics of the sample solution directly in optical density units.*

*The optical density of a solution is defined as $\text{O.D.} = \log_{10} I_0/I$ where O.D. represents the optical density, I_0 and I the intensity of the light passing through the blank and sample cell respectively. This is convenient since such a quantity is proportional to concentration when the combined Beer-Banger law is followed. This relation can be given as

$$I = I_0 e^{-\epsilon cl}$$

where I_0 and I represent the intensity of blank and sample solutions, ϵ is the molar extinction coefficient, c is the concentration in moles/liter and l is the path length of solution in centimeters.

Various chart speeds are available ranging in speed from 20 sec./division to 5 sec./division on the chart. Various scanning speeds are also available so that the spectral region being studied may be traversed at various speeds. The accuracy which may be attained with this instrument ranges from 1/2 of 1% at optical densities of less than one to about 0.2 of 1% at optical densities between one and two.

A Beckmann model G pH meter was used to determine the activity of the hydrogen ion. This instrument was standardised with buffers prepared by the National Technical Laboratories, Pasadena, California, for this purpose. Accuracies of approximately 0.01 pH units may be attained with this instrument.

Quartz cells with path lengths of 1.00 cm., 2.00 cm. and 5.00 cm. were used for reaction vessels. The volumes of these cells were measured to within 0.01 ml. All measurements given in this work were done in a 1.00 cm. quartz cell which had a volume of 2.91 ml.

All glassware, micropipettes and volumetric ware used were of the usual analytical quality.

C. Analyses

Periodate determinations were made as described by Willard and

Diehl.¹⁶ Excess potassium iodide was added to the acidified solution containing the sample. The liberated iodine was titrated with standard thiosulfate using starch as an indicator.

Standard sodium thiosulfate solution was prepared in the manner described by Willard and Furman.¹⁷ The required amount of sodium thiosulfate pentahydrate was dissolved in water to give the approximate normality desired. Potassium hydroxide and carbonate were added to shorten the time needed for the solution to stabilize. After being stored for a week the solution was standardized with potassium acid iodate the primary standard using the same method used for the determination of iodate.¹⁸

The iodate determinations were made by adding excess potassium iodide to the acidified solution containing the sample. The liberated iodine was titrated with standard thiosulfate in the usual manner.

Periodic acid was analyzed for both periodate and iodate according to the method of Muller and Friedberger.¹⁹ The solution

¹⁶H. H. Willard and H. Diehl, "Advanced Quantitative Analysis". New York, N. Y., D. Van Nostrand Company Inc. (1943) p 376.

¹⁷H. H. Willard and N. H. Furman "Elementary Quantitative Analysis". 3rd Ed., New York, N. Y. D. Van Nostrand Company Inc. (1940) p 266.

¹⁸H. H. Willard and N. H. Furman, *ibid.*

¹⁹E. Muller and O. Friedberger, *Ber.*, 35, 2652 (1902).

containing the sample was carefully buffered with bicarbonate. At this acidity the periodate was reduced to iodate with potassium iodide. Following this determination a total iodate and periodate determination was made to afford a check as to whether any iodate could be detected.

Standard potassium permanganate solution was prepared by dissolving the reagent grade solid in water followed by filtering through a sintered glass disk. Sodium oxalate was used as a primary standard for this material as in the method described by Fowler and Bright.²⁰

Manganese determinations were made by several different methods. Periodate oxidation of the manganese in acid solution to permanganic acid and comparing colorimetrically with a similarly prepared standard as described by Willard and Greathouse²¹ was one method used. The direct fluoride method²² in which manganese (II) is titrated with standard permanganate solution was also used. In other cases some manganese determinations were made gravimetrically by igniting the dry salt to Mn_3O_4 as suggested in Willard and Diehl.²³

²⁰R. M. Fowler and H. A. Bright, J. Research Nat. Bur. Standards **15**, 493 (1935).

²¹H. H. Willard and L. Greathouse, J. Am. Chem. Soc., **39**, 2366 (1917).

²²F. I. Metzger and L. E. Marrs, J. Ind. Eng. Chem., **3**, 333 (1911); **5**, 125 (1913).

²³H. H. Willard and H. Diehl, "Advanced Quantitative Analysis" New York, N. Y. D. Van Nostrand Company Inc. (1943) p. 164.

The total iodine in some iodates was determined by thermally decomposing the weighed dried salt under a current of air and subliming the iodine into a solution of potassium iodide. The iodine was then titrated with standard sodium thiosulfate solution. The decomposition was made in an all glass apparatus.

D. Method

The intense color of the permanganate ion lends itself admirably to a spectrophotometric method for following the progress of the periodate oxidation of manganese. The absorption characteristics of a potassium permanganate solution as recorded on the Cary instrument is shown in Figure 1. The molar extinction coefficient for permanganate is 2241 ± 5 at 5260 \AA as measured on the instrument used in these experiments. The metaperiodate ion has an absorption maximum at 2225 \AA , however, the interference between this peak and the permanganate absorption made measurements in this spectral region impossible. The absorption maximum of permanganate has no such fault, and it was found that at the concentrations used for manganese (II), iodic acid and perchloric acid there were no interferences from these ions. With the instrument available two methods of measurement were possible. Either the entire visible portion of the spectrum could be scanned at intervals of approximately three minutes, or the scanning mechanism could be locked at a given wavelength and the chart allowed to proceed. The latter of these

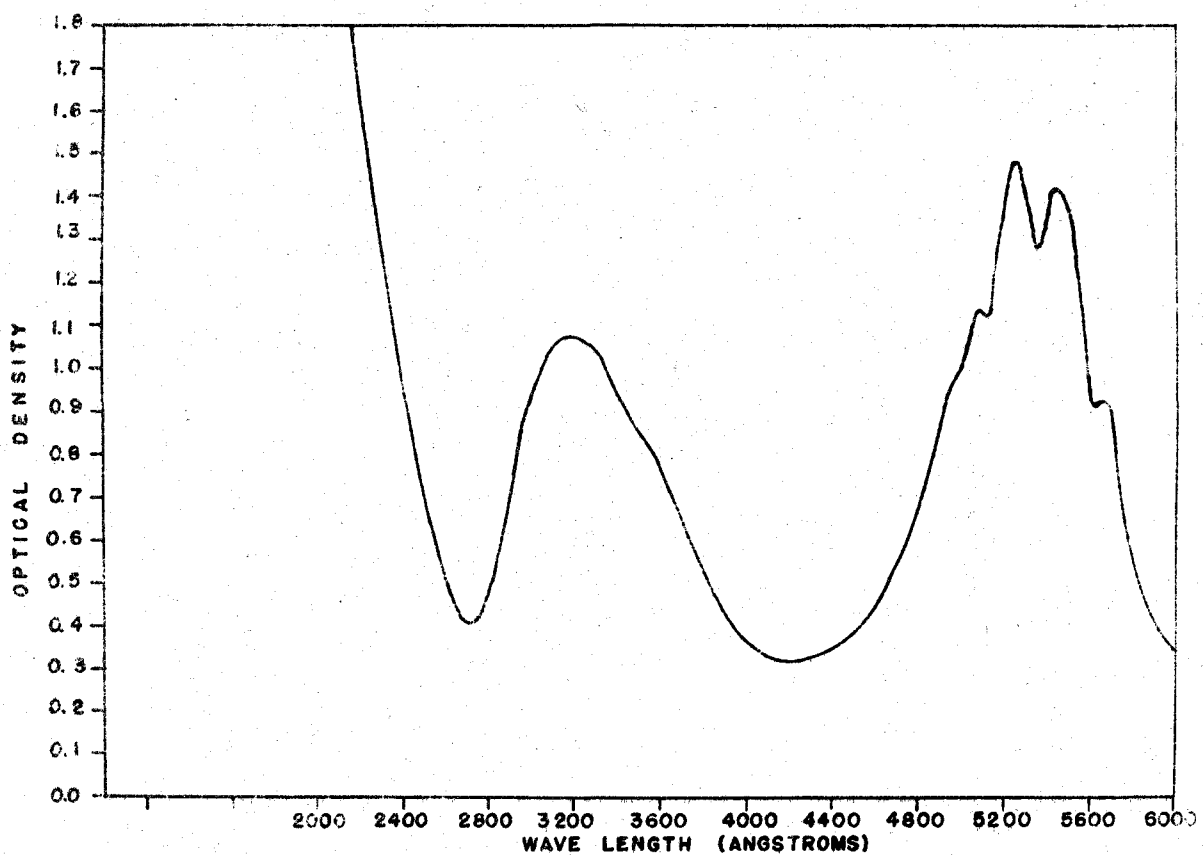


Figure 1 - Absorption characteristics of an aqueous solution of potassium permanganate on the Cary Spectrophotometer.

methods made possible an immediately available plot of permanganate concentration versus time. Examples of both types of data are shown in Figures 2 and 3.

The majority of the experiments were performed in the one centimeter quartz cells. The volume of the cell was 2.91 ml. when the meniscus was at the bottom of the neck. Calibrated micropipettes were used to measure the various amounts of each solution added.

Temperature control was attained by placing copper tanks filled with water at the desired temperature to serve as a thermal ballast in the sample chamber. When a temperature other than room temperature was used, the cell and all materials to be used were placed in a bath at the desired temperature for a sufficient time for thermal equilibrium to be attained. Experiments following the variation of temperature with time showed that the temperature of the solution remained constant to within $\pm 0.2^\circ$.

Stock solutions of persulphuric acid, manganese (II) perchlorate, iodic acid, perchloric acid and potassium permanganate were prepared in concentrations such that when diluted to volume in the quartz cell the concentrations would be in the range desired. These stock solutions were standardized by the analytical methods already described.

The general procedure followed was to pipette the desired amounts of perchloric acid and whatever other materials used into the sample cell. The manganese (II) perchlorate was added last,

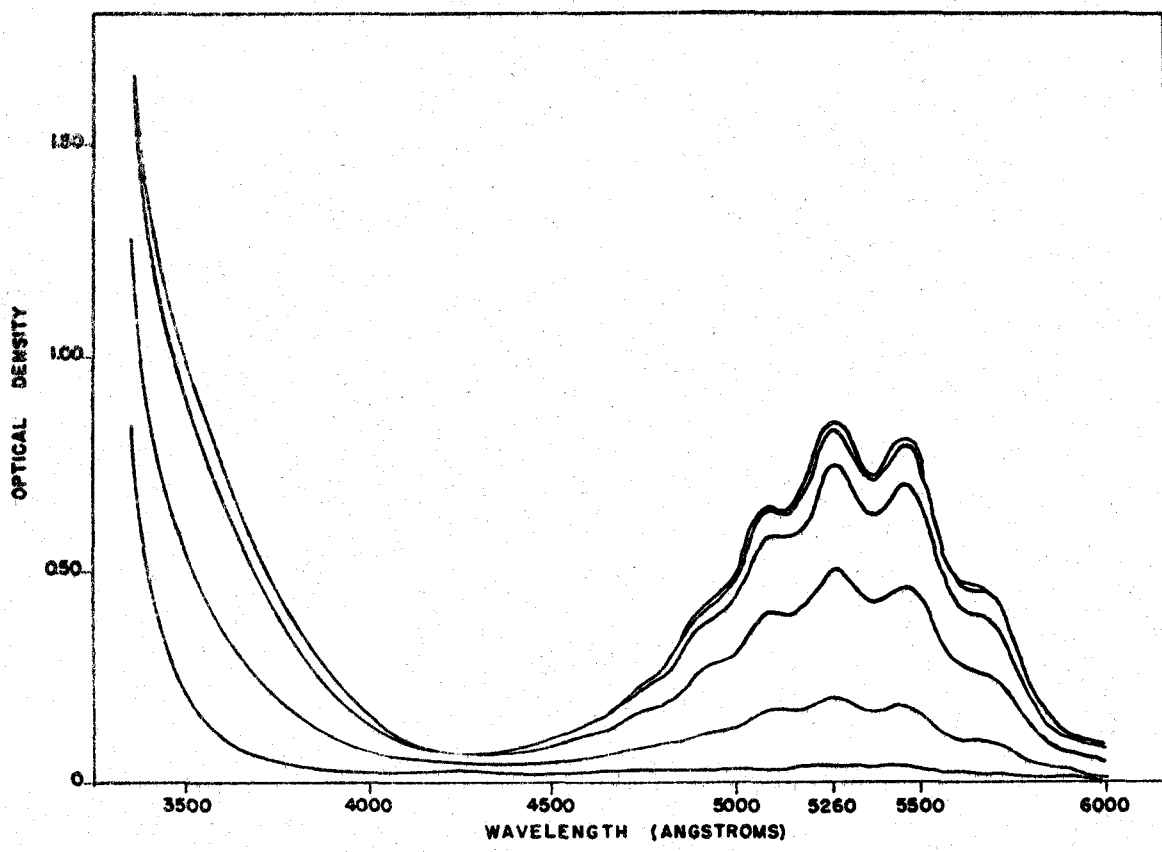


Figure 2 - Example of rata data obtained by periodic scanning.

the cell stoppered, shaken, and placed in the sample chamber of the spectrophotometer. The stop watch was started during the pipetting of the manganese (II) perchlorate. The time taken between the addition of the last reactant and the time when the spectrophotometer was turned on usually totaled about fifteen seconds. The shortest time for 98% completion of a reaction was greater than five minutes; hence, the unobserved period was always only a small part of the total time of reaction.

Preliminary experiments showed that the oxidation of manganese (II) gave a rate curve which had an "S" shape. These preliminary experiments made it possible to choose the proper acidity for minimizing the precipitation of the manganese and also to choose convenient concentrations of reactants such that the time of an experiment was within reasonable limits. After these facts were determined, the various reactions to collect experimental data were outlined.

The general method of investigation was to keep certain variables at sufficiently high concentrations so that a constant concentration of each of these could be maintained. Hydrogen ion, manganese (II), manganese (III), periodate, iodate, permanganate and ionic strength were all variables to be considered. The Cary instrument limited the amount of permanganate that could be followed; hence, it was not possible to employ large excesses of any manganese compounds since the eventual optical density of the solution would have been too high to be measured.

The above described methods were used, and the various reactions described in Table I were measured. The reactions numbered one to six inclusive were made with perchloric acid the chief variable. These results were plotted and are given as figures 3 and 4. The reactions numbered seven through eleven inclusive have the periodate concentration as the main variable. The excess periodate was always more than one hundred times the stoichiometric amount. This data was plotted and has been given in figures 5 and 6. The reactions numbered twelve through fourteen had the amount of manganese (II) as the chief variable, and the plots of these reactions are included as figure 7. The plots of reactions with iodate as the variable have been included as figure 8. The accuracy of the data in this figure is sufficient so that no data is included in Table I. The reactions numbered eighteen through twenty four inclusive have the initial amount of potassium permanganate in the presence of iodate the only variable, and these results are plotted in figure 9. The reactions numbered twenty five through twenty seven were made to determine the mode of reaction of manganese (III) iodate complex, and these plots have been given as figure 10. Reactions at 29° and 40° were made with manganese (III) and periodate to determine an activation energy. These were numbered twenty eight and twenty nine and have been plotted in figure 11. Corresponding temperature data were collected for the reaction of manganese (II), and these were numbered thirty and thirty one and have been plotted as figure 12.

