THE KINETICS OF REDOX REACTIONS INVOLVING THIOSULPHATE

by

BRONISLAW LEON WEDZICHA

A THESIS
presented for the degree of
DOCTOR OF PHILOSOPHY
in the Faculty of Science of the
UNIVERSITY OF LONDON

Bedford College, London 1973

ProQuest LLC
789 East Eisenhower Parkway
P.O. Box 1346
Ann Arbor, MI 48106-1346

ABSTRACT.

The progress of the oxidation of thiosulphate by ferricyanide ion has been followed spectrophotometrically in buffered solution over the pH range 4 - 7. Tracer studies with ^{35}S showed the presence of polythionate as the major product of oxidation, some sulphate being formed when equivalent concentrations of the reactants were used. The reaction was found to be catalysed by tetrathionate, and kinetics in the absence of products were studied as initial rates. Two rate laws, both independent of ferricyanide, were found to apply. One of these, first order with respect to hydrogen and second order with respect to thiosulphate was shown to proceed by a mechanism which has previously been observed for the initial stages of the acid catalysed decomposition of thiosulphate. No detailed mechanism was proposed for the second contributor which appeared to be dominant at high cation concentration where the order with respect to hydrogen, thiosulphate and cation was one. In the later stages, the catalysed reaction was resolved by fitting rate-$[S_4O_6^{2-}]$ data to a second degree polynomial in tetrathionate concentration. This expression was found to be equivalent to a rate law of first order with respect to ferricyanide and tetrathionate ions, in agreement with previously reported work.

Kinetic data for the oxidation of thiosulphate by iodate and by bromate ions are presented, the former reaction showing catalysis by potassium and caesium ions but not sodium ion. The latter reaction, for which only a preliminary study was made, showed general acid catalysis.

Both processes gave rate laws, with respect to thiosulphate, hydrogen and halate ions, which were the same as those reported by previous authors and the observed results were explained in terms of well established mechanisms.

ACKNOWLEDGEMENTS.

I would like to thank Professor G. H. Williams for offering me a place in the Chemistry Department at Bedford College to carry out the work described in this thesis.

My thanks are also due to my supervisor, Dr. K. E. Howlett, for his constant help and encouragement, and for his assistance with the theoretical interpretation of the results.

I wish to thank the Technical Staff in the Department of Chemistry for their assistance during the course of the work.

Finally, I gratefully acknowledge a Science Research Council Studentship which made this work possible.

B.L.W.

CONTENTS.

The reaction between thiosulphate and ferricyanide ions.

The reaction between thiosulphate and halate ions.

SECTION I.

INTRODUCTION.

INTRODUCTION.

Thiosulphate ion has been widely used in aqueous solution as a reducing agent, its most well known reaction being, perhaps, that with iodine. Some of its reactions have been reviewed by Edwards (1).

General Considerations.

There are several apparently disconnected background pieces of evidence which ought to be considered before either the kinetic investigation is begun or any results interpreted.

The structure of the ion is of importance in a mechanistic problem. Sodium methylthiosulphonate ($Na(S{-}SO_3CH_3)$) has been examined by means of X-ray crystallography (2). The sulphur-oxygen bond lengths of 1.45 ± 0.02 Å are similar to the mean value of 1.49 Å measured for $CaSO_4.2H_2O$ (3). The sulphur-sulphur bond length was found to be 1.98 Å, close to 1.97 ± 0.06 Å reported for crystalline sodium thiosulphate pentahydrate.

The nature of the latter bond is of interest. Force constants obtained from measurements made with aqueous sodium thiosulphate solutions have suggested that the S-S bond possesses considerable double bond character.

There is some uncertainty as to the length of an S-S single bond. Abrahams has reviewed the stereochemistry of sulphur (4). Pauling proposed a value of 2.08 Å, whereas on oxidation of thiosulphate to tetrathionate the distance $S{-}SO_3$ changes from 1.97 Å to a mean value of 2.11 Å. A number of compounds S_2X_2 have bond lengths of 2.04 - 2.07 Å, whilst the length 2.21 Å in S_2F_{10} would be expected to correspond to an unusually long single bond by analogy with N_2F_4 because loss of electrons to fluorine is expected. 2.04 Å is found in S_8 but some double bond character is postulated here to account for the small heat of opening of the ring.

The double bond length is probably as in the S_2 molecule in the ground state, 1.89 Å. 50 - 60% double bond character is thus expected for the sulphur-sulphur bond in thiosulphate, somewhat less than the 90% estimated for the S-O bond.

The first and second dissociation constants (corrected to zero ionic strength and of course assigning unit activity for water) for thiosulphuric acid were determined at 25°C by Page (5).

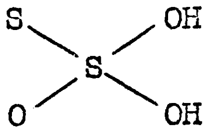
$$H_2O + H_2S_2O_3 \rightleftharpoons H_3O^+ + HS_2O_3^- \qquad K_1 = 0.25\text{ M.}$$

$$H_2O + HS_2O_3^- \rightleftharpoons H_3O^+ + S_2O_3^{2-} \qquad K_2 = 0.018\text{ M.}$$

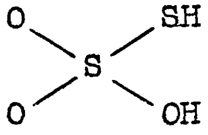
A comparison of the second dissociation constant (K_2) with that for sulphuric acid ($K_2 = 0.012$ M. at 25°C) shows that although $HS_2O_3^-$ is a slightly stronger acid than HSO_4^-, the two structures closely resemble each other.

There is no such agreement between the first dissociation constants. Page comments that dibasic acids with two equivalent ionising groups normally have first and second dissociation constants differing by a factor of about 10^5, so that both acids should have K_1 values of about 1000 if they have equivalent protons.

Two structures have been proposed for thiosulphuric acid:



(I)



(II)

the symmetric structure (I) in which the ionisable hydrogen atoms are both attached to oxygen atoms and the asymmetric structure (II) in which one hydrogen is attached to a sulphur atom. The evidence of the dissociation constants is therefore in favour of the unsymmetrical structure for thiosulphuric acid.

Bond measurements for thiosulphate suggest an equal contribution from each structure, but the asymmetric formula is strongly supported by studies on the formation of organic thiosulphates from thiols and chlorosulphonic acid. The highly coloured ferric thiosulphate complex ion is typical of the complexes formed between Fe^{3+} and compounds containing the thiol group.

The dissociation constants of phenol and thiophenol have been measured under similar conditions and the latter is the stronger acid by 3.3 units of pK. If thiosulphuric acid has the asymmetric formula, the usual empirical rules will not apply, since the two ionisable hydrogens are not equivalent, but the S-H bond should be preferentially broken.

A feature of multivalent ions is the ease with which they form ion pairs in solution with cations. Denney and Monk (6) measured the solubility of the sparingly soluble barium thiosulphate in a number of solutions of metal chlorides, in order to determine the dissociation constants of the thiosulphates of the corresponding cations. Sodium and potassium form ion pairs according to the equilibrium:

$$MS_2O_3^- \rightleftharpoons M^+ + S_2O_3^{2-}$$

while the bivalent cations studied form overall neutral ion paired species MS_2O_3. The latter were not applicable in the systems to be described as bivalent cations would lead to the precipitation of one or more components of reaction mixtures.

Davies (7) has pointed out that the mean ionic activity coefficients of many electrolytes in aqueous solution at 25°C can be represented over a considerable range of ionic strength by the equation:

$$-\log f_{\pm} = 0.505\, Z_1 Z_2 \frac{\sqrt{I}}{1 + \sqrt{I}} - 0.2\, I$$

where Z_1 and Z_2 are the magnitudes of the charges of the ions and I is the ionic strength in molarity terms. He further suggested that this relation was generally applicable, provided that the ionic strength was not too great; and later questioned whether 0.3 was not a better empirical constant than 0.2 in fitting the data.

Denney and Monk applied the original formula to their system. Dissociation constants were reported, corrected to zero ionic strength, as 0.12 and 0.21 M. for $KS_2O_3^-$ and $NaS_2O_3^-$ respectively.

These results were later used by Page in order to correct for the formation of NaS_2O_3 in his experiments to determine the stability constant for thiosulphuric acid (5). He assumed the Davies equation to be applicable even at ionic strengths as high as 0.9. The assumption seemed justified since calculated values for equilibrium constants at zero ionic strength,

$$K_0 = \frac{[H^+][S_2O_3^{2-}]}{[HS_2O_3^-]} f_2$$

(f_2 is the activity coefficient for a divalent ion) were close over the range of concentration studied.

Further the stability constants determined by Denney and Monk are in excellent agreement with conductance data of Jenkins and Monk (8) for the stability of ion pairs formed from the corresponding cations and sulphate. These were found to be 0.11 and 0.19 M. respectively.

The oxidation of thiosulphate is often accomplished in acidic media and kinetic investigations generally require the use of buffered solutions to "fix" the hydrogen ion concentration. The stabilities of free thiosulphate ion and of $HS_2O_3^-$ need consideration.

According to Sidgwick (9), thiosulphates are decomposed rapidly in acid solution to give sulphur, sulphite and other products including hydrogen sulphide and various polythionates. Above pH 5 the thiosulphate ion is present mainly as $S_2O_3^{2-}$ which is fairly stable but at higher hydrogen ion concentrations the unstable $HS_2O_3^-$ is formed which decomposes "immediately" and "irreversibly" according to:

$$HS_2O_3 \longrightarrow HSO_3^- + S$$

Stubbins (10) performed a number of experiments to check the stability of thiosulphate in acid solution. At pH 3.58 the decomposition for decimolar solutions was checked titrimetrically with iodine and found to be of the order of 1% in an hour. The infrared spectra of such decomposing solutions were recorded after precipitation with alcohol. It was shown that, under these conditions, over a period of twenty minutes, little, if any, sulphite was formed. Page (5) reached similar conclusions about the stability of thiosulphate in the acidic solutions he investigated.

The Reaction between Ferricyanide and Thiosulphate Ions.

The oxidation of thiosulphate by ferricyanide was shown by Sandved (11) to proceed at a measurable rate in aqueous solution.

Using a titrimetric technique to study the kinetics, Sandved and Holte (12) concluded that the reaction was of first order with respect to both reactants although the appropriate plots were not linear but S-shaped. The curved portions in the initial stages suggested that the reactants were involved in some sort of pre-equilibrium, a feature which was removed by the addition of ferricyanide ion. The acceleration towards the end of the reaction was traced to tetrathionate autocatalysis.

Batstone (13) discussed the significance of the ferricyanide-thiosulphate reaction in the Harcourt and Esson (14) technique for following the forward reaction between ferricyanide and iodide ion:

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

The equilibrium position for kinetically suitable mixtures is only some 2 - 10% to the right (15) and in order that the forward reaction may be followed, irreversible conditions must be approached. This is easily accomplished by the addition of thiosulphate to remove iodine as iodide ion. Further, if successive quantities of thiosulphate are added to the reaction mixture and the time lapse between each liberation of iodine, as indicated by starch, is observed, the progress of the reaction may be followed.

Clearly, the success of the method depends on the lack of any interaction, under the experimental conditions, between ferricyanide and thiosulphate ions. In view of the variability of reported results and since possible effects arising from the presence of tetrathionate ions do not appear to have been taken into consideration, Batstone (13) considered it desirable to investigate the ferricyanide-thiosulphate reaction further.

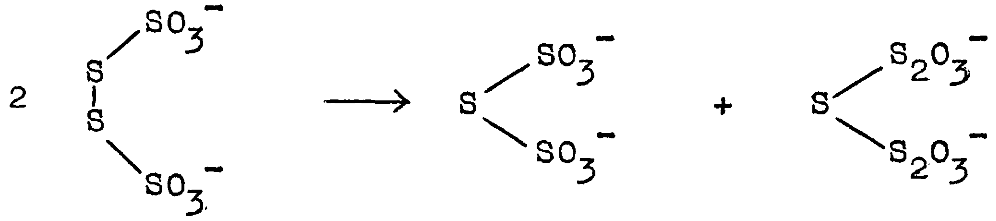
The results were in general agreement with those of Sandved and Holte (12). The reaction was found to be of first order with respect to the reactants over the pH range 7.4 - 11.2; the order with respect to hydrogen ion was one. The following mechanism was proposed as a qualitative though not completely quantitative explanation:

$$\begin{aligned}
HS_2O_3^- &+ Fe(CN)_6^{3-} \rightleftharpoons S_2O_3^- + HFe(CN)_6^{3-} \\
HS_4O_6^- &+ Fe(CN)_6^{3-} \rightleftharpoons S_4O_6^- + HFe(CN)_6^{3-} \\
S_4O_6^- &+ S_2O_3^{2-} \rightleftharpoons S_4O_6^{2-} + S_2O_3^- \\
&2\ S_2O_3^- \longrightarrow S_4O_6^{2-}
\end{aligned}$$

The accelerating and retarding effects of added tetrathionate and ferrocyanide were explained by this mechanism but at low pH values the rates of reaction were much less than those predicted from the rate equation. A large primary salt effect was observed.

The stoicheiometry of the reaction was determined by a method originally adopted by Sandved and Holte (12). Assuming the products to be ferrocyanide and tetrathionate alone, synthetic reaction mixtures, corresponding to various stages of completion, were prepared. When started these reactions proceeded at the rate expected for a normal kinetic run.

However, in neutral, weakly alkaline and weakly acidic solutions, tetrathionate undergoes a slow rearrangement into trithionate and pentathionate.



Nucleophilic displacements of sulphite groups from polythionates leading to the building up of higher polythionates have been considered by Foss (16) to be responsible for the generally accepted catalysed decomposition of tetrathionate.

In general:

$$\text{(i)} \quad S_nO_6^{2-} + S_2O_3^{2-} \rightleftharpoons S_{n+1}O_6^{2-} + SO_3^{2-}$$

$$\text{(ii)} \quad SO_3^{2-} + S_nO_6^{2-} \rightleftharpoons S_{n-1}O_6^{2-} + S_2O_3^{2-}$$

Normally, equilibrium (i) lies well to the left unless a reagent capable of removing sulphite ions is present or is added.

Foss and Kringlebotn (17) studied the reaction between thiosulphate and tetrathionate with added formaldehyde to remove sulphite as hydroxymethane sulphonate. Their results obeyed the following rate law:

$$-\frac{d[S_2O_3^{2-}]}{dt} = k\ [\text{Initial } S_4O_6^{2-}][S_2O_3^{2-}]$$

$k = 0.078\ M.^{-1}\ min^{-1}$ at 25°C and $I = 1.15$

$E = 12.0$ Kcal/mole

This rate law was interpreted by the following sequence of reactions:

$$S_4O_6^{2-} + S_2O_3^{2-} \xrightarrow{k_1} S_5O_6^{2-} + SO_3^{2-}$$
$$S_5O_6^{2-} + S_2O_3^{2-} \xrightarrow{k_2} S_6O_6^{2-} + SO_3^{2-}$$
$$S_6O_6^{2-} + S_2O_3^{2-} \xrightarrow{k_3} S_7O_6^{2-} + SO_3^{2-}$$
$$S_7O_6^{2-} + \ldots\ldots$$

where k_1, k_2, ..., k_n are all of similar value.

$$-\frac{d[S_2O_3^{2-}]}{dt} == k\ [S_2O_3^{2-}]([S_4O_6^{2-}] + [S_5O_6^{2-}] + \ldots)$$

hence, $\text{rate} = k\ [S_2O_3^{2-}][\text{Total polythionate}]$

For any run the ratios of concentrations of S_n polythionate products after some 20% reaction has occurred,

$$S_4 : S_5 : S_6 : S_7$$

were calculated as 1.0 : 0.2 : 0.02 : 0.0013.

Dithionate was found not to react under these conditions and the bimolecular rate constant for the reaction with trithionate showed a somewhat lower value of $0.0066\ M.^{-1}\ min^{-1}$.

The reaction between hydrogen sulphite and thiosulphate has been shown to occur (18):

$$4\ HSO_3^- + S_2O_3^{2-} + 2\ H^+ \longrightarrow S_3O_6^{2-} + 3\ H_2O$$

$$\text{with} \quad -\frac{d[HSO_3^-]}{dt} = k\ [HSO_3^-][S_2O_3^{2-}]^3\ [H^+]^3$$

but at 70°C and pH 3.6 - 4.1 it is slow, so that one can regard it as an unlikely contributor to the above system under the near neutral conditions normally used.

If, in a redox system, the reactivity of sulphite and of thiosulphate towards a particular oxidising agent is known, the contribution of the displacement of sulphite from polythionates to the rate of loss of oxidising agent can be determined. Sandved and Holte (12) suggested for the autocatalysis by tetrathionate a mechanism similar to that implied by the reaction involving k_1 above. They argued that this would be so provided that the reactivity of the hydrogen sulphite ion towards ferricyanide was not less than one half of that of thiosulphate.

The reaction between ferricyanide and sulphite has been examined by Swinehart (19) under a variety of conditions. The rate law was found to be as follows:

$$\text{Rate} = k\ [Fe(CN)_6^{3-}][SO_3^{2-}][M^+]$$

where, for I $\simeq$ 0.1 - 0.7 at 25°C

if $M^+ = Na^+$ $\quad k = 30\ M.^{-2}\ min^{-1}$

$E = 11.7 \pm 1.0$ Kcal/mole

$M^+ = K^+$ $\quad k = 72\ M.^{-2}\ min^{-1}$

$E = 12.6 \pm 1.0$ Kcal/mole

The major sulphur containing products were found as dithionate or sulphate according to the experimental conditions.

So far the kinetics of the ferricyanide-thiosulphate reaction have been analysed as rate constants in the region where the second order rate law appeared to apply. Here the product tetrathionate or perhaps more accurately, polythionate, is present to some extent so the apparent rate is a combination of catalysed and uncatalysed processes. Perhaps a more satisfactory solution is to interpret the concentration-time data over as much of the course of reaction as possible, in terms of a two or more term expression.

This policy was adopted by Spiro and Barreira (20) who, in order to avoid the analytical complications inherent in the titrimetric methods of the previous authors (12,13) followed the reaction spectrophotometrically by measuring the absorbance due to ferricyanide ion at 23,810 cm^{-1} where it has a molar extinction coefficient of 1020 M^{-1} cm^{-1}.

The direct reaction between the two reagents was found to be of first order with respect to thiosulphate and of half order with respect to ferricyanide. A complex term was devised to include the apparent retardation due to ferrocyanide:

$$\frac{-d[Fe(CN)_6^{3-}]}{dt} = \frac{k_1\ [Fe(CN)_6^{3-}][S_2O_3^{2-}]}{[Fe(CN)_6^{3-}]^{\frac{1}{2}} + k_1'\ [Fe(CN)_6^{4-}]^{\frac{1}{2}}}$$

The catalytic effect of tetrathionate was resolved as the sum of two terms, the first being applicable at higher concentrations, the second at lower concentrations.

$$\frac{-d[Fe(CN)_6^{3-}]}{dt} = k_2\ [S_4O_6^{2-}]^{\frac{1}{2}}[S_2O_3^{2-}] + k_3\ [S_4O_6^{2-}][S_2O_3^{2-}]$$

The tetrathionate terms were independent of hydrogen ion concentration whereas the primary reaction showed an acceleration with rising acidity by a factor of $[H^+]^{\frac{1}{6}}$. The addition of EDTA (ethylenediaminetetraacetic acid) resulted in a marked increase in rate.

The variability in the results reported by different authors shows that a reinvestigation of the kinetics of the ferricyanide-thiosulphate reaction is desirable.

A primary objective should be to isolate the rate expression corresponding to the direct reaction between ferricyanide and thiosulphate. Since complications arise from the presence of products, measurement of initial rates should afford a solution. Many spectrophotometers are now equipped with chart expansion facilities which should enable accurate measurements to be made over the first few percent of reaction.

A detailed identification of products should furnish some evidence, which may support further kinetic investigations, regarding the autocatalysis by tetrathionate.

The Oxidation of Thiosulphate by Halate Ion.

Oxyanion Oxidations.

Edwards has reviewed a number of mechanistic features common to oxyanion oxidations (21).

The rates of oxyanion reactions are markedly dependent on acid concentration. This is true both for replacement reactions such as oxygen exchange with solvent water and for redox reactions. Presumably the role of the proton is to labilise oxygen by converting it from oxide ion into hydroxide ion and on to water. The addition of protons to an oxide ion in an oxyanion should make it easier to break the bond between the oxygen and the central atom. There is a close correlation between replacement and redox reaction rates.

The only replacement process involving oxyanions for which there is adequate data is the exchange of oxygen atoms with water. The rate law for the exchange is:

$$\text{Rate} = k\,[XO_m{}^{n-}][H^+]^2$$

but for the larger central atoms in low oxidation states an expression of first order with respect to hydrogen ion is applicable.

The rate of exchange is primarily a function of the oxidation state of the central atom, the rate increasing with increase in oxidation number. However, for a set of oxyanions with the central atom in the same oxidation state, as in the halates, the size of the halogen will be the deciding factor. Thus iodate exchanges faster than chlorate. The same trend is observed in the rates of oxidations by these species and may be explained if replacement by the reducing agent in the coordination sphere of the oxyanion is an important pre-requisite to electron transfer. If the removal of an oxide ion out of an oxyanion coordination sphere is an important part of the energetics of the reaction then the influences of central atom charge and size and of acidity on rate are readily understood.

The hydrogen ion dependence is known to involve a protonation before the rate determining step because, in D_2O, the reaction has always been found to be faster than in H_2O. If protonation in the transition state was occurring the rate should be slower in D_2O than in H_2O. The more rapid rate is observed because D_3O^+ in D_2O is a stronger acid than H_3O^+ in H_2O. It is found that the rate of oxygen exchange between bromate and water is faster in D_2O than in H_2O and it is likely that most oxyanion rates of replacement follow this example. A similar solvent isotope effect is expected in redox reactions if replacement is an important aspect of the mechanism.

The Bromate-Thiosulphate Reaction.

In a previous review (1) Edwards discussed the mechanism of the oxidation of thiosulphate by bromate ion.

The rate of change of pH with reaction was measured in phthalate buffers over the range pH 4.1 - 6.5 and results showed that the reaction is of first order with respect to bromate ion, thiosulphate and hydrogen ion. It was found that inert salts lowered the rate of reaction but the kinetics did not correspond to the general mechanisms known for bromate oxidations.

The Iodate-Thiosulphate Reaction.

The oxidation of thiosulphate by iodate can be represented by the following stoicheiometry:

$$6\,H^+ + IO_3^- + 6\,S_2O_3^{2-} \longrightarrow 3\,H_2O + I^- + 3\,S_4O_6^{2-}$$

Reider (22) has measured initial rates for the reaction by a titrimetric method, following the rate of disappearance of hydrogen ion. The measurements were carried out in buffered solution and the following rate law was proposed:

$$\text{Rate} = k\,[IO_3^-]\,[H^+]^2\,[S_2O_3^{2-}]^2$$

Acetate buffers were used with salt concentration in hundredfold excess over acid to bring the hydrogen ion concentration to a suitable value for convenient rate measurements. This concentration was calculated from the following expression:

$$H^+ = 1.85 \times 10^{-5} \frac{[CH_3COOH]}{[CH_3COONa]}$$

Such a formula, however, is normally applicable only at pH close to the pK of the acid in question (4.7 for acetic acid) and calculations under the conditions stated cannot be undertaken with certainty. This is especially valid in this case where the rate is apparently very sensitive to hydrogen ion concentration.

Edwards (1) has suggested the following mechanism:

$$IO_3^- + 2\,H^+ \rightleftharpoons H_2IO_3^+ \qquad \text{(fast)}$$

$$H_2IO_3^+ + S_2O_3^{2-} \rightleftharpoons O_2I.S_2O_3^- + H_2O \qquad \text{(fast)}$$

$$O_2I.S_2O_3^- + S_2O_3^{2-} \longrightarrow IO_2^- + S_4O_6^{2-} \qquad \text{(rate determining)}$$

He further reports that measurements of pH-time curves showed the processes after the rate determining step to be by no means instantaneous.

The experimental results for kinetics of the oxidation of thiosulphate by bromate and by iodate are surrounded by an element of doubt. In one instance the kinetics are not related to a reliably known hydrogen ion concentration. In another the indirect method of pH measurement is employed to follow the progress of the reaction. It is well known that many redox systems are catalysed by the presence of conducting surfaces, and the introduction of an electrode for pH measurements may have such an effect.

Further work on both systems is desirable but an emphasis should be placed on the use of direct analytical techniques to measure the rate.

SECTION II.

THE REACTION BETWEEN FERRICYANIDE AND THIOSULPHATE IONS.

EXPERIMENTAL RESULTS.

Purity of Materials.

Whenever possible "Analar" grade reagents were used without further purification. Solutions of potassium ferricyanide were prepared by weight and used without standardisation.

Potassium thiosulphate (96%) was recrystallised twice from water made slightly alkaline with potassium hydroxide. Sulphur was found to be the major impurity. The product was dried in vacuo and its purity was determined iodimetrically. Analyses showed not less than 99.7% $K_2S_2O_3$.

Solutions of sodium and potassium acetate were prepared by neutralising standard N alkali with reagent grade glacial acetic acid. The former was prepared by dilution of "Volucon" standard volumetric concentrates, supplied by May and Baker Ltd., Dagenham.

Preparation of Thiosulphate Solutions.

Aqueous thiosulphate solutions of concentration above about 0.05 M. tend to decompose slowly depositing sulphur. If the solution is made slightly alkaline the rate of decomposition is reduced. Dissolved oxygen accelerates the reaction and solutions made up with conductivity water in an inert atmosphere tend to be more stable.

The usual procedure for making up thiosulphate solutions was to add to the weighed solid sufficient sodium tetraborate to make the solution 5×10^{-4} M. in borax and to make up to the mark with conductivity water under nitrogen. The concentration was checked by titration against potassium iodate.

When used for kinetic studies the reagent was discarded after two days although solutions remained stable for many weeks.

Preparation of Potassium Ferricyanide Solutions.

Solutions of potassium ferricyanide were prepared immediately before use. This was to eliminate any complications which may arise following the displacement of cyanide ion by water. Indeed, after several days, solutions were found to smell distinctly of cyanide.

Determination of the Products of Reaction.

It was considered that the most likely reaction products for the oxidation of thiosulphate by ferricyanide would be sulphate and various polythionates, on the following grounds:

(a) Previous workers (12,13,20) have reported finding tetrathionate as the only oxidation product in agreement with the accepted generalisation (23) that thiosulphate is oxidised to sulphate by strong oxidising agents and to tetrathionate by weaker ones. The reaction of thiosulphate with ferric ion gives tetrathionate alone (24).

(b) Foss (17) has shown that tetrathionate can undergo reaction with thiosulphate producing sulphite and higher polythionates which may subsequently disproportionate. The oxidation of sulphite by ferricyanide yields sulphate and dithionate (19).

Radiochemical Method using ^{35}S.

If thiosulphate ion, labelled with sulphur-35, is used for reaction then the products will be active to an extent dependent on their respective concentrations and, perhaps, sometimes upon which S-atom is labelled.

Ames and Willard (25) have shown that the two sulphur atoms of thiosulphate are chemically non equivalent and that exchange between the two positions does not occur. Consequently, if thiosulphate is used with one or other of the sulphur atoms labelled, the fate of that particular atom during the course of reaction may be determined. It was decided to use the sodium salt which had ^{35}S as the inner sulphur atom.

Sulphur-35 is a weak beta emitter of energy similar to carbon-14. These nuclides can conveniently be counted using liquid scintillation techniques.

Description of the Counting Apparatus.

The equipment used was an Ecko "Universal" Scintillation Counter (type N664A) which is a shielded instrument for "in vitro" counting of beta and gamma emitters. The counter comprises a thirteen stage photomultiplier tube which, together with a source coupling unit, is contained in a lead shield. The assembly is mounted in a steel case together with a wideband amplifier. The source coupling unit incorporates a light proof shutter and a spring loaded carrier to hold the pyrex sample vessels. To improve light collection a liquid coupling medium (silicone oil) is used between the sample container and the tube face. The unit was used in conjunction with an Ecko Automatic Scaler (type N530G) which also provided stabilised voltage supplies for the counter.

Principle of Operation.

Light emitted as a result of beta particle interaction with the phosphor is allowed to fall onto the target of the photomultiplier tube where it causes the release of electrons. This current is multiplied within the tube and observed at the collector as an electrical impulse of amplitude proportional to the energy exchange between the beta ray and the phosphor. The output is processed by the wideband amplifier, the gain of which may be adjusted to give the best signal-to-noise ratio for the output to the scaler. The Ecko N530G incorporates an amplitude discriminator which will only pass input pulses above a set level, continuously variable between 5 and 50 volts, thereby eliminating the greater part of the thermal noise pulses, although the high energy background will still be recorded.

Selection of a Suitable Phosphor Mixture.

The products of the reaction between Cr(VI) and thiosulphate have been examined by a radiochemical technique (10) using thiosulphate with outer sulphur atom labelled. The products were sulphate and tetrathionate.

Difficulty was encountered in optimising counting efficiency and homogeneity of the solution to be counted. Consistent results were obtained by mixing aqueous solutions 1:20 with the dioxan-based "220" phosphor supplied by Nuclear Enterprises Ltd, or 1:40 with a naphthalene-PPO-POPOP mixture in xylene-dioxan-ethanol. A 1:20 mixture with naphthalene-PPO-POPOP in dioxan to which was added 10% water was found to be effective and used with success for the counting of aqueous solutions.

The dioxan-based phosphor was used in the current work. 1 g. PPO, 0.025 g. POPOP and 12.5 g. scintillation grade naphthalene were added to a freshly opened 250 ml. bottle of dioxan (AnalaR grade). Nitrogen was bubbled through the solution, the bottle was sealed and mechanically shaken for an hour. The phosphor was stored under nitrogen in a sealed dark bottle.

Preparation of Stock ^{35}S Labelled Thiosulphate Solution.

The radioactive thiosulphate solution was prepared by dissolving in 50 ml. water, made slightly alkaline with borax (pH 9), 11 mg. sodium thiosulphate with inner sulphur atom labelled and having a specific activity of 15.7 mCi/mM. The solution had an activity of 20 uCi/ml. when work commenced.

Preparation of Mixtures for Counting.

"Ecko" coated pyrex containers (N617A) were used to hold the sample for counting. 20 ml. of the phosphor solution was transferred by means of a pipette into the sample container followed by 2 ml. water and 1 ml. of the solution under test. Since dissolved oxygen has been known to exhibit a strong quenching effect, the solution was degassed and stirred by passing nitrogen for two minutes before sealing the container. The phosphor was allowed to dark adapt for one hour, inside the instrument, prior to counting.

Selection of Optimum Working Conditions.

The best working conditions of any counter are those which give the activity of any sample to a given accuracy in the shortest time. If Rs is the count rate from the sample alone and Rb is the background count rate, it can be shown that these optimum conditions occur when Rs^2/Rb is a maximum. The variables under the control of the operator, which influence this ratio, are

(a) Photomultiplier dynode potential (HV)

(b) The amplifier gain

(c) The pulse height discriminator voltage (DB).

A set of observations for the total (Rt) and background count rates was made as a function of the photomultiplier dynode voltage at various amplifier gain settings. Graphs of Rs^2/Rb vs. HV were plotted (Rs = Rt - Rb). Table 1 summarises the results obtained from the curves, which indicate that the best settings for the two variables were:

Gain = 100;   HV = 1185 volts.

Table 1.

Variation of Efficiency with Dynode Potential.

Discriminator bias = 5 volts.

Gain	Rs^2/Rb max.	HV at max.
25	180,000	1375 V.
50	250,000	1250 V.
100	$\rangle\rangle$ 250,000	1185 V.
250	100,000	1125 V.
500	-	$\langle$ 1000 V.
1000	-	$\langle$ 1000 V.

The optimum setting for the discriminator bias was found by measuring the total and background count rates as a function of discriminator bias, the other variables being held constant at their optimum values. A curve of Rs^2/Rb vs. DB showed a broad maximum at ~~db~~ DB = 5 volts, which was taken as the best value.

It should be noted that, since a scintillation counter is an energy dependent device, the operating conditions for maximum Rs^2/Rb will differ and must be established separately for different isotopes, but once set are independent of the activity present.

To Test the Proportionality between Count Rate and Dilution.

The stock active thiosulphate (20 uCi/ml.) was diluted so as to prepare four solutions with activities over the range 1 - 10 nCi/ml. 1000 second counts were recorded for 1 ml. samples and table 2 shows that the count rate was proportional to the concentration of active species.

The maximum count rate was 163 c.p.s. and under the conditions of the experiment the counting efficiency was found to be 47%.

Table 2.

Isotope Dilution.

