I KINETICS OF THE OXIDATION OF IRON (II) BY BROMINE

II COMPLEX ION FORMATION IN THE SYSTEM IRON (III), PHOSPHORIC ACID

III KINETICS OF THE OXIDATION OF FERROCYANIDE ION BY BROMINE

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ABSTRACT

The kinetics of the oxidation of iron (II) by bromine has been studied spectrophotometrically. At (Br^-) = 0.50 M, tribromide ion was found to be the reactive bromine species, while evidence for HOBr and Br_2 reacting with iron (II) was obtained at (Br^-) $\sim 10^{-3}$ M. A mechanism involving Br_2^- is suggested, and the observed inhibition by iron (III) eliminates an alternative mechanism involving iron (IV) as an unstable intermediate. The catalytic effect of phosphoric acid was investigated.

The ultraviolet light absorption of iron (III) in phosphoric acid was studied. An attempt was made to determine the nature of the complex that is present. The presence of only one complex could not be verified.

The oxidation of ferrocyanide ion by bromine was found to proceed at a faster pace than the analogous oxidation of iron (II). Both molecular bromine and tribromide ion were found to react with ferrocyanide ion when (Br^-) = 0.05 M. The reaction appeared to be first order with respect to bromine and ferrocyanide ion at (H^+) = 0.93 M, but was found to deviate from a simple second order behaviour when the hydrogen ion concentration was decreased to 0.50 M.

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PART I: KINETICS OF THE OXIDATION OF IRON (II) BY BROMINE

INTRODUCTION

The reaction

(1) $2\ Fe^{++} + Br_3^- \text{ (or } Br_2) \rightarrow 2\ Fe^{+++} + 3\ Br^- \text{ (or } 2\ Br^-)$

is of interest because it presumably proceeds via the two one-electron steps

(2) $Fe^{++} + Br_3^- \underset{k_7}{\overset{k_2}{\rightleftharpoons}} Fe^{+++} + Br^- + Br_2^-$

(3) $Fe^{++} + Br_2^- \xrightarrow{k_3} Fe^{+++} + 2\ Br^-$

involving the formation of the unstable species, Br_2^- (or a bromine atom). The kinetics of the oxidation of iron (II) by aqueous hydrogen peroxide(1,2) and by iodine,(3) and of titanium (III) by iodine(4) indicates that these reactions proceed by analogous mechanisms involving OH radicals and I_2^-. The induction of the isomerization of maleic to fumaric acid by the reaction of iron (II) with aqueous bromine is evidence for the occurrence of bromine atoms or Br_2^- in reaction (1)(5). Several reactions due to chlorine atoms or Cl_2^- have been induced by the addition of iron (II) to chlorine solutions(6).

Several observers have made the qualitative observation that the reactions of aqueous bromine or chlorine with iron (II) are not "instantaneous"(7,8,9,10). Accordingly, it has been found in this research, that it is possible to measure the rate of reaction (1) by rapid manual operation of a Beckman spectrophotometer when the reagents are present at concentrations in the range 10^{-3}-10^{-5} M. The kinetic results confirm the reaction path consisting of steps (2) and (3) above, provide some information about the rates of reaction of molecular bromine and hypobromous acid as well as of the tribromide ion, and disprove an alternate mechanism which is based on the formation of iron (IV) as an intermediate.

EXPERIMENTAL

MATERIALS:

Weighed quantities of ferrous ammonium sulfate were dissolved in 1M perchloric acid. There was less than 2% air oxidation per month of these ca. 10^{-3}M Fe^{++} solutions (iron (III) in the solutions was estimated after the addition of phosphoric acid by the ultra-violet light absorption of the iron (III) phosphate complexes).

Weighed quantities of sodium bromate were dissolved in an excess of sodium bromide and perchloric acid to give the tribromide ion solutions. Solutions of molecular bromine, prepared by the addition of the C. P. liquid to mixed sodium perchlorate-perchloric acid solutions, were standardized iodometrically.

C. P. sodium bromide was dissolved in distilled water and a small amount of bromine was added. The excess bromine was boiled away and the solution was filtered.

Iron (III) perchlorate was prepared by dissolving ferric chloride in an excess of 60% perchloric acid and fuming the solution down to about one-third of its original volume. After two recrystallizations from water, the product gave no precipitate with silver nitrate. Iron (III) solutions in perchloric acid were standardized iodometrically.

Sodium perchlorate was prepared by neutralization of C. P. sodium bicarbonate with perchloric acid. Since sodium perchlorate is frequently used as an inert salt to adjust the ionic strength, it is important to note that the G. F. Smith Co. anhydrous product was unsatisfactory for our studies in that 0.5 M solutions were about 10^{-4} M in oxidizing impurities that reacted with iron (II).

Phosphoric and perchloric acids were of reagent quality and were not purified further. They were standardized in the usual manner.

PROCEDURE:

About 1.5 ml. of an iron (II) solution was rapidly discharged into a 1-cm. path length, glass stoppered, quartz cell which contained an equal volume of a bromine solution, or vice versa. The solutions were added from calibrated pipets which were driven by hypodermic syringes. The pipetting almost gave complete mixing, but the cell was stoppered and shaken for a few seconds to insure mixing, and then placed in a thermostated cell compartment of a Beckman model DU spectrophotometer. The first optical density reading was usually obtained about 24 seconds after mixing, and the half-time of a typical experiment was about 3 minutes. The response time of the spectrophotometer to small changes in optical density was less than a second.

EXTINCTION COEFFICIENTS:

The formal extinction coefficients, $\epsilon = D/(\Sigma\ Br_2)$, of bromine solutions, as measured in this research, are listed in Table 1.

The data of Griffith, McKeown and Winn(11) for the dissociation constant of the tribromide ion, when extrapolated to $\mu = 1.0$ and

T = 29.8°, give $K_D = (Br_2)\ (Br^-)/(Br_3^-)$ = 0.0615 mole/liter. The molecular extinction coefficients of the tribromide ion are therefore 1.123 times the ϵ 's of Table 1. (The contribution of molecular bromine to the light absorption listed in Table 1 is negligible.) The formal extinction coefficients of bromine in bromide solutions at 20.4° agreed with those calculated from the above data using K_D = 0.0570. The formal extinction coefficient of iron (III) in 0.5 M NaBr - 0.5 M $HClO_4$ was determined as 275. This value was used in correcting the observed optical densities for the small contribution due to iron (III) formed during the course of the reaction. The molecular extinction coefficient of bromine in 0.5 M $HClO_4$ and 0.5 M $NaClO_4$ at 452 mμ was measured as 93.6.

RESULTS AND DISCUSSION

A number of the experiments performed in the initial stages of the investigation are considered to be suspect, since the electric timer used was later found to be unreliable, and the techniques for making up the reagent solutions were different from those finally adopted.

The values of the rate constants in the later experiments were approximately 15% lower than the earlier ones, and had average deviations of 2% compared to 7% for the earlier ones. In the tables, the earlier and the later experiments will be grouped together where the work was merely of a repetitive nature. (The results appearing after the space in a table represent the later experiments.) The quantitative constants listed at the end of each phase of the experimental work refer to the later work. The errors listed after the constants are average deviations unless otherwise specified.

Experiments were performed which showed that neither the sulfate ion in solution due to the ferrous ammonium sulfate, nor the light from the spectrophotometer had any effect on the reaction.

All reaction rates were measured at the constant ionic strength of 1.0, maintained with sodium ions and perchlorate ions, after the desired acidity and bromide ion concentration were selected. The kinetic results for any particular run at a constant acidity and bromide ion concentration conformed to the rate law

(4) $-d\,(\Sigma\ Br_2)/dt = k\,(\Sigma\ Br_2)\,(Fe^{++})$

where $(\Sigma\ Br_2)$ is the total (formal) concentration of bromine.

THE UNINHIBITED TRIBROMIDE ION REACTION

The pertinent data are collected in Table 2. At a fixed bromide ion concentration, the constant k is independent of the initial concentrations of the reactants. The rate constant is independent of hydrogen ion concentration over the limited range studied. The dependence of k on the bromide ion concentration, $k = 30.0 \pm .5$ liters mole/sec. for $(Br^-) = 0.5M$, $k = 26.1 \pm .6$ for $(Br^-) = 0.2M$, and $k = 15.3 \pm .3$ for $(Br^-) = 0.05M$, can be explained by the assumption that tribromide ion is the reactive bromine species. If this assumption is true, the relation $k_1 = k\,(1 + K_D/(Br^-))$ must be a constant. The values of k_1 in Table 2 are calculated from this expression where K_D, the dissociation constant of the tribromide ion at $\mu = 1.0$, is taken as 0.0615 at 29.8° and 0.0570 at 20.4°. The constancy of k_1, when the bromide ion concentration is varied from 0.05 to 0.5M, shows that in this concentration range the rate law is

(5) $-d\,(\Sigma\, Br_2)/dt = k_1\,(Fe^{++})\,(Br_3^-)$.

The values of k_1 at 20.4° (21.8 ± 0.3) and 29.8° (34.0 ± 0.7) have been used to derive the equation

$$k_1 = 10^{7.59(\pm 0.36)} \exp\,(-8400\,(\pm 500)/RT).$$

The errors quoted are probable errors, not estimated safe limits of error.

At this time it is appropriate to calculate a typical experiment in detail. Table 3 and Figure 1 contain all the necessary data for an experiment that was performed at 20.4° with bromide ion and hydrogen ion each equal to 0.5M. $\epsilon = 1.08 \times 10^4$ and $\bar{\epsilon} = 304$ where ϵ and $\bar{\epsilon}$ are the formal extinction coefficients of bromine and iron (III) respectively.

(Fe^{+3}) and $\bar{D}$ were determined as follows

$$(Fe^{+3}) = 2\,(D_o - D_t)/\epsilon\ .$$

This follows from the stoichiometry of the reaction.

$$\bar{D} = (Fe^{+3})\ \bar{\epsilon}\ = 2\ \bar{\epsilon}\ (D_o - D_t)/\epsilon$$

$$D_c = D_t - \bar{D}$$

$$(\Sigma\, Br_2) = D_c/\epsilon$$

$$(Fe^{+2}) = (Fe^{+2})_o - 2\,\Delta(\Sigma\, Br_2)$$, where

$$\Delta(\Sigma Br_2) = (\Sigma Br_2)_o - (\Sigma Br_2)_t .$$

The D_o's were obtained by plotting $\sqrt{D_t}$ versus the time and extrapolating to zero time. This value for D_o and the one obtained from $D_o = \epsilon C_o$, where C_o equals the concentration of ΣBr_2 in the solution from known dilutions, usually agreed within 3%. This procedure was followed in order to maintain a check on the pipetting. The correction to the density due to the formation of iron (III) complexes never exceeded 10%.