TABLE I

Rate Data

#1 $M_{\text{HClO}_4} = 0.478$ $M_{\text{H}_5\text{IO}_6} = 0.250$ $M_{\text{Mn}(\text{ClO}_4)_2} = 3.54 \times 10^{-4}$

Note: zero absorption corresponds to 0.030 optical density units

time	0.0	1.0	3.0	5.0	7.0	9.0	10.0	11.0	13.0
O.D.	0.030	0.051	0.102	0.198	0.368	0.597	0.720	0.848	1.066

time	15.0	17.0	20.0	23.0
O.D.	1.218	1.314	1.373	1.340

#2 $M_{\text{HClO}_4} = 0.974$ $M_{\text{H}_5\text{IO}_6} = 0.250$ $M_{\text{Mn}(\text{ClO}_4)_2} = 3.54 \times 10^{-4}$

Note: zero absorption corresponds to 0.030 optical density units

time	0.0	3.0	6.0	9.0	11.0	13.0	15.0	17.0	19.0
O.D.	0.030	0.068	0.153	0.388	0.522	0.738	0.956	1.147	1.291

time	21.0	24.0	27.0	29.0
O.D.	1.386	1.460	1.487	1.492

#3 $M_{\text{HClO}_4} = 0.990$ $M_{\text{H}_5\text{IO}_6} = 0.250$ $M_{\text{Mn}(\text{ClO}_4)_2} = 3.54 \times 10^{-4}$

Note: zero absorption corresponds to 0.030 optical density units

time	0.0	3.0	6.0	9.0	11.0	13.0	15.0	17.0
O.D.	0.030	0.047	0.112	0.267	0.442	0.668	0.904	1.110

time	20.0	23.0	26.0	29.0	32.0
O.D.	1.320	1.429	1.478	1.497	1.502

#4 $M_{\text{HClO}_4} = 1.923$ $M_{\text{H}_5\text{IO}_6} = 0.250$ $M_{\text{Mn}(\text{ClO}_4)_2} = 3.54 \times 10^{-4}$

Note: zero absorption corresponds to 0.030 optical density units

time	0.0	5.0	10.0	13.0	15.0	17.0	19.0	21.0
O.D.	0.030	0.078	0.221	0.413	0.592	0.789	0.985	1.150

time	23.0	26.0	29.0	32.0	35.0
O.D.	1.277	1.395	1.460	1.488	1.497

TABLE I (continued)

#5 $M_{\text{HClO}_4} = 2.94$ $M_{\text{H}_5\text{IO}_6} = 0.250$ $M_{\text{Mn}(\text{ClO}_4)_2} = 3.54 \times 10^{-4}$

Note: zero absorption corresponds to 0.030 optical density units

time	0.0	5.0	10.0	15.0	18.0	20.0	22.0	24.0
O.D.	0.030	0.045	0.108	0.346	0.633	0.848	1.039	1.189

time	26.0	28.0	31.0	34.0	37.0
O.D.	1.292	1.358	1.412	1.438	1.447

#6 $M_{\text{HClO}_4} = 3.78$ $M_{\text{H}_5\text{IO}_6} = 0.250$ $M_{\text{Mn}(\text{ClO}_4)_2} = 3.54 \times 10^{-4}$

Note: zero absorption corresponds to 0.030 optical density units

time	0.0	3.0	6.0	8.0	10.0	11.0	12.0	13.0
O.D.	0.030	0.048	0.114	0.250	0.481	0.627	0.767	0.898

time	15.0	17.0	19.0	21.0	24.0	26.0
O.D.	1.089	1.211	1.277	1.308	1.332	1.332

#7 $M_{\text{HClO}_4} = 1.885$ $M_{\text{H}_5\text{IO}_6} = 0.500$ $M_{\text{Mn}(\text{ClO}_4)_2} = 3.54 \times 10^{-4}$

Note: zero absorption corresponds to 0.030 optical density units

time	0.0	1.0	2.0	3.0	4.0	5.0	6.0	7.0	8.0
O.D.	0.030	0.0530	0.090	0.150	0.238	0.368	0.573	0.718	0.902

time	9.0	10.0	11.0	12.0	13.0	14.0	15.0	16.0	17.0
O.D.	1.054	1.171	1.258	1.313	1.349	1.368	1.379	1.386	1.388

#8 $M_{\text{HClO}_4} = 1.885$ $M_{\text{H}_5\text{IO}_6} = 0.312$ $M_{\text{Mn}(\text{ClO}_4)_2} = 3.54 \times 10^{-4}$

Note: zero absorption corresponds to 0.030 optical density units

time	0.0	1.0	2.0	3.0	5.0	6.0	7.0	9.0
O.D.	0.030	0.052	0.083	0.127	0.290	0.412	0.558	0.873

time	10.0	12.0	14.0	16.0	18.0	21.0
O.D.	1.018	1.241	1.368	1.426	1.450	1.460

TABLE I (continued)

#9 $M_{\text{HClO}_4} = 1.885$ $M_{\text{H}_5\text{IO}_6} = 0.250$ $M_{\text{Mn}(\text{ClO}_4)_2} = 3.54 \times 10^{-4}$

Note: zero absorption corresponds to 0.030 optical density units

time	0.0	3.0	5.0	8.0	11.0	14.0	16.0	18.0
O.D.	0.030	0.050	0.080	0.172	0.352	0.637	0.849	1.043

time	21.0	24.0	27.0	31.0	37.0
O.D.	1.271	1.405	1.476	1.512	1.528

#10 $M_{\text{HClO}_4} = 1.885$ $M_{\text{H}_5\text{IO}_6} = 0.1871$ $M_{\text{Mn}(\text{ClO}_4)_2} = 3.54 \times 10^{-4}$

Note: zero absorption corresponds to 0.030 optical density units

time	0.0	5.0	10.0	15.0	20.0	23.0	25.0	28.0
O.D.	0.030	0.040	0.059	0.111	0.245	0.393	0.527	0.758

time	31.0	33.0	38.0	43.0	48.0	53.0	58.0
O.D.	0.993	1.133	1.391	1.512	1.555	1.566	1.570

#11 $M_{\text{HClO}_4} = 1.885$ $M_{\text{H}_5\text{IO}_6} = 0.1248$ $M_{\text{Mn}(\text{ClO}_4)_2} = 3.54 \times 10^{-4}$

Note: zero absorption corresponds to 0.030 optical density units

time	0.0	5.0	10.0	15.0	20.0	25.0	30.0	33.0
O.D.	0.030	0.038	0.049	0.078	0.130	0.226	0.383	0.512

time	36.0	39.0	43.0	46.0	51.0	56.0	61.0	66.0
O.D.	0.662	0.824	1.037	1.177	1.368	1.480	1.550	1.588

time	71.0
O.D.	1.600

#12 $M_{\text{HClO}_4} = 0.424$ $M_{\text{H}_5\text{IO}_6} = 0.136$ $M_{\text{KH}(\text{IO}_3)_2} = 1.94 \times 10^{-3}$

$M_{\text{Mn}(\text{ClO}_4)_2} = 3.65 \times 10^{-4}$

Note: zero absorption corresponds to 0.004 optical density units

time	0.0	5.0	10.0	15.0	17.0	19.0	22.0	25.0
O.D.	0.004	0.011	0.46	0.173	0.263	0.361	0.504	0.616

time	28.0	31.0	36.0
O.D.	0.661	0.693	0.700

TABLE I (continued)

#13 $M_{\text{HClO}_4} = 0.424$ $M_{\text{H}_5\text{IO}_6} = 0.150$ $M_{\text{KH}(\text{IO}_3)_2} = 1.94 \times 10^{-3}$
 $M_{\text{Mn}(\text{ClO}_4)_2} = 3.92 \times 10^{-4}$

Note: zero absorption corresponds to 0.020 optical density units

time	0.0	3.0	5.0	7.0	9.0	11.0	14.0	16.0
O.D.	0.020	0.039	0.079	0.161	0.299	0.468	0.678	0.753

time	18.0	21.0	24.0
O.D.	0.788	0.802	0.804

#14 $M_{\text{HClO}_4} = 0.424$ $M_{\text{H}_5\text{IO}_6} = 0.166$ $M_{\text{KH}(\text{IO}_3)_2} = 1.94 \times 10^{-3}$
 $M_{\text{Mn}(\text{ClO}_4)_2} = 7.85 \times 10^{-4}$

time	0.0	3.0	5.0	6.0	7.0	8.0	9.0	10.0	11.0
O.D.	0.020	0.060	0.184	0.311	0.479	0.678	0.875	1.056	1.197

time	12.0	14.0	16.0	18.0
O.D.	1.300	1.409	1.451	1.462

#18 $M_{\text{HClO}_4} = 0.424$ $M_{\text{KH}(\text{IO}_3)_2} = 1.94 \times 10^{-3}$ $M_{\text{H}_5\text{IO}_6} = 0.167$
 $M_{\text{Mn}(\text{ClO}_4)_2} = 3.92 \times 10^{-4}$

time	0.0	2.0	4.0	6.0	8.0	10.0	12.0	14.0	16.0
O.D.	0.0	0.03	0.022	0.048	0.097	0.166	0.249	0.340	0.433

time	18.0	20.0	22.0	24.0	26.0	28.0
O.D.	0.511	0.573	0.622	0.654	0.676	0.680

#19 $M_{\text{HClO}_4} = 0.424$ $M_{\text{KH}(\text{IO}_3)_2} = 1.94 \times 10^{-3}$ $M_{\text{H}_5\text{IO}_6} = 0.166$
 $M_{\text{Mn}(\text{ClO}_4)_2} = 3.92 \times 10^{-4}$ $M_{\text{KMnO}_4} = 3.02 \times 10^{-5}$

time	0.0	0.50	1.0	2.0	3.0	4.0	5.0	7.0	9.0
O.D.	0.063	0.067	0.080	0.113	0.159	0.209	0.253	0.378	0.483

time	11.0	13.0	15.0	17.0	19.0	21.0
O.D.	0.567	0.680	0.678	0.700	0.715	0.722

TABLE I (continued)

#20 $M_{\text{HClO}_4} = 0.424$ $M_{\text{KH}(\text{IO}_3)_2} = 1.94 \times 10^{-3}$ $M_{\text{H}_5\text{IO}_6} = 0.166$
 $M_{\text{Mn}(\text{ClO}_4)_2} = 3.92 \times 10^{-4}$ $M_{\text{KMnO}_4} = 9.06 \times 10^{-5}$

time 0.0 0.50 1.0 2.0 3.0 5.0 7.0 9.0
 O.D. 0.127 0.140 0.158 0.210 0.267 0.397 0.516 0.608

time 11.0 13.0 15.0 17.0 19.0
 O.D. 0.682 0.712 0.747 0.748 0.751

#21 $M_{\text{HClO}_4} = 0.424$ $M_{\text{KH}(\text{IO}_3)_2} = 1.94 \times 10^{-3}$ $M_{\text{H}_5\text{IO}_6} = 0.165$
 $M_{\text{Mn}(\text{ClO}_4)_2} = 3.92 \times 10^{-4}$ $M_{\text{KMnO}_4} = 1.21 \times 10^{-4}$

time 0.0 0.33 0.66 1.0 2.0 4.0 5.0 6.0 7.0
 O.D. 0.2569 0.281 0.287 0.316 0.381 0.454 0.527 0.583 0.647

time 8.0 9.0 10.0 11.0 12.0 14.0 15.0
 O.D. 0.695 0.734 0.763 0.787 0.802 0.828 0.842

#22 $M_{\text{HClO}_4} = 0.424$ $M_{\text{KH}(\text{IO}_3)_2} = 1.94 \times 10^{-3}$ $M_{\text{H}_5\text{IO}_6} = 0.163$
 $M_{\text{Mn}(\text{ClO}_4)_2} = 3.92 \times 10^{-4}$ $M_{\text{KMnO}_4} = 3.02 \times 10^{-4}$

time 0.0 0.33 0.66 1.0 2.0 3.0 4.0 5.0 6.0
 O.D. 0.687 0.697 0.721 0.750 0.852 0.951 1.034 1.99 1.150

time 7.0 8.0 9.0 11.0 13.0
 O.D. 1.187 1.216 1.232 1.250 1.260

#23 $M_{\text{HClO}_4} = 0.424$ $M_{\text{KH}(\text{IO}_3)_2} = 1.94 \times 10^{-3}$ $M_{\text{H}_5\text{IO}_6} = 0.160$
 $M_{\text{Mn}(\text{ClO}_4)_2} = 3.92 \times 10^{-4}$ $M_{\text{KMnO}_4} = 6.05 \times 10^{-4}$

time 0.0 0.33 0.66 1.0 2.0 3.0 4.0 5.0 6.0
 O.D. 1.348 1.372 1.405 1.448 1.557 1.647 1.702 1.746 1.770

time 7.0 8.0 9.0 11.0
 O.D. 1.786 1.800 1.808 1.813

TABLE I (continued)

#24 $M_{\text{HClO}_4} = 0.424$ $M_{\text{KH}(\text{IO}_3)_2} = 1.94 \times 10^{-3}$ $M_{\text{H}_5\text{IO}_6} = .157$
 $M_{\text{Mn}(\text{ClO}_4)_2} = 3.92 \times 10^{-4}$ $M_{\text{KMnO}_4} = 9.06 \times 10^{-4}$

time	0.0	0.33	0.66	1.0	1.50	2.0	3.0	4.0	5.0
O.D.	2.030	2.059	2.104	2.145	2.208	2.262	2.349	2.388	2.417

time	6.0	7.0	8.0	10.0
O.D.	2.437	2.449	2.450	2.454

#25 $C_{\text{Mn}(\text{IO}_3)_x}^{3-x} = 1$ $C_{\text{H}_5\text{IO}_6} = \frac{1}{2}$ $C_{\text{HClO}_4} = 1$ $C_{\text{IO}_3} = 1$

Note: zero absorption corresponds to 0.035 optical density units

time	0.0	0.25	0.5	0.75	1.0	1.5	2.0	2.5	3.0
O.D.	0.035	0.050	0.070	0.88	0.103	0.137	0.166	0.189	0.212

time	3.5	4.0	4.5	5.0
O.D.	0.231	0.241	0.252	0.259

#26 $C_{\text{Mn}(\text{IO}_3)_x}^{3-x} = 1$ $C_{\text{H}_5\text{IO}_6} = 1$ $C_{\text{HClO}_4} = 1$ $C_{\text{IO}_3} = 1$

Note: zero absorption corresponds to 0.045 optical density units

time	0.0	0.15	0.25	0.5	0.75	1.25	1.62	1.87
O.D.	0.045	0.074	0.094	0.129	0.162	0.187	0.215	0.229

time	2.37	2.87
O.D.	0.243	0.248

#27 $C_{\text{Mn}(\text{IO}_3)_x}^{3-x} = 2$ $C_{\text{H}_5\text{IO}_6} = 1$ $C_{\text{HClO}_4} = 1$ $C_{\text{IO}_3} = 1$

Note: zero absorption corresponds to 0.045 optical density units

time	0.0	0.25	0.37	0.5	0.75	1.0	1.25	1.50
O.D.	0.045	0.137	0.171	0.199	0.250	0.298	0.338	0.370

time	1.75	2.0	2.5	3.0	3.5
O.D.	0.392	0.410	0.429	0.438	0.441

TABLE I (continued)

#28 Reaction of $\text{Mn}(\text{IO}_3)_{3-x}$ with H_5IO_6 at 29°

Note: zero absorption corresponds to 0.053 optical density units

time	0.0	.25	.5	.75	1.0	1.5	2.0	2.5	3.0
O.D.	0.053	0.072	0.097	0.120	0.141	0.176	0.231	0.274	0.317

time	3.5	4.0	4.5	5.0	5.5
O.D.	0.350	0.380	0.401	0.415	0.430

#29 Reaction of $\text{Mn}(\text{IO}_3)_{3-x}$ with H_5IO_6 at 40°

Note: zero absorption corresponds to 0.043 optical density units

time	0.0	.25	.5	.75	1.0	1.25	1.5	1.75	2.0
O.D.	0.043	0.101	0.158	0.202	0.242	0.277	0.309	0.336	0.353

time	2.25	2.75	3.50	4.0	4.5
O.D.	0.373	0.394	0.410	0.412	0.420

#30 Reaction of $\text{Mn}(\text{ClO}_4)_2$ with H_5IO_6 at 29°

Note: zero absorption corresponds to 0.038 optical density units

time	0.0	2.0	4.0	5.0	7.0	9.0	11.0	13.0
O.D.	0.038	0.041	0.049	0.059	0.087	0.131	0.204	0.291

time	15.0	17.0	19.0	21.0	23.0	25.0	27.0
O.D.	0.394	0.489	0.506	0.627	0.654	0.688	0.704