Dilution	Total count per 1000 sec.	Count above background	10^{-6} X count X dilution
20,000	18,487	17,970	359.4
10,000	33,732	33,215	332.2
4,000	90,960	90,443	361.8
2,000	164,057	163,540	327.1

Isotope Dilution for Quantitative Product Analysis.

If to a solution containing a radioactively labelled ion is added a large excess (50:1) of the inactive salt, then the activity originally present will be diluted by the additive. The extent of this dilution is dependent on the ratio:

$$\frac{M + m}{m} \sim \frac{M}{m} \qquad \text{if } M \gg m$$

where M is the weight in grams of the inactive salt added to m grams of labelled species originally present in the sample.

Some of the salt may be recovered by partial crystallisation or precipitation. If the specific activity (that is, the activity per gram) of the product is determined, then the activity originally present in the sample may be calculated. If on the other hand, the activity of the sample is known then its weight, or concentration may be found.

This technique may be used to determine the concentration of a particular component in a mixture so long as two conditions are fulfilled:

First, the partial crystallisation or precipitation of an added salt should, on subsequent recrystallisation, yield a product free from any contaminants. Subsidiary experiments have shown (10) that when potassium sulphate, dithionate or tetrathionate were separately dissolved in mixtures possibly containing all three species, the infrared spectrum of the recovered material was identical with that of an authentic specimen.

Secondly, the exchange of radioactive label involving any of the species to be analysed should not be observable. It has been shown (26) that labelled sulphur atoms are rapidly exchanged at 60°C from both sulphide and sulphite positions between tri- and tetrathionate and between tetra- and pentathionate. After 2 hours at 60°C no exchange was observed between di- and trithionate.

Consequently the possibility of a quantitative determination of polythionates from mixtures is impossible by this method. However, it was considered worthwhile to measure the amounts (if any) of sulphate, dithionate and "tetrathionate" produced during the reaction. The last would, as a result of exchange, reflect the total polythionate concentration rather than that of itself.

Potassium salts were used throughout as they readily crystallise with no water of crystallisation. Samples of potassium salts of di- and tetrathionic acids were prepared as described in Appendix 1.

Reaction Mixture.

It was considered that the number of sulphur containing species in the product mixture should be kept to a minimum. Consequently, the reaction mixtures were prepared containing a slight excess of ferricyanide in order that all the thiosulphate might be consumed.

$$[K_2S_2O_3] = 0.045 \text{ M}; \quad [K_3Fe(CN)_6] = 0.046 \text{ M}.$$

The total volume was 50 ml. The mixture included 2 ml. stock active thiosulphate and hydrogen ion was supplied by an acetic acid/potassium acetate buffer at pH 5.1 Mixtures were allowed to react at 25°C for 24 hours.

Initial Treatment of Reaction Mixtures.

Preliminary experiments showed that the addition of potassium tetrathionate to the reacted mixture yields an intense blue colouration on warming and crystals obtained by partial precipitation with alcohol are green in colour.

This was attributed to the replacement of one or more cyanide groups from ferrocyanide by tetrathionate. Complexes of this type have been proposed to explain the appearance of a blue colour towards the end of a number of ferricyanide oxidations. These include the reaction with sulphite (19) and with thiosulphate (20). Therefore it is important to remove both ferri- and ferrocyanide before the solution can be analysed for products. Precipitation as the cupric compound offers an efficient method.

Into each of two 35 ml. capacity centrifuge tubes, fitted with ground glass stoppers, were placed 20 ml. of the reacted mixture followed by 10 ml. 0.2 M. cupric acetate solution. The tubes were shaken for several minutes and the precipitate was removed in a centrifuge at 1500 r.p.m. Finally, the solution was filtered to remove last traces of solid. Since copper is expected to interfere in much the same way as iron, excess cupric ion was removed by precipitation as the hydroxide. Each of two 20 ml. portions of filtrate were treated with 2 ml. 10% potassium hydroxide solution and the blue precipitate removed in a centrifuge at 1500 r.p.m. After filtration, the solution, 10 ml. of which were equivalent to not more than 0.1 ml. 0.01 M iodine, was used in the analysis for products.

Extraction of Products.

To individual 5 ml. portions of reaction mixture, treated to remove the iron containing species, was added about 1 g. potassium sulphate, dithionate or tetrathionate. The mixtures were warmed to 50°C and if necessary, water was added to dissolve the solid. Alcohol was added dropwise until a slight turbidity became apparent, at which stage the solution was allowed to stand for crystallisation to occur, finally cooling in ice. The crystals were filtered on a Hirsch funnel and recrystallised from warm aqueous ethanol. The product was dried at 50° over CaO in vacuo.

The dried material was used to prepare solutions for counting. Weights shown in tables 3 and 5 are those per 250 ml. of solution, although in many instances smaller volumes were prepared.

Commenting on the results shown in table 3, we can say that no dithionate was present in the reaction mixture. The activity observed as sulphate amounted to about 6% and the total recovered accounted for 72% of that put in.

The procedure adopted for the removal of the iron containing products resulted in a 4% loss of activity.

Table 3.

Analysis of Reaction Mixtures.

Background = 3773 counts/3000 sec.

Species		Wt. added to 5 ml. extract*	Wt/250 ml. for counting	3000 sec count	Due to sample	10^{-6} X activity in rxn.
SO_4^{2-}	I	1.093 g.	0.1563 g.	4,371	598	17.2
	II	1.031 g.	0.1530 g.	4,434	661	18.4
$S_2O_6^{2-}$	I	1.002 g.	0.1965 g.	3,753	-	-
	II	1.025 g.	0.2316 g.	3,853	-	-
$S_4O_6^{2-}$	I	1.368 g.	0.8910 g.	34,774	31,001	196.3
	II	1.023 g.	0.0625 g.	6,559	2,786	188.1

Sample	Dilution	3000 sec count	Due to sample	10^{-6} X activity in rxn.
1 ml. stock active thiosulphate	1,000	149,891	146,118	292.2
1 ml. extract*	500	10,556	6,783	279.8

* The extract is the reacted mixture after treatment to remove iron containing species.

To Test for Sulphur in the Iron Containing Products.

Precipitates of Cu(II) ferri- and ferrocyanide were washed free from any adsorbed sulphur containing species by suspending in 10% sodium perchlorate solution. The solid was removed in a centrifuge.

Thin films were deposited on planchets by allowing the water from several drops of a suspension to evaporate under an infrared lamp. For counting, samples were held close to the face of an "end on" Geiger Muller tube, especially suited for the counting of a and low energy B particles.

The results (table 4) show that no activity was present in the precipitated iron cyanides.

Table 4.

Analysis of Precipitates.

18,000 sec counts.

Background		4,401
Thin film	I	4,352
	II	4,475

To Test the Isotope Dilution Technique.

In view of the low recovery of ^{35}S it was decided to check the efficiency of the isotope dilution technique.

Reaction mixtures were prepared as before but in place of ferricyanide the exact amount of iodine required for equivalence was added. Under these conditions thiosulphate is quantitatively oxidised to tetrathionate (27). The mixture was diluted by a factor of 1.65 with water containing 2 ml. 10% potassium hydroxide. The resulting solution was similar to those used for the analysis of products.

The results (table 5) show complete recovery of tetrathionate activity but none was found in the recrystallised sulphate.

Table 5.

Control Experiments.

Background = 3773 counts/3000 sec.

Total activity present = 292.2×10^6 counts/3000 sec.

Species		Wt. added to 5 ml. soln.	Wt/250 ml. for counting	3000 sec count	Due to sample	10^{-6} X total activity
SO_4^{2-}	I	1.225 g.	0.1319 g.	3,781	-	-
	II	1.014 g.	0.1369 g.	3,742	-	-
$S_4O_6^{2-}$	I	1.721 g.	1.2390 g.	54,776	51,003	292.2
	II	1.926 g.	1.4715 g.	54,890	51,117	276.0

Discussion.

A rough estimate of the "active" thiosulphate suggests that, at the time of the experiment, about 1 in 1000 moles contain ^{35}S. Thus when thiosulphate is oxidised to tetrathionate the vast majority of active tetrathionate contains one ^{35}S atom presumably as $*SO_3-S-S-SO_3$.

Foss (17) suggests that

$$S_nO_6^{2-} + S_2O_3^{2-} \rightleftharpoons S_{n+1}O_6^{2-} + SO_3^{2-}$$

can occur with equlibrium lying well to the left, if undisturbed.

One might need to notice a distinction in the reaction conditions between those used for kinetic purposes and those used for radiochemistry experiments. Since we tend to use dilute solutions and the reverse reaction could be fast compared with the forward one, there will tend to be little removal of $S_nO_6^{2-}$ by thiosulphate (a) because of the reversibility and (b) because solvent cages will tend to make $S_{n+1}O_6^{2-}$ and SO_3^{2-} react together again rather than allowing sulphite to separate and be removed in some other way.

The forward reaction between thiosulphate and tetrathionate can be written to involve a variety of active and inactive partners.

If S_n represents a polythionate $S_nO_6^{2-}$

$$\begin{array}{llclcl}
\text{(I)} & S\text{-}SO_3^{2-} & + & S_4 & \longrightarrow & S_5 + SO_3^{2-} \\
\text{(II)} & S\text{-}{*SO_3^{2-}} & + & S_4 & \longrightarrow & {*S}\text{-}S_4 + SO_3^{2-} \\
\text{(III)} & S\text{-}SO_3^{2-} & + & {*S}\text{-}S_3 & \longrightarrow & {*S}\text{-}S_4 + SO_3^{2-} \\
 & & & & \searrow & S_5 + {*SO_3^{2-}} \\
\text{(IV)} & S\text{-}{*SO_3^{2-}} & + & {*S}\text{-}S_3 & \longrightarrow & {*S}\text{-}S_4 + {*SO_3^{2-}} \\
 & & & & \searrow & {*S}\text{-}S_3\text{-}S{*} + SO_3^{2-}
\end{array}$$

Of these (IV) will be negligible by a factor of 1 to 1000 compared with (II) and (III). Since the fate of the labelled sulphur is being sought encounters where both species are inactive may be ignored. The latter are present as diluents and hence only reactions (II) and (III) need be considered. All rate constants will be the same but it does not follow that the rates will be equal. When thiosulphate is oxidised to tetrathionate the same proportion of the product will be active as of reactant, that is, 1 in 1000 moles will be $*S\text{-}S_3$.

$$\text{Rate(II)} = k\,\frac{[S_2O_3^{2-}]}{1000}[S_4]$$

$$\text{Rate(III)} = k\,[S_2O_3^{2-}]\frac{[S_4]}{1000}$$

In other words the two rates will be the same and therefore both processes will be equally probable. One quarter of the sulphite formed in this way will be active.

Suppose that $S_{n+1}O_6^{2-}$ and SO_3^{2-} do separate and that the latter has a chance of reacting with pentathionate ion. The only source of the two species are reactions (II) and (III) when the radioactive label is distributed between pentathionate and sulphite in the ratio 3:1.

$$\begin{array}{llcllcl}
\text{(V)} & {}^*SO_3^{2-} & + & S_5 & \longrightarrow & {}^*S\text{-}S_3 & + \; S\text{-}SO_3^{2-} \\
\text{(VI)} & SO_3^{2-} & + & {}^*S\text{-}S_4 & \longrightarrow & {}^*S\text{-}S_3 & + \; S\text{-}SO_3^{2-} \\
 & & & & \searrow & S_4 & + \; S\text{-}{}^*SO_3^{2-}
\end{array}$$

Rate equations may be written,

$$\text{Rate(V)} = k \frac{[S\,O_3^{2-}][S_5]}{4000}$$

$$\text{Rate(VI)} = k\,[S\,O_3^{2-}]\,\frac{3[S_5]}{4000}$$

hence 3/4 of the overall change will go through (VI). In this way, upon reversal of reactions (II) and (III) only 3/8 of the activity will be returned as thiosulphate and 5/8 as tetrathionate. This represents a slight enrichment of tetrathionate activity. If the calculation for the forward reaction is repeated it will be found that sulphite will now contain 5/16 of the label, close to the limiting value of 1/3 expected after continued exchange. In practice, owing to the high dilution of the radioactive species, this situation would only be reached if the exchange was very fast. This is not so.

Subsequent reactions of S_5 or of higher polythionates with thiosulphate correspond to the propagating mechanism proposed by Foss and may be represented by reactions (II) and (III) if S_4 is replaced by the general polythionate S_n.

Two limiting situations must be considered for the initial step already discussed, (a) if no reversal has occurred and pentathionate activity is therefore 3/4 of its concentration and (b) if repeated exchange has reduced this ratio to 2/3.

In the first case

$$\frac{\text{Rate(II)}}{\text{Rate(III)}} = \frac{1}{3}$$

and hence 3/4 of the reaction will go by way of (III) to give a product in which SO_3^{2-} will contain 3/8 of the activity, the remaining 5/8 being found as S_5. If the reverse of this reaction occurs then a 1:2 distribution of the label between the two species respectively will eventually be reached.

In the second case

$$\frac{\text{Rate(II)}}{\text{Rate(III)}} = \frac{1}{2}$$

and the products would correspond to those obtained after prolonged exchange. In this case the reverse reaction is of no consequence.

According to Foss after about 20% sulphite has been produced the ratio of S_n polythionates

$$S_4 : S_5 : S_6 : S_7$$

is $\quad 1.0 : 0.2 : 0.02 : 0.0013$

and polythionates higher than S_6 are not expected to make a significant contribution.

One further consideration is required. If tetrathionate is allowed to react with sulphite then the product will be trithionate. Foss has shown that the rate constant for the reaction of the latter with thiosulphate is one power of ten smaller than that for reactions of the higher polythionates. So, from the point of view of acting as a source of sulphite groups, or higher polythionates, trithionate may be considered inert. It will, however, be formed nearly two thirds labelled.

Turning now to consider the course of the reaction in the presence of ferricyanide ion. The oxidation of sulphite by ferricyanide has been investigated by Swinehart (19). He found that if the latter was in excess, the major product was sulphate. This condition was satisfied in the present investigation and indeed no dithionate was detected.

The amount of radioactive sulphur appearing as sulphate depends on two factors.

First, on the contribution that the "tetrathionate catalysed" reaction makes towards the overall rate of loss of reactants in the ferricyanide-thiosulphate reaction. Foss has found that after 20% of the thiosulphate has reacted with tetrathionate the products began to decompose liberating sulphur. No sulphur was deposited in the reaction studied, so the contribution is not expected to be more than some 20%.

Secondly, but to a lesser extent, the amount of radioactive sulphate produced will depend on the competition between ferricyanide and polythionate for SO_3^{2-}. If polythionate is the better reactant then 1/3 of the activity will eventually end up as sulphate. Otherwise 1/4 - 1/3 will be a more realistic figure.

About 6% of the total activity was found as sulphate. Since every act of sulphite formation leads to the production of a polythionate S_5 or higher then some 12 - 18% of the activity will be present as higher polythionates. In the lower limiting case the remaining sulphur containing products will be trithionate and tetrathionate, the sum of their activities amounting to 82% of the total. In the other instance tetrathionate will be the only product. The activities of each polythionate will be nearly proportional to the molar concentration, so we can write,

$$\frac{[S_3] + [S_4]}{[S_5] + \dots} = \frac{82}{12} \sim 6.8$$

or $$\frac{[S_4]}{[S_5] + \dots} = \frac{76}{18} \sim 4.2$$

The activity due to tetrathionate was found to be 66% but this figure could be high owing to exchange during the extraction procedure. The efficiency of the technique was checked. It can only be concluded that not more than 66% of the activity, but somewhat less, was present as tetrathionate. The situation is therefore perhaps nearer the first limiting case.

The analysis figures for sulphate show that about 18% of the overall ferricyanide-thiosulphate reaction has gone by way of sulphite. The product ratios may therefore be compared with those calculated by Foss for 20% reaction,

$$\frac{[S_4]}{[S_5] + \dots} = \frac{1.0}{0.22} \sim 4.5$$

If necessary, the higher value of 6.8 observed in cases where SO_3^{2-} is not instantly removed by ferricyanide may be explained by the formation of trithionate. This will result in a depletion in the concentration of tetrathionate to yield a product which does not act as an effective source of higher polythionates. Consequently the concentration of the latter will be less than expected leading to the greater ratio. Analysis data for tetrathionate is in qualitative agreement with this conclusion.

A STUDY OF THE KINETICS OF
THE REACTION.

Preliminary Experiments.

(i) Reproducibility of Measurements.

Two analytical techniques have, in the past, been used to follow the kinetics of the ferricyanide-thiosulphate reaction; the titrimetric method first adopted by Sandved and Holte (12) and later used by Batstone (13) and the spectrophotometric technique of Spiro and Barreira (20).

The reproducibility of measurements was checked by both methods, and the effects of surface and of light on the rate of reaction were determined simultaneously.

Six identical reaction mixtures were prepared as follows:

100 ml. portions of 0.100 M. potassium ferricyanide and potassium thiosulphate were pipetted into separate 500 ml. wide mouthed conical flasks and 50 ml. phosphate buffer (pH 7.4) added to both reactants. The flasks were allowed to attain thermal equilibrium in a thermostat at 25°C. The reaction was started by mixing the contents of the two flasks and homogeneity was ensured by transferring the mixture from one vessel to the other, several times. The clock was started upon initial mixing. Two reaction mixtures, labelled A, were packed with 3.0 g. glass wool whilst two others, labelled B, were covered with metal foil to exclude light. Samples were withdrawn at timed intervals and analysed as follows:

(a) Titrimetric Determination of Thiosulphate.

20 ml. aliquots of reaction mixture were quenched in

ice/water and titrated immediately with approximately 0.02 N. iodine in the presence of starch. The colour at the endpoint was stable for at least ten minutes and it was concluded that any reaction between ferricyanide and iodide was insignificant.

(b) Spectrophotometric Determination of Ferricyanide.

2 ml. samples of reaction mixture were run into 100 ml. standard flasks and made up to the mark with water. The absorbance of this solution was determined at 420 nm. in a 1 cm. glass cell, with water in the reference compartment of a Pye Unicam SP500 spectrophotometer. At this wavelength the extinction coefficient of the ferricyanide ion is 1020 M^{-1} cm^{-1}. The efficiency of quenching by dilution was checked by measuring the absorbance over a period of ten minutes when no perceptible change occurred.

In both (a) and (b) "zero time" readings were obtained by analysis of threefold diluted ferricyanide or thiosulphate solution.

Conclusion.

Commenting on the results shown in table 6 it is seen that the apparent rate of disappearance of reactants is independent of the measurement technique. Light and surface were found to have no effect.

It can be inferred that since, under identical conditions, the rate of loss of ferricyanide is equal to the rate of loss of thiosulphate, then the stoicheiometry of the reaction is 1:1.

Table 6.

Reproducibility of Measurements.

$[K_2S_2O_3]$ = 0.0333 M. pH = 7.40

$[K_3Fe(CN)_6]$ = 0.0333 M. Temperature = 25.0 ± 0.02°C.

Time (hours)	[Thiosulphate] X 10^2 M.			[Ferricyanide] X 10^2 M.		
		A	B		A	B
0	3.33	3.33	3.33	3.33	3.33	3.33
1.0	2.65	2.65	2.65	2.49	2.57	2.50
2.0	2.17	2.19	2.17	2.07	2.12	2.08
3.0	1.73	1.75	1.74	1.65	1.69	1.68
4.0	1.39	1.41	1.40	1.33	1.39	1.36
5.0	1.15	1.17	1.17	1.09	1.15	1.15
6.0	0.99	1.01	1.01	0.94	0.98	0.98
7.0	0.87	0.88	0.89	0.83	0.88	0.88
8.0	0.79	0.79	0.80	0.76	0.78	0.78

(ii) To Investigate the Spectral Changes During Reaction.

The only materials present which absorb in the 15,000 - 40,000 wavenumber region of the spectrum are the complex cyanides of iron. Thiosulphate ion absorbs strongly beyond 40,000 cm^{-1} but in this region absorbance measurements are not so reliable.

A 250 ml. round bottomed flask, divided into two compartments, was used to prepare the reaction mixture. Buffered reactants were placed into opposite halves of the flask and allowed to equilibriate at 40°C in a thermostat. The higher temperature was chosen in order that a relatively fast reaction might be observed. The reactants were mixed by shaking the flask and the clock was started.

The reaction mixture was transferred to a 2 mm. silica cell, which was placed in the thermostatted cell compartment of a Pye Unicam SP800 recording spectrophotometer. Phosphate buffer was used in the reference beam and the temperature was maintained at 40°C.

The spectrum of the reacting mixture was scanned rapidly between 15,000 and 40,000 cm^{-1}, at timed intervals. The curves are shown in graph 1. If these spectral characteristics correspond to a quantitative conversion of ferricyanide into ferrocyanide, with no other iron containing products, then the curves ought to be reproduced by mixtures of reactant and product, such that the sum of their molar concentrations will be constant.

Six solutions containing potassium ferricyanide and ferrocyanide only, in buffered solution, were prepared at concentrations expected during the course of the kinetic run. The absorbance curves were recorded between 15,000 and 40,000 cm^{-1} at 40°C using buffer as reference. These are shown in graph 2. A spectrum of 0.1 M. sodium thiosulphate was recorded on the same chart.

Conclusion.

Commenting on the results shown in table 7, the calculated rate of reaction is independent of the wavelength at which measurements were made.

The isosbestic point for the kinetic results was found to lie at 35,040 cm^{-1}, where the solution has an absorbance of 0.920. The position was duplicated by the "synthetic" reaction mixtures (graph 2) but in this case the absorbance was 0.850. The latter did not contain thiosulphate. 0.1 M. sodium thiosulphate was found to have an absorbance of 0.050

at 35,040 cm^{-1}. Since the effects would be additive, the absorbance at the "theoretical" isosbestic point is 0.900.

At the isosbestic point the extinction coefficients of reactants and of products are equal.

$$A = E\left([\mathrm{Fe(CN)}_6^{3-}] + [\mathrm{Fe(CN)}_6^{4-}]\right)$$

where A is the absorbance and E is the extinction coefficient. The presence of such a point implies that the sum of the two concentrations is constant throughout the kinetic run. Since the position and absorbance were duplicated by mixtures of ferricyanide and ferrocyanide ion, the identity of the products has been established. The latter presupposes that any other iron containing products, which may be formed, will have different spectral characteristics from the above. This is a reasonable assumption.

The result shows that not less than 98% of the iron containing product appears as ferrocyanide ion.

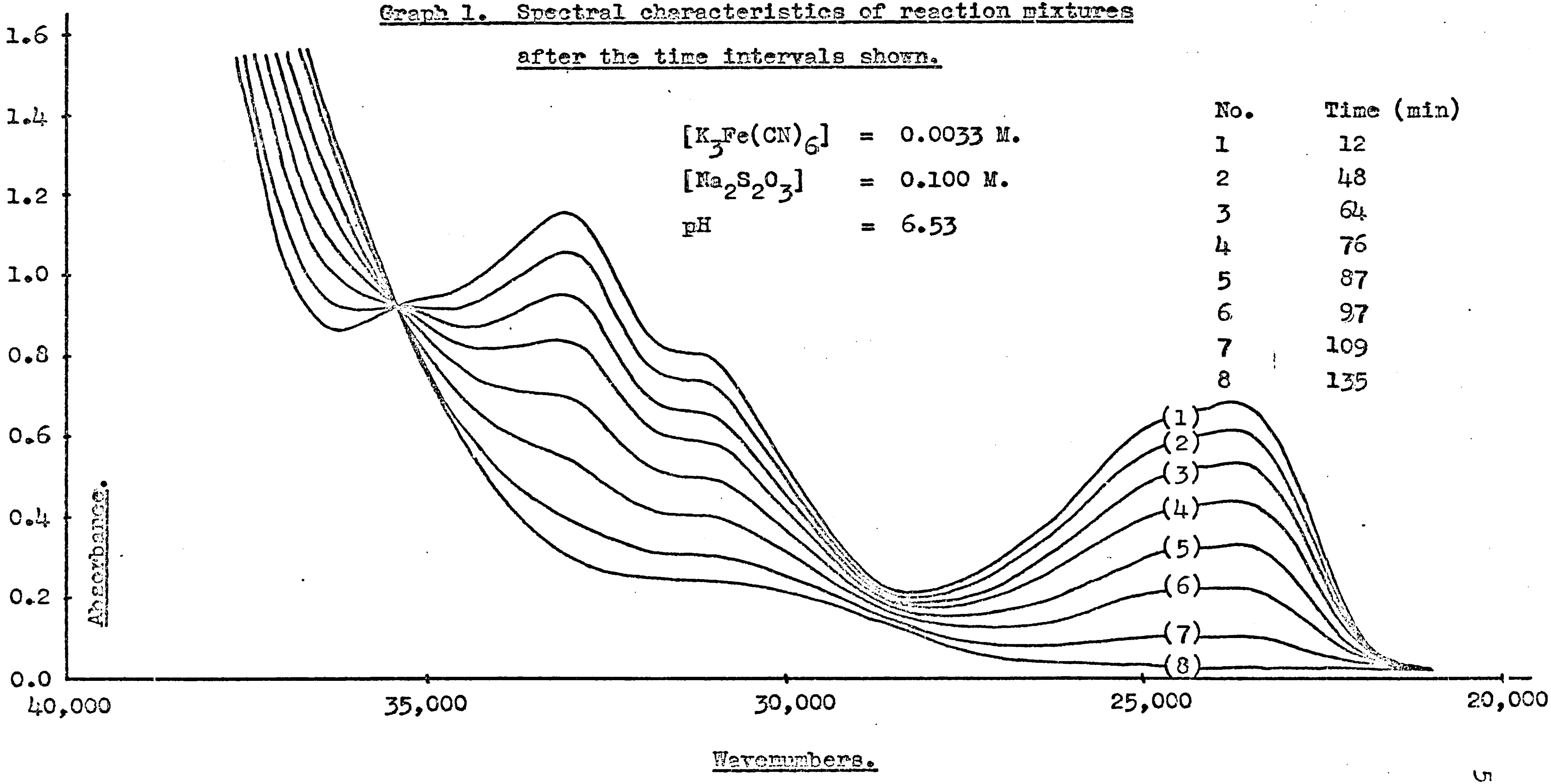
Table 7.

Reproducibility of Measurements at Various Wavelengths.

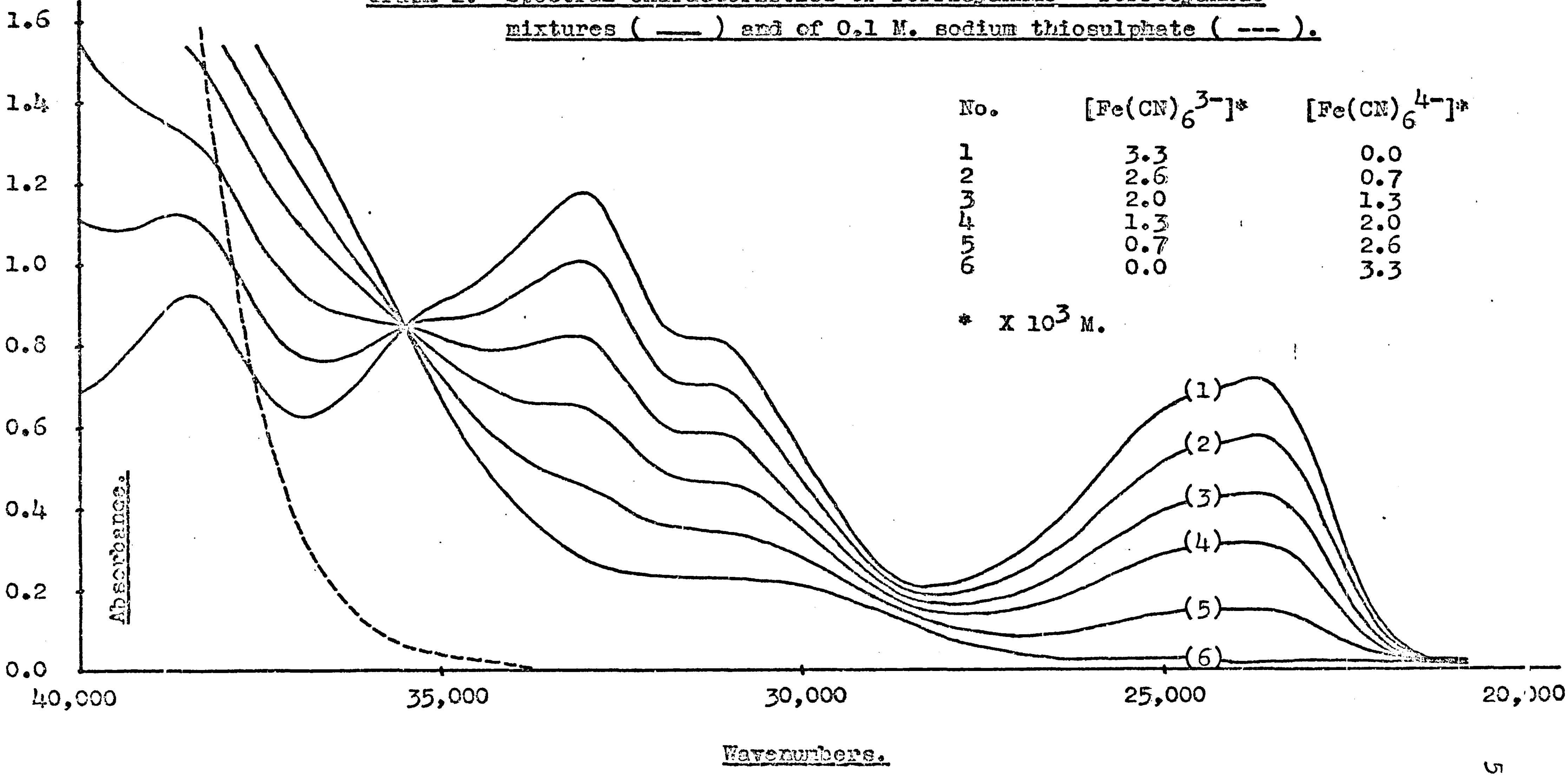
% Ferricyanide remaining at the given wavelength.

Time (mins)	23,800 cm^{-1}	31,500 cm^{-1}	33,000 cm^{-1}
12.0	95.5	99.0	98.0
48.0	85.7	87.4	87.2
64.0	73.5	73.5	75.2
76.0	60.0	61.8	61.8
87.0	43.5	45.7	46.2
97.0	28.5	29.6	30.4
109.0	11.4	13.0	13.7
135.0	0.	2.0	3.3

Graph 1. Spectral characteristics of reaction mixtures after the time intervals shown.



Graph 2. Spectral characteristics of ferricyanide - ferrocyanide mixtures (——) and of 0.1 M. sodium thiosulphate (---).



General Technique Adopted for Following the Reaction.

All kinetics experiments were carried out in the thermostatted cell compartment of a Pye Unicam SP800 recording spectrophotometer. The temperature was controlled to ± 0.02°C. The instrument was operated in the fixed wavelength mode at 23,810 cm^{-1}, in conjunction with a chart expansion unit connected to an external recorder. The latter was fitted with a synchronous chart drive motor and had been calibrated for time. All initial rate measurements were made with a scale expansion of 20 and the result was displayed on a 10" wide chart.

Equal volumes of thiosulphate and of ferricyanide were measured out by pipettes into opposite sides of a partitioned 250 ml. round bottomed flask. Buffer was added to each reactant and the mixtures allowed to attain thermal equilibrium in a thermostat. The reaction was started by shaking the flask and switching on the recorder at the same time. The mixture was transferred to a 1 cm. glass cell and placed in the spectrophotometer. The "back off" control, fitted to the scale expansion unit, was adjusted to bring the pen onto the chart, and the absorbance recorded for some time.

Initial rates were measured as the rate of change of absorbance with time, and converted into concentration units by dividing by the extinction coefficient for ferricyanide ion.

$$-\frac{d[Fe(CN)_6^{3-}]}{dt} = -\frac{d(OD)}{dt} \times \frac{1}{1020} \quad M.\ min^{-1}.$$

where t is in minutes, when a 1 cm. cell is used.

pH Measurements.

pH measurements were carried out using a Pye Dynacap pH meter in conjunction with an Ingold combined glass and calomel electrode. The instrument was calibrated by means of a 0.05 molal potassium hydrogen phthalate solution but for measurements in the near neutral regions a phosphate buffer was used. The latter was prepared from tablets supplied by Burroughs Wellcome Ltd., London. An initial difficulty was encountered when the pH of reaction mixtures was measured. The drift of reading with time was traced to a slow poisoning of the electrode by thiosulphate, a condition which took at least 24 hours to reverse by soaking in acid solution. Mixtures were prepared for pH measurement where sulphate replaced thiosulphate ion, but otherwise the conditions were identical. The steady reading given by these solutions was the same as the initial reading for reaction mixtures.