Integration of the rate expression gave

$$(6) \quad k't = \frac{2.303}{(2a - b)} \log_{10} \frac{b}{a} \frac{a - x}{b - 2x}$$

where

$$a - x = (\Sigma Br_2)$$
$$b - x = (Fe^{++})$$
$$a = (\Sigma Br_2)_o$$
$$b = (Fe^{+2})_o .$$

Therefore, the slope of the line obtained by plotting $\log_{10} \frac{(\Sigma Br_2)}{(Fe^{+2})}$ versus time equaled $k \frac{(2a - b)}{2.303}$, or when the time was plotted as minutes x 10^2

$$(7) \quad k = \frac{2.303 \text{ x slope}}{(2a - b) \text{ x } .6} = \frac{3.84 \text{ x slope}}{(2a - b)} .$$

This gave k in units of liter/mole-second.

INHIBITION BY FERRIC IONS

The results of the previous section are consistent with the reaction path of equations (2) and (3) and the assumption that $k_3 \gg k_2$. (A mechanism composed of reaction (2) followed by $Br_2^- + Br_2^- \rightarrow Br_3^- + Br^-$ is consistent with the rate data, but implausible.) If this be true, the rate constant, k_1, of Table 2 is equal to k_2. Assuming that ΔF and ΔH for the reaction $1/2\ Br_2 \rightarrow Br$ are the same in solution as in the gas phase, (the author realizes that this is only a very qualitative argument), one calculates for the reactions(12)

	ΔF^o_{298} (Kcal./mole)	ΔH^o_{298} (Kcal./mole)
(8') $Fe^{++} + Br_2 \rightarrow Fe^{+++} + Br^- + Br$	12.0	4.2
(9') $Fe^{++} + Br \rightarrow Fe^{+++} + Br^-$	-26.6	-41.8

The thermodynamic data for reactions (2) and (3) will be slightly different from those for reactions (8') and (9') because of the association of Br_2 and Br with Br^- to give Br_3^- and Br_2^-. There is evidence(13) that the dissociation constant for the reaction, $Br_2^- \rightarrow Br^- + Br$, is about 10^{-4}, i.e., substantially smaller than the dissociation constant of Br_3^-. One can therefore estimate

	ΔF^o_{298}	ΔH^o_{298}
(2) $Fe^{++} + Br_3^- \underset{k_7}{\overset{k_2}{\rightleftharpoons}} Fe^{+++} + Br^- + Br_2^-$	8.8	1.0
(3) $Fe^{++} + Br_2^- \xrightarrow{k_3} Fe^{+++} + 2\ Br^-$	-21.2	-36.4

At a finite ionic strength, the ΔF's for both reactions (2) and (3) would be more negative than the values given. The data suggest that reaction (3) is likely to be a very fast reaction but that the rate-determining reaction (2) is a difficult one that should be readily reversed, i.e., that Br_2^- can reduce iron (III). If k_7, the rate constant for the reverse of reaction (2), is of comparable magnitude to k_3, inhibition by iron (III) should be observed. In experiments with no added iron (III), there was no evidence for deviations from linearity of the plots of log $(Fe^{++})/(\Sigma\, Br_2)$ versus time over the first 50-60% of reaction where the data were usually taken. Experiments with added initial iron (III) are recorded in Table 4. The maximum iron (III) concentration that can be used is limited because of the light absorption by Fe^{+++} and $FeBr^{++}$. The predicted rate law when reaction (2) is assumed to be reversible is

$$(10)\quad -\frac{d}{dt}(\Sigma\, Br_2) = k_2\,(Fe^{++})(Br_3^-)\,\frac{1}{1 + \dfrac{k_7\,(Fe^{+++})(Br^-)}{k_3\,(Fe^{++})}}\ .$$

The quantity k in the table is the empirical rate constant defined by equation (4); the quantity k_1' is given by $k_1' = k\,(1 + K_D/(Br^-))$. According to the formulation above

$$(11)\quad k_1' = k_2/1 + k_7\,(Fe^{+++})(Br^-)/k_3(Fe^{++}).$$

The concentration of iron (III) was essentially constant during the course of the reactions; an average value of (Fe^{++}) was used in calculating $k_7(Br^-)/k_3$. The actual values of $k_7(Br^-)/k_3$ were calculated from the expression

$$(12)\quad \frac{k_7}{k_3}\,(Br^-) = \left(\frac{k_2}{k_1'} - 1\right)\frac{(Fe^{++})}{(\Sigma\ Fe^{+++})}\,(1 + K_{FeBr})$$

which is easily obtained from equation (11) and the formation constant of $FeBr^{++}$, $K_{FeBr} = (FeBr^{++})/(Fe^{+++})(Br^-) \cong 0.5$.(14)

Included in Table 4 are a set of the preliminary experiments. These earlier experiments performed at $(Br^-) = 0.5M$ give the same inhibition by iron (III) as was obtained in the later, more reliable, experiments. The author believes therefore, that the earlier experiments correctly show that there is no inhibition by iron (III) when $(Br^-) = 0.05M$. The maximum predicted decrease in rate is about 12% which would not be detected in these rather inaccurate experiments. The observed value of $k_7(Br^-)/k_3$ implies that, in the experiments with no added iron (III), there would be no observable decrease in rate for the first 50% of the reaction due to the iron (III) formed.

One may conclude therefore, that equation (10) quantitatively predicts the effect of the ferric-ferrous ratio on the rate, and that the prediction as to the effect of bromide ion is consistent with the data available.

Reaction (2) can of course, be written as

$$(2')\quad Fe^{++} + Br_3^- \underset{k_7'}{\overset{k_2}{\rightleftharpoons}} FeBr^{++} + Br_2^-.$$

In the available range of bromide ion concentrations, $FeBr^{++}$ is largely dissociated into Fe^{+++} and Br^-, so that this mechanism is kinetically indistinguishable from the one used. According to this formulation, $k_7'/k_3 = 0.27$; the species Br_2^- oxidizes Fe^{++} four times as fast as it reduces $FeBr^{++}$. It may be recalled that Taube (15) has adduced evidence for the reduction of iron (III) by Cl_2^-. The analogous reduction of iron (III) by I_2^- is a step in the reaction between iron (III) and iodide ion.(3)

An alternative mechanism for the oxidation of iron (II) by bromine involves iron (IV) as the reaction intermediate.

$$(13)\quad Fe^{++} + Br_3^- \underset{k_{14}}{\overset{k_{13}}{\rightleftharpoons}} FeBr_3^+ \quad (\text{or } Fe^{++++} + 3\ Br^-)$$

$$(15)\quad FeBr_3^+ + Fe^{++} \underset{k_{16}}{\overset{k_{15}}{\rightleftharpoons}} 2\ Fe^{+++} + 3\ Br^-.$$

To explain the observed inhibition by iron (III), one must assume that reaction (15) is reversible. The equilibrium constant for the over-all reaction (1) is then $K_1 = k_{13}\ k_{15}/k_{14}\ k_{16}$ and the predicted rate law is

$$(16)\quad -\frac{d}{dt}\ (\Sigma\ Br_2) = \frac{k_{13}(Fe^{++})(Br_3^-)}{1 + \dfrac{k_{14}}{k_{15}(Fe^{++})}} \left[1 - \frac{(Fe^{+++})^2\ (Br^-)^3}{K_1(Fe^{++})^2\ (Br_3^-)} \right].$$

This relation allows for inhibition by iron (III) only insofar as the over-all reaction (1) is reversible; since $K_1 \sim 10^9$, negligible inhibition by iron (III) is predicted by the iron (IV) mechanism in the experiments listed. The observed inhibition therefore eliminates the iron (IV) mechanism for the oxidation of iron (II) by tribromide ion. It was not possible for Hershey and Bray to eliminate the iron (IV) mechanism for the oxidation-reduction reactions in the iron-iodine system because, in this case, K is much smaller and the over-all reaction is in fact reversible.

RATE STUDIES AT LOW BROMIDE ION CONCENTRATIONS

It was apparent from Table 2 that if any information was to be obtained regarding the possibility of Br_2 and HOBr being reactants, much lower concentrations of bromide ion would have to be used. The preliminary experiments showed that there would be very little leeway in the experimental conditions for the following reasons:

(a) With $(Br^-) \sim 10^{-3}$ M, concentrations of $\Sigma Br_2 \sim 7 \times 10^{-4}$ F would have to be used to give densities of $\sim .3$. The bromide ion formed by the reaction would cause the ratio $(Br_3^-)/(Br_2)$ to increase, while (ΣBr_2) would decrease as the reaction progressed. This would possibly result in a situation where $dD_t/dt \sim 0$, or at best where D_t would be a complicated function of the time. This difficulty was surmounted by finding a wavelength, 452 mμ, where the extinction coefficients for tribromide ion and bromine were identical.

(b) The use of $\lambda = 452$ mμ, required that the concentrations of the reactants be $\sim 3 \times 10^{-3}$ F, since $\epsilon = 93.6$. At this concentration the half-time of the reaction was reduced from 3 minutes to 1 - 1 1/2 minutes.

Experiments were performed with $(H^+) = 0.5$ M and $(Br^-) \sim 10^{-3}$ M to see if the reaction went faster under these conditions than one would predict for a tribromide ion mechanism alone. When the results showed that the reaction did go faster, the acidity was varied too.

The results of one of the runs are displayed in Figure 2. The plot of log $(\Sigma Br_2)/(Fe^{++})$ has a positive second derivative because the bromide ion formed during the course of the reaction increases the tribromide ion concentration, thus accelerating the reaction. The data were analyzed in terms of the assumed rate equation

$$(17) \quad -d(\Sigma Br_2)/dt = (Fe^{++})\,(k_2(Br_3^-) + k_4(Br_2) + k_5(HOBr))$$

$$= k\,(Fe^{++})\,(\Sigma Br_2)\ .$$

The mean constants, k, were calculated from the slopes of the plot of log $(Fe^{++})/(\Sigma Br_2)$ at various times during the reaction. From these was subtracted $\bar{k}_2 = k_2\,(Br_3^-)/(\Sigma Br_2)$, the contribution of tribromide ion to the mean rate constant. The remaining term

$$(18) \quad k - \bar{k}_2 = \frac{k_4\,(Br_2) + k_5\,(HOBr)}{(\Sigma Br_2)}$$

$$= (k_4 + k_5\,K_H/(H^+)\,(Br^-))/(1 + (Br^-)/K_D)\ .$$

For $K_H^{(16)}$, the hydrolysis constant of bromine, the value 1.56×10^{-8} $(\text{mole/liter})^2$ was used. For the runs at $(H^+) = 0.87$ and $0.50M$, the quantity $k - \bar{k}_2$ was constant within the experimental error of ± 10%; for the run at $(H^+) = 0.15M$, there was a marked decrease in $k - \bar{k}_2$ as the reaction progressed. The results can all be interpreted reasonably well by the values, $k_4 = 0.76$ (liter/mole sec.) and $k_5 = 2.1 \times 10^4$ (liter/mole sec.).

Table 5 displays the data for the course of the reaction at $(H^+) = 0.15M$. Table 6 summarizes the runs at higher acidities; for the experiments of Table 6, the contribution of hypobromous acid was relatively small, and the calculated decrease in $k - \bar{k}_2$ during the course of any particular reaction was less than 15%.