#31 Reaction of $\text{Mn}(\text{ClO}_4)_2$ with H_5IO_6 at 40°

Note: zero absorption corresponds to 0.028 optical density units

time	0.0	2.0	4.0	6.0	7.0	8.0	9.0	10.0	11.0
O.D.	0.028	0.041	0.086	0.172	0.239	0.311	0.391	0.470	0.545

time	12.0	13.0	14.0	16.0	18.0	20.0
O.D.	0.607	0.659	0.700	0.747	0.769	0.773

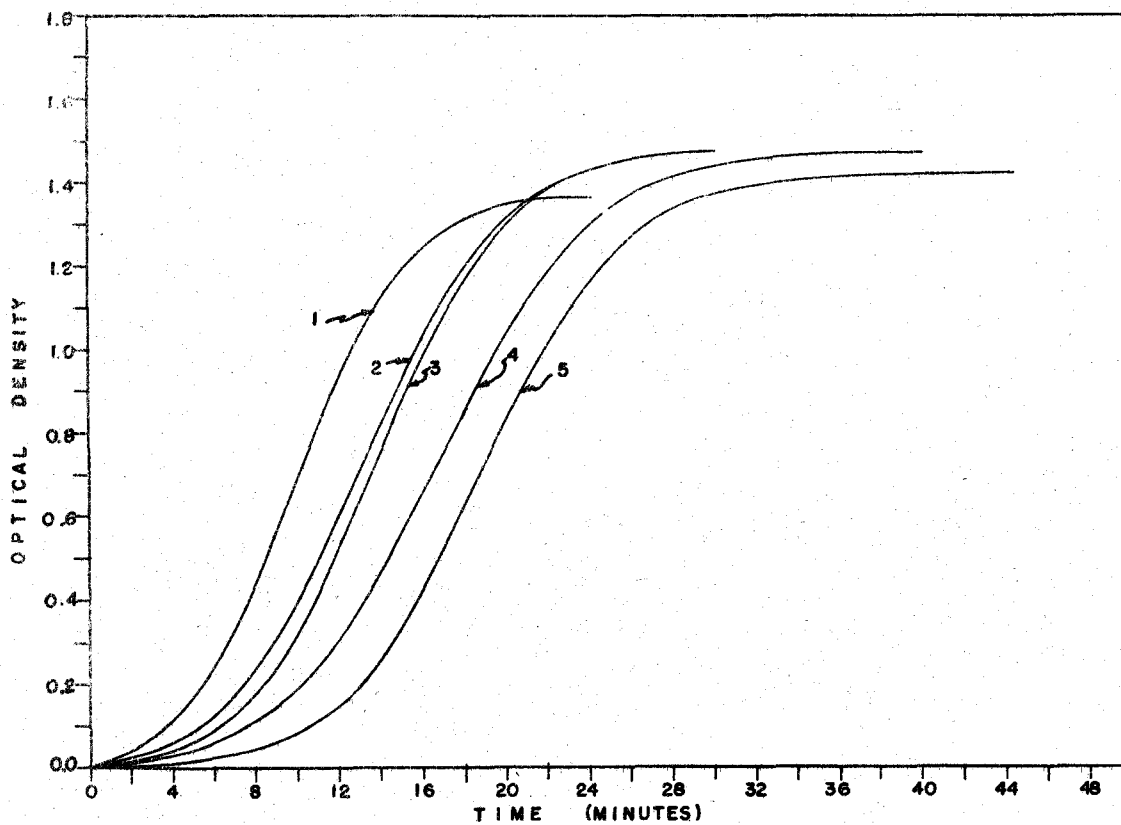


Figure 3 - Rate curves at 5260 Å

No.	M_{HClO_4}	$M_{\text{H}_5\text{IO}_6}$	$M_{\text{Mn}(\text{ClO}_4)_2}$
1	.478	.250	3.54×10^{-4}
2	.974	.250	3.54×10^{-4}
3	.990	.250	3.54×10^{-4}
4	1.923	.250	3.54×10^{-4}
5	2.94	.250	3.54×10^{-4}

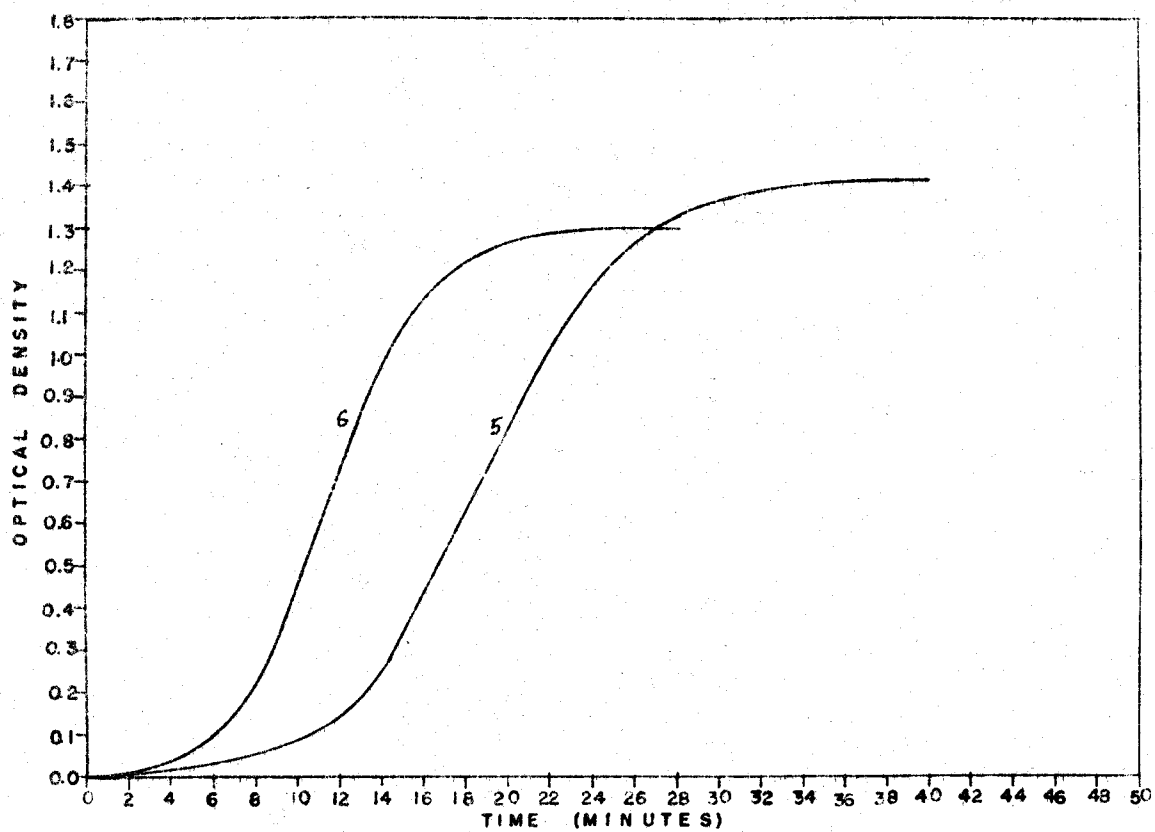


Figure 4 - Rate curves at 5260 Å

No.	M_{HClO_4}	$M_{\text{H}_5\text{IO}_6}$	$M_{\text{Mn}(\text{ClO}_4)_2}$
5	2.94	.250	3.54×10^{-4}
6	3.78	.250	3.54×10^{-4}

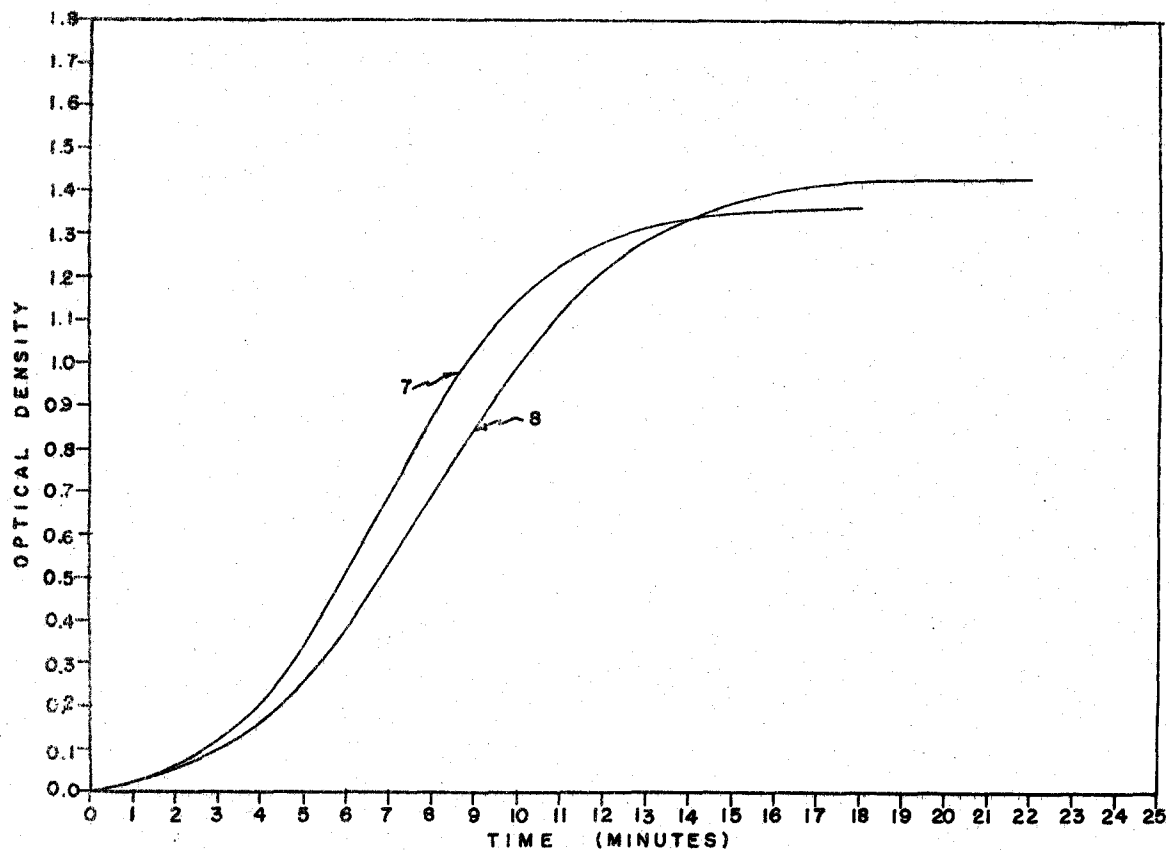


Figure 5 - Rate curves at 5260 Å

No.	M_{HClO_4}	$M_{\text{H}_5\text{IO}_6}$	$M_{\text{Mn}(\text{ClO}_4)_2}$
7	1.885	.500	3.54×10^{-4}
8	1.885	.312	3.54×10^{-4}

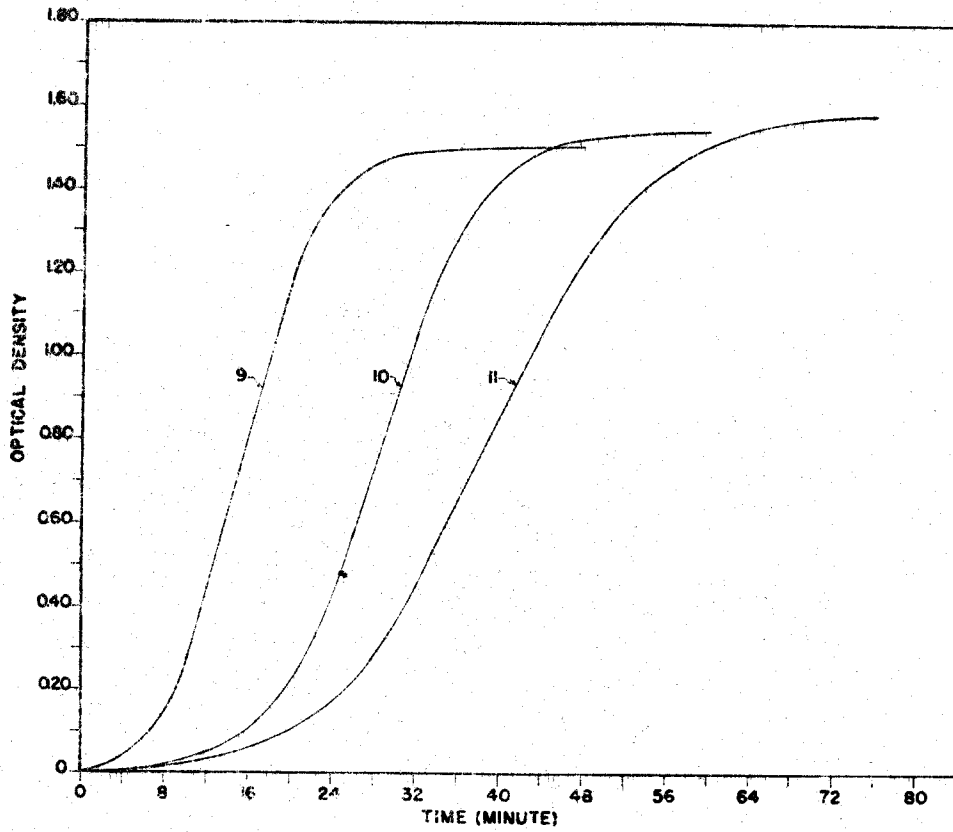


Figure 6 - Rate curve at 5260 Å

No.	M_{HClO_4}	$M_{\text{H}_5\text{IO}_6}$	$M_{\text{Mn}(\text{ClO}_4)_2}$
9	1.885	.250	3.54×10^{-4}
10	1.885	.1871	3.54×10^{-4}
11	1.885	.1248	3.54×10^{-4}