The interpretation of the pH scale has been discussed by Gold (28). The modern definition is based on the e.m.f. difference of a cell containing a standard solution in one instance and the solution under test in the other. It can be concluded that, provided the residual liquid junction potential is small, the difference in pH might express the difference between the logarithms of the hydrogen ion activities of the two solutions. Since the standardisation of the pH scale is a feature built into the pH meter, in dilute solution it is accurate to say,

$$\mathrm{pH} = -\log f_{\pm(1:1)} [\mathrm{H}^+]$$

where $f_{\pm(1:1)}$ is the mean ionic activity coefficient for a typical 1:1 electrolyte.

A limitation on the significance of pH arises from the residual liquid junction potential. This will be more important the more dissimilar the standard and test solutions are but, unless the ionic strength is high, there are experimental reasons for believing that the magnitude of this contribution is small. At high ionic strengths the error from ignoring the residual liquid junction potential is expected to be comparable with the uncertainty of the value of the mean ionic activity coefficient for the 1:1 electrolyte.

The Effect of $EDTA^{4-}$ on the Rate of Reaction.

Transition metal ions have often been identified as catalysts in redox reactions, whether by deliberate addition of salts or by their presence as impurities in the reagents used. The problem of unknown quantities being present as contaminants has often been overcome by the addition of small amounts of $EDTA^{4-}$, resulting in a lowering of the rate of reaction. The metal ion is effectively removed as a complex species and reproducible results have often been obtained only after this precaution has been taken.

Spiro and Barreira (20) however, have observed an acceleration upon adding small amounts of $EDTA^{4-}$. These results are in conflict with common expectation.

A number of experiments were carried out in which the concentration of $EDTA^{4-}$ was varied over a tenfold range. The ion was added as the disodium salt. The runs were carried out in the presence of a large excess of acetate ion to swamp any specific effects of the additive.

The optical density-time data is shown in table 8. The results are plotted in graph 3.

Table 8.

The addition of $EDTA^{4-}$.

$[S_2O_3^{2-}]$ = 0.0100 M.

$[Fe(CN)_6^{3-}]$ = 0.00100 M.

pH = 3.86

Temperature = 25.0 ± 0.02°C.

$[Na^+]$ = 0.020 M.

$[K^+]$ = 0.103 M.

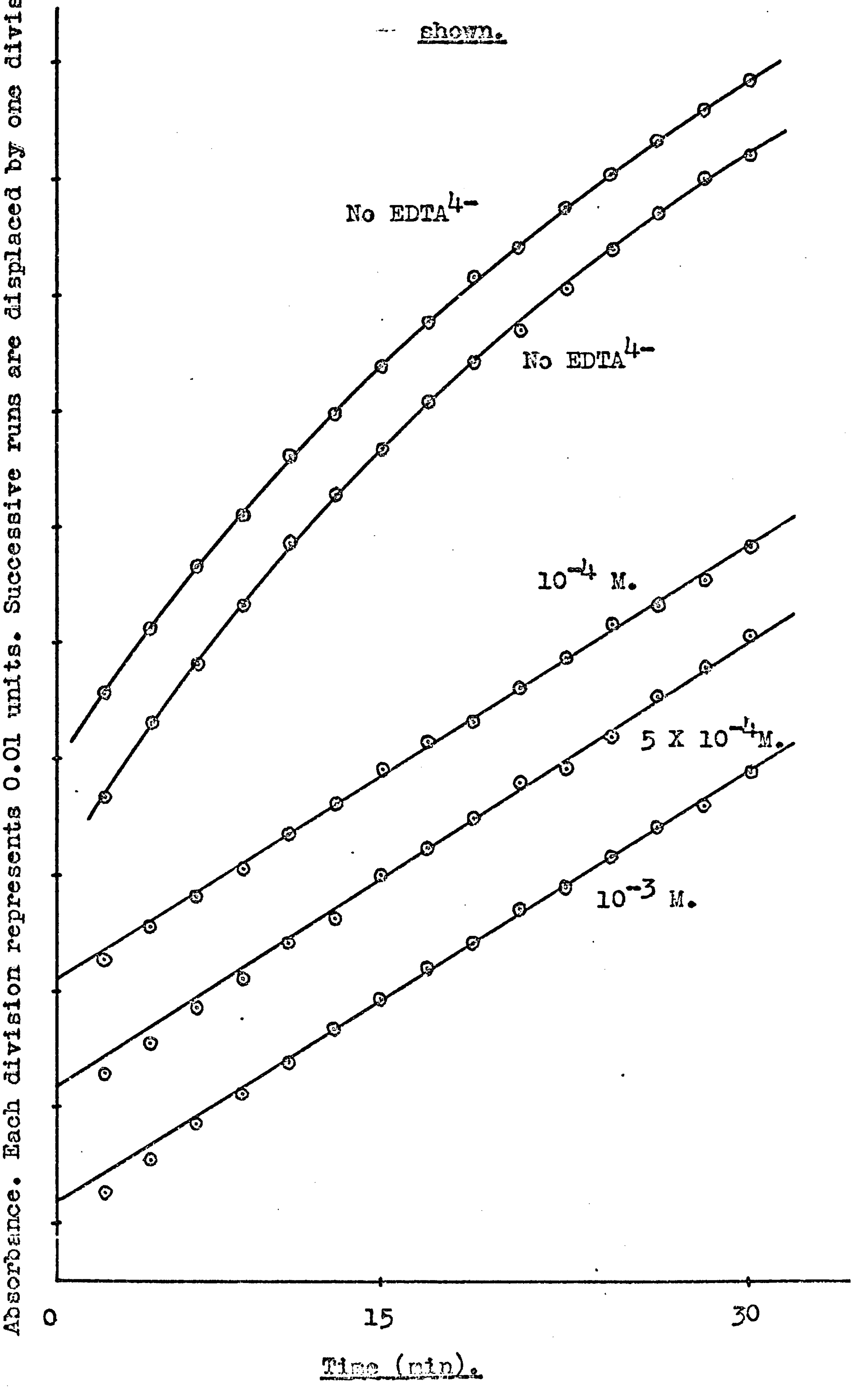
$[OAc^-]$ = 0.100 M.

Table showing changes in optical density (absorbance units) after the first observation in the presence of the amount of $EDTA^{4-}$ shown.

Time (mins)	10^{-3}M.	5 X 10^{-4}M.	10^{-4}M.	No EDTA	No EDTA
1.88	(0)	(0)	(0)	(0)	(0)
3.75	0.0026	0.0028	0.0027	0.0067	0.0056
5.63	0.0054	0.0055	0.0055	0.0130	0.0112
7.50	0.0086	0.0085	0.0081	0.0181	0.0166
9.38	0.0112	0.0110	0.0106	0.0232	0.0203
11.25	0.0138	0.0141	0.0135	0.0285	0.0260
13.13	0.0168	0.0162	0.0161	0.0327	0.0297
15.00	0.0193	0.0198	0.0190	0.0367	0.0338
16.88	0.0219	0.0223	0.0214	0.0407	0.0376
18.75	0.0240	0.0248	0.0232	0.0442	0.0415
20.63	0.0270	0.0278	0.0261	0.0469	0.0441
22.50	0.0289	0.0290	0.0286	0.0505	0.0476
24.38	0.0316	0.0318	0.0315	0.0539	0.0504
26.25	0.0341	0.0353	0.0331	0.0571	0.0532
28.13	0.0358	0.0378	0.0353	0.0600	0.0559
30.00	0.0387	0.0405	0.0382	0.0621	0.0585

All mixtures at zero time have an optical density of about 1.0.

Graph 3. Plot of optical density change vs. time in the presence of the amount of EDTA^{4-} shown.



Graph 3. Comments.

Commenting on the results plotted in graph 3, the effect of added $EDTA^{4-}$ on the first 5% of reaction is twofold. An appreciable reduction in rate is accompanied by a much more consistent and linear plot which enables initial rate measurements to be made. After the first addition there was no further effect by $EDTA^{4-}$ over a tenfold concentration change.

Table 9.

$[EDTA^{4-}]$ M.	$-\frac{d(OD)}{dt} \times 10^3$ min^{-1}	$-\frac{d[Fe(CN)_6^{3-}]}{dt} \times 10^6$ $M.\ min^{-1}$
10^{-4}	1.32	1.29
5×10^{-4}	1.39	1.36
10^{-3}	1.33	1.30

All subsequent kinetics experiments contained $EDTA^{4-}$ at a concentration of 5×10^{-4} M. The linear plots of optical density vs. time (graph 3) were typical for kinetic runs in initial rate studies. In each case the linear portion was preceded by one of slightly faster reaction.

To Determine the Order with respect to Reactants.

A number of experiments were carried out in which the concentration of one reactant was varied keeping those of all other species constant. The ionic strength was maintained by the addition of neutral salts; sodium sulphate was used to compensate for changes in thiosulphate. No such allowance was made in the case of ferricyanide ion experiments. Acetate buffers were prepared over a range of pH. These contained a constant acetate ion concentration with varying amounts of acetic acid.

The order of reaction with respect to one component was found by plotting graphs of initial rate vs. suitable functions of concentration. For a simple case,

$$\text{Initial rate} = k\,[A]^n$$

then, for an n th. order dependence a graph of initial rate vs. $[A]^n$, where $[A]$ is the concentration of a particular reactant, should be linear and pass through the origin (except in the case of a zero order reaction where initial rate is independent of $[A]$).

(a) Order with respect to $Fe(CN)_6^{3-}$.

Table 10.

$[S_2O_3^{2-}]$ = 0.0200 M.

pH = 5.17

Temperature = 25.0 ± 0.02°C.

$[Na^+]$ = 0.044 M.

$[K^+]$ = 0.200 M.

$[OAc^-]$ = 0.200 M.

$[EDTA^{4-}]$ = 5×10^{-4} M.

$[Fe(CN)_6^{3-}] \times 10^4$ M.	$-\frac{d[Fe(CN)_6^{3-}]}{dt} \times 10^7$ M. min^{-1}
1.56	6.67
4.67	6.49
6.22	6.93
10.89	6.69
12.44	6.62
14.00	6.49

The initial rate is independent of the concentration of ferricyanide ion. This is consistent with a zero order dependence.

(b) Order with respect to H^+.

Table 11.

$[S_2O_3^{2-}]$ = 0.0200 M.
$[Fe(CN)_6^{3-}]$ = 0.00100 M.
Temperature = 25.0 ± 0.02°C.

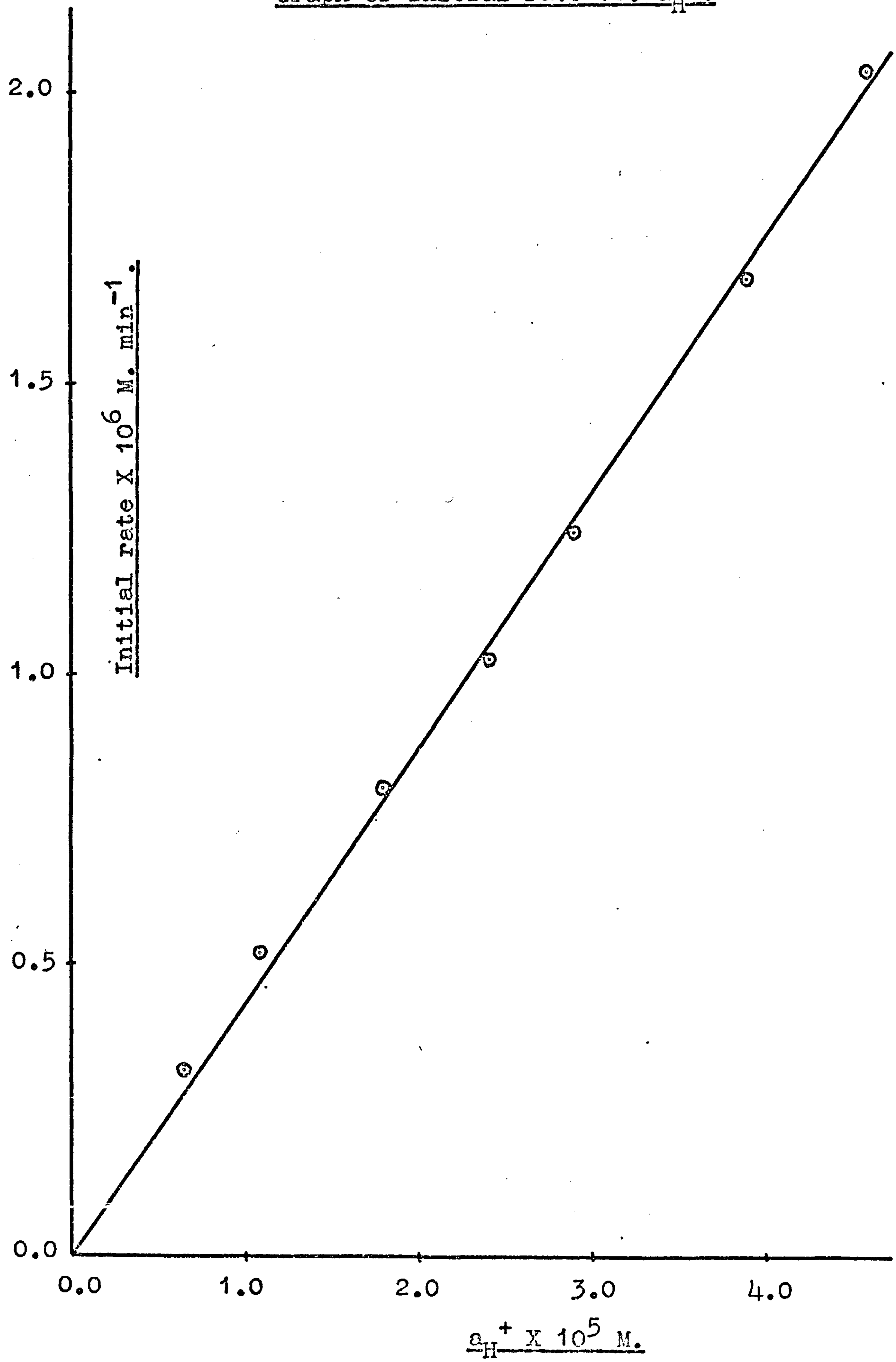
$[Na^+]$ = 0.042 M.
$[K^+]$ = 0.036 M.
$[OAc^-]$ = 0.033 M.
$[EDTA^{4-}]$ = 5×10^{-4} M.

pH	$a_{H^+} \times 10^5$ M.	$-\frac{d[Fe(CN)_6^{3-}]}{dt} \times 10^6$ M. min^{-1}
5.19	0.65	0.33
4.97	1.07	0.53
4.75	1.78	0.81
4.62	2.40	1.03
4.54	2.88	1.25
4.41	3.89	1.68
4.34	4.57	2.04

Graph 4 shows that a plot of initial rate vs. a_{H^+} is linear and passes through the origin. The order with respect to hydrogen ion is one. Although results are referred to a_{H^+} rather than to $[H^+]$, since all solutions are of equal ionic strength, this means that the ratio $a_{H^+}/[H^+]$ is constant and the conclusion about order is valid.

Graph 4.

Graph of initial rate vs. a_{H^+}.



(c) Order with respect to $S_2O_3^{2-}$.

In order to extend the range of concentration of thiosulphate over which the reaction proceeds at a conveniently measurable rate, two buffers at different pH values were used. Since the order with respect to hydrogen ion is one, the variation of pH was resolved by dividing the initial rate by the hydrogen ion activity.

Table 12.

$[S_2O_3^{2-}] + [SO_4^{2-}]$ = 0.033 M.
$[Fe(CN)_6^{3-}]$ = 0.00100 M.
Temperature = 25.0 ± 0.02°C.

$[Na^+]$ = 0.067 M.
$[K^+]$ = 0.036 M.
$[OAc^-]$ = 0.033 M.
$[EDTA^{4-}]$ = 5×10^{-4} M.

$[S_2O_3^{2-}] \times 10^2$ M.	pH	$a_{H^+} \times 10^5$ M.	$-\frac{d[Fe(CN)_6^{3-}]}{dt} \times 10^6$ M. min^{-1}
0.999	4.22	6.03	0.65
1.319	4.22	6.03	1.08
1.662	4.22	6.03	2.00
2.000	4.22	6.03	2.88
2.330	4.22	6.03	3.69
2.656	4.63	2.34	1.90
2.999	4.63	2.34	2.41

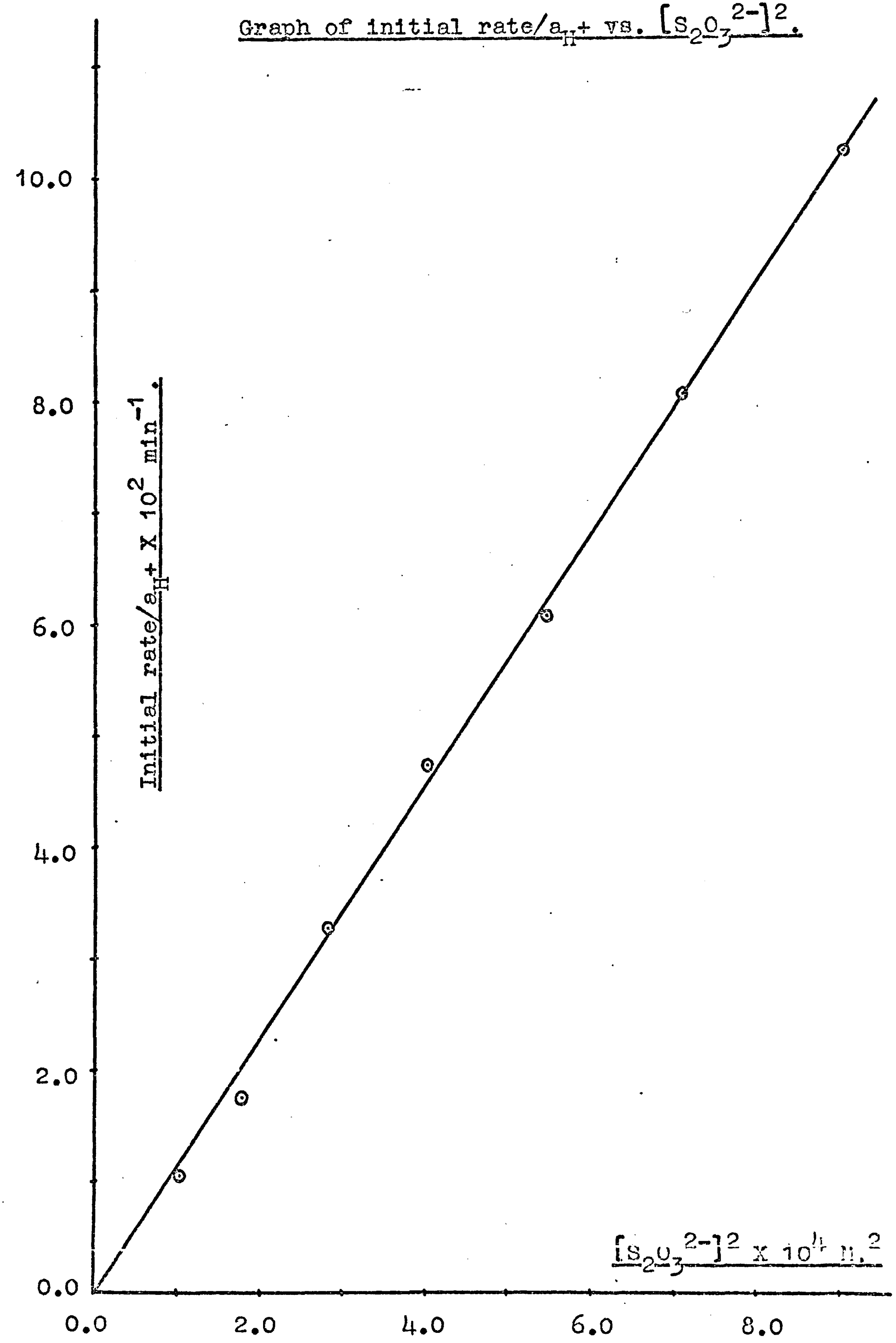
A first order rate law is not satisfied in this case. However, graph 5 (data shown in table 13) shows that a plot of (Initial rate)/a_{H^+} vs. $[S_2O_3^{2-}]^2$ gives a straight line passing through the origin. The order with respect to thiosulphate is two.

Table 13.

$[S_2O_3^{2-}]^2 \times 10^4$	$\frac{\text{Initial rate}}{a_{H^+}} \times 10^2$ min^{-1}
0.998	1.08
1.740	1.79
2.762	3.32
4.000	4.78
5.429	6.12
7.054	8.12
8.994	10.30

Graph 5.

Graph of initial rate/a_{H^+} vs. $[S_2O_3^{2-}]^2$.



The Solvent Isotope Effect on the Rate of Reaction.

In a reaction involving hydrogen ions the nature of protonation equilibria is of interest. Such systems have been known to undergo considerable modification if the solvent is changed from H_2O to D_2O. The sign and magnitude of this modification may yield valuable information in a mechanistic study.

For ferricyanide-thiosulphate mixtures in the presence of an acetate/acetic acid buffer two equilibria involving protons may be of kinetic consequence.

First, hydrogen ion produced by the buffer will depend on the dissociation constant of acetic acid. If the solvent H_2O is replaced by D_2O, the pK of the acid rises by 0.52 (29). The pH of the solution in H_2O is defined approximately by,

$$pH = pK_H + \log \frac{[OAc^-]}{[HOAc]}$$

and it is expected that a similar relationship will hold in D_2O. If the ratio of salt to acid concentration is kept constant then, provided that the activity coefficients for protons and deuterons are similar, the change of solvent to D_2O will result in an effective reduction of hydrogen ion activity by a factor of 3.3.

Secondly, hydrogen may be involved in the reaction as the ion pair $HS_2O_3^-$. The dissociation constant for the corresponding deutero acid has not been reported but comparable data is available between DSO_4^- and HSO_4^- (30). It has been shown that the hydrogen sulphate ion is structurally analogous to $HS_2O_3^-$ and any differences in the stabilities of DSO_4^- and HSO_4^- will apply to $DS_2O_3^-$ and $HS_2O_3^-$.

These data show that DSO_4^- is the weaker acid by 0.35 units of pK, a factor of 2.2. Consequently, if the reaction is of first order with respect to $[HS_2O_3^-]$, and the activity coefficient for this species is the same in both solvents, then going from H_2O to D_2O will result in a 2.2 fold increase in rate.

According to one form of the Debye Huckel theory, activity coefficients in dilute solution may be found from,

$$- \log f = \frac{A z^2 \sqrt{I}}{1 + Ba\sqrt{I}}$$

where A involves, at constant temperature, universal constants and $\epsilon^{-3/2}$, and B similarly involves $\epsilon^{-1/2}$, where ϵ is the dielectric constant of the medium. Since $Ba \sim 1$ in H_2O or D_2O at 25°C and $\sqrt{I}$ will be small, the main change in f will come from A, that is, by a factor of $\epsilon^{-3/2}$. From the data of Lewis, Olson and Maroney (31) the dielectric constant of D_2O is only some 1% less than that for H_2O and the difference is perhaps smaller as suggested by Wyman and Ingalls (32) who found the ratio $\epsilon(D_2O)/\epsilon(H_2O)$ to be 0.9963. Even if the difference is 1%, this amounts to about 1½% change in log f which, in practical terms has no significance.

Salomaa and Aalto (33) have measured, by a potentiometric method, transfer free energies for one mole of alkali metal chloride from light to heavy water

$$MCl\ (H_2O) = MCl\ (D_2O) \qquad \Delta G^o \sim 210\ \text{cal/mole}.$$

the value being dependent only on the nature of the anion since it was unaffected when different cations were used. The effect was explained by considering solvent-ion interactions. It is evident from NMR and other studies of the effects of ions on water structure that cations and anions, even when of the same formal charge and of the same size, interact very differently with surrounding water molecules. It is apparent that a cation will be surrounded by water molecules orientated such that oxygen atoms will lie in close proximity to the central atom with hydrogens pointing away. If we consider that the cation is "bonded" to the solvent through oxygen, little change in free energy is expected on going from H_2O to D_2O. On the other hand, the possible configurations of water molecules around anions are dependent on the nature of the anion, and this is expected to lead to characteristic differences in the free energies of these ions in the two solvents. The observed activity coefficients for ions in H_2O and in D_2O should be compatible with the transfer free energies. Cations are expected to have similar activity coefficients in H_2O as in D_2O, but anions must be considered individually. According to Salomaa (34) the transfer free energy for potassium chloride, $\Delta G^{o} = +219$ cal/mole at $25^{o}C$ corresponds to about 45% increase in the molar activity coefficient of the salt. For divalent ions suitable data are available (35) in the case of sulphite and of carbonate ions only, but it is clear that the values cannot be compared,

$$\frac{(f_{CO_3^{2-}})_{D_2O}}{(f_{CO_3^{2-}})_{H_2O}} = 1.47; \qquad \frac{(f_{SO_3^{2-}})_{D_2O}}{(f_{SO_3^{2-}})_{H_2O}} = 2.59$$

However, the results were considered as reasonable in view of the compatability of transfer free energies with those found for the corresponding anhydrides.

The overall picture regarding activity coefficients in D_2O is one of uncertainty, although it is clear that the Debye Huckel treatment will fail owing to its inability to take into account the specific effects which are predicted. It is true, that if such changes occurred for thiosulphate they would be incorporated in the stability constant of $DS_2O_3^-$, but since the rate of reaction apparently depends also on the concentration of $S_2O_3^{2-}$, a second and perhaps more profound effect may be observed.

If,

$$\text{Rate}_H = k\,[HS_2O_3^-][S_2O_3^{2-}] \quad = k'\,[H^+][S_2O_3^{2-}]^2$$

the rate in D_2O may be written as

$$\text{Rate}_D = 2.2\,k'\,\frac{[H^+]}{3.3}\,[S_2O_3^{2-}]^2$$

assuming no change in the activity coefficients of the various ions and where $[H^+]$ is the hydrogen ion concentration in a reaction mixture of identical composition in water.

$$\text{Hence,} \quad \frac{\text{Rate}_H}{\text{Rate}_D} \sim 1.5$$

Solutions in H_2O and in D_2O were prepared in exactly the same way.

2 ml. 0.5 M. aqueous sodium thiosulphate solution were pipetted into a 50 ml. standard flask and made up to the mark with H_2O or D_2O. In another standard flask 2 ml. 0.1 M. potassium ferricyanide and 1 ml. buffer containing 1.0 M. potassium acetate, 0.025 M. Na_2EDTA and acetic acid, were made up to the mark with solvent. Equal volumes of

the two solutions were used to prepare reaction mixtures.

In the case of water the reactants were prepared twice from the stock solutions in order to check the reproducibility of the method. For D_2O only one pair of reactants was prepared but these were used for two runs.

The experimental results are listed in table 14.

Table 14.

Solvent Isotope Effect.

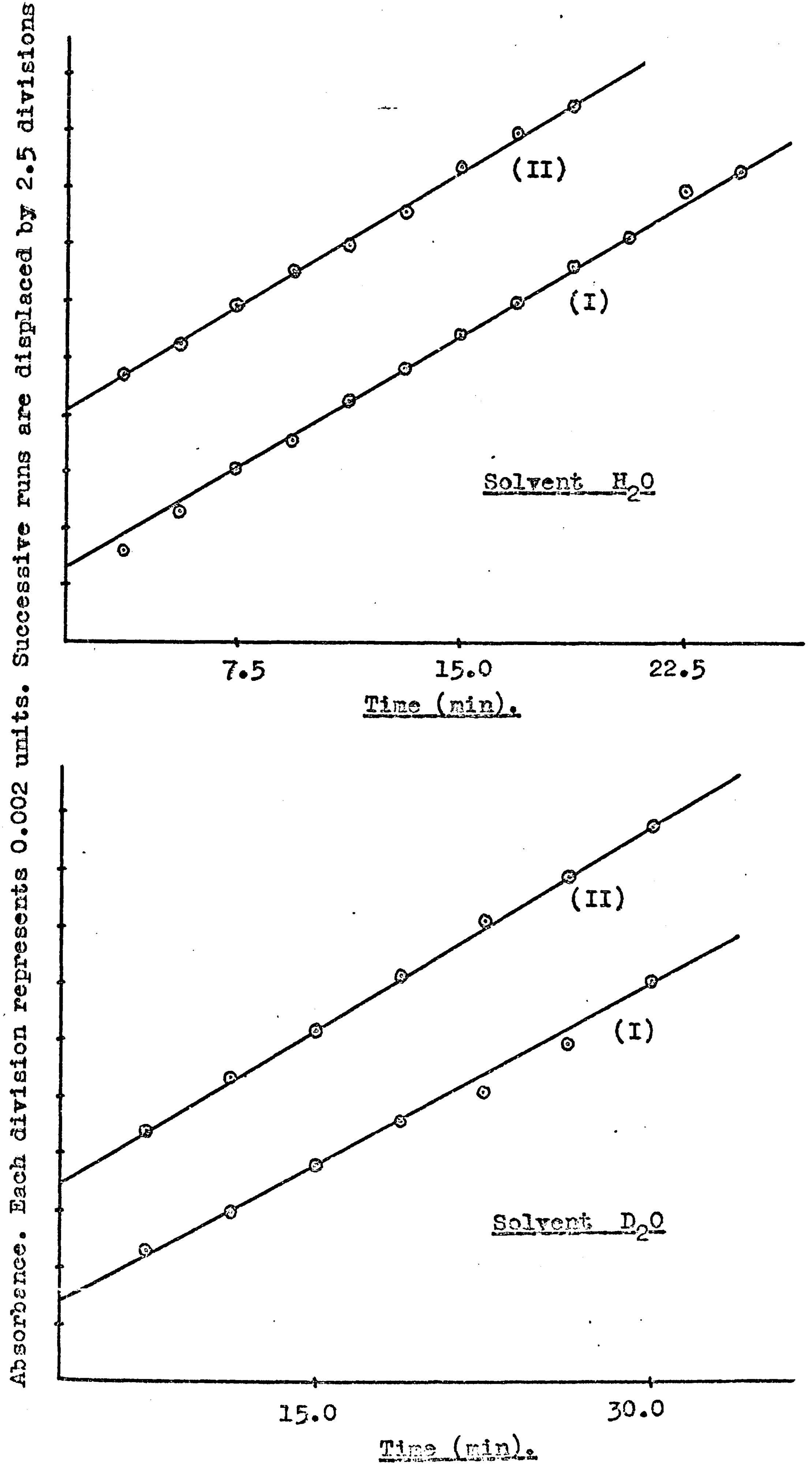
$[S_2O_3^{2-}]$	=	0.0100 M.	$[Na^+]$	=	0.021 M.
$[Fe(CN)_6^{3-}]$	=	0.00100 M.	$[K^+]$	=	0.023 M.
pH (in H_2O)	=	4.03	$[OAc^-]$	=	0.020 M.
Temperature	=	25.0 ± 0.02°C.	$[EDTA^{4-}]$	=	5 X 10^{-4} M.

Table showing changes in optical density (absorbance units) after the first observation with H_2O and D_2O as solvent.

Time (mins)	H_2O I	H_2O II	95% D_2O I	95% D_2O II
1.88	(0)	(0)		
3.75	0.0012	0.0024	(0)	(0)
5.63	0.0026	0.0035		
7.50	0.0041	0.0049	0.0026	0.0018
9.38	0.0051	0.0061		
11.25	0.0065	0.0070	0.0040	0.0037
13.13	0.0077	0.0082		
15.00	0.0089	0.0098	0.0056	0.0054
16.88	0.0100	0.0110		
18.75	0.0113	0.0120	0.0072	0.0073
20.63	0.0124			
22.50	0.0140		0.0082	0.0092
24.38	0.0147			
26.25			0.0099	0.0108
30.00			0.0121	0.0126

All mixtures at zero time have an optical density of about 1.0.

Graph 6. Plot of optical density change vs. time using H_2O or D_2O for solvent as shown.



Graph 6. Comments.

The following initial rates were measured from optical density/time graphs.

Table 15.