It is therefore assumed that molecular bromine and hypobromous acid react via the reaction paths

$$(19) \quad Fe^{++} + Br_2 \rightarrow Fe^{+++} + Br_2^- \; ; \quad k_4 = 0.76\ (\pm\ 0.2)$$

$$(20) \quad Fe^{++} + HOBr \rightarrow FeOH^{++} + Br \; ; \quad k_5 = 2.1\ (\pm\ 0.4) \times 10^4 .$$

The claim is not made that the kinetic formulation presented is the only one that will explain the data. In a reaction such as this one, where manifold possibilities for reactive species exist, it is possible for other reactions to take place in combination with any of the others suggested. The experimenter can merely suggest the most reasonable mechanism that explains the data.

CATALYSIS BY PHOSPHORIC ACID

While developing a procedure for the coulometric titration of iron (II) with electrolytically generated chlorine or bromine, using an amperometric end-point, Farrington(7) observed that the rate of reaction between halogen and iron (II) was increased by the addition of phosphoric acid. The author has made a brief study of this effect. Each run proved to be a good second-order reaction.

The reaction rate is decreased as the hydrogen ion concentration is raised. The data, displayed in Table 7, have been analyzed in terms of the rate law

$$(21)\quad -d\,(\Sigma\, Br_2)/dt = (Fe^{++})(Br_3^-)\quad (k_2 + k_{22}\,(H_2PO_4^-))$$

where $(H_2PO_4^-) = 0.015^{*}\ (H_3PO_4)/(H^+)$.(17)

The results in Table 7 were not expected to be very precise because the analysis of the experimental data involves subtraction of a substantial contribution to the optical density due to iron (III) phosphate complexes. Apart from the first entry in the table, for which the experimental error is expected to be relatively large, the data are in moderately satisfactory agreement with the assumed rate law. No other one term expression for the effect of phosphoric acid would satisfy the data as well. (In particular, a rate term, $k\,(H_3PO_4)\,(HOBr)\,(Fe^{+++})$, would correctly give the dependence on acidity but not the dependence on bromide ion concentration.) There are indications that k_{22} increases as the hydrogen ion concentration is raised, suggesting that undissociated phosphoric acid is also a catalyst. The results, however, are not sufficiently accurate to permit reliable conclusions about such finer points.

The reaction mechanism may be formulated as

$$(22)\quad Fe^{++} + Br_3^- + H_2PO_4^- \rightarrow FeH_2PO_4^{++} + Br^- + Br_2\ .$$

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[*] Griffith and McKeown give for K_1, the first ionization constant of phosphoric acid, $K_1 = 0.016$ at 30°, $\mu = 0.56$ (KCl). Lanford and Kiehl give $K_1 = 0.030$ at 30°, $\mu = .665$ ($NaNO_3$).

It is reported, however, that the main iron (III) phosphate complex in dilute acid solutions is $FeHPO_4^+$.(18) The absorption spectrum of a 10^{-3}M iron (II) solution with $(H^+) = 0.5$M and $(H_3PO_4) = 1.5$M, did not show any absorption that could be attributed to an iron (II) phosphoric acid complex.

SUMMARY OF RESULTS AT 29.8°, $\mu = 1.0$

$k_1 = k_2 = 10^{7.59(\pm 0.36)} \exp(-8400 \pm 500)/Rt$

$k_7/k_3 = 0.14\ (\pm 0.01)$

$k_4 = 0.76\ (\pm 0.2)$ liter/mole sec.

$k_5 = 2.1\ (\pm 0.4) \times 10^4$ liter/mole sec.

$k_{22} = 2.4\ (\pm 0.3) \times 10^3$ liter^2/mole^2 sec.

TABLE 1

Formal Extinction Coefficients, ϵ , of Bromine at 29.8° in 0.5M $HClO_4$, 0.5M NaBr ($\epsilon = (1/cl) \log_{10} I_o/I$)

λ (mμ)	ϵ (liter/mole cm.) x 10^{-3}
350	0.97
340	1.48
330	2.70
320	4.21
310	6.62
300	10.2
290	15.9
280	24.3
270	31.8
265	32.2
260	29.3
255	23.7
250	16.7
245	10.8

TABLE 2

Results at $(Br^-) = 0.05$, 0.2 and 0.5 M, T = 29.8° and 20.4°. All runs were at $\mu = 1.00$, maintained with Na^+ and ClO_4^- ; all runs were at $(H^+) = 0.50$ unless otherwise noted; spectrophotometric observations at $\lambda = 300$ mμ except for the indicated ones at $\lambda = 280$ mμ.

$(Fe^{++})_o$	$(\Sigma Br_2)_o$	(Br^-)	k	k_1
moles/liter x 10^5		moles/liter	liters/mole sec.	
		T = 29.8°		
4.49[a]	2.79	0.480	37.0	41.7
5.28	4.97	.480	36.8	41.5
7.50[a]	2.81	.480	33.2	37.4
10.56	2.66	.480	36.4	41.0
14.99	5.77	.480	33.1	37.3
14.99	8.31	.480	36.0	40.6
14.99	8.77	.480	33.8	38.1
14.99	8.78	.480	35.0	39.5
6.27	2.15	0.479	29.6	33.4
6.27	4.30	.483	30.5	34.4
7.42	5.62	.483	30.6	34.5
12.54	2.27	.479	39.6	33.4
12.54	4.56	.483	29.6	33.3
12.54[b,f]	4.58	.483	30.4	34.3
12.54[c,f]	4.58	.483	31.0	34.9
Average for $(Br^-) = 0.5$			30.0 ± 0.5	33.8 ± 0.5
6.27	5.36	0.196	26.5	34.8
6.27[d]	5.10	.196	25.3	33.3
12.54[e]	3.92	.209	26.6	34.4
Average for $(Br^-) = 0.2$			26.1 ± 0.6	34.2 ± 0.7

TABLE 2 (continued)

$(Fe^{++})_o$	$(\Sigma Br_2)_o$	(Br^-)	k	k_1
moles/liter x 10^5		moles/liter	liters/mole sec.	
		T = 29.8°		
7.50[a]	3.90	0.050	16.6	36.7
7.50[a]	3.95	0.050	15.9	35.2
7.50	7.98	0.050	18.6	41.1
7.50	8.07	0.050	17.7	39.1
14.99[a]	3.84	0.050	15.5	34.3
14.99[a]	4.03	0.050	15.8	34.9
14.99	7.96	0.050	17.0	37.6
14.99	8.28	0.050	17.8	39.4
12.54	12.93	0.0498	14.9	33.1
18.80	12.54	.0498	15.7	35.1
25.09	12.89	.0498	15.3	34.2
Average for (Br^-)= 0.05M			15.3 ± 0.3	34.1 ± 0.9
		T = 20.4°		
6.27	3.18	0.500	19.0	21.2
6.27[f]	5.14	0.500	18.5	20.7
12.54	3.21	0.500	19.4	21.7
12.54	5.10	0.500	19.7	22.0
18.81	3.18	0.500	19.6	21.9
18.81	5.10	0.500	19.7	22.0

Average k_1 = 21.8 ± 0.2

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[a] = 280 m . [b] $(SO_4^=) = 6.6 \times 10^{-4}M$. [c] $(SO_4^=) = 1.33 \times 10^{-3}M$.

[d] $(H^+) = 0.80M$. [e] $(H^+) = 0.65M$. [f] Excluded from average.

TABLE 3

Experimental and calculated data for a kinetics run performed at 20.4° and $(Br^-) = (H^+) = 0.5$ M.

t	D_t	$\bar{D}$	D_c	(ΣBr_2)	(Fe^{++})	$(Fe^{+2})/(\Sigma Br_2)$	$\log(Fe^{+2})/(\Sigma Br_2)$
min. x 10^2				moles/liter x 10^5			
0	.344	.000	.344	3.18	18.81	5.92	0.7723
36	.321	.001	.320	2.96	18.37	6.21	.7931
55	.310	.002	.308	2.85	18.15	6.37	.8041
71	.300	.003	.297	2.75	17.95	6.52	.8143
87	.290	.003	.287	2.66	17.77	6.68	.8248
104	.280	.004	.276	2.55	17.55	6.88	.8376
122	.270	.004	.266	2.46	17.37	7.06	.8488
178	.245	.006	.239	2.21	16.87	7.64	.8831
197	.235	.006	.229	2.21	16.69	7.87	.8960
223	.225	.007	.218	2.02	16.49	8.16	.9117
247	.215	.008	.207	1.92	16.29	8.48	.9284
291	.200	.009	.191	1.77	15.99	9.03	.9557
322	.190	.009	.181	1.68	15.81	9.42	.9741
354	.180	.010	.170	1.57	15.59	9.92	.9965
386	.170	.010	.160	1.48	15.41	10.41	1.0170
435	.160	.011	.149	1.38	15.21	11.02	1.0422
468	.150	.012	.138	1.28	15.01	11.74	1.0693
516	.140	.012	.128	1.19	14.83	12.46	1.0955
568	.130	.013	.117	1.08	14.61	13.53	1.1313

slope = 6.35×10^{-4}

$k = (3.84 \times 6.35 \times 10^{-4})/12.45 \times 10^{-5} = 19.6$ liter/mole sec.

TABLE 4

Reaction Rates with Added Iron (III) at 29.8°, $(H^+) = 0.50$, $\mu = 1.0$.

(Br^-)	$(Fe^{++})_o$ x 10^5	$(\Sigma\ Br_2)_o$ x 10^5	$(\Sigma\ Fe^{+++})_o$ x 10^4	k	k_1'	$k_7(Br^-)/k_3$
0.50	12.54	2.18	2.43	26.5	29.8	0.075
	12.54	2.19	4.86	24.8	27.8	0.061
	12.54	2.38	9.72	20.2	22.7	0.071

Average $k_7(Br^-)/k_3 = 0.069$

Preliminary Experiments

(Br^-)	$(Fe^{++})_o$ x 10^5	$(\Sigma\ Br_2)_o$ x 10^5	$(\Sigma\ Fe^{+++})_o$ x 10^4	k	k_1'	$k_7(Br^-)/k_3$
0.50	5.94	4.40	0.0	28.9	44.1	...
	5.94	4.40	1.14	33.4	37.9	0.071
	5.94	4.40	6.52	21.7	24.6	0.067
	5.94	4.40	9.78	18.8	21.3	0.061
0.05	17.99	6.60	0.0	19.7	43.6	...
	17.99	10.74	0.0	18.7	41.4	...
	7.50	5.76	12.20	20.1	44.4	x
	7.50	10.41	12.20	20.4	45.1	x
	17.99	6.16	7.36	18.8	41.6	x
	17.99	10.55	7.36	19.8	43.8	x

TABLE 5

Reaction at Low Bromide, $H^+ = 0.15$ M, 29.8°, $\mu = 1.0$.

t (min. x 10^2)	(ΣBr_2) (mole/liter x 10^3)	(Fe^{++})	log (Fe^{++})/(ΣBr_2)	(Br^-) x 10^3	k	$k - \bar{k}_2$ obsd.	$k - \bar{k}_2$ calcd.
0	2.50	3.05	0.0864	1.02			
31	2.23	2.51	.0511	1.56	2.86	2.02	2.10
39	2.16	2.37	.0403	1.70	2.86	1.95	1.99
46	2.10	2.25	.0302	1.82	2.86	1.88	1.90
55	2.03	2.11	.0170	1.96	2.86	1.81	1.81
66	1.95	1.95	.000	2.12	2.86	1.73	1.73
79	1.86	1.77	-.0214	2.30	2.86	1.63	1.65
93	1.80	1.65	-.0376	2.42	2.86	1.57	1.60
109	1.72	1.49	-.0625	2.58	2.86	1.49	1.54
138	1.61	1.27	-.1029	2.80	2.86	1.38	1.47

TABLE 6

Reactions at Low Bromide, 29.8°, $\mu = 1.0$.