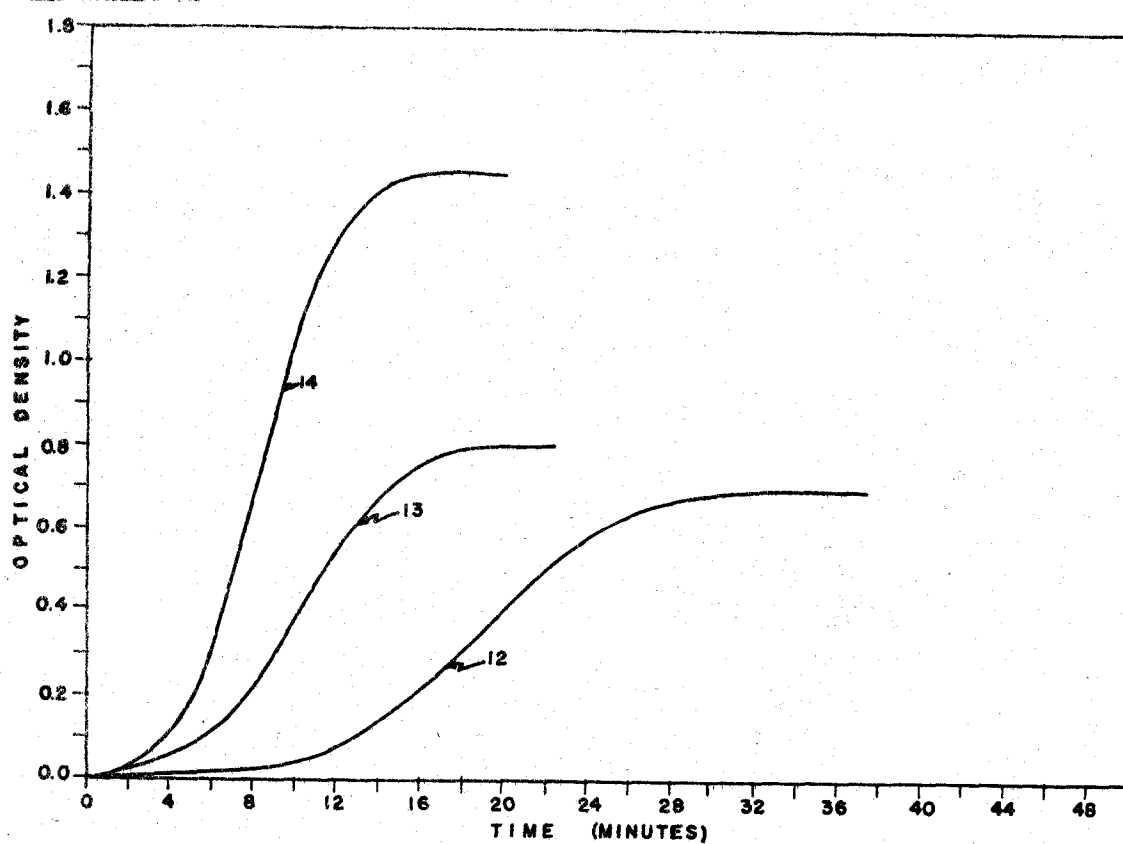


Figure 7 - Rate curves at 5260 Å

No.	M_{HClO_4}	$M_{\text{H}_5\text{IO}_6}$	$M_{\text{KH}(\text{IO}_3)_2}$	$M_{\text{Mn}(\text{ClO}_4)_2}$
12	0.424	.136	1.94×10^{-3}	3.65×10^{-4}
13	0.424	.166	1.94×10^{-3}	3.92×10^{-4}
14	0.424	.150	1.94×10^{-3}	7.85×10^{-4}

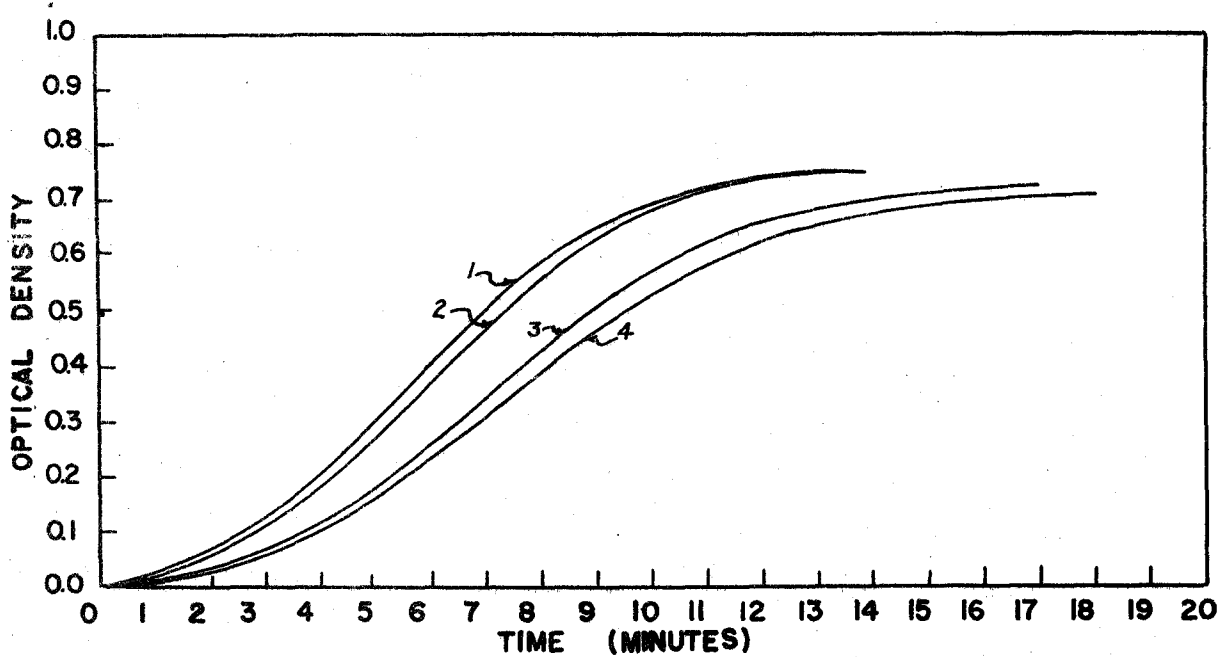


Figure 8 - Reaction rate curves

No.	$M_{\text{Mn}(\text{ClO}_4)_2}$	M_{HClO_4}	M_{HIO_3}	$M_{\text{H}_5\text{IO}_6}$
1	3.92×10^{-4}	0.424	1.13×10^{-2}	0.232
2	3.92×10^{-4}	0.424	0.379×10^{-2}	0.241
3	3.92×10^{-4}	0.424	0.15×10^{-2}	0.243
4	3.92×10^{-4}	0.424	0	0.245

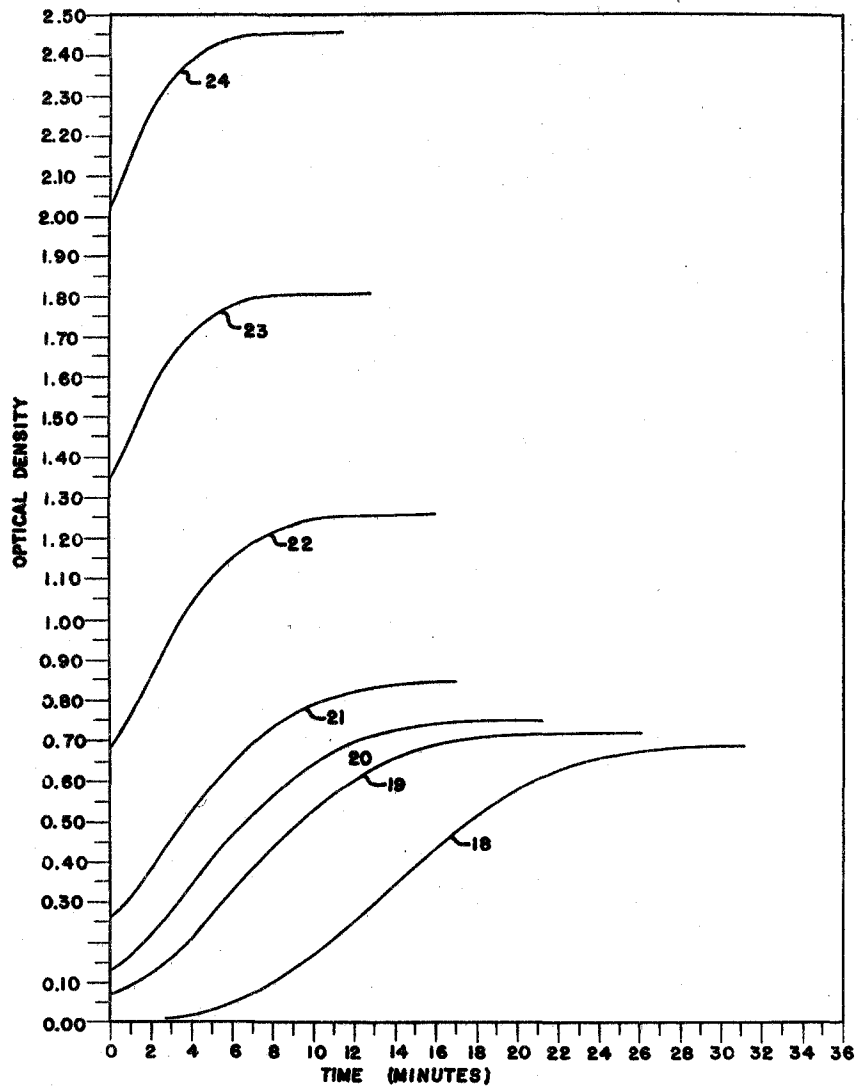


Figure 9 - Rate curves at 5260 Å

No.	M_{HClO_4}	$M_{\text{KH}(\text{IO}_3)_2}$	$M_{\text{H}_5\text{IO}_6}$	$M_{\text{Mn}(\text{ClO}_4)}$	M_{KMNO}
18	.424	1.94×10^{-3}	.167	3.92×10^{-4}	0
19	.424	1.94×10^{-3}	.166	3.92×10^{-4}	3.02×10^{-5}
20	.424	1.94×10^{-3}	.166	3.92×10^{-4}	9.06×10^{-5}
21	.424	1.94×10^{-3}	.165	3.92×10^{-4}	1.21×10^{-4}
22	.424	1.94×10^{-3}	.163	3.92×10^{-4}	3.02×10^{-4}
23	.424	1.94×10^{-3}	.160	3.92×10^{-4}	6.05×10^{-4}
24	.424	1.94×10^{-3}	.157	3.92×10^{-4}	9.06×10^{-4}

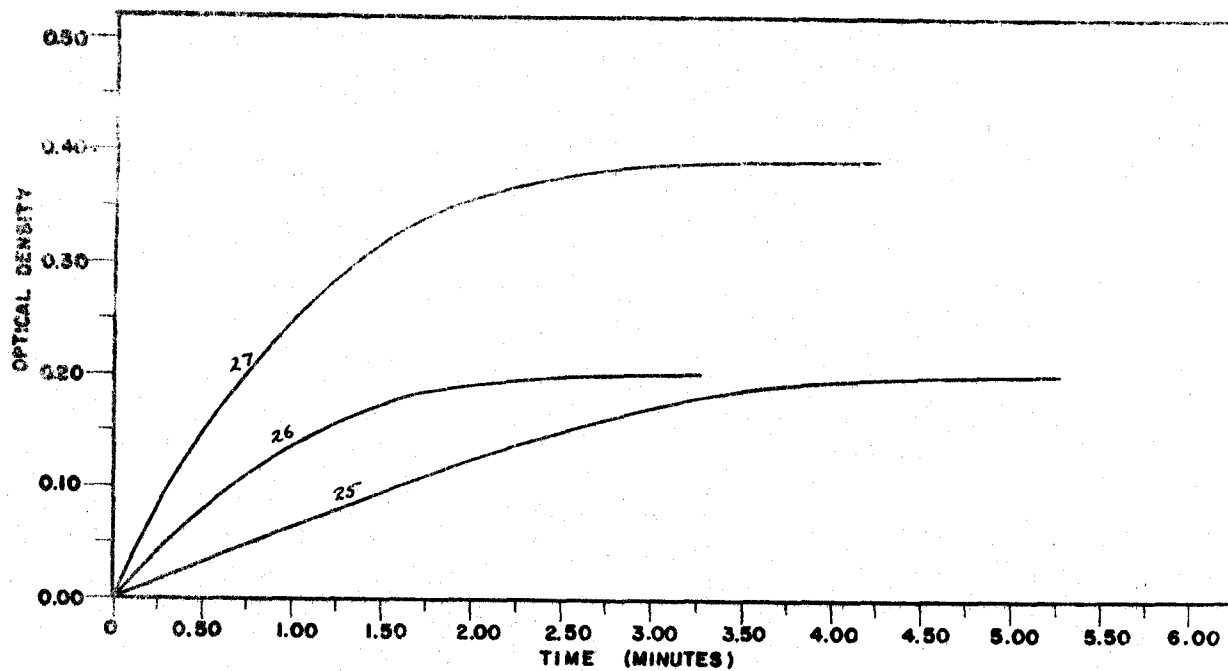


Figure 10 - Rate curves at 5260 Å

No.	$\text{Mn}(\text{IO}_3)_x^{3-x}$	H_5IO_6	HClO_4	IO_3^-
25	1	$\frac{1}{2}$	1	1
26	1	1	1	1
27	2	1	1	1

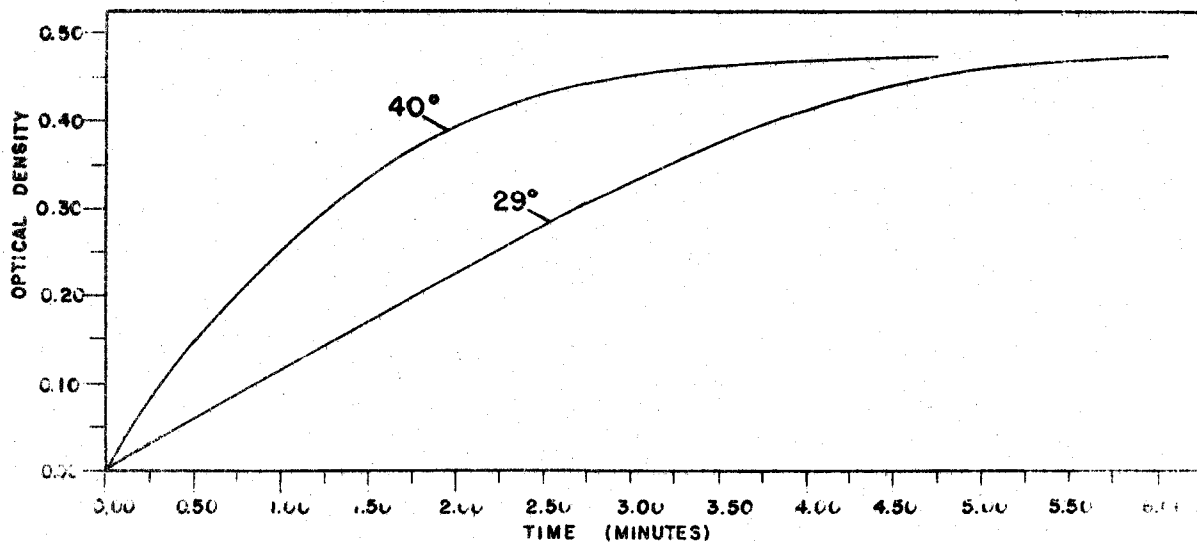


Figure 11 - Reaction curves at 29° and 40°



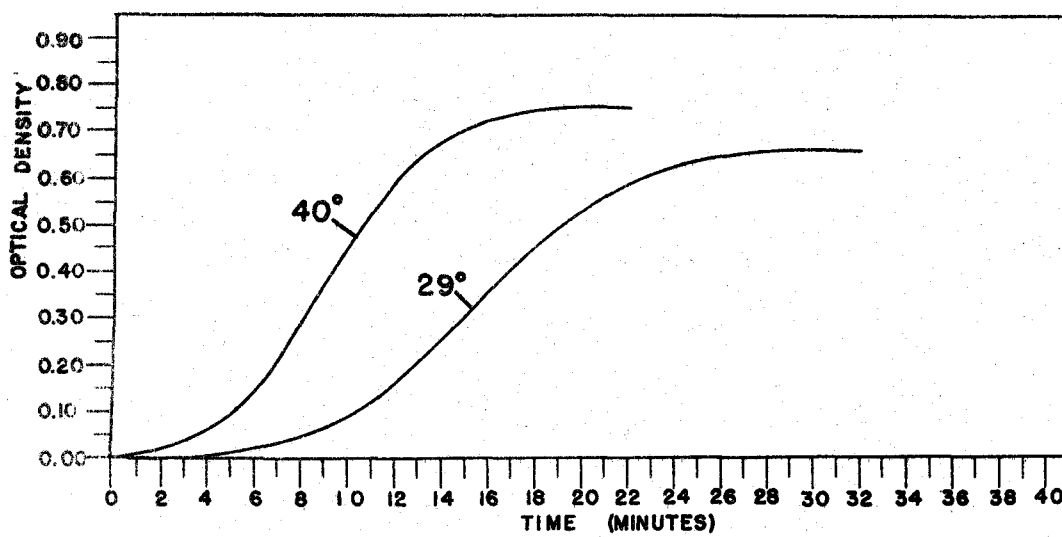


Figure 12 - Reaction curves at 29° and 40°



Reactions were made in which the spectral region from 3300 Å to 6000 Å was scanned as rapidly as possible. The original concentration of these reactions are given in Table II. A plot of the optical density at 3600 Å and at the permanganate peak at 5260 Å was made and has been included as figure 13.