Solvent	$-\frac{d[Fe(CN)_6^{3-}]}{dt} \times 10^7$ M. min^{-1}	Mean Initial Rate X 10^7 M. min^{-1}
H_2O	6.22	6.25
H_2O	6.27	
95% D_2O	4.72	4.51
95% D_2O	4.29	

It is clear that the results for water were reproducible. An apparent retardation in D_2O was observed such that,

$$\frac{\text{Rate}_H}{\text{Rate}_D} \sim 1.4$$

This is close to the value of 1.5 derived by a rather superficial approach. It is argued that since dilute solutions were used the activity coefficients for divalent ions in water are expected to approach 0.7 and the increase which may occur in going to D_2O is limited by unity. It is expected that the ratio $(f_{S_2O_3^{2-}})_{D_2O}/(f_{S_2O_3^{2-}})_{H_2O}$ will never approach the limiting value of 1.4 and consequently the effects which are of kinetic importance in the reaction are the modification of the dissociation constants for acetic acid and for $HS_2O_3^-$.

The heavy water experiments were carried out in 95% D_2O. It is generally accepted that the specific effects of

D_2O are not linearly dependent on the proportion present in mixtures with H_2O. In fact the effect obeys a quadratic law, but over a 5% addition of water it is thought likely that relative changes (which will occur in the same direction) for the two equilibria will be similar. The data are available only in the case of acetic acid.

The Effect of Added Salts on the Rate of Reaction.

The effects of addition of neutral salts to the reaction mixture can be broadly divided into two types; those arising from ionic strength changes and those due to the specific effects of anion or cation. Generally speaking both will be present in any system.

The Influence of Ionic Strength on Reaction Rate.

In an ideal solution the properties of the reactants or the activated complex would not be affected by the presence of solute molecules or ions. Real solutions containing ions deviate from ideality even at quite low concentration.

Preliminary investigations have led us to believe that the ferricyanide-thiosulphate reaction involves two molecules of thiosulphate and one proton in the slowest step of the mechanism. That is,

$$2\ S_2O_3{}^{2-} + H^+ \rightleftharpoons (\text{activated complex})^{3-} \longrightarrow \text{Products}$$

According to the Brønsted formulation, the rate constant for a real system is given by

$$k = k_o \frac{f^2_{S_2O_3{}^{2-}}\ f_{H^+}}{f_{\text{complex}}} \qquad (i)$$

where k_o is the rate constant when the activity coefficient function is unity.

If the activity coefficient of an ion in water at 25°C is represented by the equation

$$-\log f = 0.505\ z^2\ F(I)$$

where z is the charge on the ion and F(I) is some function of ionic strength, then equation (i) becomes,

$$\log k = \log k_0 - 0.505\ (2 \times 4 + 1 - 9)\ F(I)$$

$$\text{hence } k = k_0$$

In other words, if the rate law is obeyed without any other species participating in the rate determining step, then ionic strength will have no effect on the rate of reaction.

Specific Effects.

Apparent anomalies to the Brønsted theory of salt effects are numerous. A possible explanation which has often been suggested is that they are due to association between oppositely charged ions to form ion pairs or complexes. These could modify the reaction in two ways. In the first place they would have to be taken into account when calculating the true concentrations of reactants and therefore the ionic strength of the medium. Secondly, one or more of such ion pairs may be involved in the rate determining step, thus altering the charge of the activated complex and hence the ionic type of the reaction, and also possibly modifying the reactivity of the system in a more profound way as well.

In general, association between univalent ions will effectively be absent in dilute solution; between univalent and bivalent ions it will usually be appreciable except at the highest dilutions; and between ions of higher charge it will be universal and nearly always extensive. Since two negatively charged multivalent ions are involved, ion pairs with cations must be taken into consideration.

Experiments were carried out in which reaction mixtures contained only one cation, either sodium or potassium ion.

The ionic strength was varied between 0.068 and 0.388 by the addition of potassium nitrate and up to 0.548 with sodium nitrate. The salt was added with the buffer which was prepared to approximately the same pH for each run. Solutions contained a constant acetate concentration with variable amounts of acetic acid. All other parameters were held constant. The results are summarised in tables 16 and 17.

Table 16.

The addition of Na^+.

$[S_2O_3^{2-}]$ = 0.0100 M. $[K^+]$ = 0.003 M.

$[Fe(CN)_6^{3-}]$ = 0.00100 M. $[OAc^-]$ = 0.033 M.

Temperature = 25.0 ± 0.02°C. $[EDTA^{4-}]$ = 5×10^{-4} M.

$[NaNO_3]$ M.	$[Na^+]_{tot.}$ M.	I*	pH	$-\frac{d[Fe(CN)_6^{3-}]}{dt} \times 10^7$ M. min^{-1}
-	0.054	0.071	4.15	6.30
0.080	0.134	0.151	4.16	6.03
0.160	0.214	0.231	4.14	5.80
0.240	0.294	0.311	4.10	5.99
0.320	0.374	0.391	4.01	7.52
0.400	0.454	0.471	4.06	6.45
0.480	0.534	0.551	3.98	7.30

* Calculated from initial reactant concentrations.

Table 17.

The Addition of K^+.

$[S_2O_3^{2-}]$ = 0.00996 M. $[Na^+]$ = 0.001 M.
$[Fe(CN)_6^{3-}]$ = 0.00100 M. $[OAc^-]$ = 0.033 M.
Temperature = 25.0 ± 0.02°C. $[EDTA^{4-}]$ = 5×10^{-4} M.

$[KNO_3]$	$[K^+]_{tot.}$	I*	pH	$-\frac{d[Fe(CN)_6^{3-}]}{dt} \times 10^7$
M.	M.			M. min^{-1}
-	0.056	0.070	4.11	8.10
0.054	0.110	0.123	4.14	7.76
0.107	0.163	0.177	4.15	8.65
0.160	0.216	0.230	4.12	8.63
0.267	0.323	0.337	4.09	9.44
0.320	0.376	0.390	4.09	10.00

* Calculated from initial reactant concentrations.

Nature of Ions and Ion Pairs Present.

Extensive listings of the stability constants of complexes formed between hydrogen or metal ions and a variety of organic and inorganic ligands are available (36).

The ion capable of being the most highly charged in the reaction mixture is $EDTA^{4-}$. There is general agreement regarding pK values for the second and third dissociation constants of H_4EDTA, which are reported to be 2.67 and 6.16 at 25°C respectively. Consequently, at pH 4 the majority will be present as the divalent ion H_2EDTA^{2-}. Ferricyanide ion, on the other hand, does not form stable ion pairs with protons. In fact, the third dissociation constant of $H_3Fe(CN)_6$ is too large to obtain evidence of any complex formation.

Over the percentage of reaction studied, the amount of ferrocyanide produced will be negligible. Thiosulphate will exist mainly as the divalent species $S_2O_3^{2-}$ which, at pH 4, is expected to be in at least 100 to 1 molar excess over $HS_2O_3^-$. The acids of all monovalent anions will be fully dissociated.

If tables of stability constants are scanned it is evident that, unless some specialised interaction occurs, the equilibrium constants for ion pair dissociation are, to a first approximation, dependent on two factors only: the nature of the metal ion and the charge type of the ligand.

Using results reported for sulphate and thiosulphate, the stability constants for NaL^- and KL^- (L is the ligand) are 0.21 and 0.11 M. at 25°C respectively. In view of the lack of suitable data regarding other divalent ligands, it has to be assumed that these values will be generally applicable. Since the number of trivalent anions is relatively small, there is a corresponding lack of information regarding their ion pairs. The stability constant for $KFe(CN)_6^{2-}$ is reported as 0.08 M. at 25°C.

Calculation of Ion Pair Concentrations.

The results of measurements carried out in D_2O are consistent with the rate being dependent on $[HS_2O_3^-]$. The concentration of the latter depends on the free thiosulphate present, which, in view of possible ion pair formation, will be less then that put in.

The divalent anion concentration is comprised of thiosulphate and H_2EDTA^{2-}. Ferricyanide amounts to some 10% of this and its stability constant with potassium ion is not remote from that expected for KL^-. Hence, to a good approximation $[Fe(CN)_6^{3-}]$ may be included as a contributor to the total $[L^{2-}]$, for the calculation of ion pair concentrations.

The stability constants above, have been quoted as those corrected to zero ionic strength. From these values of Ko, the dissociation constant (K) for a solution of particular ionic strength I, may be calculated from

$$K = Ko \times 10^{2.02\,F(I)}$$

$$\text{where} \quad F(I) = \frac{\sqrt{I}}{1 + \sqrt{I}} - 0.2\,I$$

Let the initial concentration of metal ion (M^+) be "a", and that of L^{2-}, "b". If, at equilibrium the concentration of ion pair formed is "x",

$$\begin{array}{cccc} ML^- & \rightleftharpoons & M^+ & + & L^{2-} \\ x & & (a-x) & & (b-x) \end{array}$$

$$K = \frac{(a-x)(b-x)}{x}$$

hence

$$x^2 - (a+b+K)\,x + ab = 0$$

This quadratic may be solved for x,

$$x = \frac{-B - \sqrt{B^2 - 4AC}}{2A}$$

(The positive root gives an answer which is inadmissible)

where $A = 1$, $B = -(a+b+K)$ and $C = ab$.

It is now a simple matter to determine equilibrium concentrations of metal ion and of ligand. These are given the subscript "T" to denote "true" values. $[S_2O_3^{2-}]_T$ may be calculated by proportion from $[L^{2-}]_T$.

Table 18 shows the results of such a calculation using the experimental data listed in tables 16 and 17. It is apparent that improved values I_T for the ionic strength are within 6%, in the worst case, of the ionic strength I obtained from reactant concentrations. This is considered sufficiently close in view of the assumptions made not to warrant a second approximation.

Hydrogen ion concentrations were calculated from

$$H^+ = \log^{-1} (0.505\ F(I) - pH)$$

and the third order rate constant k_3, which is expected to be independent of the ionic strength of the medium is given by

$$k_3 = \frac{\text{Initial rate}}{[S_2O_5^{2-}]^2\ [H^+]}$$

Table 18.

M^+	I	K*	$10^3[ML^-]$*	$10^3[L^{2-}]_T^*$	$10^3[S_2O_3^{\ 2-}]_T^*$	$[M^+]_T^*$	I_T	$10^5[H^+]$*	$10^{-2}k_3$**
Na^+	0.071	0.523	1.057	10.442	9.098	0.053	0.068	8.86	0.86
	0.151	0.670	1.892	9.607	8.371	0.132	0.146	9.22	0.93
	0.231	0.766	2.486	9.013	7.853	0.212	0.225	9.99	0.94
	0.311	0.831	2.981	8.518	7.421	0.291	0.304	11.19	0.97
	0.391	0.873	3.424	8.075	7.036	0.371	0.383	13.94	1.09
	0.471	0.899	3.835	7.664	6.678	0.450	0.462	12.52	1.16
	0.551	0.912	4.224	7.275	6.339	0.530	0.541	15.11	1.20
K^+	0.070	0.272	1.887	9.512	8.307	0.054	0.066	9.69	1.21
	0.123	0.328	2.806	8.593	7.505	0.107	0.118	9.49	1.45
	0.177	0.369	3.435	7.964	6.955	0.160	0.170	9.56	1.87
	0.230	0.401	3.942	7.457	6.512	0.212	0.222	10.45	1.95
	0.337	0.443	4.760	6.639	5.798	0.318	0.327	11.50	2.44
	0.390	0.457	5.104	6.295	5.498	0.371	0.379	11.59	2.85

* M.

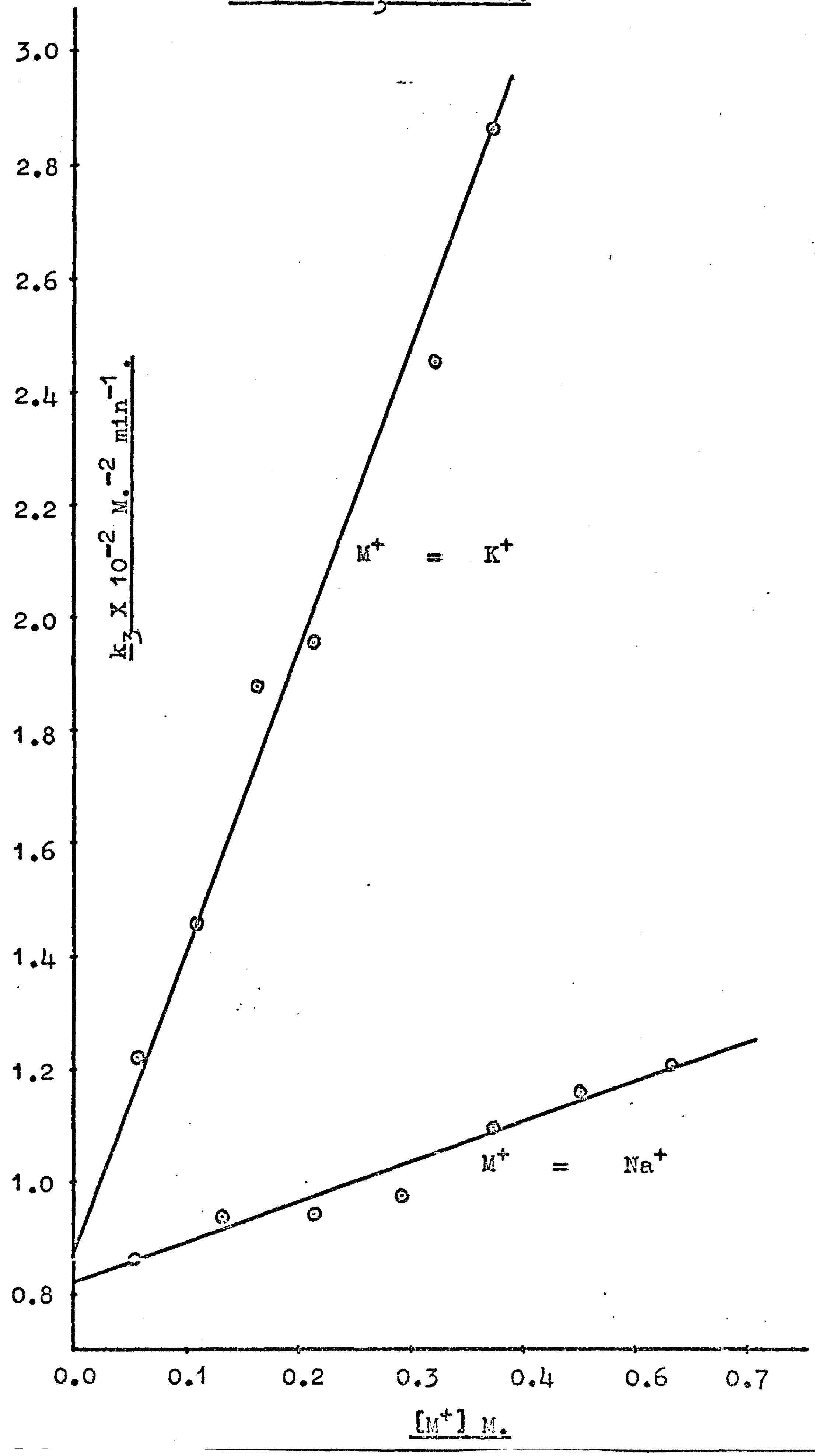
** M^{-2} min^{-1}

$[L^{2-}]$ = 0.0115 M. for M^+ = Na^+

$[L^{2-}]$ = 0.0114 M. for M^+ = K^+

Graph 7.

Graph of k_3 vs. $[M^+]$.



Graph 7, Comments.

It is clear that the rate of reaction is dependent both on the nature and on the amount of cation present. However, if graphs of k_3 vs. $[M^+]$ are extrapolated to zero concentration, an uncatalysed rate is predicted in both cases, with $k_3 = 82$ and 87 $M.^{-2}$ min^{-1} for sodium and potassium ion respectively. It is considered that these results are sufficiently close to be regarded as the same. Therefore a mean value may be taken. If,

$$\text{Rate}_o \quad = \quad 85\,[S_2O_3{}^{2-}]_T^2\,[H^+] \quad M.\ min^{-1}$$

then, since rate_o is expected to be independent of ionic strength, the residual rate due to the catalysed reaction under any conditions may be calculated,

$$\text{Rate}_r \quad = \quad \text{Rate}_{obs} \quad - \quad \text{Rate}_o$$

where rate_{obs} is the experimental initial rate under the specified conditions.

The following rate law was found to fit the results:

$$\text{Rate}_r \quad = \quad 10^{-3.03\,F(I)}\,(3.2[Na^+]_T + 23.4[K^+]_T)\,([S_2O_3{}^{2-}]_T\,[H^+])\ M.\ min^{-1}$$

The overall rate will be the sum of rate_o and rate_r and therefore it may be predicted from the complete rate expression. The values are compared with observed initial rates in table 19.

Table 19.

M^+	$Rate_o$	Predicted $Rate_r$	Predicted $Rate_{obs}$	$Rate_{obs}$
Na^+	6.23	0.36	6.59	6.30
	5.49	0.58	6.07	6.03
	5.24	0.77	6.01	5.80
	5.24	0.99	6.23	5.99
	5.87	1.38	7.25	7.52
	4.75	1.36	6.11	6.45
	5.16	1.80	6.96	7.30
K^+	5.68	2.68	8.36	8.10
	4.54	3.53	8.07	7.76
	3.93	4.12	8.05	8.65
	3.77	4.93	8.70	8.63
	3.29	6.19	9.48	9.44
	2.98	6.58	9.56	10.00

All rates are X 10^7 M. min^{-1}.

There is general agreement between observed and predicted rates. The first order dependence with respect to thiosulphate is consistent with the findings of Spiro and Barreira (20) who measured the progress of the ferricyanide-thiosulphate reaction in 2 M. salt solution.

The Effect of Temperature on the Rate of Reaction.

The rate of reaction was measured at a variety of temperatures under two sets of conditions. In one case dilute, buffered solutions of sodium salts were used with no additions, in order to simulate, as closely as possible, the reaction independent of cation. In the other case potassium ion was added so that a predominantly catalysed reaction may be observed.

The energy of activation for the reaction was calculated from the Arrhenius relationship,

$$k = A\, e^{-E/RT}$$

a plot of $\log_{10}$Initial rate vs. $1/T^{o}K$ giving a slope of $E/2.303\,R$, when initial rates refer to experiments carried out under identical conditions of concentration.

Table 20.

$[Na^+] = 0.052$ M. $[S_2O_3^{2-}] = 0.010$ M. pH 4.15

T^oC	$10^3/T^oK$	$-\frac{d[Fe(CN)_6^{3-}]}{dt} \times 10^7$ M. min^{-1}	$7 + \log_{10}$ Init. Rate
15.0	3.472	2.57	0.410
20.0	3.413	4.01	0.603
25.0	3.356	6.62	0.821
30.0	3.300	10.59	1.025
35.0	3.247	17.08	1.223

See graph 8.

Table 21.

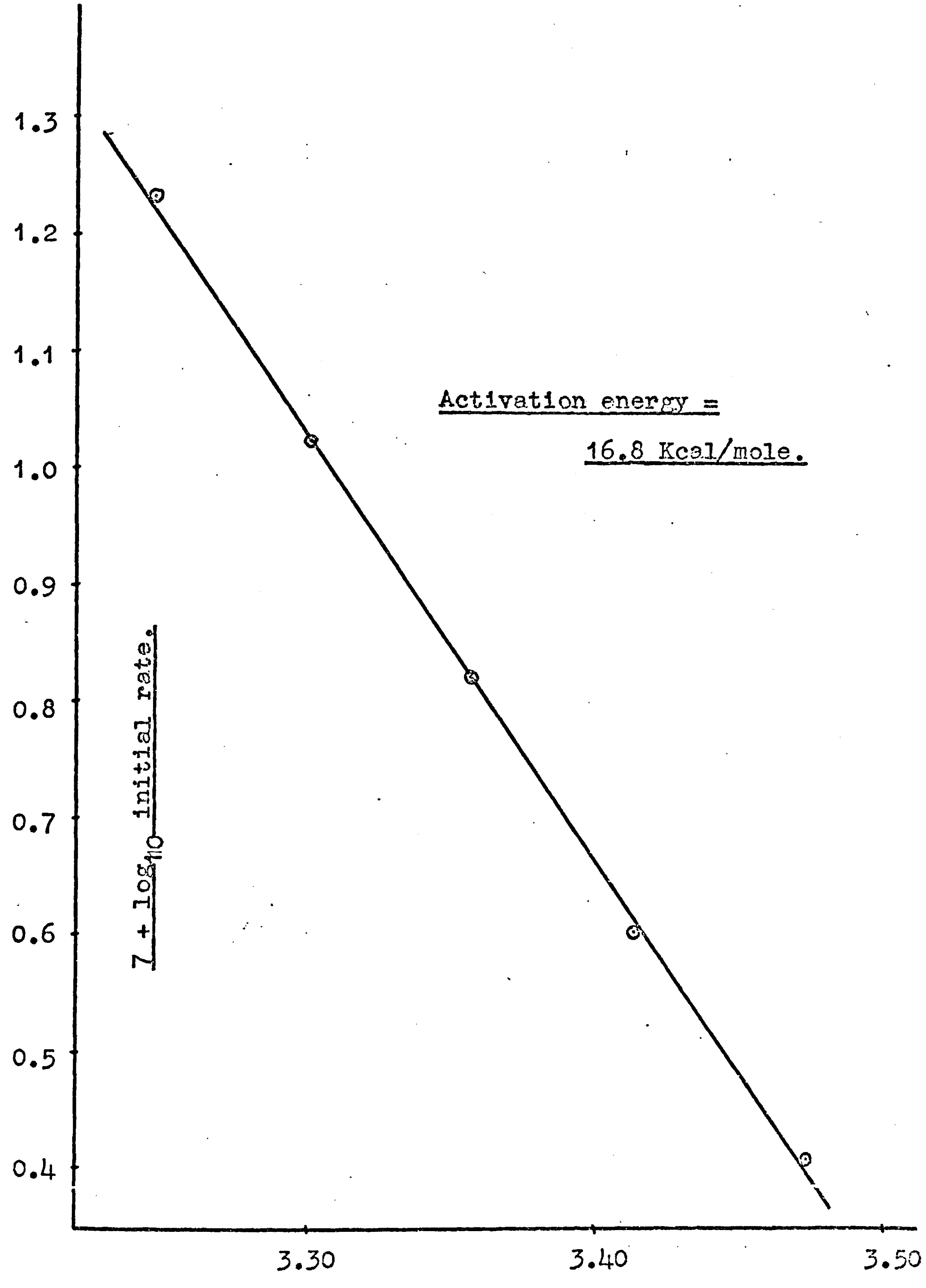
$[K^+]$ = 0.356 M. $[S_2O_3^{2-}]$ = 0.005 M. pH 3.91

T^oC	$10^3/T^oK$	$-\frac{d[Fe(CN)_6^{3-}]}{dt} \times 10^7$ M. min^{-1}	$\log_{10}$ 7 + Init. Rate
20.0	3.413	2.16	0.335
25.0	3.356	3.22	0.509
30.0	3.300	5.23	0.719
35.2	3.245	8.89	0.949
40.0	3.195	13.73	1.138

See graph 9.

Graph 8.

Arrhenius plot for reaction where $[Na^+] = 0.052$ M.

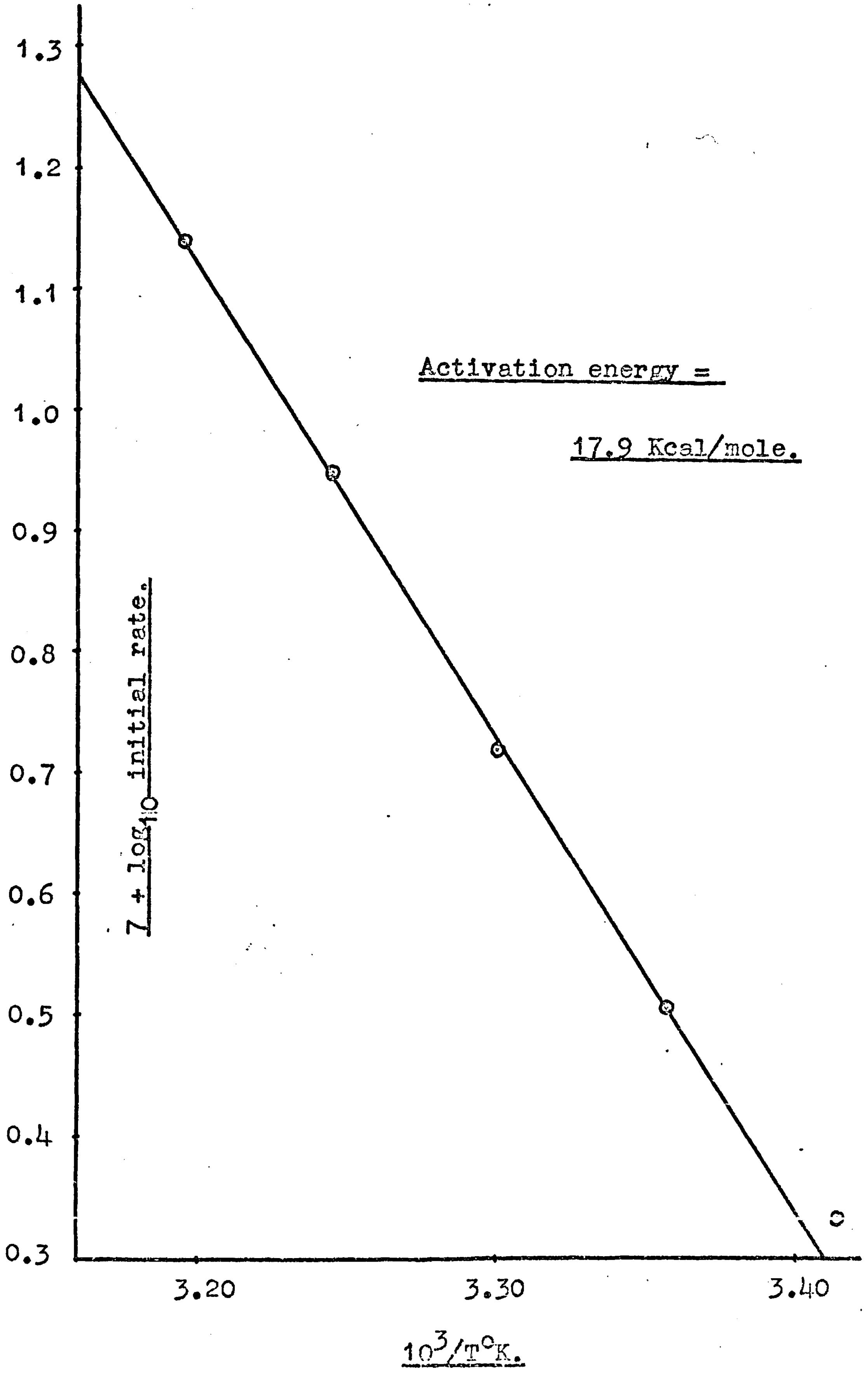


$10^3/T^oK$.

Graph 9.

Arrhenius plot for reaction where

$[K^+] = 0.356$ M.



Activation energy =

17.9 Kcal/mole.

The Effect of Added Reaction Products on the Rate of Reaction.

It has been reported (12,13,20) that the addition of tetrathionate has a catalytic effect on ferricyanide-thiosulphate mixtures, but the presence of ferrocyanide causes a retardation. It was decided to check these observations and to see whether they are significant when the concentrations of both products are of the order of those expected after half of the reaction has occurred.

Reaction mixtures were prepared as before. Tetrathionate was introduced as a solution of the potassium salt into the thiosulphate compartment of the reaction vessel, immediately prior to the start of the experiment. In order to investigate the effect of ferrocyanide ion a suitable quantity of solid potassium ferrocyanide was used during the preparation of stock ferricyanide solution.

6.64×10^{-4} M. $K_4Fe(CN)_6$ in a 5 mm. glass cell was found to have a negligible absorbance at 23,810 cm^{-1}, and tetrathionate is transparent at this wavenumber.

Concentration-time data are shown in table 22.

Table 22.

The Effect of Reaction Products on Rate.

$[S_2O_3^{2-}]$ = 0.108 M.

$[Fe(CN)_6^{3-}]$ = 0.00133 M.

pH = 7.38

Temperature = 25.0 ± 0.02°C.

$[K^+]$ = 0.825 M.

$[EDTA^{4-}]$ = 5×10^{-4} M.

Table of optical density (absorbance units) as a function of time at the concentration of added ferrocyanide and tetrathionate shown. 5 mm. cells were used.

Time (mins)	No additioms	$[S_4O_6^{2-}] = 3.22 \times 10^{-4}$ M.			$[Fe(CN)_6^{3-}] = 6.64 \times 10^{-4}$ M.	
		A	B	C	A	B
0.0	0.672	0.679	0.678	0.679	0.678	0.679
4.0		0.514	0.464	0.614		
10.0		0.316	0.595	0.516		
15.0	0.633	0.158	0.538	0.428		
20.0		0.045	0.466	0.337		
25.0		0.019	0.378	0.253		
30.0	0.590	0.017	0.275	0.180	0.587	0.595
35.0			0.169	0.121		
40.0			0.078	0.077		
45.0	0.527		0.027	0.049	0.528	0.530
50.0			0.009	0.030		
60.0	0.407				0.413	0.403
75.0	0.218				0.237	0.222
90.0	0.010				0.067	0.040

Table 22. Comments.

The rate of reaction was apparently unaffected by the addition of ferrocyanide ion at a concentration expected after 50% completion and consequently the species will have no kinetic effect when deliberate additions are not made.

The expected acceleration was observed for experiments containing added tetrathionate ion. The results obtained here, however, were clearly irreproducible. Table 23 shows the results of initial rate measurements carried out on reaction mixtures containing added tetrathionate ion.

Table 23.

$[S_2O_3^{2-}]$ = 0.100 M.
pH = 5.72
Temperature = 25.0 ± 0.02°C.
$[K^+]$ = 0.133 M.
$[Na^+]$ = 0.199 M.
$[EDTA^{4-}]$ = 5×10^{-4} M.

Table of initial rates $\times 10^6$ M. min^{-1} at the concentration of added tetrathionate shown.

$[S_4O_6^{2-}] \times 10^4$ M.	$[Fe(CN)_6^{3-}]$ M.	
	0.00100	0.00200
0.00	6.26	6.05
5.11	9.38	11.75
* 5.11	95.15	132.98

* Started after tetrathionate had been in contact with thiosulphate for 30 mins.

The irreproducibility of the rate of reaction in the presence of added tetrathionate may, in part, be attributed to its reaction with thiosulphate, presumably forming sulphite. However, since this inconsistency is apparent even when tetrathionate is added immediately before the start of the reaction, it is suspected that the origin of the effect is somewhat more complicated. Consequently, the generally accepted method to find the effect on rate of a particular reactant, that is, to vary its concentration keeping that of all other species constant is not applicable for tetrathionate. A solution should be sought by measuring the reproducible concentration-time curves for reaction mixtures containing no added products, and fitting a rate law to individual kinetic runs.

To Derive a Rate Expression which will hold over a Large Percentage of Reaction.

It is expected that, at any instant, the rate of the ferricyanide-thiosulphate reaction will be given by a complex rate expression consisting of terms to describe the contributions from the initial and the catalysed stages. According to Spiro and Barreira (20) the latter is itself complex in nature, and consequently a rate expression of this type will be difficult to integrate. Under such circumstances it may be helpful to determine the value of the rate from the concentration-time data and plot it against concentration. Since the rate expression is usually the simplest mathematical form of describing the kinetics of a reaction, it may be possible to see a relationship between rate and concentration. Such a relationship may, for example, be a power series in concentration. It is important, therefore to be able to measure with sufficient accuracy the rate of reaction at any given time or concentratiom.

The following method was adopted. The rate was determined, at various times, by a graphical method of drawing tangents, with the aid of a mirror, to concentration-time curves at some 30 points. The rate of loss of ferricyanide was then plotted against time to smooth out the random variations inherent in this method of measurement, and the results were examined alongside corresponding tetrathionate concentration, which is believed to be important in the later stages of the reaction. The amount was calculated assuming only quantitative conversion of thiosulphate to tetrathionate.

Graph 10 shows a typical plot of rate vs. $[S_4O_6^{2-}]$ the data being obtained from table 24. Here and in subsequent tables where the use of computing was made the tetrathionate concentration is denoted by "[TETRA]" M. The rate is defined as $-d[Fe(CN)_6{}^{3-}]/dt$ M. min^{-1} and for all the numerical data powers of ten are denoted by "E". The graph suggests that the simplest relationship between the two variables is a quadratic one of the form,

$$\text{Rate} = A + B\,[S_4O_6{}^{2-}] + C\,[S_4O_6{}^{2-}]^2$$

where A, B and C are constants for a particular run. If these rate constants are evaluated under various conditions then a more detailed relationship may be proposed.