$(Fe^{++})_o$ x 10^3	$(\Sigma Br_2)_o$ x 10^3	(Br^-) x 10^3	(H^+)	k	$k - \bar{k}_2$ obsd.	$k - \bar{k}_2$ calcd.
3.32	2.73	1.72	0.50	2.19	1.01	1.02
4.15	2.75	2.08	.50	2.32	1.09	1.01
4.15	3.39	2.28	.50	2.45	1.03	0.97
3.32	3.39	1.39	.50	2.35	1.18	1.03
3.05	2.97	1.69	.87	1.87	0.87	0.94

TABLE 7

Catalysis by Phosphoric Acid, 29.8°, $\mu = 1.0$.

$(Fe^{++})_o$ x 10^5	$(\Sigma Br_2)_o$ x 10^5	(ΣH_3PO_4)	(H^+)	$k_2 + k_{22}(H_2PO_4^-)$	k_{22} x 10^{-3}
Experiments at $(Br^-) = 0.5M$					
7.42*	5.69	0.089	0.516	47.1	5.22
12.54	4.56	.149	.516	43.9	2.35
7.42	5.59	.178	.516	44.9	2.17
7.42	5.56	.267	.516	48.9	1.98
12.54	4.46	.297	.516	46.1	1.44
12.54	4.43	.445	.516	62.4	2.26
7.42	5.62	.446	.516	56.8	1.81
7.42	5.71	.534	.516	70.6	2.42
Experiments at $(Br^-) = 0.2M$					
6.27	4.71	0.149	0.147	64.3	2.19
6.27	5.42	.149	.300	53.1	2.69
6.27	5.24	.149	.491	47.6	3.07
6.27	5.27	.149	.646	45.5	3.40
6.27	4.85	.446	.344	74.6	2.18
6.49	4.82	.461	.508	70.4	2.75
6.27	5.20	.446	.646	60.2	2.59

Average $k_{22} = 2.4\ (\pm 0.3) \times 10^3$

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* Excluded from the average.

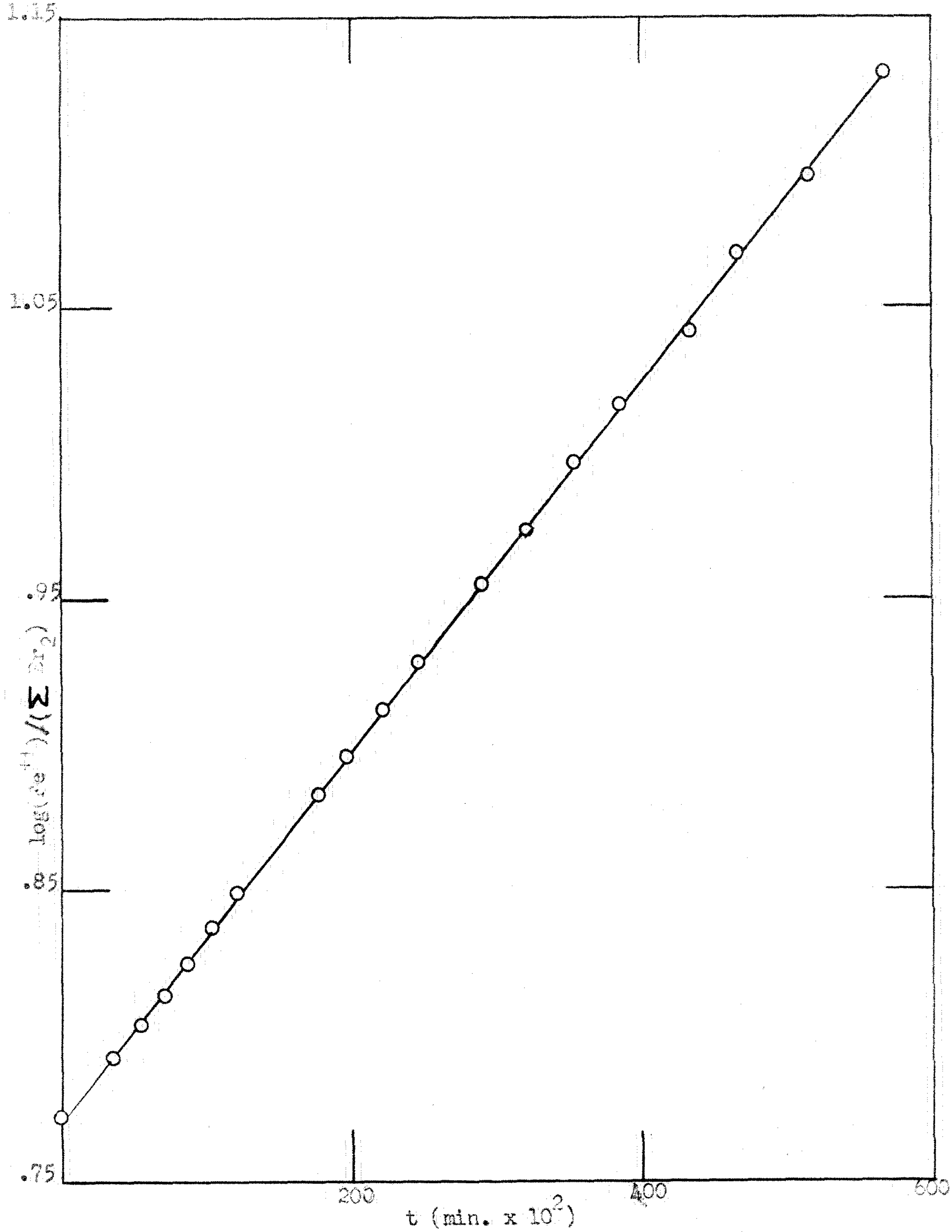

Figure 1

Plot of log $(Fe^{++})/(\Sigma Br_2)$ versus time for an experiment performed at 20.4° and $(Br^-) = (H^+) = 0.5$F. $(\Sigma Br_2)_o = 3.18 \times 10^{-5}$M, and $(Fe^{++})_o = 18.81 \times 10^{-5}$F. $\lambda = 300$ mμ.

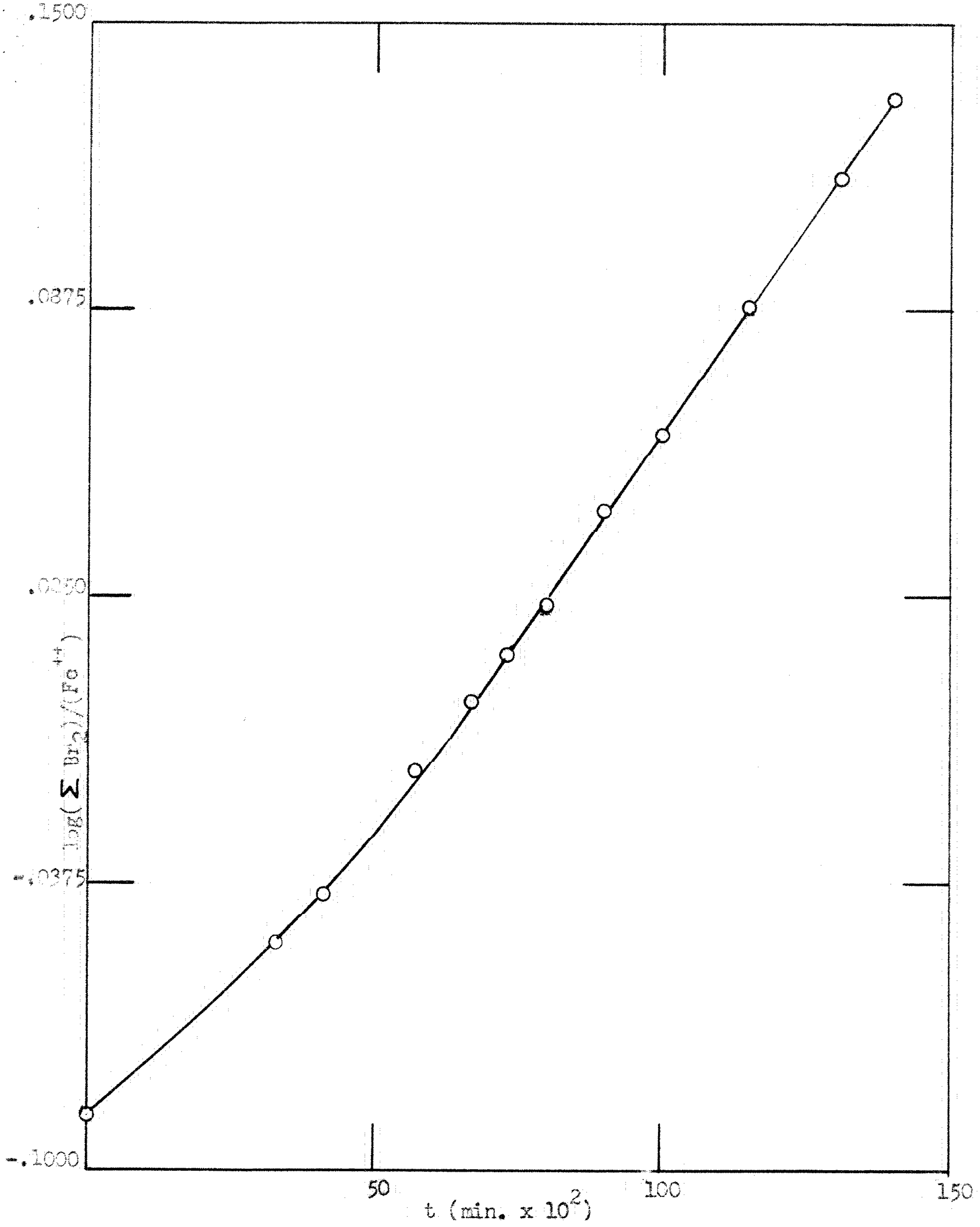

Figure 2
Plot of log (Σ Br2)/(Fe^{++}) versus time for an experiment performed at 29.3° with (Σ Br2)$_o$ = 3.39 x 10^{-3}F, (Fe^{++})$_o$ = 4.15 x 10^{-3}F, (Br^-)$_o$ = 1.02 x 10^{-3}F, (H^+) = .5M and μ = 1.0 at 452 mμ .