E. Appendix

During exploratory and preliminary experiments it was noticed that while adding a solution of potassium permanganate to a solution of manganese (II) perchlorate in the presence of excess iodic acid a purple gray precipitate was formed. This material was not similar to any compound of manganese that was familiar to the author; hence, the properties and composition of this material were investigated since such information might be of assistance in postulating the path and intermediates of the reaction being investigated.

Further experimentation led to the tentative hypothesis that the material might be manganese (III) iodate, and the literature was searched to determine if such a compound had been noted previously. Berg²⁴ reported a compound believed to be a double iodate of manganese, $\left[\text{Mn}^{\text{II}} \text{Mn}^{\text{IV}} (\text{IO}_3)_6 \right]$, however, neither his description or method of preparation of this material corresponded to the one prepared.

²⁴A. Berg, Compt. Rend., 128, 674 (1899).

TABLE II

Initial Concentrations for Scanning Reactions

Reaction	$M_{\text{Mn}^{II}}$	$M_{\text{H}_5\text{IO}_6}$	M_{HClO_4}	M_{MnO_4}	M_{KIO_3}
1A	3.92×10^{-4}	.263	.424	0	0
2A	3.92×10^{-4}	.263	.424	0	3.1×10^{-3}
3A	3.92×10^{-4}	.263	.424	0	6.2×10^{-6}
4A	3.92×10^{-4}	.263	.424	3×10^{-4}	3.1×10^{-3}
5A	3.92×10^{-4}	.131	.424	3×10^{-4}	Sat.
6A	3.92×10^{-4}	.131	.424	6×10^{-4}	Sol
7A	3.92×10^{-4}	.263	.424	0	0
8A	3.92×10^{-4}	.131	.424	0	0

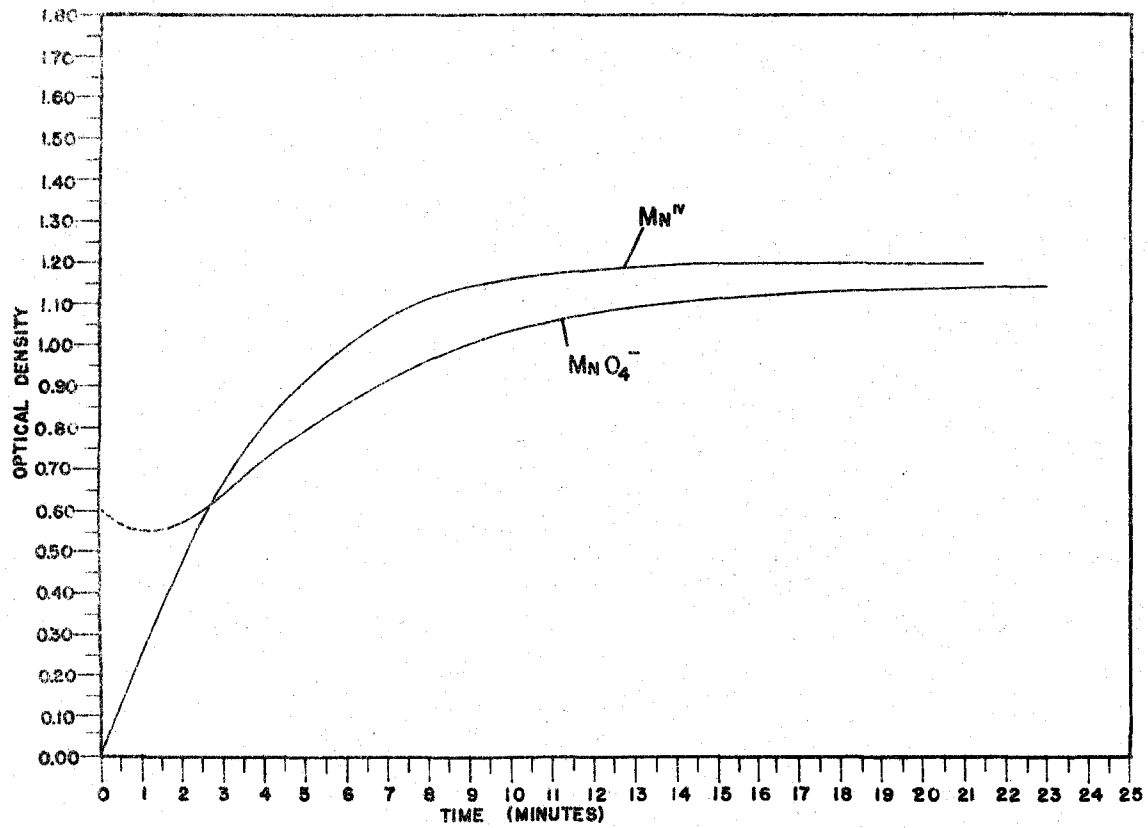


Figure 13 - Rate curves at 5260 Å and 3600 Å; Mn^{IV} O.D. obtained by difference.

Berg's work left something to be desired since several attempts by the author and others in the laboratory did not reproduce his results.

The most satisfactory method for the preparation of the purple gray material found was to precipitate the material with iodic acid from ethanol-water solutions of manganese (III) fluoride complex. A sample procedure follows: 2 gms. of potassium permanganate were dissolved in 50 ml. of water, and the resulting solution was added to a solution containing 10 gms. of manganese (II) chloride tetrahydrate in the presence of excess hydrofluoric acid. The total volume was about 200 ml. A solution containing 33 gms. of iodic acid in 85% ethanol was added. The volume was such that the final ethanol concentration was about 50%. The precipitate was filtered upon a sintered glass disk as rapidly as possible and thoroughly washed with water-ethanol mixtures. The final wash was with 95% ethanol in order to remove as much water as possible. The filtered material was then placed in a vacuum dessicator and allowed to dry for several hours until no odor of alcohol could be detected over the dried material. It was later determined that the material could safely have the alcohol removed by drying at around 80° in a suitable oven. Yields of approximately 75% were obtained by the above method.

Analyses of this material for iodine, iodate and manganese led to the conclusion that the material was manganese (III) iodate.

The analyses and theoretical composition have been shown below.

	<u>Analysis</u>	<u>Theoretical</u>
Manganese	9.41 \pm .05%	9.47%
Iodine	63.8 \pm 2%	65.7%
Iodometric Oxidation Equivalent	17.96 \pm .004	18.00 equivalents/580 gms.

The manganese determinations were made by both periodate oxidation to permanganate followed by colorimetric comparison with a similarly prepared manganese standard, and by ignition in air of the weighed dry salt to Mn_2O_4 . Both methods gave identical results within the experimental error. The iodine determinations were made by collecting the free iodine in potassium iodide solution following thermal decomposition of a weighed sample, and titrating with standard thiosulfate solution. These analyses along with the chemical properties of the salt were taken as evidence for the compound, manganese (III) iodate.

Manganese (III) iodate prepared as described is a purple gray material which decomposes upon heating to give free iodine and Mn_2O_4 . The dry salt is remarkably stable in air for a manganese (III) salt, even to the extent that after drying at 100° for several hours no decomposition was noted. When placed in water it reacts giving a yellow solution probably containing colloidal manganese (IV) oxide. It is possible to precipitate the salt from solutions of manganese (III)

fluoride or sulfate complex by the addition of iodic acid. The salt when treated with a concentrated solution of iodic acid, gives a violet solution apparently containing an iodate complex of manganese (III). The absorption characteristics of this complex have been included as figure 14.

An X-ray powder diagram of this material using Cu K radiation was made by Mr. P. H. Lewis. Since this information is sometimes useful in the identification of a material the estimated intensities and $\sin^2 \theta$ values for manganese (III) iodate have been included as Table III.

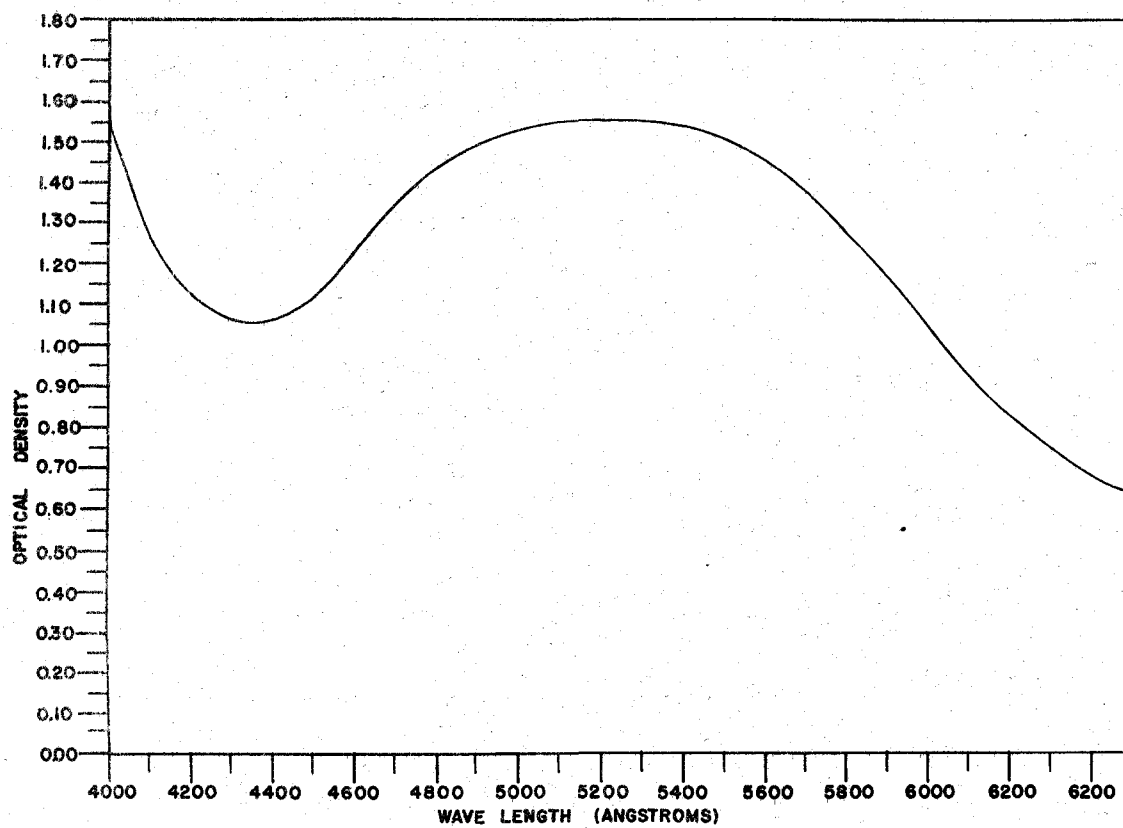


Figure 14 - Absorption character of manganese (III) iodate

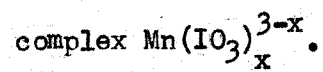


TABLE III

X-Ray Powder diagram of $\text{Mn}(\text{IO}_3)_3$ using $\text{Cu K}\alpha$ radiation

Intensity	$\sin^2 \theta$
W	0.0390
W	0.0435
S ⁺	0.0475
W ⁻	0.0560
W ⁻	0.0594
M ⁺	0.0741
W ⁺	0.0825
W ⁺	0.0854
W ⁺	0.0911
W ⁻	0.0972
W ⁺	0.1166
M	0.1222
W ⁺	0.1318
S ⁻	0.1659
M ⁺	0.1962
W	0.2141
W ⁺	0.2232
W ⁺	0.2312
W	0.2483
W ⁻	0.2655
W	0.2969
W ⁺	0.3053
W	0.3162
W	0.3450
W ⁻	0.3798
W	0.3883

III. DISCUSSION AND RESULTS

A. Manganese (III)

A cursory examination of the experimental data brought out the fact that two entirely different types of rate curves existed depending upon whether manganese (II) or manganese (III) were the starting material. Manganese (II) gave an "S" shaped rate curve indicative of at least a two step process, while manganese (III) gave rate curves of the more conventional shape. An "S" curve indicated at least two steps because the initially increasing rate could mean only that some reactant's concentration was increasing with time; and since only manganese (II) was present originally, an intermediate must have been building up or the product must have been reacting with the manganese (II).

The rate curves numbered twenty five, twenty six and twenty seven are those with manganese (III) iodate as the initial form of manganese. Sufficient iodic acid was kept present to prevent precipitation of the manganese. A plot of the logarithm of the final optical density minus the optical density at a given time versus the time was made and has been included as figure 15 for the three reactions mentioned. These plots were straight lines which indicate that this reaction was first order in the unreacted manganese present.

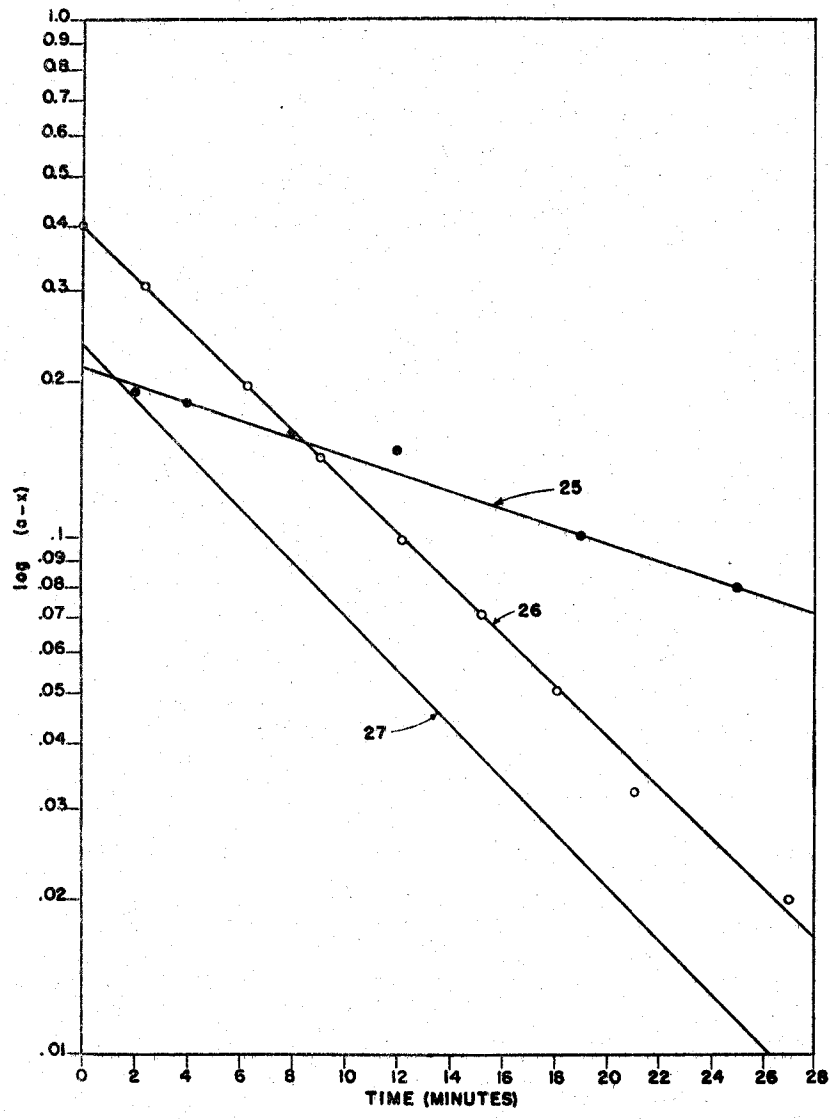


Figure 15 - Semilogarithmic plots of $\log (OD_{final} - OD)$ versus time for the oxidation of $Mn(IO_3)_x^{3-x}$.