Polynomial regression was used to fit the quadratic expression to rate-concentration data, a computer program being used for this purpose. This was available as a number of library subroutines known as "Scientific Subroutine Packages" which, when called by a master program, are capable of carrying out polynomial regression to a degree limited only by the accuracy of the machine. The main program for the specific purpose in hand was written with the aid of the manual (37) relating to the library routines in question, and is listed in appendix II.

The results of calculations are given in tables 24 - 32, the coefficients of regression being shown with their standard deviations alongside. The latter should be a measure of the constancy of the coefficients during the course of a kinetic run. The predicted rate was calculated by putting values of A, B and C into the rate expression and the residual rate is the difference between observed and predicted values.

The units of A are M. min^{-1}; of B, min^{-1}; and of C, M.$^{-1}$ min^{-1}.

Graph 10.

Graph of rate vs. [$S_4O_6^{2-}$] during a typical run.

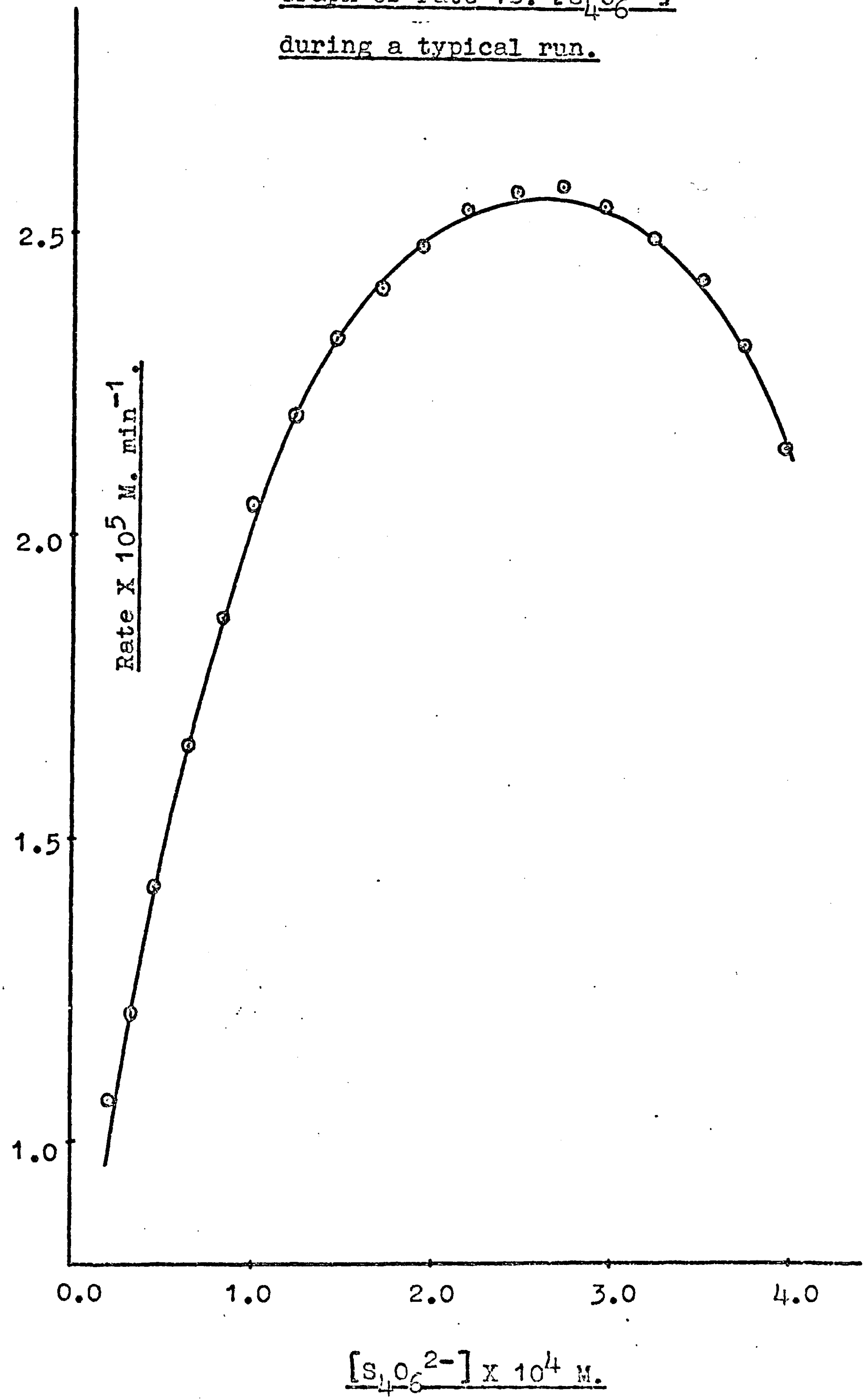


TABLE 24.

POLYNOMIAL REGRESSION. TO FIT KINETIC DATA TO QUADRATIC RATE LAW.

$[S_2O_3^{2-}]$ = 0.198 M.

$[Fe(CN)_6^{3-}]$ = 0.00100 M.

pH = 5.75

$[EDTA^{4-}]$ = 5×10^{-4} M.

Temperature = 25.0 ± 0.02°C.

$[Na^+]$ = 0.398 M.

$[K^+]$ = 0.123 M.

$[OAc^-]$ = 0.120 M.

COEFFICIENTS OF REGRESSION

A = .8744E-05

B = .1360E+00 +OR- .4321E-02

C = -.2641E+03 +OR- .1040E+02

TABLE OF RESIDUALS

[TETRA]	RATE	PREDICTED	RESIDUAL
.200E-04	.107E-04	.114E-04	-.707E-06
.320E-04	.121E-04	.128E-04	-.674E-06
.450E-04	.142E-04	.143E-04	-.128E-06
.620E-04	.165E-04	.162E-04	.321E-06
.800E-04	.186E-04	.179E-04	.648E-06
.990E-04	.205E-04	.196E-04	.863E-06
.121E-03	.220E-04	.213E-04	.710E-06
.144E-03	.233E-04	.228E-04	.412E-06
.168E-03	.241E-04	.241E-04	-.242E-07
.193E-03	.248E-04	.252E-04	-.350E-06
.218E-03	.254E-04	.258E-04	-.436E-06
.244E-03	.257E-04	.262E-04	-.490E-06
.271E-03	.258E-04	.262E-04	-.419E-06
.296E-03	.255E-04	.259E-04	-.375E-06
.322E-03	.250E-04	.251E-04	-.188E-06
.349E-03	.243E-04	.240E-04	.225E-06
.372E-03	.232E-04	.228E-04	.437E-06
.394E-03	.215E-04	.213E-04	.176E-06

TABLE 25.

POLYNOMIAL REGRESSION. TO FIT KINETIC DATA TO QUADRATIC RATE LAW.

$[S_2O_3^{2-}]$ = 0.119 M. $[Na^+]$ = 0.398 M.
$[Fe(CN)_6^{3-}]$ = 0.00100 M. $[K^+]$ = 0.123 M.
pH = 5.75 *$[N(Et)_4^+]$ = 0.079 M.
$[EDTA^{4-}]$ = 5×10^{-4} M. $[Cl^-]$ = 0.238 M.
Temperature = 25.0 ± 0.02°C. $[OAc^-]$ = 0.120 M.

* Added to adjust ionic strength.

COEFFICIENTS OF REGRESSION

A = .4387E-05
B = .8119E-01 +OR- .1049E-02
C = -.1341E+03 +OR- .2535E+01

TABLE OF RESIDUALS

[TETRA]	RATE	PREDICTED	RESIDUAL
.110E-04	.552E-05	.526E-05	.256E-06
.180E-04	.596E-05	.581E-05	.155E-06
.280E-04	.647E-05	.656E-05	-.854E-07
.380E-04	.710E-05	.728E-05	-.179E-06
.490E-04	.784E-05	.804E-05	-.204E-06
.630E-04	.873E-05	.897E-05	-.240E-06
.780E-04	.972E-05	.990E-05	-.184E-06
.920E-04	.108E-04	.107E-04	.383E-07
.110E-03	.118E-04	.117E-04	.124E-06
.128E-03	.128E-04	.126E-04	.237E-06
.148E-03	.137E-04	.135E-04	.234E-06
.169E-03	.144E-04	.143E-04	.142E-06
.191E-03	.150E-04	.150E-04	.175E-07
.213E-03	.155E-04	.156E-04	-.668E-07
.237E-03	.160E-04	.161E-04	-.137E-06
.261E-03	.163E-04	.164E-04	-.143E-06
.285E-03	.166E-04	.156E-04	-.840E-07
.312E-03	.167E-04	.167E-04	.553E-08
.337E-03	.166E-04	.165E-04	.716E-07
.362E-03	.162E-04	.162E-04	.154E-07
.387E-03	.158E-04	.157E-04	.268E-07
.409E-03	.152E-04	.152E-04	-.927E-09

TABLE 26.

POLYNOMIAL REGRESSION, TO FIT KINETIC DATA TO QUADRATIC RATE LAW.

$[S_2O_3{}^{2-}]$ = 0.040 M.

$[Fe(CN)_6{}^{3-}]$ = 0.00100 M.

pH = 5.75

$[EDTA^{4-}]$ = 5 X 10^{-4} M.

Temperature = 25.0 ± 0.02°C.

$[Na^+]$ = 0.398 M.

$[K^+]$ = 0.123 M.

*$[N(Et)_4{}^+]$ = 0.159 M.

$[Cl^-]$ = 0.476 M.

$[OAc^-]$ = 0.120 M.

* Added to adjust ionic strength.

COEFFICIENTS OF REGRESSION

A = .6736E-06

B = .2145E-01 +OR- .2093E-03

C = -.3375E+02 +OR- .6147E+00

TABLE OF RESIDUALS

[TETRA]	RATE	PREDICTED	RESIDUAL
.140E-04	.960E-06	.967E-06	-.734E-08
.220E-04	.112E-05	.113E-05	-.923E-08
.310E-04	.129E-05	.131E-05	-.162E-07
.390E-04	.148E-05	.146E-05	.211E-07
.490E-04	.169E-05	.164E-05	.463E-07
.650E-04	.192E-05	.193E-05	-.539E-08
.800E-04	.217E-05	.217E-05	-.376E-08
.980E-04	.243E-05	.245E-05	-.218E-07
.118E-03	.271E-05	.273E-05	-.250E-07
.140E-03	.300E-05	.302E-05	-.153E-07
.162E-03	.328E-05	.326E-05	.170E-07
.188E-03	.353E-05	.351E-05	.164E-07
.214E-03	.374E-05	.372E-05	.214E-07
.243E-03	.390E-05	.389E-05	.665E-08
.274E-03	.400E-05	.402E-05	-.174E-07
.305E-03	.405E-05	.408E-05	-.266E-07
.336E-03	.409E-05	.407E-05	.191E-07

TABLE 27.

POLYNOMIAL REGRESSION. TO FIT KINETIC DATA TO QUADRATIC RATE LAW.

$[S_2O_3^{2-}]$ = 0.198 M. $[Na^+]$ = 0.398 M.

$[Fe(CN)_6^{3-}]$ = 0.00200 M. $[K^+]$ = 0.126 M.

pH = 5.75 $[OAc^-]$ = 0.120 M.

$[EDTA^{4-}]$ = 5×10^{-4} M.

Temperature = 25.0 ± 0.02°C.

COEFFICIENTS OF REGRESSION

A = .8227E-05

B = .1114E+00 +OR- .1113E-02

C = -.8005E+02 +OR- .1346E+01

TABLE OF RESIDUALS

[TETRA]	RATE	PREDICTED	RESIDUAL
.300E-04	.121E-04	.115E-04	.603E-06
.500E-04	.136E-04	.136E-04	.329E-08
.700E-04	.155E-04	.156E-04	-.132E-06
.950E-04	.179E-04	.181E-04	-.187E-06
.125E-03	.208E-04	.209E-04	-.101E-06
.165E-03	.240E-04	.244E-04	-.428E-06
.200E-03	.275E-04	.273E-04	.196E-06
.245E-03	.308E-04	.307E-04	.863E-07
.295E-03	.339E-04	.341E-04	-.222E-06
.345E-03	.369E-04	.371E-04	-.230E-06
.400E-03	.399E-04	.400E-04	-.766E-07
.465E-03	.428E-04	.427E-04	.836E-07
.530E-03	.451E-04	.448E-04	.320E-06
.600E-03	.464E-04	.462E-04	.155E-06
.675E-03	.471E-04	.469E-04	.155E-06
.745E-03	.470E-04	.468E-04	.215E-06
.815E-03	.454E-04	.458E-04	-.441E-06

TABLE 28.

POLYNOMIAL REGRESSION. TO FIT KINETIC DATA TO QUADRATIC RATE LAW.

$[S_2O_3^{2-}]$	=	0.079 M.	$[Na^+]$	=	0.398 M.
$[Fe(CN)_6^{3-}]$	=	0.00200 M.	$[K^+]$	=	0.126 M.
pH	=	5.75	*$[N(Et)_4^+]$	=	0.119 M.
$[EDTA^{4-}]$	=	5×10^{-4} M.	$[Cl^-]$	=	0.357 M.
Temperature	=	25.0 ± 0.02°C.	$[OAc^-]$	=	0.120 M.

* Added to adjust ionic strength.

COEFFICIENTS OF REGRESSION

A = .3019E-05

B = .3542E-01 +OR- .1288E-02

C = -.2047E+02 +OR- .2022E+01

TABLE OF RESIDUALS

[TETRA]	RATE	PREDICTED	RESIDUAL
.200E-04	.330E-05	.372E-05	-.420E-06
.450E-04	.460E-05	.457E-05	.281E-07
.850E-04	.620E-05	.588E-05	.318E-06
.140E-03	.780E-05	.758E-05	.223E-06
.185E-03	.900E-05	.887E-05	.128E-06
.210E-03	.960E-05	.956E-05	.444E-07
.290E-03	.114E-04	.116E-04	-.171E-06
.315E-03	.121E-04	.121E-04	-.469E-07
.380E-03	.134E-04	.135E-04	-.125E-06
.495E-03	.154E-04	.155E-04	-.139E-06
.525E-03	.160E-04	.160E-04	.245E-07
.615E-03	.172E-04	.171E-04	.136E-06

TABLE 29.

POLYNOMIAL REGRESSION. TO FIT KINETIC DATA TO QUADRATIC RATE LAW.

$[S_2O_3^{2-}]$ = 0.040 M. $[Na^+]$ = 0.398 M.

$[Fe(CN)_6^{3-}]$ = 0.00200 M. $[K^+]$ = 0.126 M.

pH = 5.75 *$[N(Et)_4^+]$ = 0.159 M.

$[EDTA^{4-}]$ = 5×10^{-4} M. $[Cl^-]$ = 0.476 M.

Temperature = 25.0 ± 0.02°C. $[OAc^-]$ = 0.120 M.

* Added to adjust ionic strength.

COEFFICIENTS OF REGRESSION

A = .1049E-05

B = .1637E-01 +OR- .3428E-03

C = -.1046E+02 +OR- .6972E+00

TABLE OF RESIDUALS

[TETRA]	RATE	PREDICTED	RESIDUAL
.100E-04	.113E-05	.121E-05	-.820E-07
.150E-04	.130E-05	.129E-05	.747E-08
.300E-04	.150E-05	.153E-05	-.310E-07
.550E-04	.194E-05	.192E-05	.221E-07
.850E-04	.245E-05	.237E-05	.850E-07
.105E-03	.272E-05	.265E-05	.674E-07
.155E-03	.333E-05	.333E-05	-.496E-08
.190E-03	.377E-05	.378E-05	-.115E-07
.250E-03	.446E-05	.449E-05	-.273E-07
.320E-03	.518E-05	.522E-05	-.356E-07
.405E-03	.594E-05	.596E-05	-.221E-07
.500E-03	.665E-05	.662E-05	.325E-07

TABLE 30.

POLYNOMIAL REGRESSION. TO FIT KINETIC DATA TO QUADRATIC RATE LAW.

$[S_2O_3^{2-}]$ = 0.101 M. $[K^+]$ = 0.273 M.
$[Fe(CN)_6^{3-}]$ = 0.00133 M. *$[N(Et)_4^+]$ = 0.017 M.
pH = 4.70 $[Cl^-]$ = 0.050 M.
$[EDTA^{4-}]$ = 5×10^{-4} M. $[OAc^-]$ = 0.033 M.
Temperature = 25.0 ± 0.02°C.

* Added to adjust ionic strength.

COEFFICIENTS OF REGRESSION

A = .2282E-04

B = .1679E+00 +OR- .1851E-01

C = -.2858E+03 +OR- .2652E+02

TABLE OF RESIDUALS

[TETRA]	RATE	PREDICTED	RESIDUAL
.780E-04	.338E-04	.342E-04	-.377E-06
.116E-03	.379E-04	.384E-04	-.550E-06
.158E-03	.415E-04	.422E-04	-.712E-06
.202E-03	.447E-04	.451E-04	-.371E-06
.247E-03	.476E-04	.469E-04	.749E-06
.295E-03	.499E-04	.475E-04	.243E-05
.344E-03	.504E-04	.467E-04	.365E-05
.390E-03	.454E-04	.448E-04	.579E-06
.434E-03	.390E-04	.418E-04	-.284E-05
.473E-03	.349E-04	.383E-04	-.338E-05
.510E-03	.317E-04	.341E-04	-.240E-05
.542E-03	.289E-04	.298E-04	-.946E-06
.572E-03	.264E-04	.253E-04	.107E-05
.598E-03	.241E-04	.210E-04	.310E-05

TABLE 31.

POLYNOMIAL REGRESSION. TO FIT KINETIC DATA TO QUADRATIC RATE LAW.

$[S_2O_3^{2-}]$ = 0.101 M.
$[K^+]$ = 0.273 M.
$[Fe(CN)_6^{3-}]$ = 0.00133 M.
*$[N(Et)_4^+]$ = 0.027 M.
pH = 5.36
$[Cl^-]$ = 0.040 M.
$[EDTA^{4-}]$ = 5×10^{-4} M.
$[OAc^-]$ = 0.053 M.
Temperature = 25.0 ± 0.02°C.

* Added to adjust ionic strength.

COEFFICIENTS OF REGRESSION

A = .1209E-04
B = .7483E-01 +OR- .1849E-02
C = -.1162E+03 +OR- .2721E+01

TABLE OF RESIDUALS

[TETRA]	RATE	PREDICTED	RESIDUAL
.380E-04	.153E-04	.148E-04	.537E-06
.640E-04	.166E-04	.164E-04	.200E-06
.990E-04	.182E-04	.184E-04	-.156E-06
.126E-03	.194E-04	.197E-04	-.270E-06
.152E-03	.205E-04	.208E-04	-.275E-06
.183E-03	.215E-04	.219E-04	-.388E-06
.216E-03	.225E-04	.228E-04	-.326E-06
.253E-03	.234E-04	.236E-04	-.178E-06
.287E-03	.240E-04	.240E-04	.123E-07
.311E-03	.242E-04	.241E-04	.847E-07
.338E-03	.243E-04	.241E-04	.201E-06
.362E-03	.243E-04	.239E-04	.358E-06
.386E-03	.242E-04	.237E-04	.549E-06
.410E-03	.238E-04	.232E-04	.574E-06
.432E-03	.231E-04	.227E-04	.381E-06
.409E-03	.223E-04	.232E-04	-.947E-06
.479E-03	.214E-04	.213E-04	.141E-06
.497E-03	.205E-04	.206E-04	-.639E-07
.519E-03	.195E-04	.196E-04	-.112E-06
.540E-03	.185E-04	.186E-04	-.933E-07
.558E-03	.176E-04	.176E-04	-.478E-07
.575E-03	.166E-04	.167E-04	-.810E-07
.593E-03	.156E-04	.156E-04	.159E-07
.608E-03	.145E-04	.146E-04	-.113E-06

TABLE 32.

POLYNOMIAL REGRESSION. TO FIT KINETIC DATA TO QUADRATIC RATE LAW.

$[S_2O_3^{2-}]$ = 0.101 M. $[K^+]$ = 0.273 M.
$[Fe(CN)_6^{3-}]$ = 0.00133 M. $*[N(Et)_4^+]$ = 0.030 M.
pH = 5.78 $[Cl^-]$ = 0.037 M.
$[EDTA^{4-}]$ = 5×10^{-4} M. $[OAc^-]$ = 0.060 M.
Temperature = 25.0 ± 0.02°C.

* Added to adjust ionic strength.

COEFFICIENTS OF REGRESSION

A = .4316E-05
B = .5991E-01 +OR- .1650E-02
C = -.8177E+02 +OR- .2774E+01

TABLE OF RESIDUALS

[TETRA]	RATE	PREDICTED	RESIDUAL
.150E-04	.570E-05	.520E-05	.540E-06
.280E-04	.630E-05	.593E-05	.371E-06
.450E-04	.690E-05	.685E-05	.538E-07
.630E-04	.760E-05	.777E-05	-.166E-06
.850E-04	.840E-05	.882E-05	-.417E-06
.109E-03	.930E-05	.987E-05	-.575E-06
.132E-03	.104E-04	.108E-04	-.399E-06
.161E-03	.115E-04	.118E-04	-.342E-06
.192E-03	.128E-04	.128E-04	-.432E-08
.224E-03	.140E-04	.136E-04	.367E-06
.262E-03	.148E-04	.144E-04	.401E-06
.297E-03	.153E-04	.149E-04	.403E-06
.336E-03	.155E-04	.152E-04	.286E-06
.374E-03	.153E-04	.153E-04	.150E-07
.412E-03	.149E-04	.151E-04	-.219E-06
.449E-03	.145E-04	.147E-04	-.231E-06
.484E-03	.140E-04	.142E-04	-.158E-06
.521E-03	.134E-04	.133E-04	.659E-07
.550E-03	.126E-04	.125E-04	.681E-07
.581E-03	.117E-04	.115E-04	-.223E-07

Tables 24 - 32, Discussion.

The Addition of $N(Et)_4^+$ to Maintain Ionic Strength.

The large radius (4.0 Å) and the low charge of the tetraethylammonium ion make it a potentially suitable reagent for the study of ionic strength effects where ion pairing is to be avoided. This policy was adopted to compensate for changes in ionic strength for the present series of experiments but in the light of further evidence the validity of these measurements should be checked.

The limited information available regarding specific effects of tetraethylammonium ions suggests that they are less efficient catalysts than sodium or potassium, a result which is consistent with the larger ionic radius. However, for a number of reactions involving anions, the magnitude of the effect seems to depend on the charge of the activated complex. In the case of the ferricyanide-iodide reaction the sign of the salt effect is reversed on going from potassium to $N(R)_4^+$ where R is methyl or ethyl. Indelli (38) explained this result qualitatively by considering the high polarisability of the quarternary ammonium salt and consequently its ability to cluster around a highly charged activated complex, preventing the smaller ions from getting sufficiently close to exert any appreciable short range action. In a recent paper, Giacomelli (39) attributed the apparently anomalous behaviour to a possible hydrophobic effect of the ion which, if incorporated in the activated complex, would alter drastically the hydration and consequently the energetics of the transition state. It may even be argued that the presence of a quarternary ammonium salt could modify the stability constants for possible ion pairs in the reaction mixture.

No quantitative interpretation of the effect of tetraalkylammonium ion on reaction rate has yet been reported and it is impossible to even make a qualitative prediction as to whether an acceleration or a retardation is to be expected for the reaction in question. All subsequent calculations were carried out assuming that $N(Et)_4^+$ is inert towards ion pair formation and any kinetic features should appear in the final result.

Significance of the "Zero" Order Term.

The intercept (A) of the rate vs. $[S_4O_6^{2-}]$ curve at zero concentration corresponds to the reaction occurring when none of this product is present, and therefore it refers to what has previously been measured directly as the initial rate. The rate law governing this initial stage has been shown to be

$$-\frac{d[Fe(CN)_6^{3-}]}{dt} = 85\,[S_2O_3^{2-}]_T^2\,[H^+]$$
$$+\ 10^{-3.03}\,F(I)\,(3.2[Na^+]_T + 23.4[K^+]_T)\,[H^+][S_2O_3^{2-}]_T$$
$$M.\ min^{-1}$$

at 25°C and $[OAc^-] = 0.033$ M. (see page 84).

The concentrations of thiosulphate and metal ions (subscript T) in this expression are those obtained after considering the formation of possible ion pairs, notably $NaS_2O_3^-$ and $KS_2O_3^-$. Since reaction mixtures contained both sodium and potassium ion it is necessary to consider the relevant equilibria for the two cations simultaneously.

$$NaS_2O_3^- \rightleftharpoons Na^+ + S_2O_3^{2-}$$
$$KS_2O_3^- \rightleftharpoons K^+ + S_2O_3^{2-}$$

Let us assume, as usual, that the ion pair equilibria are very rapidly established. If the initial concentrations of sodium, thiosulphate and potassium ions are "a", "b" and "c" respectively, and the amounts of $NaS_2O_3^-$ and $KS_2O_3^-$ present at equilibrium are "x" and "y" respectively then, for sodium ion,

$$K_{Na} = \frac{(a - x)(b - x - y)}{x}$$

$$\text{or} \quad y = b - x - \frac{K_{Na} \; x}{(a - x)} \quad \ldots. \text{(i)}$$

and, for potassium ion

$$K_K = \frac{(c - y)(b - x - y)}{y}$$

$$\text{or} \quad x = b - y - \frac{K_K \; y}{(c - y)} \quad \ldots. \text{(ii)}$$

where K_M refers to the stability constant of the ion pair $MS_2O_3^-$ under the experimental conditions, calculated as described on page 80. The total divalent anion (L^{2-}) concentration (see also page 79) was considered in the place of thiosulphate.

Equations (i) and (ii) were solved simultaneously for x and y by a method of successive approximations. Values of x were guessed and inserted into equation (i) in order to calculate y. The result was substituted into equation (ii) and a new value for x derived. On the basis of this result a better value of x was guessed and fed into equation (i). The iteration was repeated until the x obtained at the end of the calculation was close to that put in. The results are shown in table 33. Initial rates were calculated from the overall rate expression shown above and experimentally observed rates are compared alongside.

Table 33.

I	$[L^{2-}]$ M.	10^2 x M.	10^2 y M.	$10^2[L^{2-}]_T$ M.	$10^2[S_2O_3{}^{2-}]_T$ M.	$10^6[H^+]$ M.	Predicted rate X 10^6 M. min^{-1}	Observed rate X 10^6 M. min^{-1}
0.72	0.200	4.841	2.572	12.587	12.461	2.57	3.51	*8.74
0.72	0.121	3.008	1.661	7.431	7.308	2.57	1.25	4.39
0.72	0.042	1.071	0.617	2.512	2.392	2.57	0.15	0.67
0.73	0.201	4.853	2.639	12.608	12.420	2.56	3.48	*8.23
0.73	0.082	2.059	1.188	4.953	4.772	2.56	0.55	3.02
0.73	0.043	1.093	0.644	2.563	2.384	2.56	0.15	1.05
0.40	0.103	-	3.511	6.789	6.657	28.53	11.99	22.82
0.41	0.103	-	3.502	6.798	6.666	6.25	2.63	12.09
0.41	0.103	-	3.502	6.798	6.666	2.38	1.00	4.32

* No $N(Et)_4{}^+$ present for these runs.

Table 33, Comments.

It is immediately apparent that predicted rates are quite different from those observed experimentally. In two instances kinetic runs were carried out where no tetraethylammonium ion had been added and in these cases the measured rate should have been predicted. The only difference in experimental conditions between the runs used for the derivation of the kinetic equation (see tables 16 and 17) and those carried out in the present investigation, which has not been taken into account, is the higher buffer concentration in the latter case. Since a good first order plot for hydrogen ion was obtained (graph 4) in experiments with variable acid but constant acetate ion concentration, general acid catalysis is thought unlikely. However, general base catalysis, that is, a reaction step involving the concentration of acetate ion, cannot be ruled out. Other bases might also need to be considered.

It was found that the third order rate constant for the first term of the rate law referring to the initial rate was dependent on acetate ion concentration, this dependence being as follows,

$$k_3 = 38 + 1400\,[\mathrm{OAc}^-]$$

Table 34 compares values for k_3 calculated from the above expression with those found from initial rates, where,

$$k_3 = \frac{\text{Initial rate} - 10^{-3.03}\,F(I)\,(3.2[\mathrm{Na}^+] + 23.4[\mathrm{K}^+])[\mathrm{S_2O_3}^{2-}][\mathrm{H}^+]}{[\mathrm{S_2O_3}^{2-}]^2\,[\mathrm{H}^+]}$$

and the values for thiosulphate and metal ion concentration are "true" values.

Table 34.

$[OAc^-]$ M.	k_3 predicted $M.^{-2}\ min^{-1}$	k_3 experimental $M.^{-2}\ min^{-1}$
0.033	84	85(1)
0.120	206	216(2)
0.120	206	199(3)
0.200	318	317(4)

(1) See page 84

(2) Refer to tables 24 and 33

(3) Refer to tables 27 and 33

(4) Refer to table 10. Here $[Na^+]$ was considered to be negligible.

There is general agreement between experimental and calculated values over a sixfold range of acetate ion concentration. An ionic strength term for the acetate catalysed reaction has not been included since it was considered that the data would not be sufficiently sensitive to show any trends in this respect.

Table 35 lists initial rates calculated for the present series of experiments taking into account the acetate ion concentration. The measured values are shown alongside for comparison together with the remaining variables, that is, $[N(Et)_4^+]$ and $[Cl^-]$.

Considerable discrepancy still exists between observed and predicted rates when either tetraethylammonium or chloride ion is present. For a reaction of this complexity it is thought unlikely that any unambiguous result can be obtained from so few kinetics experiments, since involvement of the two ions in question is possible in any of the three reaction steps proposed.

Table 35.

$[N(Et)_4^+]$ M.	$[Cl^-]$ M.	Predicted rate X 10^6 M. min^{-1}	Observed rate X 10^6 M. min^{-1}
-	-	8.34	8.74
0.079	0.238	2.91	4.39
0.159	0.476	0.33	0.67
-	-	8.25	8.23
0.119	0.357	1.25	3.02
0.159	0.476	0.33	1.05
0.017	0.050	11.86	22.82
0.027	0.040	3.38	12.09
0.030	0.037	1.39	4.32

Significance of the "First" and "Second" Order Terms.

Owing to the large number of variables present in the reaction mixtures it is unlikely that any correlations between kinetic runs will be meaningful, however a number of conclusions may be drawn regarding individual experiments where almost all these variables are constant. The thiosulphate concentration was regarded as constant during the course of a kinetic run. The "first" and "second" order terms of the quadratic rate expression,

$$-\frac{d[Fe(CN)_6^{3-}]}{dt} = A + B\,[S_4O_6^{2-}] + C\,[S_4O_6^{2-}]^2$$

are considered to refer to the tetrathionate catalysed part of the reaction, observable once the reaction is under way.

It must be remembered that this relationship is purely a mathematical one where $[S_4O_6^{2-}]$ refers to $\frac{1}{2}([Fe(CN)_6^{3-}]_o - [Fe(CN)_6^{3-}])$ where $[Fe(CN)_6^{3-}]_o$ is the initial ferricyanide concentration.

If the proposals of Batstone (13) are adopted to explain the tetrathionate catalysed step, the following overall rate law is expected:

$$-\frac{d[Fe(CN)_6^{3-}]}{dt} = A + k\,[Fe(CN)_6^{3-}][S_4O_6^{2-}]$$

However, since

$$[Fe(CN)_6^{3-}] = [Fe(CN)_6^{3-}]_o - 2[S_4O_6^{2-}]$$

the equation becomes

$$-\frac{d[Fe(CN)_6^{3-}]}{dt} = A + k\,[Fe(CN)_6^{3-}]_o[S_4O_6^{2-}] - 2\,k[S_4O_6^{2-}]^2$$

that is, a second degree polynomial in $[S_4O_6^{2-}]$ as found during the present investigations, where $B = k\,[Fe(CN)_6^{3-}]_o$ and $C = -2\,k$. Consequently, if the rate law is correct, a certain relationship between B and C must hold, namely:

$$C = -\frac{2\,B}{[Fe(CN)_6^{3-}]_o}$$

Table 36 compares, for individual runs, calculated C values from experimentally derived B values with the coefficient of $[S_4O_6^{2-}]^2$ obtained by polynomial regression on rate-concentration data.

The agreement between observed and calculated values for C is considered to be good and this supports the rate law suggested by Batstone.

Table 36.