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PART II: COMPLEX ION FORMATION IN THE SYSTEM IRON (III), PHOSPHORIC ACID

INTRODUCTION

Nearly one hundred years ago, Claus(1) noted that the addition of phosphoric acid or a phosphate salt would decolorize a solution containing iron (III) thiocyanate complexes. Since that time many other investigators have reported similar evidence for the existence of a complex between iron (III) and phosphoric acid, i.e., the decolorization of a ferric chloride solution(2) and the interference of small amounts of phosphate with a colorimetric determination of iron (III) as a thiocyanate complex.(3) Bonner and Yost(4) devised an analytical determination of iron (II) with sodium hypochlorite, by utilizing the fact that the free iron (III) concentration was greatly reduced in solutions that contained excess phosphate. Bonner and Romeyn(5) found that the oxidation of iron (II) by iodine, in the presence of phosphoric acid, failed to go to completion when the solution was approximately 3 N in sulfuric acid, but that it was quantitative when the sulfuric acid concentration was lowered to 0.1 N. Furthermore, they tried to find evidence for an iron (III) phosphate complex in 3 N sulfuric acid by means of a potentiometric titration of a ferrous-ferric solution with phosphoric acid. The titration produced a smooth curve without an inflection point and thus gave no indication of stoichiometric complex formation upon the addition of the equivalent amount of reagent.

A quantitative study of the equilibrium between iron (III) and phosphoric acid was made by Lanford and Kiehl(6) in which they determined that the complex was $FeHPO_4^+$; a spectrophotometric analysis using the absorption of ferric thiocyanate was the method used.

During the study of the accelerating effect of phosphoric acid on the reaction between bromine and ferrous ion, the author discovered that the ferric phosphate complex strongly absorbed ultraviolet light. Further investigations of the ultraviolet absorption spectra in this system were carried out.

EXPERIMENTAL

Solutions of $Fe(ClO_4)_3$ were prepared as described on page 3 of this thesis. Phosphoric acid solutions were prepared by dilution of 85% phosphoric acid and were standardized as recommended by Swift(7).

The optical densities of solutions of constant (Fe^{+3}) and varying (H_3PO_4), listed in Tables 1 - 4, were measured in 1 cm. cells with a Beckman Model DU spectrophotometer.

RESULTS AND DISCUSSION

First a derivation will be given which will clarify the analysis of the data:

Assume that only one complex is formed.

(1) $Fe^{+++} + H_3PO_4 \rightleftharpoons FeH_{3-n}PO_4^{3-n} + nH^+$

(2) $$K_p' = \frac{(FeH_{3-n}PO_4^{3-n})(H^+)^n}{(Fe^{+++})\ (\Sigma\, H_3PO_4)}$$

(3) where $(\Sigma\ H_3PO_4) = (\Sigma\ H_3PO_4)_o - (FeH_{3-n}PO_4^{3-n})$.

Let $FeH_{3-n}PO_4^{3-n}$ be designated as FeP.

(4) Define $K_p = K_p'/(H^+)^n$.

The total optical density of a solution containing iron (III) and phosphoric acid is

(5) $D_T = D_{Fe^{+++}} + D_{FeOH^{++}} + D_{FeP}$,

and at a constant acidity

(6) $= \epsilon_{Fe^{+++}} (Fe^{+++}) + \epsilon_{FeOH^{++}} K_H'(Fe^{+++}) + \epsilon_{FeP} (FeP)$

where $(Fe^{+++}) K_H = (FeOH^{++}) (H^+)$, and $K_H = K_H' (H^+)$.

(7) $D_T - (Fe^{+++}) (\epsilon_{Fe^{+++}} + \epsilon_{FeOH^{++}} K_H') = \epsilon_{FeP} (FeP)$

(8) but $(Fe^{+++}) = (Fe^{+++})_o - ((FeOH^{++}) + (FeP))$

(9) Define $\bar{\epsilon} = \epsilon_{Fe^{+++}} + \epsilon_{FeOH^{++}} K_H'$.

(10) Then $D_T - (Fe^{+++})_o \bar{\epsilon} + \bar{\epsilon} ((FeOH^{++}) + (FeP)) = \epsilon_{FeP}(FeP)$.

(11) Define $D_T - (Fe^{+++})_o \bar{\epsilon} = D_c$

(12) $D_c = (FeP) (\epsilon_{FeP} - \bar{\epsilon}) - (FeOH^{++}) \bar{\epsilon}$.

The second term on the right hand side of equation (12) is 5% or less of the first term and has been neglected in all subsequent calculations. Then

(13) $D_c = (FeP) (\epsilon_{FeP} - \bar{\epsilon})$.

If equations (2), (4) and (8)(neglecting $(FeOH^{++})$) are combined with equation (13) and the expression is rearranged, equation (14) is the result.

$$(14)\quad \frac{(Fe^{+++})_o}{D_c} = \frac{1}{(\Sigma\ H_3PO_4)} \quad \frac{1}{K_p\ (\ \epsilon_{FeP} - \bar{\epsilon}\ )} + \frac{1}{\epsilon_{FeP} - \bar{\epsilon}} .$$

It is seen from equation (14) that a plot of $(Fe^{+++})_o/D_c$ versus $1/(\Sigma\ H_3PO_4)$ will give a straight line having a slope of $1/K_p\ (\ \epsilon_{FeP} - \bar{\epsilon}\ )$ and an intercept of $1/(\ \epsilon_{FeP} - \bar{\epsilon}\ )$. It should be recalled that the equation, in this form, is valid only when the concentration of $(\Sigma\ H_3PO_4)$ is so low that just the first complex species is formed.

A typical experiment will now be calculated in detail. Table 5 contains all the necessary data. Under the experimental conditions, $\bar{\epsilon}$ equaled 76, and the corrections to the total observed densities were: -0.0375 for $(Fe^{+++}) = 4.94 \times 10^{-4}$ F and -0.0225 for $(Fe^{+++}) = 2.96 \times 10^{-4}$ F. A trial value of $K_p = 600$ yielded an average value of 551 for $\epsilon_{FeP} - \bar{\epsilon}$. (This result for $\epsilon_{FeP} - \bar{\epsilon}$ was obtained by solving for (FeP), using equations (2) and (4), at arbitrary values of $(H_3PO_4)_o$, and then substituting (FeP) into equation (13) and solving for the desired quantity.)

The values listed under (FeP) in Table 5 were then obtained by dividing D_c by 551 for all $(\ \Sigma\ H_3PO_4)_o$, and $(\Sigma\ H_3PO_4)$ was obtained by using equation (3). Since this kind of analysis requires an accurate determination of both the slope and the intercept, these quantities were obtained by a least squares analysis of the data. Figure 1 displays the best straight line obtained by this analysis. The equations $\Sigma y = a\Sigma x + nb$, and $\Sigma xy = a\Sigma x^2 + b\Sigma x$ were used to determine the slope and the intercept, where $y = (Fe^{+++})_o/D_c$, $x = 1/(\Sigma H_3PO_4)$, a = the slope and b = the intercept. It is seen from equation (14) that $1/b = (\epsilon_{FeP} - \bar{\epsilon})$ and $b/a = K_p$. The value of K_p obtained from the plot was 576; this should be compared with $K_p = 535$, which was obtained from the first approximation that $K_p = 462$. The values $K_p = 572$ and $(\epsilon_{FeP} - \bar{\epsilon}) = 544$ were then chosen as the best values at $\lambda = 320$ mμ and $(H^+) = 0.10F$.

The linearity of the plot in Figure 1 tends to support the original assumption that only one iron (III) phosphate complex was formed in the concentration range used. It must be emphasized, however, that this is not a very stringent test; the least squares method gives a K_p and $(\epsilon_{FeP} - \bar{\epsilon})$ that fit the data best, therefore, it would be difficult to detect a gradual curvature at higher phosphoric acid concentrations.

Table 6 contains the values of K_p, $\epsilon_{FeP} - \bar{\epsilon}$, and $K_p(\epsilon_{FeP} - \bar{\epsilon})$ that were obtained in this research at various wavelengths and acidities. (These results were obtained by using the data contained in Tables 1 - 4 with one exception: at $(H^+) = 0.05M$ only the data at $(Fe^{+++})_o = 4.94 \times 10^{-4}F$ were considered to be suspect due to the use of glassware that had not been cleaned. By looking at the data in Table 4, one is able to see that the data at the two iron (III) concentrations are not consistent.

Therefore the results at $(H^+) = 0.05M$ must be considered as being the least reliable obtained.) As was expected from equation (4), K_p decreases with increasing acidity. It is seen in Table 6 that $(\epsilon_{FeP} - \bar{\epsilon})$ is not a constant at the different hydrogen ion concentrations ($\bar{\epsilon}$ varies very little in the range of acidities used), which it should be if only one complex is formed. The variation in $(\epsilon_{FeP} - \bar{\epsilon})$ can be attributed to either: the error in extrapolating the experimental data in order to obtain the intercept in equation (14), or to the formation of additional complexes. Assuming that only one complex is formed, one can best observe the variation of K_p with acidity by comparing values of $K_p(\epsilon_{FeP} - \bar{\epsilon})$. It can be seen from equation (14) that the quantity $K_p(\epsilon_{FeP} - \bar{\epsilon})$ is obtainable with greater accuracy than is K_p; the latter quantity requires an accurate knowledge of $(\epsilon_{FeP} - \bar{\epsilon})$, and the slope is much less dependent upon which straight line is drawn through the points, than is the intercept. The quantity, $K_p(\epsilon_{FeP} - \bar{\epsilon})$, is found to vary inversely with acidity, too.

To eliminate any extraneous acid effects from equation (2), a correction must be made for the first dissociation of phosphoric acid. Define

$$(15) \quad K_T' = \frac{(FeP)\ (H^+)^n}{(Fe^{+++})\ (H_3PO_4)} \qquad \text{and} \qquad K_T = \frac{K_T'}{(H^+)^n}$$

(16) where $\frac{(H^+)\ (H_2PO_4^-)}{(H_3PO_4)} = K_1$

(17) and $(H_3PO_4) = (\Sigma\ H_3PO_4) - (H_2PO_4^-)$.

The value $K_1 = 3.02 \times 10^{-2}$ was chosen, since this is the value adopted by Lanford and Kiehl.(6)

In order to determine n in equation (15), the ratios of $K_T\ (\epsilon_{FeP} - \bar{\epsilon})$ were determined at a particular wavelength and various acidities. In Table 7, ρ_1, ρ_2 and ρ_3 equal the ratios of $K_T\ (\epsilon_{FeP} - \bar{\epsilon})$ at $(H^+) = 0.10$ and 0.20 F, $(H^+) = 0.05$ and 0.1 F and $(H^+) = 0.05$ and 0.20F respectively. If there is only one complex formed, these ratios are actually the ratios of K_T at the two different acidities. By dividing log ρ_1 and log ρ_2 by log 2, one obtains n = 1.45 and 1.87 respectively. This means, if the data are taken at face value, that there are two complex species, $FeH_2PO_4^{++}$ and $FeHPO_4^+$.

Lanford and Kiehl(6) obtained a value of $K_T = 1550$ at 30° and $\mu = 0.655$ ($NaNO_3$) and $(H^+) = 0.10M$. The average value of K_T, at 29.8°, $\mu = 0.20$ ($NaClO_4$) and $(H^+) = 0.10M$, obtained in this research was 602. Any correction in K_1 or K_T, due to the difference in ionic strengths used, would only make the two values for K_T diverge even further. They obtained a value of n = 2.02, which proved that the complex ion was $FeHPO_4^+$.