Application of the well known relation was made to determine the order of the reaction in periodate:

$$(3) \quad n = 1 + \frac{\log \frac{\tau_1}{\tau_2}}{\log \frac{a_2/a_1}{1}}$$

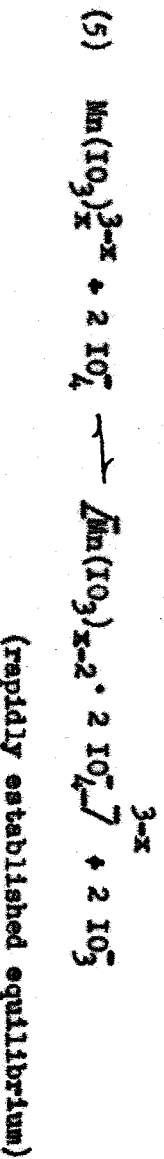
where n is the order, τ_1 and τ_2 the time taken to complete a given fraction of the reaction, and a_1 and a_2 are the concentrations. The results of these calculations showed that the order in periodate was 2.0 ± 0.1 for fractional reactions of 0.25, 0.50, 0.75 and 0.90. These results suggested an explanation of the mechanism of this reaction.

The rate expression is then the following:

$$(4) \quad \frac{d[MnO_4^-]}{dt} = k [HIO_4^-] [Mn(10_3)]^x$$

where k is the rate constant and the C 's represent the concentrations of the reactants and product.

A mechanism for the reaction of manganese (III) with periodate was postulated which satisfied the observed rate relations. This is given below.



These reactions explained the observed orders for the observed

rates. The replacement of the iodate by periodate in the complex was postulated because the small concentration of ionic manganese (III) in solution. This would make difficult an explanation by collision of the observed third order. The value obtained for the rate constant when molarities were used was $110 \text{ liter}^2 \text{ moles}^{-2} \text{ sec.}^{-1}$ assuming that essentially all of the manganese (III) was present in the complex.

The rate curves for the reaction of manganese (III) with periodate at 29° and 40° given in figure 16 made possible the calculation of the activation energy of this reaction. The equation used for this was

$$(7) \quad \frac{d(\log k)}{d\left(\frac{1}{T}\right)} = - \frac{\Delta E}{2.303 R}.$$

The value obtained was 16.7 kilocalories.

B. Manganese (II)

An analysis using the initial slopes of the "S" shaped rate curves for the reaction of manganese (II) with periodate was not possible. The method used to attempt a determination of reaction orders was to compare the rate of reaction at a given fraction of the reaction in the vicinity of the maximum rate. At such points the concentration of reactants other than the main variable was assumed to be the same and these rates were then compared with the various concentrations. When such a procedure was followed the per-

iodate order was determined to be one throughout the concentration range studied. A plot of the periodate concentration versus the rate at half reaction has been included as figure 16. The plot was linear indicating an order of one. Similar treatment of the rates at one quarter and three quarter reaction yielded a similar result.

The experiments with varying initial permanganate concentrations were not particularly suited to such an analysis, however, measurement of the maximum rates made possible the determination of the permanganate order. A plot of the maximum rate versus the square root of the permanganate concentration yielded a linear plot indicating a order of one half.

The experiments with varying initial amounts of manganese (II) shown in figure 6 made possible the determination of the manganese (II) order. The maximum rate was measured, and this was corrected for the varying permanganate concentration using the order already attained for permanganate. Corrections were made for the slightly different periodate concentrations used. Plotting yielded the manganese (II) order as one.

The effect of adding perchloric acid was more complex and a plot of the rate versus acidity has been included as figure 17. A definite minimum in the rate occurs at an acid concentration of about 1.5 molar.

Experiments with varying iodate concentrations made evident only that iodate was the only variable observed which accelerated the rate

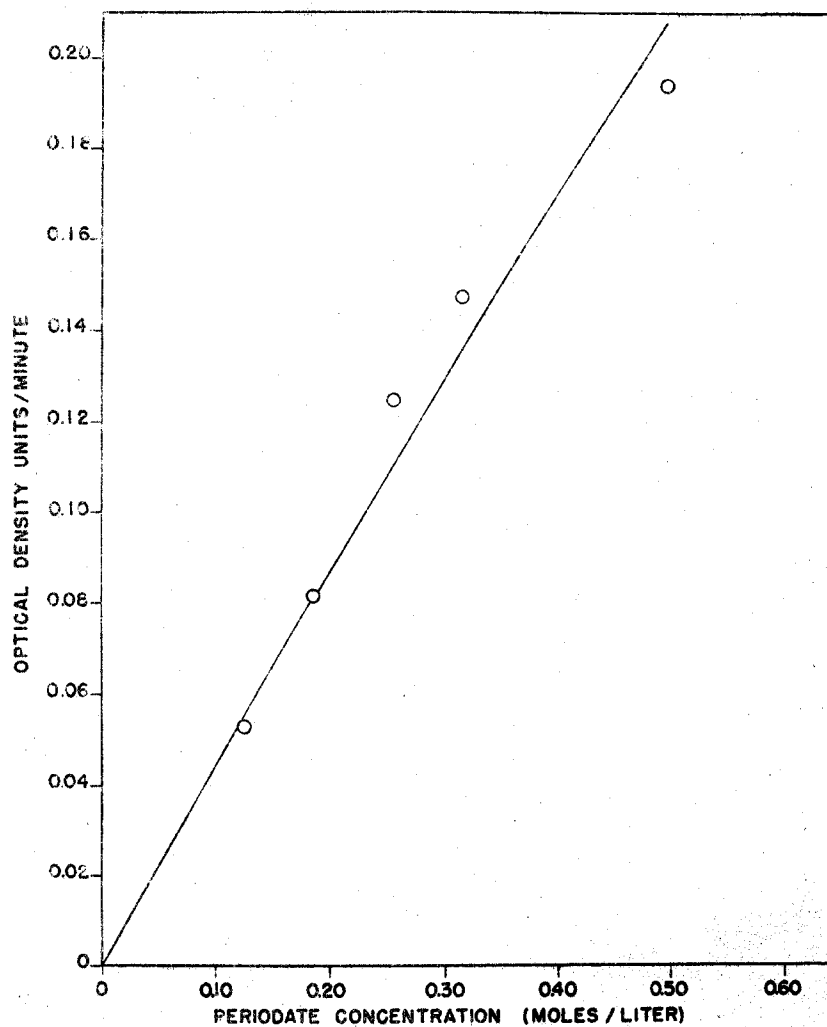


Figure 16 - Linear plot of the maximum oxidation rate of manganese (II) at various periodate concentrations.

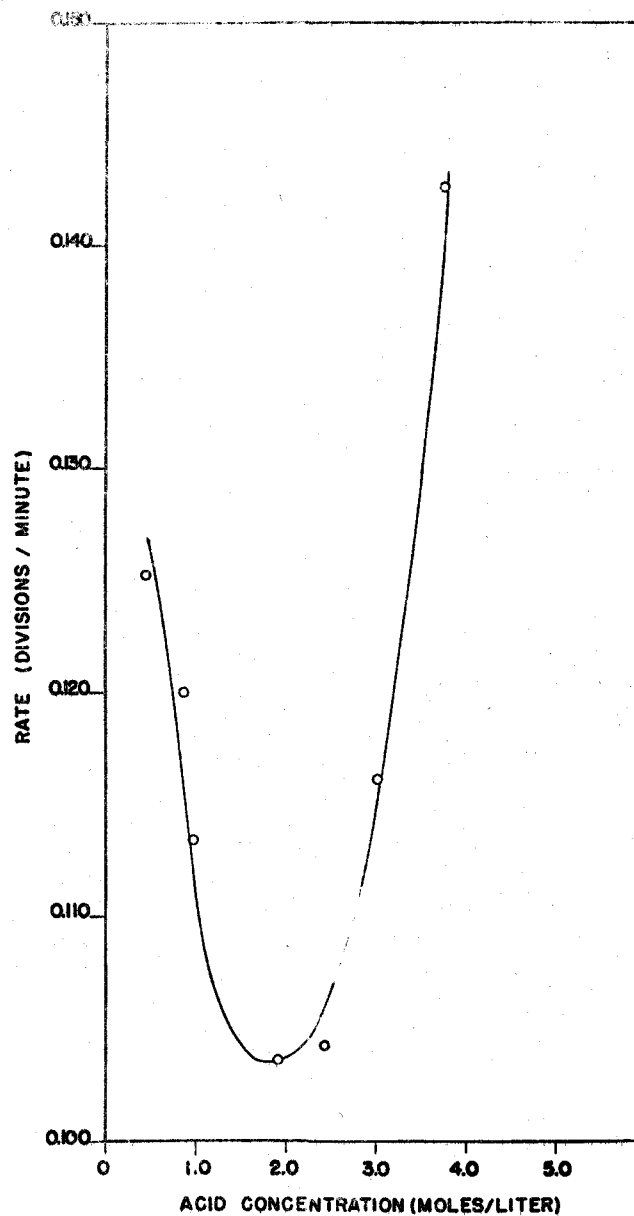


Figure 17 - Variation of rate at various perchloric acid concentrations.

and raised the final extinction. Large excesses of iodate seemed to slow the rate. The variation of rate with ionic strength as determined by Strickland and Spicer⁴ has been included as figure 18.

The foregoing results yielded several facts which any proposed reaction mechanism must explain. These are summarized below.

1. The final extinction of permanganate was not a simple linear function of the manganese present. The slower reactions were usually those with the greater final extinction. Reactions accelerated by iodate were an exception to this rule.

2. The separate addition of iodate and permanganate shortened the time to the inflection point of the rate curve. The addition of both iodate and permanganate to the reaction made this time very short.

3. The addition of small amounts of manganese (IV oxide shortened the time necessary for reaction although the reaction of manganese (IV) oxide with periodate was negligible.

4. A long induction period was observed for the reaction in the absence of the above accelerative influences.

5. The periodate order for the rate was 1.0.

6. The permanganate order was about 0.5.

7. The manganese (II) order was 1.0.

8. A minimum rate with varying acid concentration was observed at about 1.5 M perchloric acid.

9. Increasing the ionic strength increased the reaction velocity.

10. Manganese (III) iodate was oxidized to permanganate in

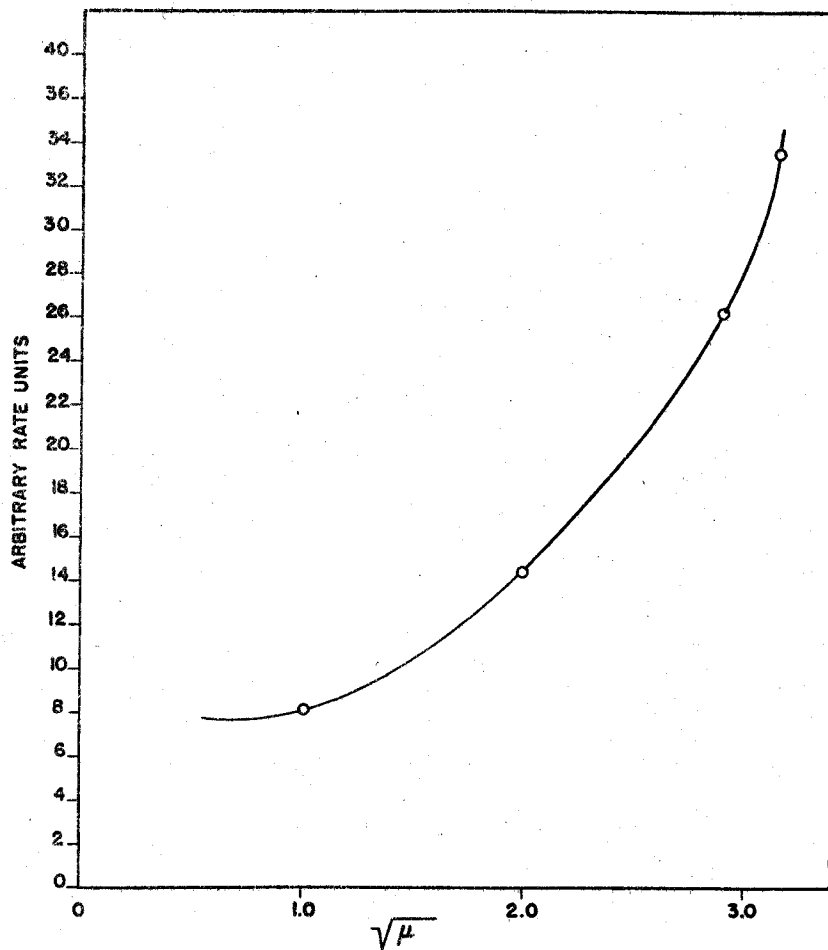


Figure 18 - Variation of rate with ionic strength.

a second order periodate first order manganese reaction.

The times to various parts of the reaction have been defined differently by various writers. In this work the induction period is used as the time necessary before 0.05 optical density units for permanganate is present. The incubation period is the time necessary to reach the maximum reaction rate.

Postulating that the reaction between periodate and manganese (II) be slow was necessary because of the induction period observed in the absence of complexing agents. The known instability of any available intermediate oxidation state in the absence of complexing agents for the storing of appreciable amounts of manganese was the reason for this postulate. This same fact argued for assigning a high specific rate to the reaction between periodate and the intermediate to form permanganate as the product.

The permanganate order observed coupled with its behavior in shortening the induction period suggested a reaction involving this species and manganese (II) resulting in an intermediate state. Manganese (III) was a logical first choice for an intermediate state since the behavior of this state with periodate already had been determined. The radioactive exchange work of Polissar²⁵ showed a rapid manganese (II), (III) exchange in the presence of complexing agents and could be explained by a rapid manganese (II), (III), (IV)

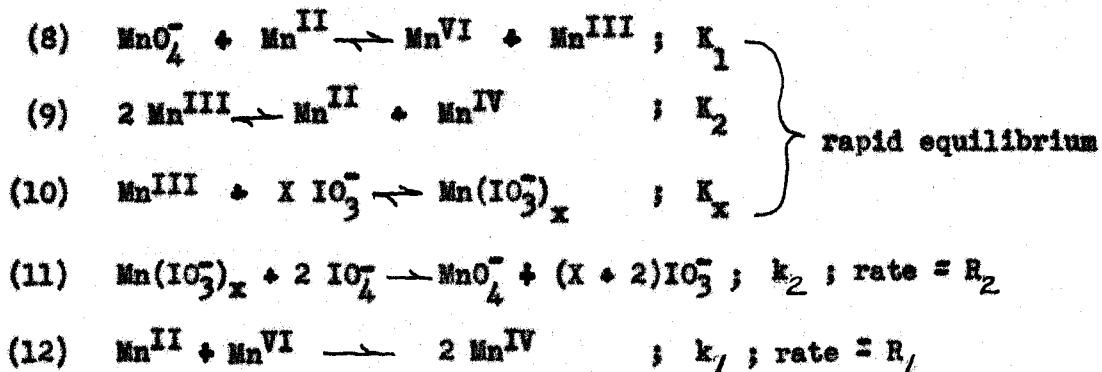
²⁵M. Polissar, J. Am. Chem. Soc., **58**, 1372 (1936).

exchange. The work of Tomkins²⁶ on the Guyard reaction offered information to be considered for the interaction of permanganate and manganese (II). He reported a reaction order of one for permanganate and manganese (II), while an order of negative one was found for the hydrogen ion. Heterogeneous catalysis was also noted. The experimental work in this investigation of the Guyard reaction appeared to be reliable. The mechanism proposed was not satisfactory since 40% of the precipitated manganese (IV) oxide was required to form directly from the reaction of manganese (II) and manganate although the author stated that this did not contribute to an appreciable extent. The equilibrium between permanganate, manganate, manganese (III) and manganese (II) proposed does not contradict any radioactive exchange studies and does furnish an explanation of complexing agents for manganese (III) upon the Guyard reaction.