B min^{-1}	$[Fe(CN)_6^{3-}]_o \times 10^3$ M.	Calculated C $M.^{-1}$ min^{-1}	Observed C $M.^{-1}$ min^{-1}
0.136	1.00	- 272	- 264
0.081	1.00	- 162	- 134
0.021	1.00	- 42	- 34
0.111	2.00	- 111	- 80
0.035	2.00	- 35	- 20
0.016	2.00	- 16	- 10
0.168	1.33	- 253	- 286
0.075	1.33	- 113	- 116
0.060	1.33	- 90	- 82

These findings must be considered along with other evidence. A possible mechanism which has already been discussed in connection with the radiochemical analysis of products is that catalysis may be due to the reaction of thiosulphate with tetrathionate, or more correctly, polythionate, followed by a removal of sulphite by ferricyanide ion. Such a reaction would have to involve thiosulphate in the rate expression; however the experimental conditions were not suitable to arrive at a conclusion in this respect. The product analysis data also led one to suspect that, perhaps, the removal of sulphite by ferricyanide was not instantaneous as originally thought. In the limiting case if, owing to the low concentration present, the latter process is slow relative to the rate of production of sulphite,

$$S_2O_3^{2-} + S_4O_6^{2-} \xrightarrow{fast} S_5O_6^{2-} + SO_3^{2-}$$

$$SO_3^{2-} + Fe(CN)_6^{3-} \xrightarrow{slow} Fe(CN)_6^{4-} + SO_4^{2-}$$

then,

$$\text{Rate} = k' [S_2O_3^{2-}][S_4O_6^{2-}][Fe(CN)_6^{3-}]$$

consistent with the observations made under conditions of constant thiosulphate ion concentration. The stoicheiometric equation for the catalysed reaction will be given by

$$S_4O_6^{2-} + S_2O_3^{2-} + Fe(CN)_6^{3-} \longrightarrow S_5O_6^{2-} + SO_4^{2-} + Fe(CN)_6^{4-}$$

where tetrathionate could be replaced by any polythionate species, such as the one formed in the specific reaction shown above. In the calculation of the coefficients A, B and C it was assumed that the loss of two moles of ferricyanide ion led to the formation of one mole of tetrathionate. However, if the reaction in question leads to the production of sulphate, as is suggested, then the catalysed step will not cause an increase in the amount of tetrathionate present; it will not deplete the total polythionate concentration either. Instead, the species $S_nO_6^{2-}$ will be quantitatively converted to $S_{n+1}O_6^{2-}$ which, to all intents and purposes, is kinetically indistinguishable from its parent.

The only source of tetrathionate is the primary reaction. Since this is of zero order with respect to ferricyanide ion and since pH and $[S_2O_3^{2-}]$ are regarded as constant during the course of a kinetic run then, after a time t mins, the rate of the said process will be given by the initial rate, and the amount of tetrathionate formed may be found from,

$$[S_4O_6^{2-}] = \tfrac{1}{2} A\, t \quad M.$$

If the rate of the catalysed reaction is proportional to $[Fe(CN)_6^{3-}][S_4O_6^{2-}]$, as supported by the results in table 36, then the experimental data for individual runs ought to be satisfied when $[S_4O_6^{2-}]$ is calculated only from the initial rate. An experiment was selected where the fit to the quadratic rate law was good and the calculated C value matched the observed (see table 36). The kinetic run chosen is that shown in table 24 and the relevant data are listed in table 37.

Table 37.

$$A = [S_4O_6^{2-}]; \quad B = [Fe(CN)_6^{3-}]; \quad k = \frac{\text{Rate} - 0.87 \times 10^{-5}}{A\ B}$$

Time (mins)	10^4 A M.	10^3 B M.	10^8 A B $M.^2$	10^5 Rate M. min^{-1}	k $M.^{-1}$ min^{-1}
0	0	1.000	0	0.87	-
4	0.17	0.958	1.63	1.06	117
8	0.35	0.905	3.17	1.42	174
12	0.52	0.832	4.33	1.85	226
16	0.70	0.745	5.22	2.20	255
20	0.87	0.646	5.62	2.41	274
24	1.05	0.540	5.67	2.54	295
28	1.22	0.429	5.23	2.58	327
32	1.40	0.321	4.49	2.50	363
36	1.57	0.215	3.38	2.32	429

The inconsistency in k suggests that the calculation of $[S_4O_6^{2-}]$ from the initial rate alone does not represent the true situation. In fact a somewhat higher concentration than that shown above is required in the later stages of the reaction.

A mechanism which is proposed must involve a method whereby sulphate is produced, although the amount may be quite small. The primary reaction cannot be considered as the source since tetrathionate ion must in some way be formed to participate in the subsequent catalysis, unless, of course, the latter species was originally present as an impurity. This possibility is considered doubtful because of the high quality reagents used in this work. The radiochemical analysis for sulphate was consistent with a mechanism involving sulphite as intermediate however it is conceivable that this route may correspond to only a small fraction of the observed change. In fact, so far we have considered numerically two limiting situations; one where no sulphate is formed and one where only sulphate is formed as a result of the tetrathionate catalysis.

It may be argued that since for radiochemical work the amount of ferricyanide used was nearly 50 times that present for the experiment under consideration, the probability of the ferricyanide-sulphite reaction, which is known to be of first order with respect to ferricyanide ion, will be reduced correspondingly, here. This is evidence that the extent of the reaction proceeding via sulphite to sulphate, which the product analysis showed to be in the region of 20%, may be very small indeed in the kinetic work and the major catalytic change could lead to the productiom of tetrathionate, as oxidation product, by some other route. Thus the "working" tetrathionate concentration will correspond closely to that used originally for the evaluation of the coefficients A, B and C, and the rate law proposed by Batstone for the catalytic reaction is satisfactory.

SECTION III.

THE REACTION BETWEEN FERRICYANIDE AND THIOSULPHATE IONS.

DISCUSSION.

GENERAL DISCUSSION.

Some properties of the thiosulphate ion in isolation and the findings on the ferricyanide-thiosulphate reaction available to date were reviewed in the introduction.

Experimental data has been used to derive a mathematical expression in the form of a rate equation encompassing as many variables of the reacting system as possible.

The ferricyanide-thiosulphate reaction has been found to involve two distinct processes, the first, proceeding in the absence of any products whilst the second, which is dominant in the later stages of reaction involves the participation of tetrathionate ion.

The Initial Stages of Reaction.

The initial rate has been shown to fit the following rate expression:

$$-\frac{d[Fe(CN)_6^{3-}]}{dt} = k\,(1 + 37[OAc^-])\,[S_2O_3^{2-}]^2\,[H^+] + k'\,([Na^+] + 7.3[K^+])\,[S_2O_3^{2-}][H^+]$$

where k' incorporates the ionic strength term predicted by the Brønsted theory. The corresponding term for the acetate catalysed reaction has not been considered in the derivation of the expression since the kinetics results were not sufficiently sensitive to permit the necessary calculation. The activation energies connected with k and k' are 16.8 and 17.9 Kcal/mole respectively. The solvent isotope effect is consistent with $HS_2O_3^-$ being one of the reacting species in the mechanism connected with the first term of the rate equation.

The dependence of rate on ferricyanide concentration is of zero order and for this reason the reaction is unique in the field of redox systems involving thiosulphate where, invariably, the oxidising agents constitute a term in the rate expression. The implication is that thiosulphate undergoes a spontaneous rate determining change in the buffered medium so as to facilitate subsequent electron removal by ferricyanide.

Thiosulphate readily decomposes in acid solution and will exchange oxygen atoms with solvent water. The mechanisms of these two processes have been considered in literature and since they constitute two out the three possible spontaneous changes which thiosulphate can undergo in acidified solution (the third possibility being hydrogen ion exchange between protonated forms and water), it is deemed worthwhile to review the available information.

The Acid Catalysed Decomposition of Thiosulphate.

The formation of sulphur as a product of the decomposition of thiosulphate in acidified solution has been of interest to colloid chemists, however very few of these widely reported investigations shed light on the mechanism of the reaction.

A kinetic investigation was carried out by La Mer and coworkers (40). The measurements were made by observing scattered light at 400 mu. Since the concentration of sulphur required to be present in solution before discreet particles may be observed (3.1×10^{-6} g. atoms S/litre) is known, the time required for the "Tyndall" beam to appear was used as a measure of the initial rate of production of the element.

The measurements referred to an extremely small percentage of reaction where the products are expected to be sulphite ion and elemental sulphur. The reaction is also expected to be free from the complications which, in the later stages produce numerous polythionates.

The initial rate of production of sulphur was given by:

$$\frac{d[S]}{dt} = k\,[S_2O_3^{2-}]^{3/2}\,[H^+]^{1/2}$$

and was explained by the following mechanism:

$$HS_2O_3^- + S_2O_3^{2-} \xrightarrow{k_1} [HS_2O_3.S_2O_3]^{3-}$$

$$[HS_2O_3.S_2O_3]^{3-} \xrightarrow{k_2} SO_3^{2-} + HSO_3^- + 2\,S$$

where, at an ionic strength of 0.016, $k_1 = 0.31$ M.$^{-1}$ min^{-1} and $k_2 = 0.14$ min^{-1}. No activation parameters were determined in this case.

The rate of production of sulphite was measured titrimetrically and was found to obey the following rate law:

$$\frac{d[SO_3^{2-}]}{dt} = k\,[S_2O_3^{2-}]^2\,[H^+]$$

These kinetics results were confirmed by Davis (41) who explained them on the basis of the following reaction scheme:

$$HS_2O_3^- + S_2O_3^{2-} \longrightarrow HS_3O_3^- + SO_3^{2-}$$

$$HS_3O_3^- + S_2O_3^{2-} \longrightarrow HS_4O_3^- + SO_3^{2-}$$

$$\vdots$$

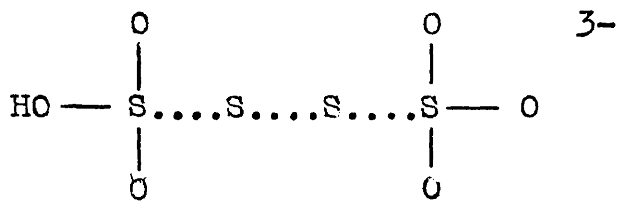
finally $HS_8O_3^- + S_2O_3^{2-} \longrightarrow S_8 + HSO_3^- + SO_3^{2-}$

The work of La Mer and of Davis was criticised by Agarwala and coworkers (42). By considering the natural abundance of the isotopes ^{34}S and ^{32}S they investigated the kinetic isotope effect on the reaction. Their findings were in favour of a bimolecular mechanism with respect to thiosulphate:

$$2\ S_2O_3^{2-} \rightleftharpoons [SO_3....S....S....SO_3]^{4-} \longrightarrow 2\ SO_3^{2-} + S$$

where, in the transition state one of the thiosulphate molecules loses a sulphur atom to the other, the sulphur-sulphur-sulphite bond of this second molecule breaking simultaneously.

Since the authors do not consider that protonation of thiosulphate will lead to any isotopic fractionation, the activated complex, or a species from which the activated complex will be derived, has the structure:



$$\mathrm{HO{-}\overset{O}{\underset{O}{S}}....S....S....\overset{O}{\underset{O}{S}}{-}O}\quad ^{3-} \qquad .....\ (i)$$

where the sulphur-sulphur bonds will be extended to greater than the normal single bond length.

It was argued that the mechanisms presented by the previous two authors are invalid on the basis of predicting an isotope effect not observable experimentally. For the purpose of this discussion, where only the initial stages of the mechanism could be of importance (since on completion, sulphur is produced and no evidence of colloidal sulphur was found in ferricyanide-thiosulphate mixtures), all mechanisms propose the existence of at least structure (i), or even a species with S-S bonds fully made as was possibly visualised by La Mer.

The Exchange of Oxygen between Thiosulphate and Water.

The exchange of ^{18}O between thiosulphate ion and water has been measured at 60 - 100°C and pH 5.3 - 6.5 (43). The rate was found to be of first order with respect to thiosulphate and of first order with respect to hydrogen ion:

$$\text{Rate} = k\,[S_2O_3^{2-}][H^+]$$

General acid catalysis was not observed, nor was the reaction catalysed by chloride ions. The rate constant, which was of the order of 1200 $M.^{-1}$ min^{-1} at 80°C, was independent of ionic strength over the range I = 0.01 - 0.04 and one measurement above an ionic strength of 1. The exchange was faster in D_2O than in H_2O with $k_{H_2O}/k_{D_2O} = 0.63$ and the activation energy was 13.4 Kcal/mole.

The lack of an effect of ionic strength on rate is not consistent with the rate equation. According to the Brønsted theory for the formation of a singly charged activated complex, presumably $HS_2O_3^-$ from H^+ and $S_2O_3^{2-}$, the rate constant k for a real system is related to that under ideal conditions (k_o) by:

$$k = k_o \frac{f_2 f_1}{f_1} = k_o f_2$$

where f_1 and f_2 denote activity coefficients for singly and doubly charged ions respectively. Hence,

$$\log k = \log k_o - 2.02\, F(I)$$

In other words a graph of log k vs. F(I) should have a slope of -2.02. This is not so. The authors argued that this may in part be due to the breakdown of the Debye-Huckel limiting law at the ionic strengths encountered experimentally. Even if this is so, a retardation of rate with increase in ionic strength should still be observable under these conditions at such low ionic strengths.

Perhaps the most serious shortcoming of this investigation is the use of unbuffered reaction mixtures for some critical experiments, such as the determination of the order with respect to thiosulphate. It is difficult to imagine that the pH of thiosulphate solutions at various concentrations will be constant even though they may have been prepared carefully from high quality reagents. The protonation equilibrium

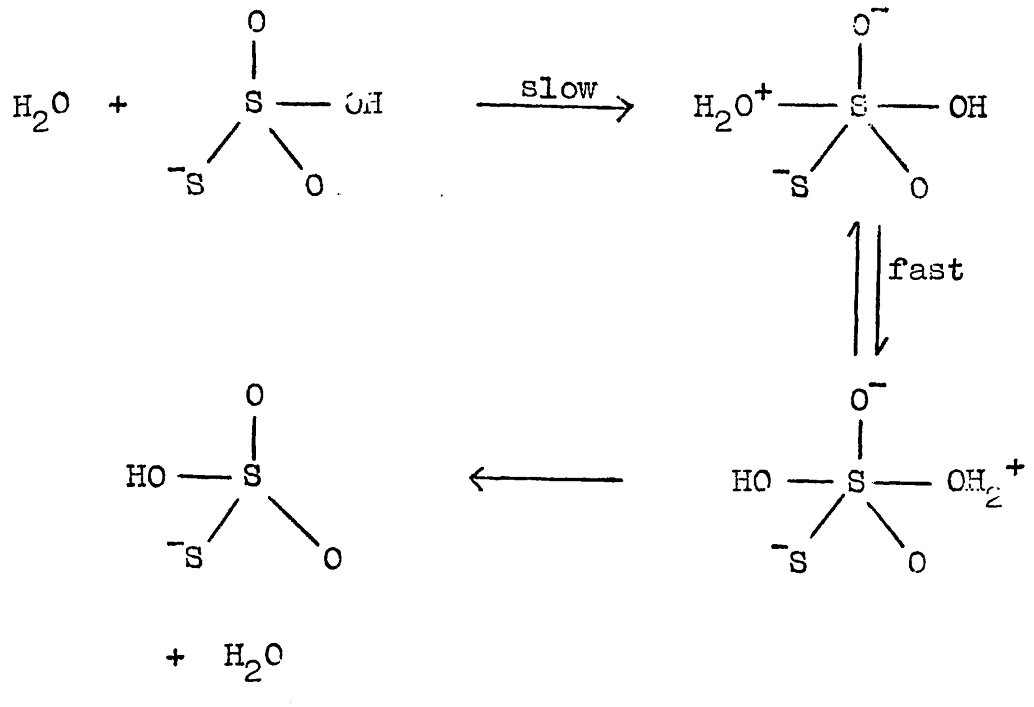
$$H^+ + S_2O_3^{2-} \rightleftharpoons HS_2O_3^-$$

will tend to remove hydrogen ions at higher thiosulphate concentration whilst the greater ionic strength of the medium will modify the dissociation constant of water (Kw) according to

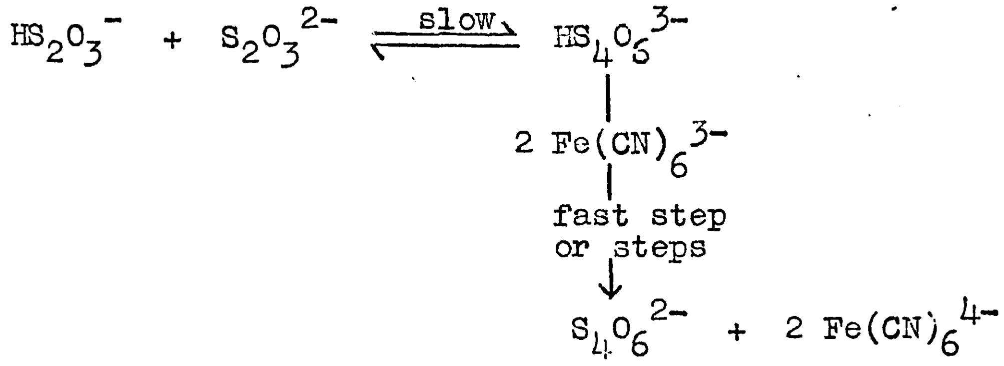
$$\log Kw = -14 - 1.01\ F(I).$$

Although this difficulty was acknowledged by the authors it is hard to believe that the actual pH may be calculated from the two considerations given above.

A mechanism which is consistent with the proposed rate equation involves the attack of water on the central sulphur atom in an SN2 type reaction,



Turning now to consider the mechanism of the initial stages of the ferricyanide-thiosulphate reaction. The first term of the rate equation suggests a reaction between the two species $HS_2O_3^-$ and $S_2O_3^{2-}$, greatly accelerated in the presence of carboxylate ion. Complex formation between the two reactants has been proposed as the rate determining event for the acid catalysed decomposition of thiosulphate ion. A pathway involving such an intermediate could be important in the present investigation.



$$HS_2O_3^- + S_2O_3^{2-} \xrightleftharpoons{\text{slow}} HS_4O_6^{3-}$$

$$HS_4O_6^{3-} \xrightarrow[\text{fast step or steps}]{2\,Fe(CN)_6^{3-}} S_4O_6^{2-} + 2\,Fe(CN)_6^{4-}$$

According to La Mer (40) the second order rate constant for the formation of the complex ion from $HS_2O_3^-$ and $S_2O_3^{2-}$ is 0.31 $M.^{-1}$ min^{-1}. This value was calculated assuming

0.01 M. to be the dissociation constant for $HS_2O_3^-$, that is,

$$0.01 = \frac{[H^+][S_2O_3^{2-}]}{[HS_2O_3^-]}$$

No adjustment was made for the ionic strength of the medium, but since this was kept constant throughout the investigation, this does not constitute an error. Hence,

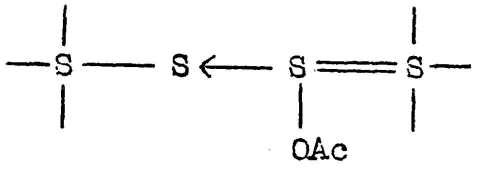
$$[HS_2O_3^-] = 100\,[H^+][S_2O_3^{2-}]$$

and $$\text{Rate} = 31\,[H^+][S_2O_3^{2-}]^2 \quad M.\ min^{-1}.$$

The third order rate constant compares most favourably with a value of 38 $M.^{-2}\ min^{-1}$ calculated for the first term of the rate expression for the ferricyanide-thiosulphate reaction in the absence of carboxylate ion (see page 111). The value is independent of ionic strength.

No activation parameters or solvent isotope effect data are available for the acid catalysed decomposition of thiosulphate ion.

According to La Mer and coworkers the intermediate species is fairly stable in aqueous solution, the first order rate constant for decomposition being 0.14 min^{-1}. This corresponds to a half life of some 5 minutes. Agarwala and coworkers (42), on the other hand, favour a four centred reaction with synchronous cleavage of two $S\text{-}SO_3$ bonds and the formation of an S_2 molecule. The nature of the intermediate should explain general base catalysis, that is, the presence of anions should favour the formation of the species. If sulphur-sulphur bonds are formed between two thiosulphate ions they may be a result of overlap of filled $p\pi$ orbitals on one sulphur with the empty $d\pi$ orbitals of the other, this type of bonding being frequently found between sulphur and oxygen atoms (44). Under such circumstances the electron donating atom will aquire a partial positive charge and it could be conceived that anions will act so as to stabilise the charge thus:



$$-\overset{|}{\underset{|}{S}}-S\leftarrow\underset{\underset{OAc}{|}}{S}=\overset{|}{\underset{|}{S}}-$$

enhancing the stability of the complex and resulting in the observed catalysis. If this is so, the addition of anions should also have the effect of reducing the rate of decomposition of thiosulphate in acid solution.

An intermediate of the type proposed by La Mer is clearly preferred in this discussion. The oxidation of the complex by ferricyanide will be fast

$$HS_4O_6^{3-} + Fe(CN)_6^{3-} \begin{array}{l} \nearrow \; HFe(CN)_6^{3-} + S_4O_6^{3-\cdot} \\ \searrow \; Fe(CN)_6^{4-} + HS_4O_6^{2-} \end{array}$$

the sulphur containing species formed in each case being a free radical. Terminating processes can be devised to give tetrathionate as the only product:

$$S_4O_6^{3-} + Fe(CN)_6^{3-} \longrightarrow S_4O_6^{2-} + Fe(CN)_6^{4-}$$

$$HS_4O_6^{2-} + Fe(CN)_6^{3-} \begin{array}{l} \nearrow \; HS_4O_6^{-} + Fe(CN)_6^{4-} \\ \searrow \; S_4O_6^{2-} + HFe(CN)_6^{3-} \end{array}$$

or by radical disproportionation followed by dimerisation,

$$HS_4O_6^{2-} \longrightarrow HS_2O_3^{-} + S_2O_3^{-}$$

$$S_4O_6^{3-} \longrightarrow S_2O_3^{2-} + S_2O_3^{-}$$

$$2\ S_2O_3^{-} \longrightarrow S_4O_6^{2-}$$

The second term of the initial rate equation suggests a somewhat different process to that postulated above, for the first term. The mechanism must, as in the previous case, be a spontaneous change which thiosulphate can undergo, since there is no involvement of ferricyanide ion in the rate equation. The reaction is of first order with respect to hydrogen ion and to thiosulphate ion and is of first order with respect to cation. Although there are some similarities in the kinetics to those reported for the exchange of oxygen between thiosulphate ion and water (43) there is a difference of 4.5 Kcal/mole in the activation energies for the two processes.

The activated complex is expected to have the composition MHS_2O_3. It may be argued that if mutual repulsion is the cause of the inability of $S_2O_3^{2-}$ and $Fe(CN)_6^{3-}$ to come sufficiently close for electron transfer, then ion pairing of one or other reactant with cations should assist such an encounter.

The rate expression suggests the following reaction scheme:

$$H^+ + S_2O_3^{2-} + M^+ \underset{}{\overset{\text{slow}}{\rightleftharpoons}} MHS_2O_3 \xrightarrow[\text{fast}]{Fe(CN)_6^{3-}} \text{products}$$

where the equilibrium concentration of the intermediate MHS_2O_3 is estimated to be of the order of 10^{-6} M. Ion pairing equilibria of this type are usually set up rapidly. The rate of a normal bi-molecular process, when the concentrations of reactants are of the order of 10^{-6} and 10^{-4} M., with a pre-exponential term of 10^{9} and a small activation energy, will be fast, and thus the low concentration of the intermediate cannot be held to account for the slow rate of reaction. Further, under such conditions, it is likely that $Fe(CN)_6^{3-}$ attack would become rate determining.

The mechanism requires of the order of 18 Kcal/mole whereas the addition of H^+ and M^+ would be expected to have an activation energy of only 0 to 6 - 8 Kcal/mole. Presumably, further energy is required to render the intermediate specialised in some way.

Once MHS_2O_3 is formed no large electronic concentration (- charge) resides on, say, the outer sulphur atom and it is possible that water, or even some base present in solution, could attack and consequently facilitate electron loss. The slow step could then be the formation of a bond (for example, to sulphur) and such a process would require activation energy.

More accurately, a mechanism may thus be written as follows:

$$\begin{tikzcd} H^+ + S_2O_3^{2-} + M^+ \arrow[r, shift left, "\text{fast}"] & MHS_2O_3 \arrow[l, shift left] \arrow[r, shift left, "\text{slow}"] & \text{(activated complex)} \arrow[l, shift left] \arrow[d, "Fe(CN)_6^{3-}\ \text{fast}"] \\ & & \text{products.} \end{tikzcd}$$

Since, at any instant, some 25% of $HS_2O_3^-$ may exist in the "thiol" form, the possible reaction of this group with ferricyanide should be mentioned.

Organic thiols are readily oxidised by ferricyanide to the corresponding dithio-compound, for example,

$$2\ C_8H_{17}SH \xrightarrow{Fe(CN)_6^{3-}} (C_8H_{17}S-)_2$$

The mechanism of these oxidations has been discussed by Wiberg and coworkers (45). The reactions are almost universally base catalysed and it is generally accepted that the species RS^- is involved in an electron abstraction by ferricyanide to give the free radical $RS^{\bullet}$ which may subsequently dimerise. Although some of these oxidations are known to proceed in acid solution where a mechanism of proton abstraction by ferricyanide has been postulated, the kinetic evidence is not considered sufficiently conclusive to enable an analogy to be drawn.

Oxidation of the activated complex will be fast:

$$\begin{tikzcd}
 & HFe(CN)_6^{3-} + MS_2O_3^{\bullet} \\
MHS_2O_3 + Fe(CN)_6^{3-} \arrow[ur] \arrow[dr] & \\
 & Fe(CN)_6^{4-} + MHS_2O_3^{+}
\end{tikzcd}$$

$$\begin{tikzcd}
 & M^+ + HS_2O_3^{\bullet} \\
MHS_2O_3^{+} \arrow[ur] \arrow[dr] & \\
 & H^+ + MS_2O_3^{\bullet}
\end{tikzcd}$$

followed by subsequent dimerisation of the free radicals

$$2\ (M^+ \text{ or } H^+)S_2O_3^{\bullet} \longrightarrow (H^+ \text{ or } M^+)S_4O_6^- + H^+ \text{ or } M^+$$

Tetrathionate ion has been proposed as the major product of the initial reaction step.

The Later Stages of Reaction.

A computer program was used to calculate rate constants in the later stages of reaction where it was found to be strongly catalysed by the presence of tetrathionate ion. The rate was found to be of first order with respect to tetrathionate and ferricyanide ions. That is,

$$\text{Rate} = k\,[S_4O_6^{2-}][Fe(CN)_6^{3-}]$$

but the possible involvement of thiosulphate and of hydrogen ion was not resolved owing to the unpredictable kinetic effects of tetraethylammonium ion, which was added to maintain ionic strength.

It was shown that, unless ferricyanide is present at a relatively high concentration, as was the case for the determination of products by tracer techniques where equimolar quantities of ferricyanide and of thiosulphate were used, the possible reaction by way of sulphite

$$S_4O_6^{2-} + S_2O_3^{2-} \rightleftharpoons S_5O_6^{2-} + SO_3^{2-}$$
$$SO_3^{2-} + Fe(CN)_6^{3-} \longrightarrow \text{products}$$

does not occur. Ferrocyanide, verified spectrophotometrically to be the major iron containing product (see page 48) was found not to affect the rate of reaction, when present at concentrations corresponding to 50% completion. The possibility of cyanide substitution by sulphur containing species was eliminated both on the grounds of the spectrophotometric measurements and since no activity was found in precipitates of Cu(II) compounds of complex iron cyanides when experiments were carried out on reaction mixtures labelled with ^{35}S.

Since the rate equation is not complete as far as reactants are concerned, any mechanism proposed is likely to be erroneous.

The following sequence of events was suggested by

Batstone (13) to explain the kinetics over a wide range of reaction, presumably referring to the tetrathionate catalysed process, which was found to be of first order with respect to reactants and to hydrogen ion.

$$HS_2O_3^- + Fe(CN)_6^{3-} \rightleftharpoons S_2O_3^- + HFe(CN)_6^{3-}$$

$$HS_4O_6^- + Fe(CN)_6^{3-} \rightleftharpoons S_4O_6^- + HFe(CN)_6^{3-}$$

$$S_4O_6^- + S_2O_3^{2-} \rightleftharpoons S_4O_6^{2-} + S_2O_3^-$$

$$2\ S_2O_3^- \longrightarrow S_4O_6^{2-}$$

The lack of further kinetic data prevents any possible improvements being made.

SECTION IV.

THE REACTION BETWEEN FERRICYANIDE AND THIOSULPHATE IONS.

CONCLUSION.

CONCLUSION.

The oxidation of thiosulphate by ferricyanide ion has been shown to proceed by way of three distinct routes, two occurring simultaneously in the initial stages of reaction, whilst the third is catalysed by the presence of the product, tetrathionate.

One of the concurrent processes involves, in the rate determining step, attack of free thiosulphate on the protonated form,

$$HS_2O_3^- + S_2O_3^{2-} \rightleftharpoons HS_4O_6^{3-}$$

to give an adduct through S-S bonding between the outer sulphur atoms. Since this type of bonding would occur by electron donation from one atom to the other, the partial positive charge remaining on the donor atom may be stabilised by the presence of anions and this possibility has been used to explain the observed catalytic effect on rate, of acetate ion. The activation energy was found to be 16.8 Kcal/mole. On the basis of the close resemblance of this reaction to the acid catalysed decomposition of thiosulphate, it is proposed that the intermediate is sufficiently stable to have a half life of several minutes in isolation, presumably extended in the presence of anions. The activated complex is rapidly oxidised by ferricyanide to tetrathionate by way of sulphur containing free radicals of the type, $S_4O_6^{3-}$ and subsequently $S_2O_3^-$.

The second of the two concurrent processes involves a fast pre-equilibrium between cation, hydrogen ion and thiosulphate ion followed by subsequent rate determining rearrangement of this uncharged intermediate in the presence of water or some base.

$$M^+ + H^+ + S_2O_3^{2-} \underset{}{\overset{fast}{\rightleftharpoons}} MHS_2O_3 \underset{}{\overset{slow}{\rightleftharpoons}} \text{(activated complex)}$$

Oxidation of the activated complex by ferricyanide is fast and mechanisms involving either straightforward electron transfer or hydrogen abstraction are considered possible. The latter may be analogous to the oxidation of organic thiols by ferricyanide under some conditions. Terminating processes are of free radical type to give tetrathionate as the only product. The activation energy is 17.9 Kcal/mole.

It is hoped that this summary of the two processes comprising the initial rate will stimulate further research into this and related reactions. Since the rate determining change which occurs is independent of the presence of oxidising agent, the system described is perhaps one of the simplest reacting mixtures which the experimentalist can contrive, that is, a thiosulphate ion and a proton. Other additives can be kept low. Since the formation of intermediate is of interest, the oxidising agent can be omitted altogether, and a knowledge of the kinetics under these conditions, in dilute solution could serve to teach a great deal regarding the structure of, and the environment around, the thiosulphate ion. Such fundamental knowledge could be of considerable value in further work on the oxidation of thiosulphate.

It is envisaged that initial kinetic studies on the basic system should be to correlate conclusively the results of the first part of this conclusion with the decomposition of thiosulphate. It may be speculated that the reaction which is of first order with respect to M^+, H^+ and $S_2O_3^{2-}$ may fit into the same overall process in the light of accurate kinetic data.

The mechanism operating in the later stages of the ferricyanide-thiosulphate reaction has not been included owing to the lack of suitable kinetic data, however first order dependence of rate on tetrathionate and on ferricyanide concentration has been confirmed. It is considered however, that the approach used to evaluate the rate constants in this investigation is a most satisfactory method of dealing with the kinetics of the process and it is sincerely hoped that work may be undertaken in the future on a thorough kinetic investigation with a similar mathematical approach.

SECTION V.

THE REACTION BETWEEN HALATE AND THIOSULPHATE IONS.

EXPERIMENTAL RESULTS.

Purity of Materials.

Whenever possible "AnalaR" grade reagents were used without further purification. Reagent grade (99 - 101%) $NaIO_3.H_2O$ was used for the preparation of iodate solutions which were standardised before use against thiosulphate of known concentration. This was prepared as previously described on page 24. Thiosulphate solutions for kinetic work were prepared in a similar manner.

Solutions of NaH_2PO_4 and K_2HPO_4 were prepared by titrating reagent grade orthophosphoric acid or AnalaR grade potassium dihydrogen orthophosphate with N. sodium or potassium hydroxide respectively. The alkali was prepared by dilution of "Volucon" standard volumetric concentrates, supplied by May and Baker Ltd., Dagenham.