On the basis of comparison with other iron (III) complexes, one would expect iron (III) to form higher complexes in a stepwise manner until the hexacoordinated complex is formed. For example, the iron (III) thiocyanate ,(9) and the iron (III) halide(10) complexes form successively higher complexes as the concentration of complexing agent is increased. Since phosphoric acid is at best only bidentate, one would expect to see complexes with up to three molecules of phosphate bound to one of iron (III).

The argument is offered here that both Lanford and Kiehl and the author may have been measuring the composite equilibrium constant of two or more phosphate complexes and perhaps two complexes that differ by one proton, instead of the single equilibrium constant they thought they were measuring. The evidence in support of this thesis follows:

(a) Table 6 indicates that $\epsilon_{FeP} - \bar{\epsilon}$ is a function of acidity, and furthermore that $\lambda = 280$ mμ gives erratic results at high and low acidities. This suggests that there are two or more species which have different absorption spectra. (These species may be either higher phosphate complexes, or complexes differing only by the dissociation of a proton.)

(b) Tables 1 and 2 show that there is an increase in optical density with increasing (H_3PO_4) at all wavelengths, and then a decrease at high (H_3PO_4) at several wavelengths when (H^+) = 0.10 M. The decrease in density is, of course, explained by the formation of a higher phosphate complex that has smaller extinction coefficients at the wavelengths concerned.

(c) Davidson and Whiteker(8), who used a radioactive isotope, ion-exchange method, obtained a value of $K_T' \sim 30$ at $(H^+) = 1.0M$ and $\mu = 1.0$ ($NaClO_4$), and furthermore, found that there is a strong indication that higher complexes are formed. The author worked at $(H_3PO_4) = 10^{-3} - 10^{-4}F$ and obtained a value for $K_T' \sim 6$; Lanford and Kiehl obtained $K_T' = 15.5$ while using $(H_3PO_4) = 10^{-2} - 10^{-3}$; Davidson and Whiteker obtained $K_T' \sim 30$ at $(H_3PO_4) = .06 - .05F$. This summary supports the conclusion that higher complexes are being formed at higher (H_3PO_4). There appear to be two or more phosphate complexes. (This does not include the large number of possibilities where two or more complexes differ only in the number of protons which are coordinated with the complex.)

An additional interesting fact is that the complexes formed in the system iron (III), phosphoric acid do not form "instantaneously". Solutions containing phosphoric acid and iron (III), having concentrations of $\sim 5 \times 10^{-4}F$, were mixed rapidly and placed in a spectrophotometer. It was found that, 22 seconds after mixing, a change in density corresponding to only 75% of the total observed change in density had occurred.

TABLE 1

Values of D_c for $(Fe^{+++})_o = 4.94 \times 10^{-4}$ F, at 29.8°, $\mu = 0.20$ ($NaClO_4$ and $HClO_4$) and ($HClO_4$) = 0.10 M.

$(\Sigma\ H_3PO_4)_o$ (mole/liter)	280	290	300 (mμ)	310	320
9.07×10^{-5}	.063	.045	.031	.021	.013
2.27×10^{-4}	.106	.099	.067	.042	.025
2.90	.133	.116	.085	.053	.030
4.35	.196	.181	.137	.090	.054
4.53	.204	.199	.137	.085	.048
7.25	.311	.276	.206	.132	.072
9.07	.371	.358	.248	.160	.092
1.02×10^{-3}	.389	.356	.262	.167	.092
1.10	.416	.375	.277	.176	.097
1.81	.546	.501	.373	.241	.137
2.72	.636	.594	.435	.280	.157
4.54	.746	.679	.510	.325	.180
6.35	.826	.740	.543	.346	.188
9.07	...	.769	.566	.360	.197
4.53×10^{-2}	...	.880	.640	.380	.199
3.02×10^{-1}	...	1.03	.672	.366	.174
9.07	...	1.03	.651	.331	.148
$(Fe^{+++})_o\ \bar{\epsilon}$	.454	.221	.108	.060	.038

TABLE 2

Values of D_c for $(Fe^{+++})_o = 2.47 \times 10^{-4}$ F, at 29.8°, $\mu = 0.20$ $(NaClO_4$ and $HClO_4) = 0.10M$.

$(\Sigma\ H_3PO_4)$ (mole/liter)	280	290	300	310	320
			(mμ)		
4.53×10^{-5}	.008	.008	.005	.004	...
9.07	.021	.019	.012	.009	...
2.27×10^{-4}	.054	.051	.036	.024	...
2.90	.070	.063	.043	.027	...
4.35	.094	.085	.060	.036	.021
4.53	.106	.096	.066	.043	.026
5.76	.121	.110	.080	.048	.027
7.25	.141	.128	.093	.058	.031
1.02×10^{-3}	.189	.169	.123	.078	.044
1.81	.267	.239	.172	.110	.061
2.72	.315	.284	.206	.132	.074
4.53	.382	.342	.246	.156	.086
6.35	.413	.371	.270	.170	.092
9.07	.430	.400	.296	.182	.104
4.53×10^{-2}	.545	.480	.340	.201	.106
3.02×10^{-1}	.640	.534	.356	.192	.092
9.07	.669	.522	.330	.167	.077
$(Fe^{+++})_o$ $\bar{\epsilon}$	.227	.110	.054	.030	.019

TABLE 3

Values of D_c at 29.8°, $\mu = 0.20$, $(HClO_4) = 0.20$ M.

$(\Sigma H_3PO_4)_o$ (mole/liter)	280	290	300 (mμ)	310	320
			$(Fe^{+++})_o = 4.94 \times 10^{-4}$ F		
4.53×10^{-4}	.100	.093	.068	.042	.024
9.07	.199	.186	.126	.081	.047
13.59	.284	.252	.180	.115	.065
18.12	.376	.333	.241	.157	.094
22.65	.420	.374	.269	.169	.097
$(Fe^{+++})_o \bar{\epsilon}$	.445	.205	.091	.043	.023
			$(Fe^{+++})_o = 2.47 \times 10^{-4}$ F		
4.53×10^{-4}	.065	.060	.043	.029	.018
9.07	.102	.093	.067	.043	.023
13.59	.147	.131	.092	.058	.034
18.12	.196	.173	.125	.082	.052
22.65	.222	.193	.137	.087	.052
$(Fe^{+++})_o \bar{\epsilon}$	.223	.102	.045	.022	.012

TABLE 4

Values of D_c at 29.8°, $\mu = 0.20$, $(HClO_4) = 0.05$ M.

(Σ H_3PO_4) (mole/liter)	280	290	300	310	320	330
			(mμ)			
$(Fe^{+++})_o = 4.94 \times 10^{-4}$ F						
1.13×10^{-4}	.130	.114	.084	.056	.032	.014
2.27	.264	.232	.175	.115	.065	.030
2.27	.246	.229	.177	.115	.068	.032
3.40	.390	.352	.764	.176	.104	.054
4.53	.432	.397	.297	.195	.112	.054
4.53	.406	.388	.296	.196	.115	.055
5.67	.491	.449	.338	.223	.127	.062
6.80	.529	.528	.380	.251	.144	.070
9.07	.589	.593	.436	.286	.166	.083
11.34	.639	.638	.466	.304	.174	.086
$(Fe^{+++})_o = 2.47 \times 10^{-4}$ F						
1.13×10^{-4}	.057	.053	.038	.026	.013	.009
2.27	.108	.105	.080	.056	.034	.018
2.27	.116	.097	.072	.046	.024	.013
3.40	.154	.140	.104	.067	.038	.019
4.53	.189	.173	.128	.087	.050	.024
4.53	.193	.173	.130	.085	.049	.025
5.67	.215	.197	.147	.096	.054	.027
6.80	.252	.233	.178	.120	.072	.037
9.07	.307	.278	.213	.147	.092	.057
11.34	.321	.283	.213	.139	.080	.038

TABLE 5

Sample Calculation of K_p and ($\epsilon_{FeP} - \bar{\epsilon}$) at 29.8°, $\mu = 0.20$ and $(HClO_4) = 0.10$ F at $\lambda = 320$ mμ .

$(Fe^{+++})_o$	$(\Sigma H_3PO_4)_o$	D_c	(Fe P)	(ΣH_3PO_4)	$(\Sigma H_3PO_4)^{-1}$	$(\Sigma H_3PO_4)^{-2}$	$(Fe^{+++})_o/D_c$	$(Fe^{+++})_o/D_c(\Sigma H_3PO_4)_o$
(mole/liter x 10^4)			(mole/liter x 10^4)			10^{-6}	10^5	
4.94	2.27	.0255	.46	1.81	5525	30.55	1936	107.06
	2.90	.0305	.55	2.35	4255	18.10	1619	68.84
	4.35	.0545	.99	3.36	2978	8.85	906	26.98
	4.53	.0485	.88	3.65	2740	7.50	1018	27.89
	7.25	.0725	1.32	5.93	1685	2.84	680	11.46
	9.07	.0925	1.68	7.39	1350	1.82	534	7.21
	10.15	.0925	1.68	8.47	1180	1.39	534	6.30
	11.00	.0975	1.77	9.23	1084	1.17	506	5.48
2.96	4.35	.0255	.46	3.89	2570	6.60	1160	29.80
	5.80	.0325	.59	5.21	1920	3.68	910	17.47
	7.25	.0375	.68	6.57	1520	2.31	789	11.99
	10.15	.0525	.95	9.20	1085	1.18	564	6.65
TOTALS					27892	85.99	11156	327.13

$K_p = 576$

$\epsilon_{FeP} - \bar{\epsilon} = 542$

TABLE 6

Values of K_p, $(\epsilon_{FeP} - \bar{\epsilon})$ and $K_p(\epsilon_{FeP} - \bar{\epsilon})$ at 29.8° and $\mu = 0.20$ ($NaClO_4$).

λ (mμ)	K_p	$\epsilon_{FeP} - \bar{\epsilon}$	$K_p(\epsilon_{FeP} - \bar{\epsilon}) \times 10^{-3}$
	$(H^+) = 0.20$ F		
320	90	1288	116
310	80	2492	200
300	187	1904	356
290	121	3816	460
280	35	13190	457
Average	103 ± 41		
	$(H^+) = 0.10$ F		
320	572	544	311
310	460	1064	490
300	290	2497	726
290	527	2163	1140
280	462	2628	1215
Average	462 ± 70		
	$(H^+) = 0.05$ F		
320	847	1033	875
310	920	1690	1550
300	850	2700	2230
290	1060	3100	3280
280	3515	1965	6900
Average	919 ± 71*		

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* Excluding the value at $\lambda = 280$ mμ.

TABLE 7

Ratios of K_T ($\epsilon_{FeP} - \bar{\epsilon}$) at Different Hydrogen Ion Concentrations.

λ(mμ)	ρ_1	ρ_2	ρ_3
320	3.03	3.45	10.45
310	2.77	3.88	10.75
300	2.31	3.77	8.70
290	2.80	3.54	9.92
280	3.01	6.98	21.00
Average*	2.73	3.66	9.96
	n = 1.45	n = 1.87	n = 1.66

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* Excluding the values at λ = 280 mμ.