The foregoing led to the postulation of a mechanism which was tentatively accepted subject to its success in explaining the observed data. It should be noted that this mechanism applies to the region of high rates, i.e. the situation which exists when considerable amounts of permanganate and iodate are present. The very slow reactions in the initial portion of the reaction result because these

²⁶ C. C. Tomkins, Trans. Faraday Soc., **38**, 131 (1942).

ions are not present. The mechanism proposed follows:



The equilibria were postulated to be rapid enough that equilibrium conditions could be assumed. The other reactions were chosen as irreversible and the means of shifting the position of equilibrium.

A derivation for a rate expression follows:

For convenience Roman numerals have been chosen to represent the concentrations of each of oxidation states of manganese. These concentrations are proportional to the activity at constant ionic strength which was the condition under which the reaction was studied. The letter D has been used the operator, d/dt .

$$(13) \quad R_1 = k_1 (\text{II})(\text{VI})$$

$$(14) \quad R_2 = k_2 (\text{III})(\text{IO}_4^-)_2$$

The conservation of manganese assuming $D(\text{VI}) = 0$ requires

$$(15) \quad D(\text{II}) + D(\text{III}) + D(\text{IV}) = -D(\text{VII}) = R_1 - R_2$$

The conservation of electrons in the lower oxidation states requires

$$(16) \quad 2 D(\text{II}) + 3 D(\text{III}) + 4 D(\text{IV}) = 6 R_1 - 3 R_2$$

Differentiation of the constant K_2 requires

$$(17) \quad (II)(III) D(IV) + (IV)(III) D(II) - 2 (II)(IV) D(III) = 0$$

Solving equations (15), (16), (17) simultaneously

$$(18) \quad D(IV) = \frac{3 R_1 (IV)(III) - 8 (II)(IV) R_1 + 2 (II)(IV) R_2}{(II)(III) + (IV)(III) + 4 (II)(IV)}$$

$$(19) \quad D(III) = 4 R_1 - R_2 - 2 D(IV)$$

$$(20) \quad D(II) = - 3 R_1 + D(IV)$$

Assuming $(II) \gg (III) \gg (IV)$

$$(21) \quad 4 R_1 = R_2$$

or

$$(22) \quad 4 k_1 (II)(VI) = k_2 (III)(IO_4^-)^2$$

$$(23) \quad \text{and since } k_1 = \frac{(VII)(III)}{(VIII)(II)}$$

$$(24) \quad (III) = 2 \sqrt{\frac{k_1 k_2}{k_2}} \frac{(VII) \frac{1}{2} (III)}{(IO_4^-)}$$

which makes

$$(25) \quad D(VII) = R_2 - R_1 \sim 3/4 R_2 = 3/2 k_2 \sqrt{k_1 k_1} (VII) \frac{1}{2} (II)(IO_4^-)$$

The derived rate expression gave the observed orders for manganese (II), periodate and permanganate. The explanation of the other facts with this mechanism was made readily. The variation of final extinction with rate was assumed to be caused by precipitation of manganese (IV), either as the hydrated oxide or as a periodate. Evidence resulted from reactions followed by traversing the spectral region, 3500 Å to 6000 Å, periodically. The ratio of the optical density at 5260 Å to that at 3600 Å for pure potassium permanganate

solutions was found to be about 0.47 while those from the periodate oxidations possessed values of greater than one. The ratio was higher for those reactions where the final extinction was least. Colloidal solutions of manganese (IV) show increasing absorption at lower wavelengths. It was possible to subtract the optical density caused by permanganate at 3600 Å and actually plot the formation of the manganese (IV). An example of this is shown in figure 13. A periodate of manganese (IV) could be postulated also, and the reddish brown precipitate obtained in reactions at low acidity was evidence for this.

The variation of rate with acid strength was explained by combining the repression of ionization of periodic acid and the effect of increasing ionic strength. The expression for periodate ion is

$$(26) \quad \frac{(IO_4^-)}{(H_5IO_6)} = \frac{K_a}{(H^+)}$$

when concentrations are substituted for activities. It should also be noted that in all experimental work described that no orders were determined except in reactions whose ionic strength were essentially constant. Further effects of hydrogen ion upon other ions in solution certainly could occur.

An explanation for the success of various acids used in this oxidation became apparent when it was noted that the order of complexing for manganese (III) was the same as the order recommended. The order was found to be phosphoric acid > sulfuric acid > nitric acid.

The effect of increasing iodate concentration upon the rate shown in figure 8 can be explained by the increased ability to form the manganese (III) iodate complex. Sufficient iodate should depress the rate because of the equilibrium which



would be driven to the left when iodate in excess of that necessary to complex the manganese (III) was present. This explains the slower rates observed when manganese (III) iodate complex was the initial material.

The reactions performed at 29° and 40° made it possible to calculate the activation energy for this reaction. These curves have been included in figure 12. The value obtained was about 14 kilocalories at half reaction. Higher values were observed at earlier times because of the higher barriers found in the reactions during the induction period.

The lowering of the final extinction reported by Strickland and Spicer⁴ in sulfuric acid solutions as the acid concentration increases was not caused by incomplete oxidation, but is caused by the polymerization or dehydration of ions to form an uncolored compound. This conclusion was reached as the result of scanning solutions

⁴J. D. Strickland and G. Spicer, Analytica chimica Acta, 5, 517 (1949).

of potassium permanganate in various sulfuric acid-water mixtures. The activity of water in such solutions has been measured by Shankman and Gordon.²⁸ Solutions were prepared with a constant molar concentration of potassium permanganate and a known mole fraction of sulfuric acid. The original lowering of the 5260 Å peak for permanganate was directly proportional to the activity of water in these solutions as shown in figure 19. A polymerization such as



could be involved, however, hydrogen ion activity information would be necessary to determine if this is the case.

C. Analytical Significance

The results of this work made possible listing certain recommendations in regard to using this oxidation for analytical purpose.

These have been listed below:

1. Acids such as phosphoric, sulfuric and iodic whose anions are known to stabilize the manganese (III) valence state are to be preferred to insure complete reaction.

2. Only a small excess of potassium periodate or periodic acid is necessary to insure completeness of reaction and is to be desired.

²⁸S. Shankman and A. R. Gordon, J. Am. Chem. Soc., 61, 2370 (1939).

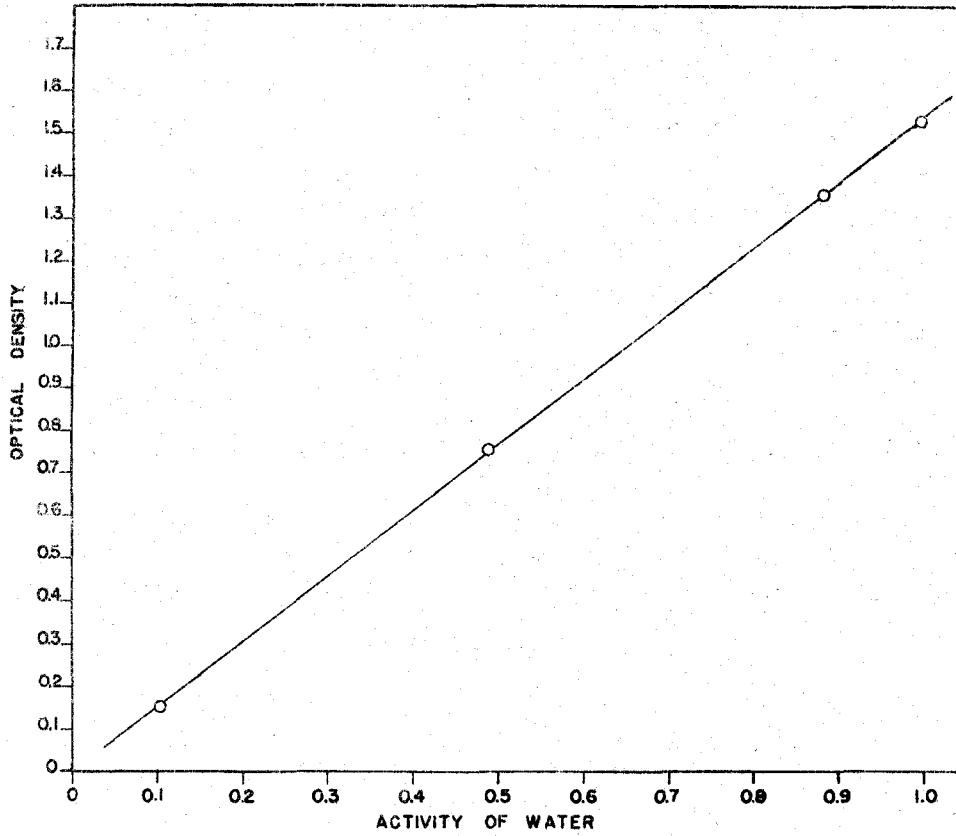


Figure 19 - Variation of the optical density at 5260 Å for permanganate solutions on sulfuric acid water mixtures versus the activity of water.

3. Too high acid concentrations, especially concentrations at which the activity of water is very low, should be avoided since these concentrations will lower the sensitivity of the method because of the lowered extinction coefficient of the permanganate ion formed.

4. The recommendation that the reaction be performed at high temperatures made by Willard and Greathouse²⁹ is well made since the solubility of manganese (IV) is increased at these temperatures allowing a greater concentration of manganese (IV) to exist in solution before precipitation will occur thus aiding in the obtaining of the desired maximum extinction.

5. The standard with which the sample is compared should be prepared preferably from manganese in an equivalent valence state and under similar conditions in regard to periodate, manganese and acid concentrations.

D. Suggested Experiments

During the course of these experiments several phenomena were observed which suggested experiments which might be of interest if further pursued. These have been described below:

1. The existence of the iodate complex of manganese (III) led to considerations concerning how the ionic species in solution might

²⁹H. H. Willard and L. Greathouse, *J. Am. Chem. Soc.*, **39**, 2366 (1917).

be determined. The method of continuous variations was ruled out since the manganese (III) ion is not stable in aqueous solutions. The work of Schaffer and Hammaker³⁰ on the composition of the fluoride complex of manganese (III) might be applicable to the determination of this composition. Their method combined the use of spectrophotometric and potentiometric data for the purpose of obtaining a plot whose slope leads to the number of anions present in the complex. The iodate complex absorption characteristics have been determined, figure 14, and a silver iodate electrode might be used for the potentiometric measurement of iodate activity.

2. Various concentrations of iodic acid were used as a solvent for the manganese (III) iodate prepared. Equilibria appear to exist for these solutions which might be described as below.



The existence of two different solid phases was very evident. One appeared identical in appearance to manganese (II) iodate while the other was a dark reddish brown. The existence of manganese (IV) iodate has been suggested by Berg and the appearance of this solid phase appeared identical with that obtained by prolonged heating hydrated manganese (IV) oxide with iodic acid. The phase rule when applied to the above solutions with three phases coexisting in equilibrium allows no composition degrees of freedom, and this result

³⁰E. R. Scheffer and E. M. Hammaker, *J. Am. Chem. Soc.*, **72**, 2575 (1950).

was apparently in accord with spectrophotometric data since the same absorption curve was always obtained when the two solid phases were present. It would seem possible that further extension of the electromotive force, spectrophotometric method would allow this equilibrium constant to be measured. Perhaps consistent values for the free energy of formation of a manganese (IV) salt could thus be attained.

3. Further work on the composition of manganese (IV) iodate and periodate was suggested by these same experiments along with those made during the kinetic studies.

IV. SUMMARY

The chemical kinetics of the oxidation of manganese to permanganate ion with periodate was studied by spectrophotometric methods. The reaction of periodate ion with manganese (III) was found to be first order in manganese (III) and second order in periodate. A mechanism satisfying these orders was proposed. The reaction between manganese (III) and periodate was found to be first order in manganese, periodate and half order in permanganate, and a mechanism was proposed which explained these orders along with other facts which were found by the author. Various substantiating evidence for this proposed mechanism was given.

A previously unknown salt of manganese (III) was isolated. Methods of preparation were determined, and analyses of the material were made. The compound was determined to be manganese (III) iodate, and some of its properties were noted. The existence of an iodate complex of this compound was shown to exist, and the absorption characteristics of this complex were determined.

Recommendations concerning the procedure for the periodate oxidation of manganese for analytical determinations were proposed together with suggestions for further experiments coming from the work described.

Part II THE SOLUBILITY, ACTIVITY COEFFICIENTS AND ACTIVITY
PRODUCT OF MANGANESE (II) IODATE

I. INTRODUCTION

The solubility of manganese (II) iodate in water has been reported as 0.5 g/100g H₂O and as insoluble.^{1,2} The variation of solubility with temperature, the activity coefficients, and the activity product were not described.

This investigation was initiated as the result of kinetic studies in this laboratory involving the oxidation of manganese (II) in solution containing iodate. The solubility of manganese (II) iodate in water at various temperatures and in aqueous solutions of potassium iodate, manganese (II) perchlorate, and sodium chloride were determined. The results have been used to compute the activity coefficients, activity product and the heat of solution of manganese (II) iodate.

¹C. F. Rammelsberg, Fogg. Ann., 55, 66 (1842).

²A. Ditte, Ann. Chim. Phys., (6), 21, 157 (1890).

II. EXPERIMENTAL

A. Materials

Manganese (II) iodate was prepared by precipitation from aqueous solutions of reagent grade iodic acid and manganese (II) chloride. After several washings the vacuum dried salt was analyzed for manganese, iodine, and iodate. The results of these analyses indicated 13.52% Mn and 0.0148 iodometric equivalents per gram. Theoretical values for $Mn(IO_3)_2$ are 13.57% Mn and 0.01482 equivalents/gram. Water redistilled from alkaline permanganate was used throughout these experiments; its conductance was found to be about 10^{-6} mhos/cm.

B. Analyses

The manganese determinations were made by oxidation to permanganic acid with periodic acid according to the procedure of Willard and Greathouse.³ Manganese (II) iodate was also ignited to Mn_2O_4 , and weighed. The iodate determinations were made iodometrically in acid solution. The sodium thiosulfate used to titrate the liberated iodine was standardized against potassium iodate prepared by the J. T. Baker Chemical Company by the procedure described by Willard and Furman.⁴

³H. H. Willard, and L. Greathouse, *J. Am. Chem. Soc.*, **39**, 2366 (1917).

⁴H. H. Willard, and N. H. Furman, "Elementary Quantitative Analysis" p. 269.

C. Preparation of Solutions

All solutions were prepared by weighing dried salts and adding a measured volume of water to these salts in a glass stoppered flask.

D. Apparatus

A water thermostat with a temperature control of $\pm .02^\circ$ was used for temperatures below 45° . Effective stirring and agitation were provided by means of a Burrel shaker.