Reagent grade casesium nitrate was used without further purification. Solutions were prepared by weight assuming the theoretical composition for the salt. BaS_2O_3 was obtained from British Drug Houses Ltd., Poole. It was washed with water several times and dried in vacuo before use.

Preliminary Experiments.

(a) Stoicheiometry of the Reaction.

The overall reaction between iodate and thiosulphate has been represented by the following stoicheiometric equation (22):

$$IO_3^- + 6\,H^+ + 6\,S_2O_3^{2-} \longrightarrow I^- + 3\,H_2O + 3\,S_4O_6^{2-}$$

No experimental evidence is available for this and it was decided to check whether the reactants were consumed in the molar ratios suggested.

A reaction mixture was prepared having the following composition:

$[IO_3^-]$ = 0.0100 M. $[HOAc]$ = 0.0987 M.

$[S_2O_3^{2-}]$ = 0.1001 M. $[NaOAc]$ = 0.100 M.

After 24 hours, when the desired reaction was presumed to have gone to completion, unaccompanied by any side reaction, portions of the solution were analysed for thiosulphate by titration with standard iodine, and for acetic acid by pH titration with 0.1 N sodium hydroxide.

Results.

Table 38.

	Initial M.	Final M.	Change M.
$[IO_3^-]$	0.0100	-	0.0100
$[S_2O_3^{2-}]$	0.1001	0.0424	0.0577
$[HOAc]$	0.0987	0.0422	0.0565

The results show that equal amounts of thiosulphate and of acid were used up during the reaction but the ratio of these to iodate consumed does not exceed 5.8:1. This was considered to be sufficiently close to the accepted ratio of 6:1, expected for oxidations by iodate where the latter is reduced to iodide ion and the reducing agent undergoes a one electron oxidation.

(b) Reproducibility of Measurements.

Empirically, the best way of following the iodate-thiosulphate reaction would be to measure the rate of loss of hydrogen ion, by titrating reaction mixtures for acid with sodium hydroxide. The method offers two advantages. First, upon initial addition of alkali, the pH of the medium will be raised thereby effectively quenching the reaction. Secondly, the additive will be quite inert in the reaction mixture and will not lead to any complications arising from side effects.

Reider found that the rate of reaction was conveniently measurable when experiments were carried out in a buffer with a composition corresponding to a pH well above the upper limit of an acetate buffer, possibly around neutrality. This would lie within the pH range of a phosphate buffer pK 7.2, which was selected for the present experiments.

The titration of the dihydrogen orthophosphate ($H_2PO_4^-$) ion with alkali has been treated by Vogel (46). The pH change at the end point is somewhat slow and it is required that a suitable indicator should have a sharp transition range centred close to pH 9.7. An indicator recommended for this titration is thymolphthalein. However, the appearance of the blue colour was found to be gradual and evident even in the early stages of the titration. Thus, it was difficult to ascertain exactly when the end point had been reached. Vogel suggests that a sharper colour change may be obtained using an indicator consisting of a mixture of phenolphthalein and a-naphtholphthalein which changes from pale rose, through green to violet at pH 9.6. However, repeated determinations gave widely differing results, the cause being attributed to a difficulty in identifying the correct colour change. As a result of these tests the use of acid-base indicators was abandoned and the method of pH titration was adopted.

Reaction mixtures were prepared as follows. 100 ml. portions of 0.1005 M. sodium thiosulphate and 0.1014 M. sodium iodate were pipetted into separate 500 ml. wide mouthed conical flasks. 50 ml. buffer was added to each and the solutions allowed to attain thermal equilibrium in a thermostat. The reaction was started by mixing the contents of the two flasks and the mixture was transferred from one vessel to the other to ensure homogeneity. The clock was started at the first addition.

At timed intervals, 20 ml. portions of reaction mixture were run into 50 ml. water in a 100 ml. beaker containing a magnetic stirrer and a Pye "Ingold" combined electrode to monitor the pH of the solution. The stirring was started and 0.1 N. sodium hydroxide added rapidly from a 10 ml. microburette until the pH rose to about 8.4, after which the titration was completed by small additions of the alkali. For each titration, graphs of pH vs. time, and a first derivative were plotted, the end point being found from the maximum of the latter graph. Four kinetic runs were carried out in this manner to determine the effect of physical conditions on rate. The first, A, was under normal laboratory conditions. In B the reaction vessel was wrapped in metal foil to exclude light. C was packed with 3.0 g. glass wool to study the effect of surface. Since the addition of $EDTA^{4-}$ is expected to render any potential transition metal catalysts inactive (see page 55) an experiment, labelled D, was carried out where 0.12 g. Na_2EDTA had been added to the iodate half of the reaction mixture. Upon mixing, this rendered the reaction 10^{-3} M. in $EDTA^{4-}$.

Since the technique of pH titration is somewhat tedious and lengthy an alternative method of analysis was sought. The titration of thiosulphate ion with iodine may be feasible provided that the possible side reaction of iodide is considered. The reaction of iodide with iodate has been examined by Barton and Wright (47) who found

$$-\frac{d[IO_3^-]}{dt} = 1.8 \times 10^{10} [IO_3^-][I^-]^2 [H^+]^2 \quad M. \ min^{-1}$$

at 25°C and I = 1.0 and, at low buffer concentration, ignoring the less important terms describing the specific effects of carboxylate and phosphate ions. Reider found a similar rate law to hold for the iodate-thiosulphate reaction, thiosulphate ion replacing iodide in the rate expression. Here the fifth order rate constant found by measuring the loss of hydrogen ion was 2.4×10^{14} $M.^{-4}$ min^{-1} and, if this is a realistic figure, then, under similar conditions the latter reaction would proceed at least 1000 times faster than the rate of loss of iodide ions in the former, the contribution of this to the overall rate being insignificant.

A reaction mixture, labelled E, prepared as above was analysed for thiosulphate as follows: At timed intervals 20 ml. aliquots were withdrawn and titrated rapidly with 0.02 N. iodine (in KI) using starch as indicator. When the titration was complete some of the mixtures were left to stand for a period of time. No deepening of the starch-iodine colour was apparent after ten minutes.

Table 39 summarises the results of preliminary experiments labelled A - E.

Table 39.

Reproducibility of Measurements.

$[IO_3^-]$ = 0.0338 M.

$[S_2O_3^{2-}]$ = 0.0335 M.

pH = 7.22

Temperature = 25.0 ± 0.02°C.

$[Na^+]$ = 0.300 M.

$[HPO_4^{2-}]$ = 0.084 M.

$[H_2PO_4^-]$ = 0.032 M.

Table of % reaction as a function of time for kinetics experiments labelled A - E.

Time (mins)	A	B	C	D	E
30	6.3	5.6	6.2	7.5	6.2
60	11.6	11.0	11.8	13.4	11.8
90	16.7	16.0	16.2	17.8	16.8
120	20.9	20.6	20.9	21.8	21.5
150	24.8	24.4	24.9	27.4	25.6
180	28.7	27.9	28.7	29.6	29.3
210	31.8	31.2	32.1	32.7	33.0
240	34.8	34.2	35.2	35.5	36.1
270	37.6	37.0	37.4	38.3	39.3
300	40.1	39.5	39.9	40.8	42.1
330	42.3	41.8	42.7	42.7	44.2
360	44.2	43.7	-	44.9	46.4

Table 39. Comments.

The rate of reaction was found to be quite reproducible and independent of the physical effects of surface and of light. There was no change in rate upon addition of a small amount of $EDTA^{4-}$.

When the progress of the reaction was followed by analysis for thiosulphate, the rate of loss of the latter was found to be similar to the rate of disappearance of hydrogen ion. This result is predicted from the stoicheiometry and should hold even if, in the later stages of reaction, the iodide formed reacts with iodate to give iodine.

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

Subsequent oxidation of thiosulphate by iodine should be fast and result in the same overall stoicheiometry for the combined process as observed for the iodate-thiosulphate reaction.

The discrepancy of some 4% in concentration as measured by the two analytical techniques after 50% reaction, was attributed to side effects of the iodimetric technique, but, in terms of rate up to 25% of reaction, the apparent acceleration was considered negligible.

Titration of thiosulphate with iodine was adopted generally for kinetic studies in this section. No preliminary experiments were carried out on the reaction involving bromate ion, but it was expected that the relative reactivity of thiosulphate and of **iodide** towards bromate would be similar to that described for iodate.

Since the reaction is expected to be of high overall order with respect to reactants and integration of possible rate expressions will thus be difficult, especially so after the variation of pH has been included, initial rates were studied as a function of concentration. The early stages of the reaction are also free from any effects arising from the presence of iodide ion.

General Technique Adopted for Following the Reaction.

All kinetics experiments were carried out in a thermostat controlled to ± 0.02°C. Mixtures of thiosulphate and buffer, and of halate and buffer were placed into separate 500 ml. wide mouthed conical flasks and the stoppered containers were allowed to attain thermal equilibrium in the thermostat. The reaction was started by pouring the contents of one flask into the other and thorough mixing was ensured by transferring the mixture from one vessel to the other several times. The start of the reaction was taken to be the first addition.

The total reaction volume was 300 ml. At timed intervals 20 ml. portions of reaction mixture were run into a quantity of iodine, just short of that required for equivalence. Starch was added and the titration completed to the blue colouration of the starch-iodine complex.

The observations were made over the first 10% of reaction and initial rates for the disappearance of thiosulphate were calculated from graphs of $[S_2O_3^{2-}]$ vs. time. These were linear over at least 5% of reaction in most cases.

The apparatus used for the measurement of pH and some general principles necessary for its interpretation have already been described (see page 53). Measurements for the iodate-thiosulphate reaction were carried out over a period of time on a sample of reaction mixture withdrawn at the beginning of the kinetic run. The consumption of hydrogen ion was apparent by a slow rise in pH and initial values were found by extrapolation of pH-time curves to zero time. In the case of bromate-thiosulphate mixtures the poisoning of the electrode, which proved troublesome in the investigation of the ferricyanide-thiosulphate reaction, was again evident. Consequently, mixtures for pH measurements were prepared with sulphate replacing thiosulphate ion, all other conditions being kept the same. Such solutions proved very satisfactory during the study of the latter reaction.

To Determine the Order with respect to Reactants for the Reaction of Thiosulphate with Iodate and with Bromate Ions.

Several experiments were carried out in which the concentration of one reactant was varied keeping those of all other species constant. The ionic strength was maintained by the addition of neutral salts; sodium or potassium nitrate and sodium sulphate were used to compensate for changes in sodium iodate or potassium bromate and sodium thiosulphate concentration respectively.

For the study of hydrogen ion dependences, phosphate buffers were prepared as described in Appendix III. Sets of solutions contained constant sodium, potassium and divalent anion concentration and were also of constant ionic strength. For the iodate-thiosulphate reaction the total phosphate concentration ($[H_2PO_4^-] + [HPO_4^{2-}]$) varied from 0.036 - 0.042 M. over the range of pH studied, whereas this concentration was kept constant for the reaction involving bromate ion.

The order of reaction with respect to one component was found by plotting graphs of initial rate vs. suitable functions of concentration. For a simple case

$$\text{Initial rate} = k\,[A]^n$$

then, for an n th. order dependence, a graph of initial rate vs. $[A]^n$, where $[A]$ is the concentration of a particular reactant, should be linear and pass through the origin.

(I) The Iodate-Thiosulphate Reaction.

(a) Order with respect to IO_3^-.

Table 40.

$[IO_3^-] + [NO_3^-]$ = 0.100 M.

$[S_2O_3^{2-}]$ = 0.0332 M.

pH = 7.29

Temperature = 25.0 ± 0.02°C.

$[Na^+]$ = 0.370 M.

$[HPO_4^{2-}]$ = 0.090 M.

$[H_2PO_4^-]$ = 0.019 M.

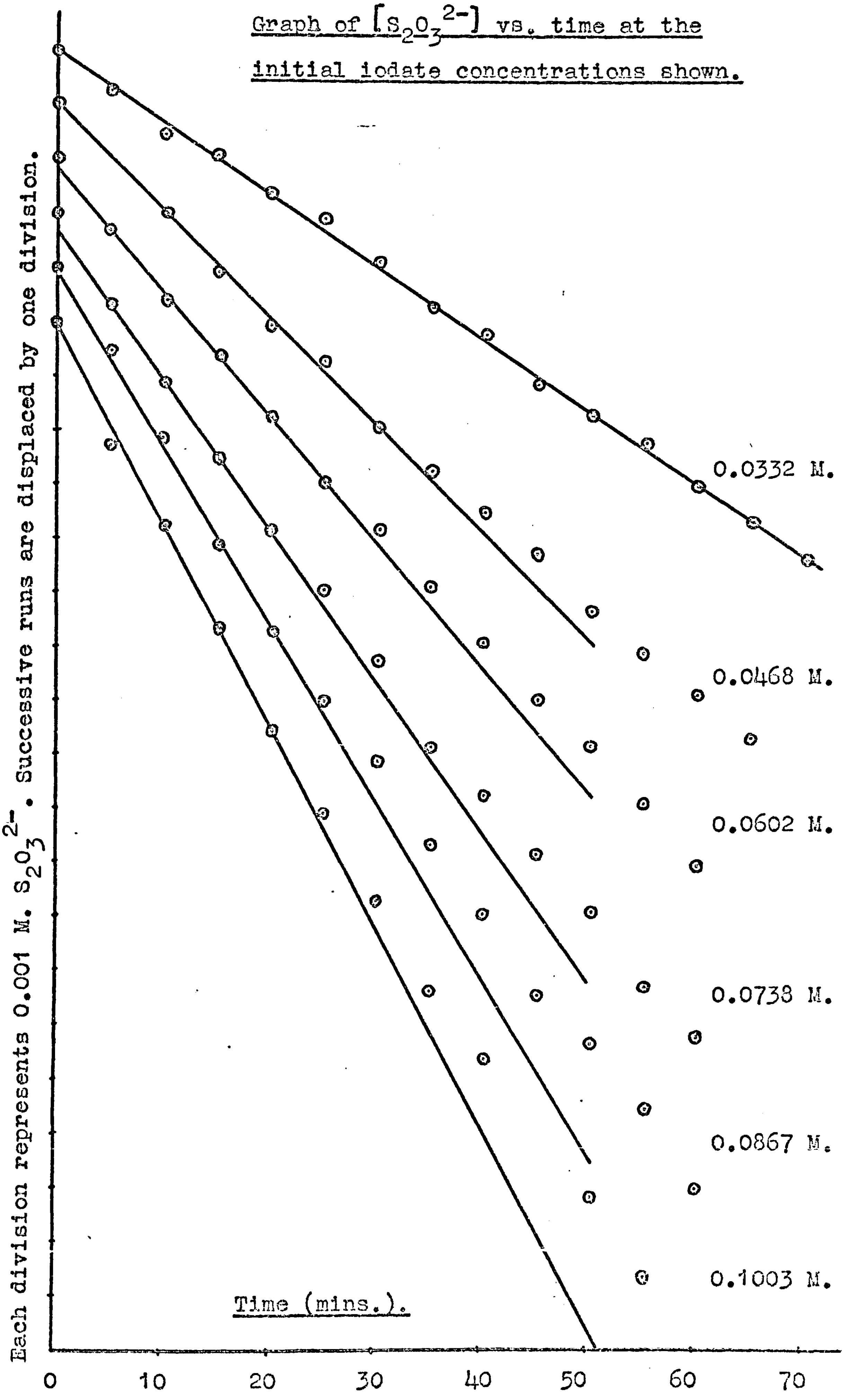
Table of $[S_2O_3^{2-}]$ M. as a function of time for the initial iodate concentrations (M.) shown at the head of each column.

Time (mins)	0.0332	0.0468	0.0602	0.0738	0.0867	0.1003
0	0.03320	0.03320	0.03320	0.03320	0.03320	0.03320
5	0.03305	-	0.03294	0.03286	0.03289	0.03274
10	0.03289	0.03280	0.03268	0.03258	0.03258	0.03246
15	0.03281	0.03258	0.03248	0.03229	0.03219	0.03207
20	0.03268	0.03239	0.03225	0.03203	0.03186	0.03170
25	0.03258	0.03225	0.03201	0.03181	0.03160	0.03138
30	0.03243	0.03201	0.03184	0.03155	0.03138	0.03106
35	0.03227	0.03186	0.03162	0.03124	0.03107	0.03073
40	0.03215	0.03170	0.03142	0.03105	0.03081	0.03047
45	0.03198	0.03155	0.03121	0.03083	0.03052	-
50	0.03186	0.03134	0.03103	0.03062	0.03033	0.02997
55	0.03176	0.03119	0.03083	0.03034	0.03009	0.02967
60	0.03160	0.03103	0.03059	0.03016	0.02980	0.02941
65	0.03147	0.03088				
70	0.03134					

See graph 11.

Graph 11.

Graph of $[S_2O_3^{2-}]$ vs. time at the initial iodate concentrations shown.



Graph 11. Comments.

The concentration-time graphs plotted in this study are typical of those obtained throughout the work on the oxidation of thiosulphate by halate ion. To avoid repetition the raw experimental data will be omitted for subsequent kinetic runs.

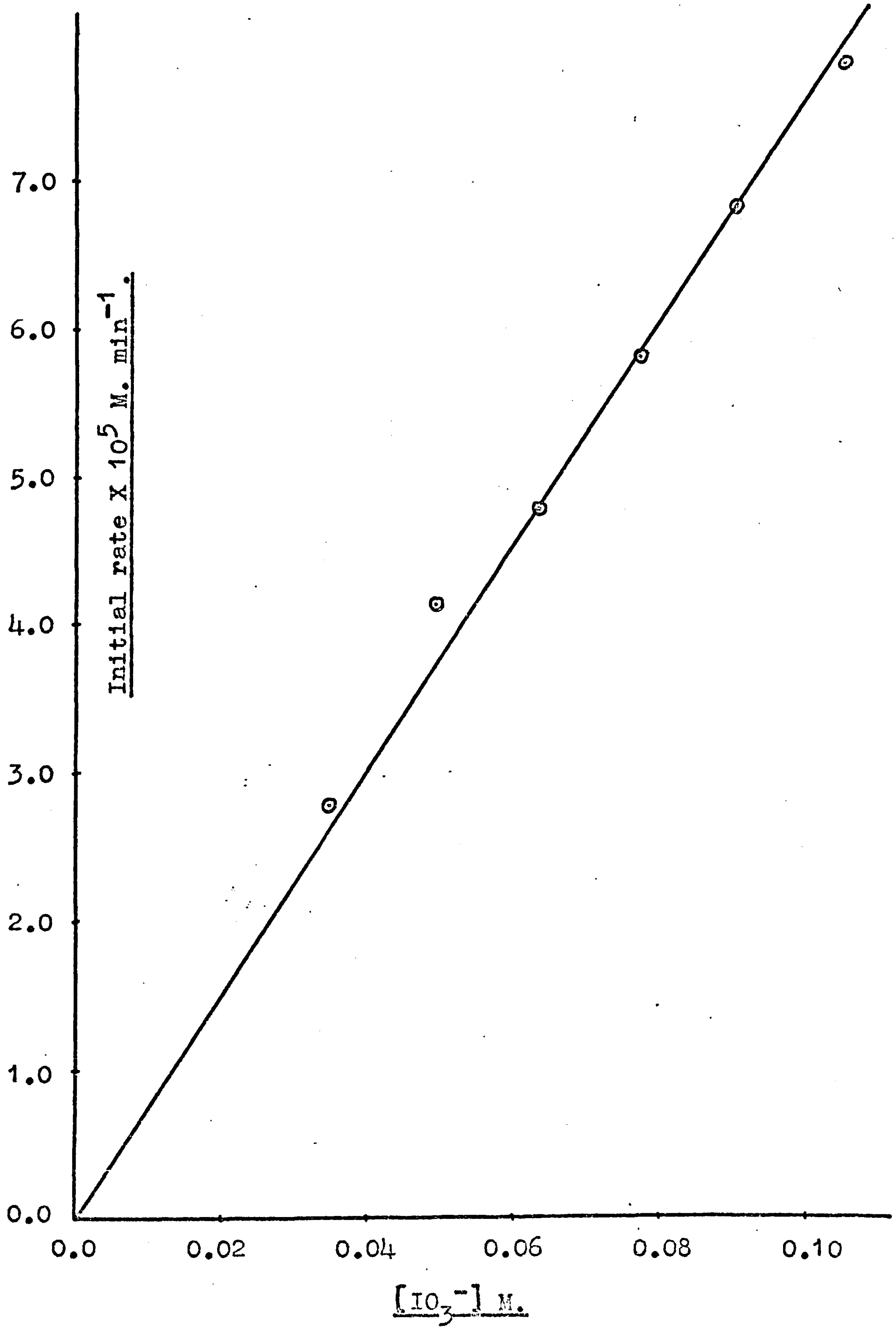
Table 41.

$[IO_3^-]_0$ M.	$-\frac{d[S_2O_3^{2-}]}{dt} \times 10^5$ M. min^{-1}
0.0332	2.66
0.0468	3.98
0.0602	4.60
0.0738	5.58
0.0867	6.56
0.1003	7.48

Graph 12 shows that a plot of initial rate vs. $[IO_3^-]_0$ (data shown in table 41) is linear and passes through the origin. The order with respect to iodate is one.

Graph 12.

Graph of initial rate vs. $[IO_3^-]$.



(b) Order with respect to $S_2O_3^{2-}$.

Table 42.

$[IO_3^-]$ = 0.0350 M.

$[S_2O_3^{2-}] + [SO_4^{2-}]$ = 0.052 M.

pH = 7.32

Temperature = 25.0 ± 0.02°C.

$[Na^+]$ = 0.340 M.

$[HPO_4^{2-}]$ = 0.090 M.

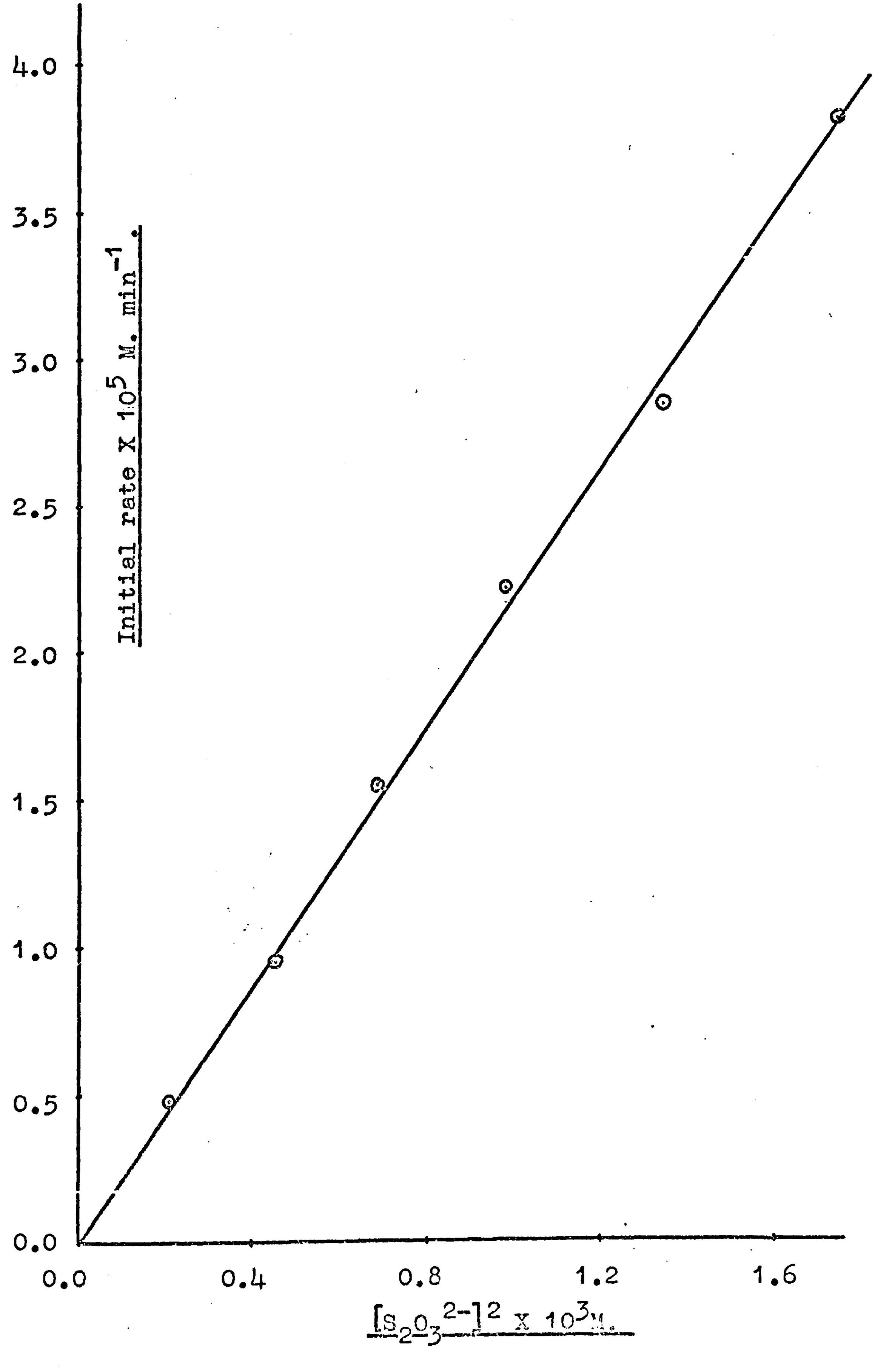
$[H_2PO_4^-]$ = 0.019 M.

$[S_2O_3^{2-}]_o$ M.	$[S_2O_3^{2-}]^2 \times 10^3$ $M.^2$	$-\frac{d[S_2O_3^{2-}]}{dt} \times 10^5$ $M.\ min^{-1}$
0.0140	0.197	0.48
0.0209	0.437	0.95
0.0260	0.676	1.55
0.0313	0.980	2.22
0.0365	1.332	2.85
0.0416	1.731	3.82

A first order rate law is not satisfied in this case. However, graph 13 shows that a plot of initial rate vs. $[S_2O_3^{2-}]_o^2$ gives a straight line passing through the origin. The order with respect to thiosulphate is two.

Graph 13.

Graph of initial rate vs. $[S_2O_3^{2-}]^2$.



(c) Order with respect to H^+.

Buffers prepared as in Appendix IIIa.

Table 43.

$[IO_3^-]$ = 0.0249 M.
$[S_2O_3^{2-}]$ = 0.0256 M.
Temperature = 25.0 ± 0.02°C.

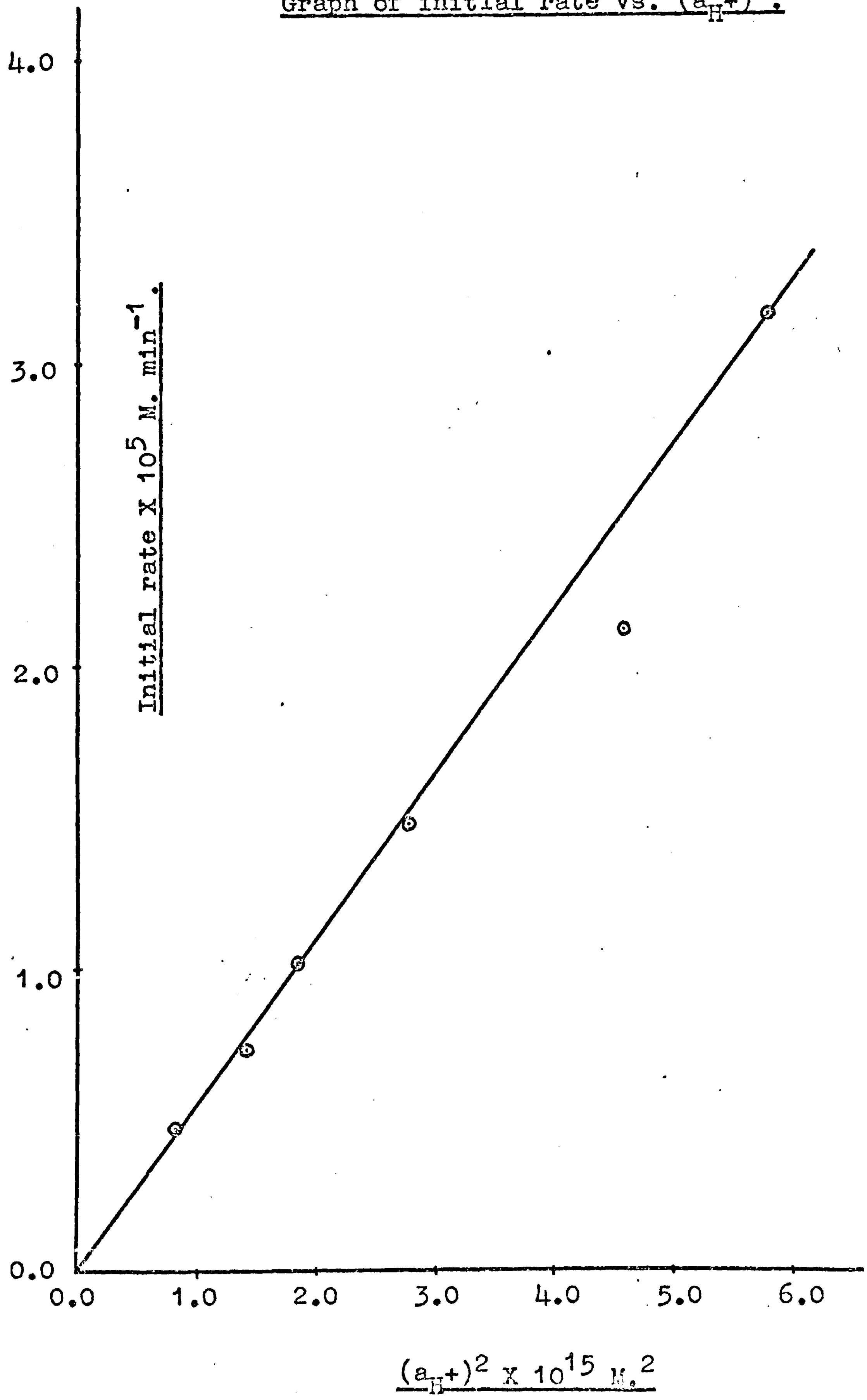
$[Na^+]$ = 0.076 M.
$[K^+]$ = 1.000 M.
$[HPO_4^{2-}]$ = 0.033 M.
$[H_2PO_4^-] + [NO_3^-]$ = 0.967 M.

pH	$a_{H^+} \times 10^8$	$(a_{H^+})^2 \times 10^{15}$	$-\frac{d[S_2O_3^{2-}]}{dt} \times 10^5$
	M.	$M.^2$	$M.\ min^{-1}$
7.55	2.82	0.80	0.48
7.43	3.72	1.38	0.73
7.37	4.27	1.82	1.02
7.28	5.25	2.76	1.48
7.17	6.76	4.57	2.12
7.12	7.59	5.76	3.15

A first order rate law is not satisfied in this case. However, graph 14 shows that a plot of initial rate vs. $(a_{H^+})^2$ gives a straight line passing through the origin. The order with respect to hydrogen ion is two.

Graph 14.

Graph of initial rate vs. $(a_{H^+})^2$.



(II) The Bromate-Thiosulphate Reaction.

(a) Order with respect to BrO_3^-.

Table 44.