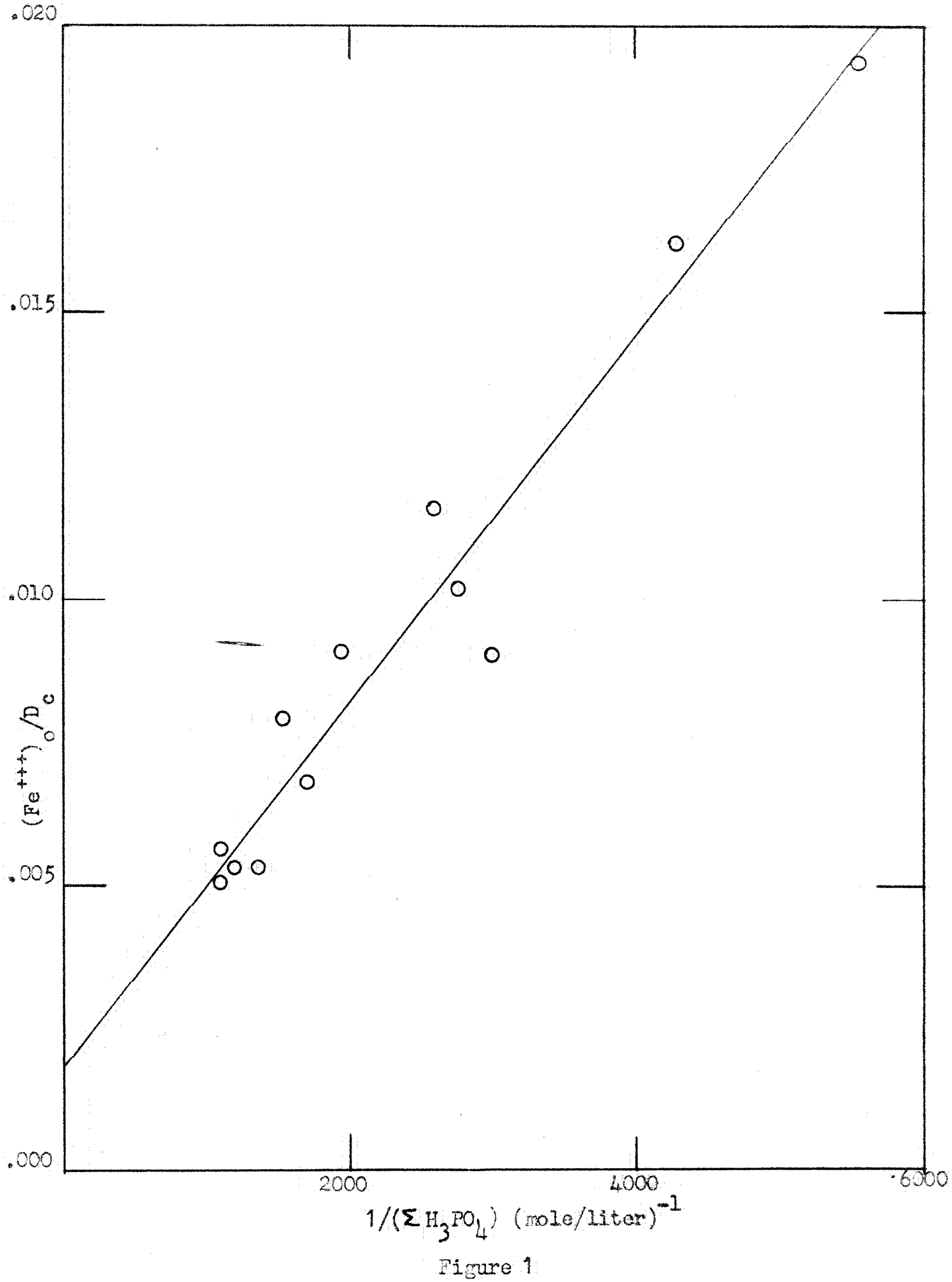

Figure 1

Plot of $(Fe^{+++})_o/D_c$ versus $1/(\Sigma H_3PO_4)$ at 320 mμ with $\mu = 1.00(NaClO_4)$, $(H^+) = 0.1$ M and T = 29.8°.

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PART III: KINETICS OF THE OXIDATION OF FERROCYANIDE ION BY BROMINE

INTRODUCTION

In view of the fact that the doubly, positively, charged ferrous ion reacted about forty times faster with the singly, negatively, charged tribromide ion than with the neutral bromine molecule,(1) the reaction between ferrocyanide ion and bromine was studied to determine the kinetics, and particularly to distinguish among the various possible reacting species.

Unfortunately, several difficulties (which shall be discussed in some detail later) made the formulation of a detailed mechanism impossible. However, interesting quantitative and semi-quantitative observations were made.

The only similar work of a quantitative nature that has been done, was a short series of experiments on the reaction between iodine and ferrocyandie ion performed by Saal.(2) He determined that the reaction was bimolecular, and, unjustifiably, decided that the reactants were I_2 and $Fe(CN)_6^{= =}$. This work is criticized by the author, because the "anomalous" results obtained by Saal when he varied the ionic strength and the chloride ion concentration can be explained if both I_2 and I_2Cl^- are reactants.

The induction of the isomerization of maleic to fumaric acid by the reaction between bromine and ferrocyanide ion is evidence for the occurrence of bromine atoms or Br_2^- in this reaction.(3) Taube,(4) however, reported that the chlorination of maleic acid was not induced when ferrocyanide ion was added to a solution containing maleic acid and chlorine; this was interpreted as meaning that no Cl atoms were produced in the reaction $Cl_2 + 2\,Fe(CN)_6^{= =} \rightarrow 2\,Cl^- + 2\,Fe(CN)_6^{- - -}$.

The stoichiometry of the reaction

$$(1)\quad 2\,Fe(CN)_6^{= =} + Br_2 \rightleftharpoons 2\,Fe(CN)_6^{- - -} + 2\,Br^-$$

has been substantiated by several investigators.(5) It has also been stated that bromine does not attack ferricyanide ion.(6) The stoichiometry of reaction (1) was checked spectrophotometrically in this research, by adding a 1.0×10^{-3} F ferrocyanide solution, which was .8 F in hydrogen ion, to a 3.7×10^{-4} F bromine solution that was 1.0 F in bromide ion, and then subtracting the contribution due to ferrocyanide from the observed optical density at various wavelengths. The resultant plot of density versus wavelength agreed almost quantitatively with the published spectrum of ferricyanide ion.(7)

EXPERIMENTAL

PROCEDURE AND MATERIALS

In general, the kinetic experiments were carried out in a manner similar to those performed in the reaction between iron (II) and bromine.(1) The only modifications introduced were those required by the higher observed rate constants (5 - 10 times larger). Solutions having concentrations of approximately 1×10^{-5} F and $1 - 4 \times 10^{-5}$ F of bromine and ferrocyanide respectively, were discharged into a 10 cm path length, glass stoppered, quartz cell, which had a volume of approximately 30 ml.. Two 20 ml. hypodermic syringes, which were discharged simultaneously, with the aid of a wooden handle, through a y-shaped glass mixing chamber, were used to fill the cell. Completeness of mixing was insured by inverting the reaction cell several times.

Potassium ferrocyanide was recrystallized twice from hot, distilled water. Weighed quantities of anhydrous potassium ferrocyanide were dissolved in distilled water to make up stock solutions which were freshly prepared a short time before the experiments were performed. A very fast reaction (completed in less than 40 seconds) occurred, which produced ferricyanide ion, when the ferrocyanide solution was diluted with 1 F $HClO_4$. The extent of oxidation was approximately 2×10^{-6} mole/liter of ferrocyanide.

EXTINCTION COEFFICIENTS

Using the extrapolated value(8) $K_D = (Br_2)(Br^-)/(Br_3^-) = 0.058$, the following formal extinction coefficients at 25°, $= 1.0$, and $\lambda = 300$ mμ for ΣBr_2 were calculated from the extinction coefficients of the tribromide ion: 5320 at $(Br^-) = 0.05$ M, 7300 at $(Br^-) = 0.10$ M, and 8860 at $(Br^-) = 0.15$ M. The value for the extinction coefficient for ferricyanide at this wavelength was 1600(7).

The optical density of solutions of ferrocyanide ion was measured at various acidities. A maximum density was found at pH's between 2 and 3 at those wavelengths where the extinction coefficient of ferricyanide greatly exceeded that of ferrocyanide. Qualitative observations verified the fact that a maximum in the rate of formation of a substance which absorbed strongly at $\lambda = 420$ mμ occurred at the same pH's as mentioned above. The observed phenomenon can be attributed mainly to the air oxidation of ferrocyanide to ferricyanide, which is catalyzed by ultra-violet light.(9) It would be interesting to observe the optical densities of ferrocyanide solutions as a function of pH in the absence of oxygen.

Reliable results, however, were obtained in solutions that had pH's either $\leqslant 0.3$ or $\geqslant 6.0$. In Table 1 one may observe the interesting fact that the absorption spectra of ferrocyanide ion are different in acidic and basic solutions. Using Zotov and Nekrasov's values for the third and fourth dissociation constants* of $H_4Fe(CN)_6$ and assuming that they are correct in saying that $H_4Fe(CN)_6$ and $H_3Fe(CN)_6^-$ behave like strong acids,(10) one can say that the extinctions coefficients at high acidity in Table 1 refer to $H_2Fe(CN)_6^=$ while the ones in approximately neutral solution refer to $Fe(CN)_6^{= =}$.

In all the experiments performed, an ionic strength of .98 ± 0.2 was maintained with Na^+ and ClO_4^-; the temperature was always 25.1° ± .2°.

The method of analyzing the kinetic data is exactly the same as outlined in Part I of this thesis. The correction to the observed density decrement due to the formation of ferricyanide ion was very large (approximately equal to the observed change in density). Unless there is a statement made to the contrary, the graphs of $\log (\Sigma Fe(CN)_6^{= =})/(\Sigma Br_2)$ versus time which correspond to

$$(2) \quad -\frac{d(\ Br_2)}{dt} = k\ (\Sigma\ Br_2)\ (\Sigma\ Fe(CN)_6^{= =}),$$

gave reasonably good straight lines for the first 50 - 60% of the reaction. In the tables, those experiments that are marked with asterisks are considered by the author to be less reliable than the others, since the calculated and extrapolated initial points did not agree well.

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* $K_3 = 10^{-3}$ and $K_4 = 5 \times 10^{-5}$ at infinite dilution.

In all the experiments listed in the tables, the acidities of the ferrocyanide and bromine solutions were approximately the same before they were mixed. This was done to eliminate the possibility of any acid catalyzed reaction being modified, due to a "slowly" attained equilibrium involving one of the reactants.

RESULTS AND DISCUSSION

The best conditions for performing the experiments were high acidity and low bromide ion concentration. As the acidity was lowered, the reaction became faster, and the results became increasingly unreliable.

$(H^+) = .93$ F, $(Br^-) = 0.05$ F

In Table 2 are listed the results of the experiments performed at $(H^+) = 0.93$ F and $(Br^-) = 0.05$ F. The experiments completed under these conditions are considered to be the most reliable performed in this investigation. Furthermore, the absence of any obvious trend of the bimolecular constant with changing ferrocyanide or bromine concentration, supports the belief that the rate determining step of reaction (1), can be expressed by equation (2). The value of k was found to be 138 ± 10% liter/mole sec. under these conditions.