E. Procedure

Solutions of manganese (II) iodate were agitated for twenty four hours at 25° and 45° . The volume of these solutions was approximately 200 ml. After withdrawing and analyzing 25 ml. aliquots from these samples, the flasks were placed in the other temperature bath and shaken for six hours. Aliquots were again withdrawn and analyses made. The solubility obtained at each temperature checked to within $\pm .02\%$. This was taken to indicate that reversible equilibrium had been attained. Manganese (II) iodate was agitated at 1° and 25° with aqueous solutions of manganese (II) perchlorate and potassium iodate. The aliquots taken from these were accurately weighed so that an approximation of the density could be made. Concentrations were expressed in molalities (moles/1000gms H_2O throughout).

The solutions containing manganese (II) perchlorate and sodium chloride were analyzed by adding hydrochloric acid and potassium iodide and titrating the liberated iodine with sodium thiosulfate. The concentration of sodium chloride was determined from the weights of the salt and the water added. The aliquots from the solutions containing potassium iodate were oxidized to permanganate with periodic acid in sulfuric acid solution and compared colorimetrically in a Beckman Model DU spectrophotometer at a wave length of 5260 Å with a standard prepared by identical treatment from a standard solution of manganese (II) perchlorate. The solubilities of the pure salt at high temperatures were determined in an exactly similar fashion. The manganese (II) iodate was always present in considerable excess. The pH of each aliquot was taken with a Beckman Model G pH meter to determine the hydrogen ion activity.

III. DISCUSSION AND RESULTS

The solubility of manganese (II) iodate in water and in aqueous solutions of sodium chloride, potassium iodate, and manganese (II) perchlorate are tabulated in Table I and shown graphically in Figure 1. Its solubility in water at various temperatures is shown graphically in Figure 2.

Activity coefficients of the manganese (II) iodate in the aqueous solutions of sodium chloride were evaluated from the change in solubility with ionic strength. The solubility at zero ionic strength was obtained by an extrapolation of the ion attraction expression for the mean activity coefficient for a 2-1 or 1-2 electrolyte at 25°. The expression given by Harned and Owen was used:⁵

$$-\log \gamma_{\pm} = \frac{1.017 \mu_{\pm}^{\frac{1}{2}}}{1 + 0.3281 B \mu_{\pm}^{\frac{1}{2}}} \quad (1)$$

where γ_{\pm} is the mean ionic activity coefficient, μ_{\pm} is the ionic strength and B is a constant determined from the experimental data. In place of γ_{\pm} the equivalent expression m°/m was substituted where m is the molality of a saturated solution and m° the concentration of a saturated solution at zero ionic strength. Thus

⁵H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," New York, N. Y., Reinhold Publishing Co. (1950) p 39.

TABLE I

Solubility Data For Manganese (II) Iodate

Temperature	Solubility	$\mu \frac{1}{2}$	M _{NaCl}	M _{KIO₃}	M _{Mn(ClO₄)₂}	pH
3°	0.00568	0.1310	0.00			4.03
3°	0.00621	0.1637	0.01007			3.83
3°	0.00625	0.2110	0.02462			3.95
3°	0.00751	0.2843	0.0554			3.80
3°	0.00786	0.3670	0.1108			3.88
3°	0.00902	0.6610	0.4070			3.91
25°	0.00658	0.1407	0.0			4.03
25°	0.00694	0.1760	0.01007			3.84
25°	0.00761	0.2179	0.02462			3.94
25°	0.00836	0.2840	0.05540			3.80
25°	0.00896	0.3681	0.11080			3.86
25°	0.01041	0.6630	0.4070			3.90
25°	0.00474	0.1454		0.00688		4.13
25°	0.00211	0.1688		0.02213		4.28
25°	0.0006846	0.2554		0.06218		4.10
25°	0.000301	0.3335		0.1091		4.43
25°	0.00397	0.635			0.1138	1.40
25°	0.00531	0.192			0.010305	3.00
25°	0.00560	0.180			0.00743	2.63
45°	0.00713					
90°	0.00854					

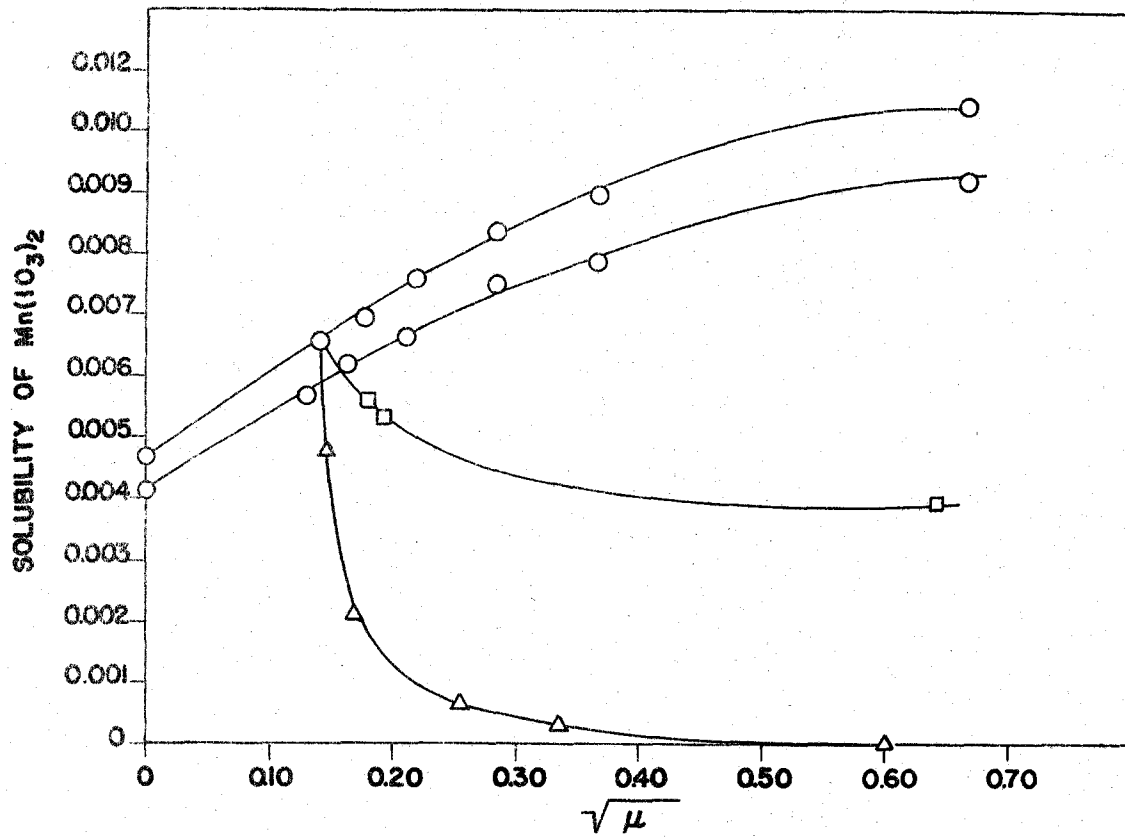


Figure 1 - Solubility of manganese (II) iodate in aqueous solutions of sodium chloride, potassium iodate and manganese (II) perchlorate.

O - Sodium Chloride

Δ - Potassium Iodate

\square - Manganese (II) Perchlorate

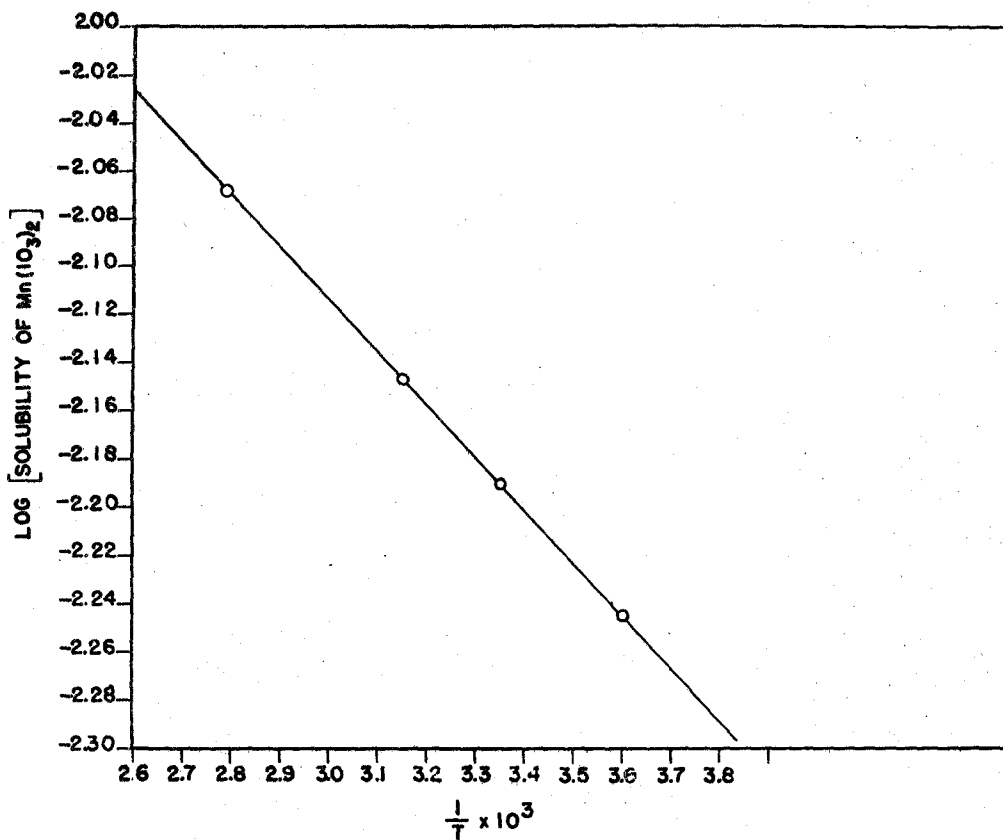


Figure 2 - Plot of $\log [\text{solubility } Mn(IO_3)_2]$ versus the reciprocal absolute temperature $\times 10^3$.

when m was expressed as a function of μ the constants m_0 and B were determined from the smoothed curve in the vicinity of low ionic strength. The values of m_0 at 3° and 25° respectively were 4.67×10^{-3} and 4.10×10^{-3} . The fit of expression 1 to the experimental data has been shown in Figure 1.

The solubility product for a 1-2 or 2-1 electrolyte is given as

$$K_{sp} = 4 M_0^3 \quad (2)$$

where K_{sp} is the solubility product and M_0 is the solubility at zero ionic strength. The value obtained at 25° was $4.33 \times 10^{-7} M_0^3$. The activity coefficients of manganese (II) iodate and of manganese (II) perchlorate were calculated from the relation

$$K_{sp} = \gamma_{\pm}^3 (M^2 10^{-3}) (M_{Mn^{++}}) \quad (3)$$

The activity coefficients have been given graphically in Figure 3.

The activity coefficients of manganese (II) chloride at ionic strength of from 0.3 to 2.0 given by Robinson and Stokes from potentiometric data have also been plotted on this graph.⁶ It is apparent that manganese (II) iodate behaves in a similar manner. It should be noted that complete dissociation of the electrolyte has been assumed in these calculations.

The heat of solution of manganese (II) iodate was calculated

⁶R. A. Robinson, and R. H. Stokes, *Trans. Faraday Soc.*, **36**, 1137 (1940).

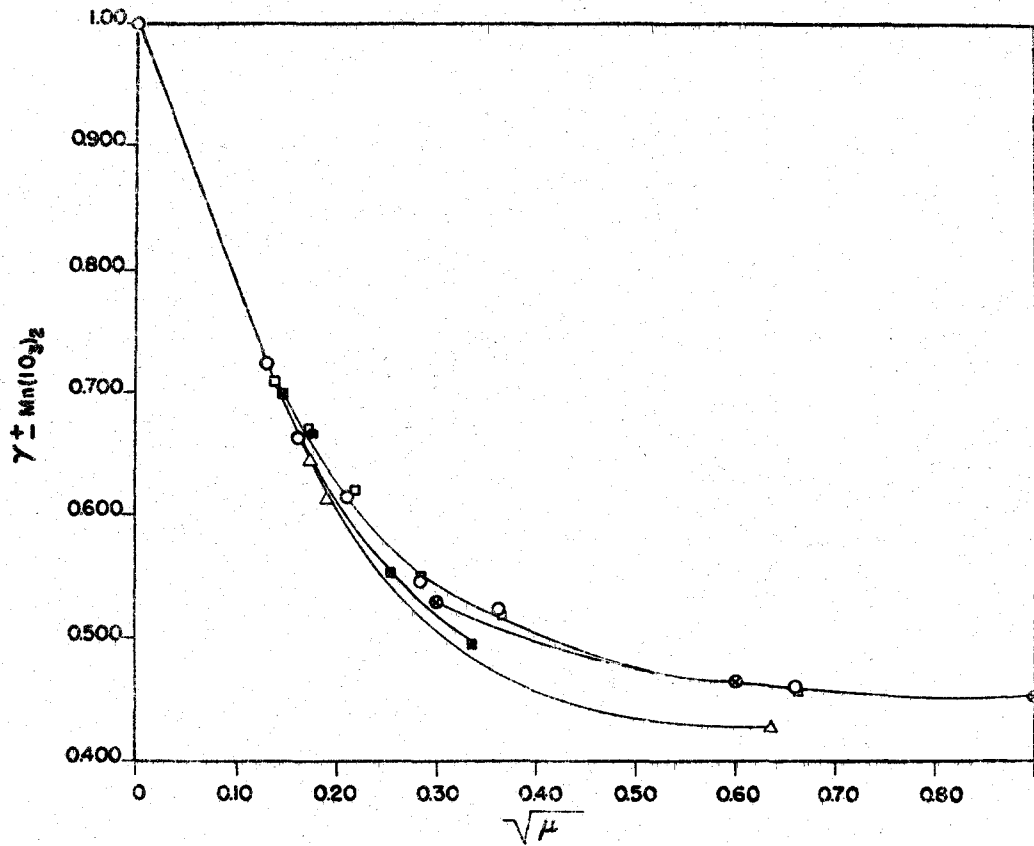


Figure 3 - Mean activity coefficients of manganese (II) iodate in aqueous solutions of sodium chloride, potassium iodate, and manganese (II) perchlorate.

○ NaCl @ 3°

□ NaCl @ 25°

△ Mn(ClO₄)₂ @ 25°

■ KIO₃ @ 25°

⊗ $\gamma_{\pm} \text{MnCl}_2$ by EMF measurements

from the slope of the solubility-temperature curve by using the well-known thermodynamic relations:

$$\frac{d (\log K_{sp})}{d \left(\frac{1}{T} \right)} = - \frac{\Delta H}{2.303 R} \quad (4)$$

The value obtained was 2900 calories/mole in the temperature range of 3° to 25°.

For the reaction (equation 5)



the free energy change at 25° was computed as 8680 calories. Using the above value for the heat the value obtained for the entropy change was - 19.4 calories/degree mole. Taking 28.0 entropy units as the standard entropy for the iodate ion⁷ and assuming that the ionic entropy of manganese (II) is the same as ferrous ion⁸ (- 25.9 e. u.). The standard entropy of solid manganese (II) iodate was calculated to be 49.5 entropy units.

⁷W. M. Latimer, K. S. Pitzer, and W. V. Smith, *J. Am. Chem. Soc.*, **60**, 1829 (1940).

⁸W. M. Latimer, "Oxidation Potentials", New York, N. Y., Prentice-Hall, Inc., 1938. p. 219.

IV. SUMMARY

The solubility of manganese (II) iodate in water at temperatures from 0° - 90° and in aqueous solutions of sodium chloride, potassium iodate and manganese (II) perchlorate at 25° have been determined. The activity coefficients of manganese (II) iodate in these solutions at 25° have been calculated from these solubilities. The activity product and heat of solution of manganese (II) iodate have been calculated as 4.33×10^{-7} and 2900 calories/mole respectively.

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