EFFECT OF ACIDITY

In Table 3 are displayed the results of experiments performed at $(H^+) = 0.50$ M and $(Br^-) = 0.50$ M. The first three experiments show that at constant bromine concentration, the "constant" k decreases with increasing ferrocyanide concentration. Experiments were then performed to determine the dependence, if any, of the rate constant on bromine concentration. The last two sections of Table 3 show that k is independent of the bromine concentration over the range studied, and they indicate that the trend in k with ferrocyanide is beyond the experimental error.

It is clear that the reaction proceeds more rapidly at $(H^+) = 0.50$ M than at 0.93 M; however, in view of the unexplained trend of the second order rate constant with ferrocyanide ion concentration at the lower acidity, as well as the large experimental error, no quantitative conclusions about the hydrogen ion dependence of the rate law can be made.

Table 4 affords more information, for, although the trend with respect to ferrocyanide ion concentration seems to remain, the difference between the values obtained at high and low ferrocyanide concentrations now falls well within the large experimental error and can be disregarded. The composite average for all ten experiments done at $(H^+) = 0.73$ M and $(Br^-) = 0.05$ M is $k = 208 \pm 14\%$. If this is combined with the value $k = 138 \pm 10\%$ at $(H^+) = 0.93$ M and $(Br^-) = 0.05$ M, a value of $n = 1.7 \pm 0.9$ results, where $k = k'/(H^+)^n$. The large experimental error therefore masks the nature of the reacting ferrocyanide species.

A reasonable extrapolation of the value of K_3(10), where $K_3 = (H^+)(HFe(CN)_6^{---})/(H_2Fe(CN)_6^{=})$, from 10^{-3} at zero ionic strength to 1.8×10^{-2} at $\mu = 1.0$ by using the expression $\log_{10} f_x = - 0.50 z_x^2 \sqrt{\mu}/(1 + \sqrt{\mu})$, indicates that most of the ferrocyanide, at $(H^+) = 0.50 - 0.93$ M, is in solution as $H_2Fe(CN)_6^=$. An inverse acid dependence of 1.7 indicates that both $HFe(CN)_6^{---}$ and $Fe(CN)_6^{----}$ are the major reacting species; however, either one reacting alone would also fit the data within the experimental error.

BROMIDE ION DEPENDENCE

Table 5 shows that changing the (Br^-) from .05 to .15 M at $(H^+) = 0.73$ M does not change the rate constant. By raising the bromide ion concentration by a factor of 3, the bromine concentration was reduced by a factor of 2, while the tribromide ion concentration was increased by 58%. The independence of the rate on bromide ion concentration means that the rate constants, involving Br_2 and Br_3^- as the reacting species are about the same at $(H^+) = .73$ M; furthermore, this means that the reaction cannot involve HOBr, at the concentrations of hydrogen ion and bromide ion used, since the concentration of this species would be lowered by a factor of 6 when the (Br^-) was increased from 0.05 to 0.15 M.

In order to see whether Br_2 and Br_3^- reacted with the same species, three experiments were performed at $(H^+) = 0.50$ M and $(Br^-) = 0.05$, 0.10, and 0.15 M. Table 6 shows that varying the bromide ion concentration at this lower acidity also had no great effect on the rate constant.

The conclusion one reaches is that the rate determining step of reaction (1) can be expressed as some combination of the following reactions:

(3) $Br_2 + HFe(CN)_6^{-\,-\,-}$

(4) $Br_3^- + HFe(CN)_6^{-\,-\,-}$

(5) $Br_2 + Fe(CN)_6^{=\,=}$

(6) $Br_3^- + Fe(CN)_6^{=\,=}$

If Br atoms are involved as Wachholtz(3) suggested, then the following mechanism would probably prevail:

(7) $\Sigma\, Br_2 + \Sigma\, Fe(CN)_6^{-\,-} \rightleftharpoons Fe(CN)_6^{-\,-\,-} + Br_2^-$

(8) $Br_2^- + \Sigma\, Fe(CN)_6^{=\,=} \longrightarrow Fe(CN)_6^{-\,-\,-} + 2\, Br^-$

Table 7 shows the effect of added ferricyanide on k at constant initial bromine and ferrocyanide concentrations. The "inhibition" is apparently small, and in view of the large experimental error obtained in this investigation, the question of the reversibility of reaction (7) must be left as an unanswered problem.

ERRORS

Concentrations of the order of 3×10^{-6} F would have given half-times greater than three minutes under all experimental conditions. Unfortunately, an "instantaneous" oxidation of a small amount of ferrocyanide by an impurity in the perchloric acid prevented the use of these dilute solutions. The concentrations of bromine that were used required the use of $\lambda = 300\ m\mu$ to give the proper optical densities. Large corrections due to the optical density of the ferricyanide formed were necessary at this wavelength. The fact that the reaction was half over in 1 - 1 1/2 minutes in the experiments performed at the lower acidities, made the estimation of the zero time more critical.

TABLE 1

The Formal Extinction Coefficients* of Ferrocyanide Solutions $\sim 10^{-3}$ F in Acid and Neutral Solutions.

λ (mμ)	ϵ at (H^+) $\sim$ .9 F	ϵ at pH $\sim$ 6.5
260	956	2430
270	615	1710
280	421	1090
290	322	625
300	328	367
305	333	311
310	351	311
315	342	298
320	338	319
325	304	304
330	277	309
340	189	254
350	112	177
360	55	100
370	27	54

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[*] Reproducible to about ± 5%.

TABLE 2

Results at $(H^+) = 0.93$ M and $(Br^-) = 0.05$ M.

$(\Sigma\ Br_2)$	$(\Sigma\ Fe(CN)_6^{=\,=})$	k
(mole/liter x 10^6)		(liter/mole sec.)
7.33	28.35	143
8.21	23.72	119
8.10	34.50	144
10.25	8.78	138
10.15	18.66	163
10.15	30.00	*155
10.70	34.50	141
10.53	39.41	115
13.36	34.50	122

Average 138 ± 10%

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* See page 52.

TABLE 3

Results at $(H^+) = 0.50$ M and $(Br^-) = 0.05$ M.

(ΣBr_2)	$(\Sigma Fe(CN)_6^{\equiv\,=})$		k
(mole/liter x 10^6)			(liter/mole sec.)
9.40	10.35		*474
9.40	22.39		369
9.40	34.37		267
		Average	370 ± 19%
9.02	36.00		*329
9.17	34.90		276
12.21	36.00		302
15.31	36.00		279
		Average	297 ± 6%
8.64	18.00		573
12.04	18.00		389
15.05	18.00		424
		Average	462 ± 16%

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* See page 52.

TABLE 4

Results at $(H^+) = 0.73$ and $(Br^-) = 0.05$ M.

$(\Sigma\ Br_2)$	$(\Sigma\ Fe(CN)_6^{= =})$	k
(moles/liter x 10^6)		(liter/mole sec.)
8.14	35.00	205
8.80	33.50	209
8.84	39.00	245
10.62	35.00	159
13.41	35.00	168
		Average 197 ± 14%
8.08	15.70	233
9.21	14.80	238
12.31	14.80	*260
13.72	15.70	165
15.60	14.70	197
		Average 219 ± 14%

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* See page 52.

TABLE 5

Results at (H^+) = 0.73 M and Variable (Br^-).

(ΣBr_2)	$(\Sigma Fe(CN)_6^{\equiv})$	(Br^-)	k	Average k
(mole/liter x 10^6)		(mole/liter)	(liter/mole sec.)	
8.80	33.50	.05	*209	227 ± 8%
8.84	39.00	.05	245	
9.18	39.00	.10	203	208 ± 2.4%
9.55	33.50	.10	213	
8.86	33.50	.15	253	245 ± 3%
9.20	39.00	.15	237	
		Average	227 ± 8%	

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* See page 52.

TABLE 6

Results at $(H^+) = 0.50$ M and Variable (Br^-).

(ΣBr_2)	$(\Sigma Fe(CN)_6^{= =})$	(Br^-)	k
(mole/liter x 10^6)		(mole/liter)	(liter/mole sec.)
9.17	34.90	.05	*276
9.55	34.90	.10	*405
8.86	34.90	.15	*266
		Average	316 ± 19%

TABLE 7

Results at $(H^+) = .73$, $(Br^-) = 0.05$ M and Variable $(Fe(CN)_6^{- - -})_o$.

(ΣBr_2)	$(\Sigma Fe(CN)_6^{= =})$	$(Fe(CN)_6^{- - -})_o$	
(mole/liter x 10^6)			liter/mole sec.)
6.14	19.25	0.00	251
5.54	19.25	13.1	228
5.54	19.25	23.7	186

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* See page 52.

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PROPOSITIONS

1. The reaction between iodine and ferrocyanide ion should be reinvestigated by a spectrophotometric method. Saal's "anomolous" results(1) can be explained if both I_2Cl^- and I_2 are considered as reactants.

2. The high cross sections of certain metals for "slow" neutrons suggest a scheme for detecting these metals in the presence of the more common metals. For example, 0.5% indium in iron should be detectable by this method.(2)

3. The suggestion has been made that in reactions where P is very small, where $k = Pz \exp(-E/RT)$, as in the Menschutkin reaction, one might be able to bring P closer to unity if the very small dissociation constant of the alkyl halide is considered.(3) A method of testing this hypothesis is proposed.

4. (a) A method is suggested for determining the maximum difference in bond energy for $H \ldots O_2H$ and $H \ldots O_2$.
(b) Dainton and Collinson are quoted as stating(4) that by using H_2O^{18} they determined that the reaction $OH + H_2O_2 \rightarrow H_2O + HO_2$ is much faster than $OH + HO^*H \rightarrow HOH + O^*H$,

where the OH radicals are produced by the photolysis of H_2O_2. The proposal is made that any method using H_2O^{18} could not possibly reveal any information on that subject.

5. The failure of zinc to come down in its proper place in semi-micro qualitative analysis schemes should be fully studied by the use of radioactive zinc.

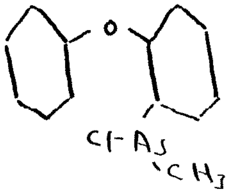
6. The air oxidation of ferrocyanide ion should be investigated as a function of pH. Qualitative observations indicate that the maximum formation of ferricyanide takes place at a pH that corresponds to a maximum $HFe(CN)_6^{---}$ concentration.(5)

7. Qualitative observations have been made on the complexing between titanium (IV) and hydrogen peroxide.(6) An interpretation of these observations is proposed. A program for research in the field of titanium complex ion formation is suggested.

8. The system iron (II), phosphate buffer should be investigated for complex ion formation by either a radioactive, ion-exchange method, or by a method involving

a change in pH. A complex formed in this system would explain the catalytic effect of phosphoric acid in the reaction between iron (II) and bromine.

9. Optical isomerism has been observed in tervalent arsenic when two of its bonds are part of a ring.(7) It is proposed that an arsenic compound such as



be tested for optical isomerism.

10. It is suggested that all graduate students read some of the papers presented in the first few volumes of the Royal Society of London, Philosophical Transactions.

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