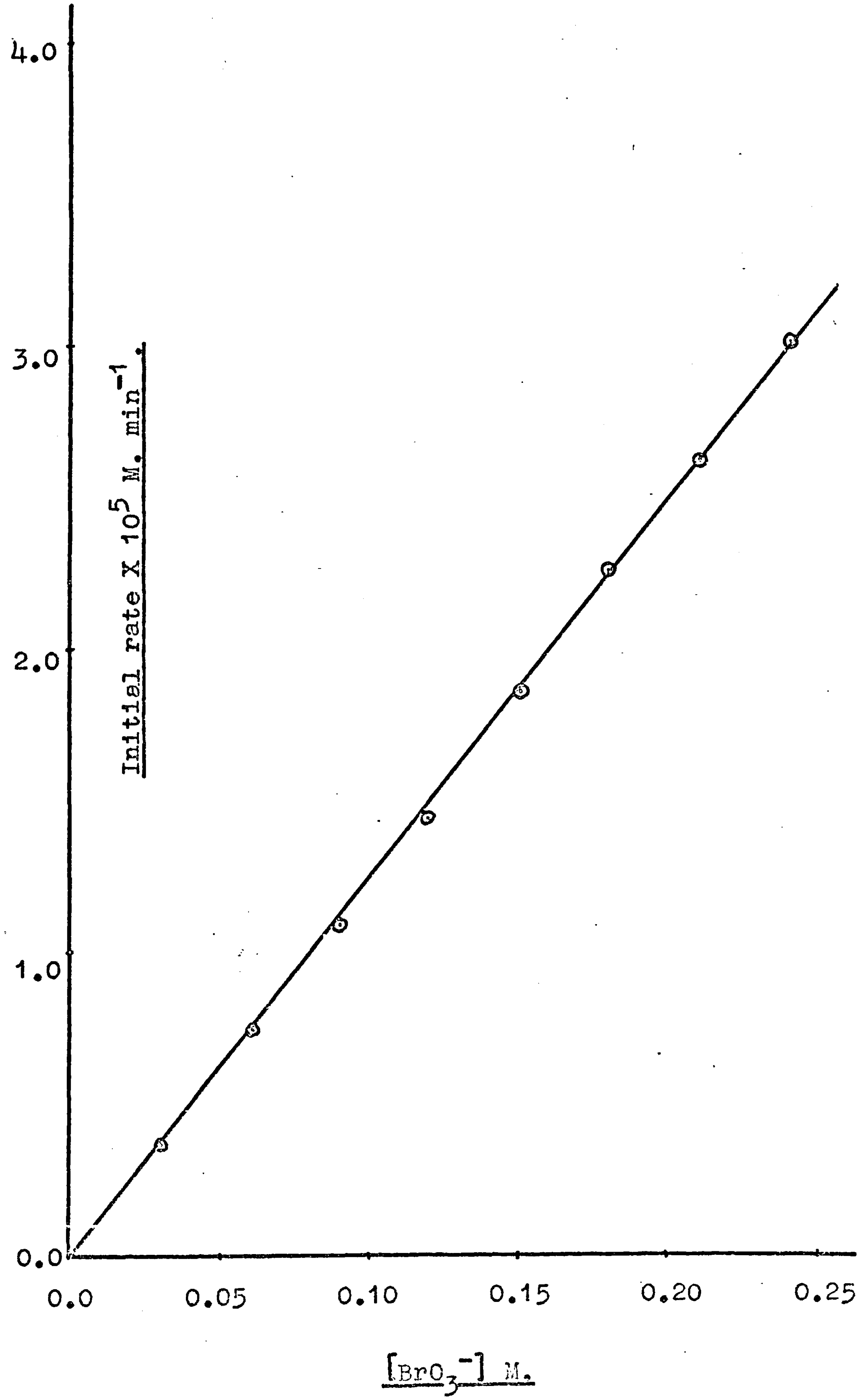
$[NO_3^-] + [BrO_3^-]$ = 0.250 M.
$[S_2O_3^{2-}]$ = 0.0200 M.
pH = 6.54
Temperature = 25.0 ± 0.02°C.
$[Na^+]$ = 0.040 M.
$[K^+]$ = 0.400 M.
$[HPO_4^{2-}]$ = 0.050 M.
$[H_2PO_4^-]$ = 0.050 M.

$[BrO_3^-]$ M.	$-\frac{d[S_2O_3^{2-}]}{dt} \times 10^5$ M. min^{-1}
0.0313	0.37
0.0625	0.75
0.0938	1.09
0.1250	1.44
0.1563	1.86
0.1875	2.26
0.2188	2.62
0.2500	3.01

Graph 15 shows that a plot of initial rate vs. $[BrO_3^-]_0$ is linear and passes through the origin. The order with respect to bromate is one.

Graph 15.

Graph of initial rate vs. $[BrO_3^-]$.



(b) Order with respect to $S_2O_3^{2-}$.

Table 45.

$[BrO_3^-]$ = 0.0200 M.

$[S_2O_3^{2-}] + [SO_4^{2-}]$ = 0.050 M.

pH = 5.68

Temperature = 25.0 ± 0.02°C.

$[Na^+]$ = 0.125 M.

$[K^+]$ = 0.108 M.

$[HPO_4^{2-}]$ = 0.012 M.

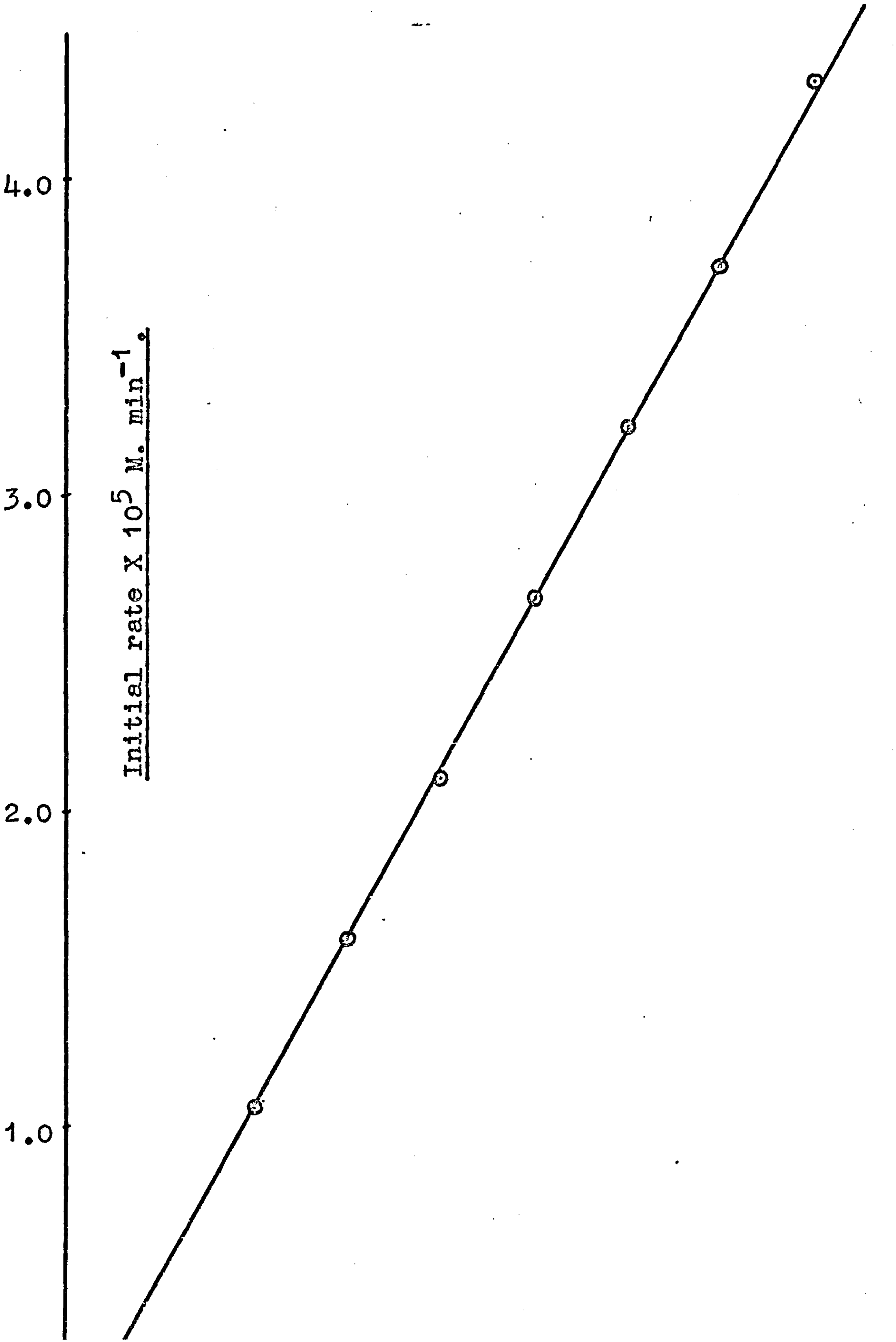
$[H_2PO_4^-]$ = 0.088 M.

$[S_2O_3^{2-}]$ M.	$-\frac{d[S_2O_3^{2-}]}{dt} \times 10^5$ M. min^{-1}
0.0125	1.06
0.0188	1.60
0.0250	2.10
0.0313	2.67
0.0375	3.21
0.0438	3.72
0.0500	4.31

Graph 16 shows that a plot of initial rate vs. $[S_2O_3^{2-}]_o^2$ is linear and passes through the origin. The order with respect to thiosulphate is one.

Graph 16.

Graph of initial rate vs. $[S_2O_3^{2-}]$.



(c) Order with respect to H^+.

Buffers prepared as in Appendix IIIb.

Table 46.

$[BrO_3^-]$ = 0.100 M.

$[S_2O_3^{2-}]$ = 0.0200 M.

Temperature = 25.0 ± 0.02°C.

$[Na^+]$ = 0.040 M.

$[K^+]$ = 0.400 M.

$[HPO_4^{2-}] + [SO_4^{2-}]$ = 0.100 M.

$[H_2PO_4^-] + [NO_3^-]$ = 0.100 M.

pH	$a_{H^+} \times 10^7$ M.	$-\frac{d[S_2O_3^{2-}]}{dt} \times 10^5$ M. min^{-1}
7.14	0.72	0.26
6.95	1.12	0.45
6.63	2.34	1.15
6.53	2.95	1.46
6.41	3.89	2.11
6.21	6.03	3.50

The experimental results do not satisfy first or second order rate laws, since the linear first order plot does not pass through the origin and a second order plot is curved. If,

$$\text{Initial rate} = k\,[A]^n$$

then, taking logarithms,

$$\log_{10} \text{Initial rate} = n \log_{10} [A] + \log_{10} k$$

Hence, a graph of $\log_{10}$ initial rate vs. $\log_{10}$ $[A]$ will have a slope of n, the order of reaction with respect to A.

Table 47.

pH	$6 + \log_{10}$ Initial rate
7.14	0.415
6.95	0.653
6.63	1.061
6.53	1.164
6.41	1.324
6.22	1.544

From graph 17 (data shown in table 47) n = 1.24. According to Edwards (1) the order with respect to hydrogen ion is one; the high value observed here implies that the reaction may undergo general acid catalysis to some extent, that is, the rate also depends on the concentration of one or more of the acids present. The obvious possibility is $H_2PO_4^-$, and the following rate law was found to be consistent with the observations:

$$\frac{\text{Initial rate}}{a_{H^+}} = 24 + 475\,[H_2PO_4^-]$$

Table 48 shows a comparison between initial rates predicted from the above rate expression and those observed under experimental conditions. $[H_2PO_4^-]$ was found from appendix IIIb, where the preparation of the buffer mixtures is described.

There is a close agreement between observed and predicted values.

Table 48.

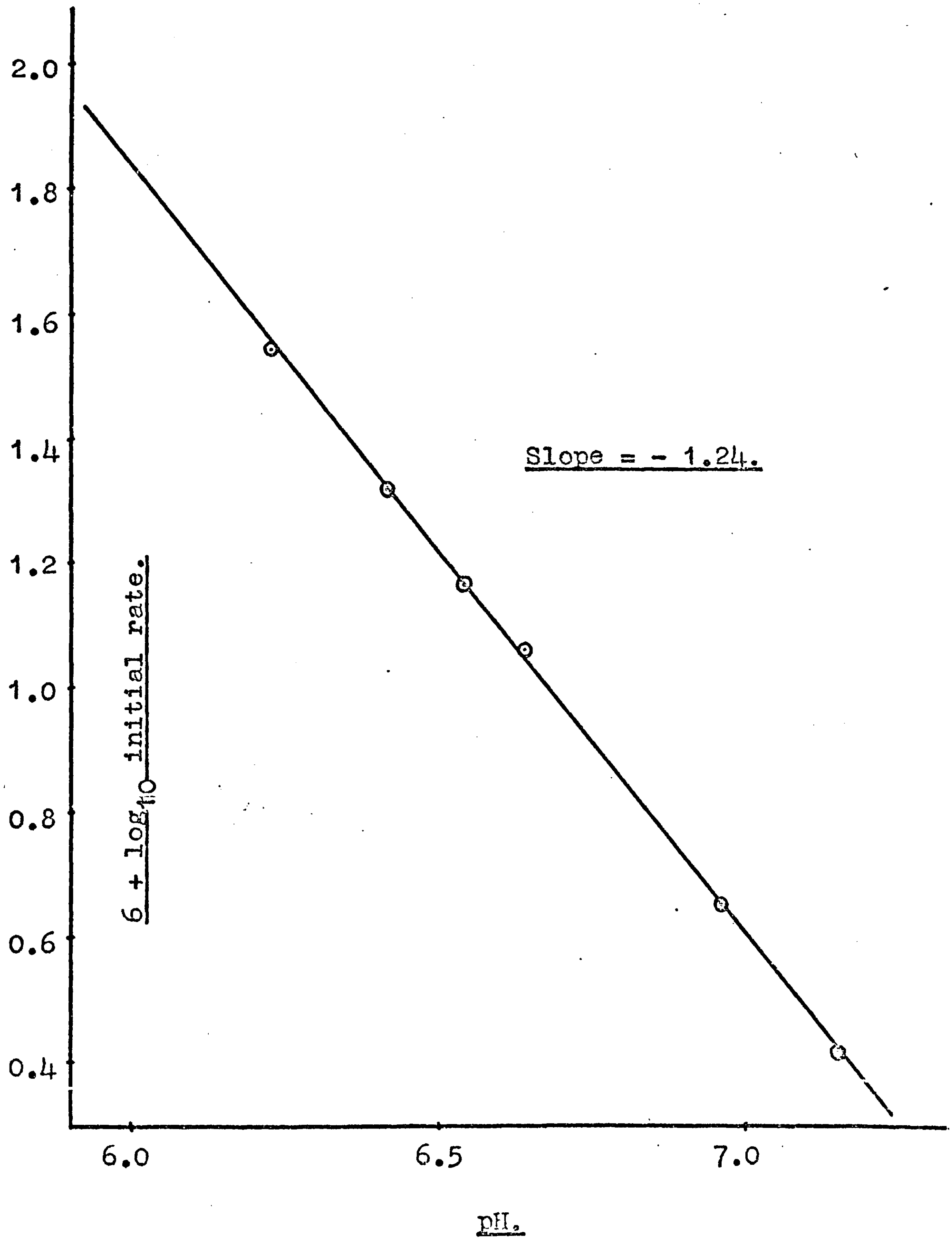
$a_{H^+} \times 10^7$ M.	$[H_2PO_4^-]$ M.	Predicted rate X 10^5 M. min^{-1}	Observed rate X 10^5 M. min^{-1}
0.72	0.0250	0.26	0.26
1.12	0.0333	0.45	0.45
2.34	0.0500	1.12	1.15
2.95	0.0556	1.49	1.46
3.89	0.0625	2.09	2.11
6.03	0.0714	3.49	3.50

Note.

All subsequent kinetics experiments on the oxidation of thiosulphate by halate ion were carried out for the reaction involving iodate.

Graph 17.

Graph of $\log_{10}$ initial rate vs. pH.



The Solvent Isotope Effect on the Rate of Reaction.

Preliminary experiments to determine the order with respect to reactants have shown that two hydrogen ions are involved in the events leading up to the rate determining step. Since the position of protonation equilibria is generally modified on changing the solvent from H_2O to D_2O, the isotope effect, which is assumed to be in the same direction for each of the two hydrogen ions involved in this investigation, will be additive and may consequently be quite marked. Barton and Wright (47) have found that the ratio of rate constants k_D/k_H for the possibly analogous iodate oxidation of iodide ion is 9.8, representing a very large increase in rate in D_2O.

It was considered that a knowledge of the solvent isotope effect on the iodate thiosulphate-reaction would be of considerable mechanistic value.

Solutions for kinetic studies in H_2O and in D_2O were prepared in exactly the same way. 0.200 g. * $Na_2HPO_4.2H_2O$ and 0.500 g. KIO_3 were weighed directly into a 50 ml. volumetric flask. 2 ml. aqueous 0.75 M. KH_2PO_4 were added and the solution made up to the mark with H_2O or D_2O. The thiosulphate part of the reaction mixture was prepared by dilution of 2 ml. aqueous 1.00 M. $Na_2S_2O_3$ to 50 ml. with H_2O or D_2O. Equal volumes of iodate and of thiosulphate solutions were used for kinetic work and 10 ml. aliquots of reaction mixture were withdrawn for analysis.

---

* $Na_2HPO_4.2H_2O$ was prepared by drying the decahydrate salt over anhydrous calcium chloride for several weeks. The composition of the salt was found to be 99.5% $Na_2HPO_4.2H_2O$ by pH titration with HCl before use.

In the case of H_2O the reactants were prepared twice, the thiosulphate being made up from its stock solution, in order to check the reproducibility of the method.

The experimental results are listed in table 49.

Table 49.

Solvent Isotope Effect.

$[IO_3^-]$ = 0.0234 M.
$[S_2O_3^{2-}]$ 0.0200 M.
pH (in H_2O) 7.57

Table of $[S_2O_3^{2-}]$ M. as a function of time in the solvents shown.

Time (mins)	H_2O	H_2O	96% D_2O
0	0.02000	0.02000	0.02000
30			0.01991
40	0.01987	0.01987	
60			0.01982
80	0.01974	0.01972	
90			0.01975
120	0.01963	0.01962	
150			0.01958
160	0.01949	0.01949	
200	0.01939	0.01939	
210			0.01937
240	0.01925	0.01924	
280	0.01911	0.01910	

Table 49, Comments.

It is evident from the experimental figures that the preparation of reagents and the method of following the reaction is reproducible in H_2O. Practically no kinetic isotope effect was observed on changing the solvent from H_2O to D_2O.

Some difficulties arising from an attempt to explain solvent isotope effects of this type have been previously dealt with in connection with the ferricyanide-thiosulphate reaction (see page 66). A satisfactory explanation was evolved by considering the modification to the possible protonation equilibria, arising from the solvent change, and their subsequent effect on the concentration of a suitable kinetically important intermediate.

The modification to the hydrogen ion content of the reaction mixture must be the first consideration. A phosphate buffer, consisting of a mixture of $H_2PO_4^-$ and HPO_4^{2-} ions, was used in the present investigation, the pH of such a system being given by:

$$pH = pK + \log_{10} \frac{[HPO_4^{2-}]}{[H_2PO_4^-]}$$

Provided that the ratio of "acid" to "salt" is kept constant the pH of the medium will depend on the pK of the acid, $H_2PO_4^-$. According to Rule and La Mer (48) the dihydrogen orthophosphate ion is a weaker acid in D_2O by 0.56 units of pK, but a more recent study (30) suggests that the ΔpK, that is, the difference between the pK in D_2O and in H_2O, is a somewhat higher value of 0.64. A mean value of 0.60 is considered acceptable and represents an effective reduction in the hydrogen ion concentration by a factor of 4.

According to Edwards (1,21) the fate of hydrogen ions in the iodate-thiosulphate reaction is a fast two stage pre-equilibrium with iodate to form the "superacid" $H_2IO_3^+$, that is:

$$IO_3^- + H^+ \rightleftharpoons HIO_3$$

$$HIO_3 + H^+ \rightleftharpoons H_2IO_3^+$$

the mechanism of oxidation being analogous to oxygen exchange between the anion and water. The latter reaction has recently been studied by means of oxygen-17 nuclear magnetic resonance (49) where a rate law, second order with respect to hydrogen and first order with respect to iodate, was observed at high acid concentrations. The mechanism involving a double protonation was proposed, however the identity of the species is expected to be somewhat more complex than that put forward by Edwards. Heavy hydration of the iodate ion is supported by its low conductance compared with that of chlorate or bromate ion, and the initial protonation is best written as:

$$H_3O^+ + IO_3^- \rightleftharpoons H_3IO_4$$

The composition of the di-protonated form is not known, it may possibly be $H_6IO_5^+$ or $H_4IO_4^+$.

In order to explain the observed solvent isotope effect for the iodate-thiosulphate reaction it is necessary to consider not only the effect of solvent change of the two protonation equilibria, but also on the possible factors arising from the de-aquation of iodate during its rate determining interaction with thiosulphate.

The effect of solvent change on "HIO_3" is known, "DIO_3" being the weaker acid by 0.3 units of pK (50). The remaining variables are as yet unknown and consequently a theoretical value for the solvent isotope effect in this investigation cannot be calculated. A useful guideline could have been obtained from the solvent isotope effect on the rate of exchange of oxygen between iodate and water, however no such work has yet been reported.

A possibility which must be considered is one where the reacting species are $HS_2O_3^-$ and HIO_3, that is:

$$HS_2O_3^{2-} + HIO_3 + S_2O_3^{2-} \rightleftharpoons (\text{complex})^{3-} \longrightarrow \text{products}$$

The effect of D_2O on the stability constant of the former ion pair has been considered during the investigation of the ferricyanide-thiosulphate reaction, whereas oxygen exchange between IO_3^- and H_2O will occur in weakly acidic media with a rate law which is of first order with respect to hydrogen ion and iodate ion. A Δ pK value of 0.35 for $HS_2O_3^-$ and 0.30 for "HIO_3" represents an effective increase in the concentration of the species by a factor of 2.2 and 2.0 respectively. It should be noted that the ΔpK value for "HIO_3" takes into account any effect of aquation changes on going from free iodate to the acid form,

A rate equation in D_2O may be written in terms of the various concentrations in H_2O as follows:

$$\text{Rate}_D = k' \frac{2.2 \times 2.0}{4.0 \times 4.0} [HS_2O_3^-][HIO_3][S_2O_3^{2-}]$$

where k' is the rate constant in H_2O.

$$\text{Hence} \qquad \frac{\text{Rate}_D}{\text{Rate}_H} = 0.28$$

A retardation of rate in D_2O is thus predicted. However, in the light of the previous evidence it is likely that considerable involvement of water will still occur prior to the rate determining step, modifying the isotope effect in some unknown way. For this reason a quantitative correlation between observed and predicted solvent isotope effects cannot be made here.

The difference in isotope effects between that observed for the iodate-iodide reaction (47), $k_D/k_H = 9.8$, and that found for the iodate-thiosulphate reaction, the mechanisms of which are likely to be analogous, has to be explained. If the discrepancy is due to the different states of aquation of the various intermediates required to build up the activated complex, then the magnitude and direction of the effect will depend on a large number of unknowns and at this stage the problem is insoluble. However, since no details of the reaction conditions for H_2O/D_2O experiments were given in the paper, it may be speculated that, in order to avoid complications arising from the solvent isotope effect on the buffer, the latter was omitted. Under these circumstances the effective fourfold reduction in hydrogen ion, calculated for the phosphate buffer system in our case, does not arise in the unbuffered system and this represents a possible sixteenfold increase in rate of reaction. The result found by Barton and Wright was some ten times greater than that observed for the iodate-thiosulphate reaction, in approximate agreement with the above supposition.

The Effect of Added Salts on the Rate of Reaction.

Some properties of reactant mixtures and of the activated complex in the presence of added neutral salts have already been discussed in connection with the ferricyanide-thiosulphate reaction (see page 75). It was found that, after specific effects of ion association had been taken into account, a rate equation could be written which was consistent with the Brønsted formulation for a non ideal system.

The iodate-thiosulphate reaction has been shown to involve two thiosulphate ions, two hydrogen ions and one iodate ion in the slowest step of the mechanism,

$$2\ S_2O_3^{2-} + 2\ H^+ + IO_3^- \rightleftharpoons (\text{activated complex})^{3-} \longrightarrow \text{products}$$

According to the Brønsted theory the rate constant for a real system is given by:

$$k = k_o \frac{f^2_{S_2O_3^{2-}}\ f^2_{H^+}\ f_{IO_3^-}}{f_{(\text{complex})^{3-}}} \qquad \ldots.\ (i)$$

where k_o is the rate constant when the activity coefficients (denoted by f) are unity.

If the activity coefficient of an ion in water at 25°C is represented by the equation:

$$-\log_{10} f = 0.505\ z^2\ F(I)$$

where z is the charge on the ion and F(I) is some function of ionic strength, then equation (i) becomes:

$$\log_{10} k = \log_{10} k_o - 0.505\ (2 \times 4 + 2 \times 1 + 1 - 9)\ F(I)$$

or,

$$\log_{10} k = \log_{10} k_o - 1.01\ F(I)$$

That is, a retardation in rate should accompany an increase in ionic strength if F(I) is positive.

A series of kinetic experiments was carried out containing various amounts of added sodium or potassium nitrate within the range of ionic strength 0.2 - 0.8, the initial concentration of all other species being kept constant.

The experimental results are listed in table 50.

Table 50.

$[S_2O_3^{2-}]$ = 0.0252 M. $[H_2PO_4^-]$ = 0.0067 M.
$[IO_3^-]$ = 0.0252 M. $[HPO_4^{2-}]$ = 0.0333 M.
Temperature = 25.0 ± 0.02°C.

$[Na^+]$ M.	$[K^+]$ M.	$[NO_3^-]$ M.	pH	I*	$-\frac{d[S_2O_3^{2-}]}{dt} \times 10^5$ M. min^{-1}
0.142	0.007	-	7.44	0.21	0.64
0.242	0.007	0.100	7.33	0.31	0.86
0.142	0.107	0.100	7.37	0.31	0.96
0.342	0.007	0.200	7.23	0.41	1.03
0.142	0.207	0.200	7.30	0.41	1.17
0.442	0.007	0.300	7.16	0.51	1.26
0.142	0.307	0.300	7.24	0.51	1.41
0.542	0.007	0.400	7.11	0.61	1.50
0.142	0.407	0.400	7.21	0.61	1.64
0.642	0.007	0.500	7.07	0.71	1.57
0.142	0.507	0.500	7.21	0.71	1.80
0.742	0.007	0.600	7.06	0.81	1.83
0.142	0.607	0.600	7.20	0.81	1.95

* Calculated from initial reactant concentrations.

Calculation of Ion Pair Concentrations.

The possible interactions between oppositely charged ions constitute major deviations from the Brónsted theory. As a result of ion pairing, "free" reactant concentration may, depending on the charge of the species in question, be very much less than that put in. Consequently, if a species is rendered inactive by ion association, this loss must be taken into account. Even if an ion paired reactant is as reactive as the free species, ion association must be considered when calculating the true ionic strength of the medium.

The tendency for ions of unlike charge to form complexes has already been considered for the ferricyanide-thiosulphate reaction (see page 76). It can be concluded that, in the present system, where the most highly charged anions are $S_2O_3^{2-}$ and HPO_4^{2-}, the only ion pairs which reach a significant concentration will be $MS_2O_3^-$ and $MHPO_4^-$ where M^+ is Na^+ or K^+. In general,

$$ML^- \rightleftharpoons M^+ + L^{2-}$$

where L^{2-} is a divalent ligand. It has also been shown that the dissociation constant of ML^- is, to a first approximation, independent of the nature of L^{2-} but depends only on its charge and on the nature of M^+. Hence:

$$[L^{2-}] = [S_2O_3^{2-}] + [HPO_4^{2-}]$$

The experimental data shown in table 50 may be considered as arising from two types of system as far as the calculation of ion pairs is concerned.

(a). The first type is one where only one cation is present to any appreciable extent.

Considering the equilibrium with sodium ion,

$$NaL^{-} \rightleftharpoons Na^{+} + L^{2-}$$

for an initial concentration "a" of Na^{+} and "b" of L^{2-} then, if at equilibrium the amount of NaL^{-} is "x",

$$K = \frac{(a - x)(b - x)}{x}$$

where the equilibrium constant K, for a real system is given by:

$$K = Ko \times 10^{2.02\ F(I)}$$

where Ko = 0.21 M. and

$$F(I) = \frac{\sqrt{I}}{1 + \sqrt{I}} - 0.2\ I$$

Hence, $x^2 - (a + b + K)\ x + ab = 0$

The quadratic may be solved for x,

$$x = \frac{-B - \sqrt{B^2 - 4\ AC}}{2\ A}$$

(the positive root gives an answer which is inadmissible) where A = 1; B = -(a + b + K) and C = ab.

(b). The second type of system contains both sodium and potassium ions at comparable concentration. The two possible equilibria must be considered simultaneously:

$$NaL^{-} \rightleftharpoons Na^{+} + L^{2-}$$

$$KL^{-} \rightleftharpoons K^{+} + L^{2-}$$

If, at equilibrium the amount of KL^{-} formed is "y" for an initial potassium ion concentration "c" then,

$$K_{Na} = \frac{(a - x)(b - x - y)}{x}$$

or
$$y = b - x - \frac{K_{Na} \quad x}{a - x} \qquad \text{..... (ii)}$$

and

$$K_K = \frac{(c - y)(b - x - y)}{y}$$

or
$$x = b - y - \frac{K_K \quad y}{c - y} \qquad \text{..... (iii)}$$

where K_{Na} and K_K denote the dissociation constants for NaL^- and KL^- respectively under real conditions. Ko for KL^- is 0.11 M.

Equations (ii) and (iii) may be solved for x and y by a method of successive approximations as outlined on page 108.

The calculations for the two types of system were carried out on the experimental data with $[L^{2-}] = b = 0.0585$ M. The results for x and y together with the relevant equilibrium constants are given in table 51. The values $[L^{2-}]_T$ and $[S_2O_3{}^{2-}]_T$ are equilibrium concentrations, the subscript "T" being used to denote "true" values. The latter concentration was found by simple proportion from $[L^{2-}]_T$ and these new values were used to calculate an improved value, I_T for the ionic strength.

Table 51.

I	$[Na^+]$ M.	$[K^+]$ M.	K_{Na} M.	K_K M.	x M.	y M.	$[L^{2-}]_T$ M.	$[S_2O_3^{\ 2-}]_T$ M.	I_T
0.21	0.142	0.007	0.745	-	0.00887	-	0.04963	0.02138	0.19
0.31	0.242	0.007	0.831	-	0.01265	-	0.04585	0.01975	0.28
0.31	0.142	0.107	0.831	0.435	0.00686	0.00946	0.04218	0.01817	0.27
0.41	0.342	0.007	0.881	-	0.01581	-	0.04269	0.01839	0.37
0.41	0.142	0.207	0.881	0.462	0.00576	0.01546	0.03728	0.01606	0.36
0.51	0.442	0.007	0.907	-	0.01862	-	0.03988	0.01718	0.47
0.51	0.142	0.307	0.907	0.475	0.00503	0.02013	0.03334	0.01436	0.46
0.61	0.542	0.007	0.915	-	0.02122	-	0.03728	0.01606	0.56
0.61	0.142	0.407	0.915	0.479	0.00451	0.02399	0.03000	0.01292	0.55
0.71	0.642	0.007	0.910	-	0.02367	-	0.03483	0.01500	0.66
0.71	0.142	0.507	0.910	0.477	0.00411	0.02727	0.02712	0.01168	0.64
0.81	0.742	0.007	0.895	-	0.02600	-	0.03250	0.01400	0.75
0.81	0.142	0.607	0.895	0.469	0.00379	0.03018	0.02453	0.01057	0.74

Table 51, Comments.

Table 51 shows that the true ionic strength is somewhat less than that calculated from reactant concentration. It is possible to repeat the calculation using these new values to find more accurate $[L^{2-}]_T$ however this was not considered justified in the light of the approximations already made. The deviation at lower ionic strengths is certainly within the limits of error of the function of ionic strength whereas, at higher values of I, F(I) passes through a broad maximum, a large change in ionic strength representing a small increment in F(I).

The values I_T were considered as the best results for the ionic strength of the medium and were used in subsequent calculations.

Table 52 gives the information which was used to calculate the rate constant in the following rate equation:

$$-\frac{d[S_2O_3^{2-}]}{dt} = k_5 \times 10^{-1.01\ F(I)} [S_2O_3^{2-}]^2 [H^+]^2 [IO_3^-]$$

where the hydrogen ion concentration is given by

$$[H^+] = \log_{10}^{-1} (0.505\ F(I) - pH)$$

(see page 53).

Table 52.

$[IO_3^-] = 0.0252$ M.

I_T	$\log^{-1}-1.01\ F(I)$	$10^8\ [H^+]$ M.	$[S_2O_3^{2-}]_T$ M.	$-\frac{d[S_2O_3^{2-}]}{dt} \times 10^5$ M. min^{-1}	$10^{-14}\ k_5$ M.$^{-4}$ min^{-1}	$[K^+]$ M.
0.19	0.539	4.90	0.02138	0.64	4.29	-
0.28	0.509	6.61	0.01975	0.86	3.93	-
0.27	0.512	6.03	0.01817	0.96	6.20	0.098
0.37	0.493	8.32	0.01839	1.03	3.54	-
0.36	0.494	7.08	0.01606	1.17	7.27	0.192
0.47	0.483	10.00	0.01718	1.26	3.51	-
0.46	0.484	8.32	0.01436	1.41	8.10	0.288
0.56	0.480	11.22	0.01606	1.50	3.82	-
0.55	0.480	8.91	0.01292	1.64	10.23	0.385
0.66	0.479	12.30	0.01500	1.57	3.82	-
0.64	0.479	8.91	0.01168	1.80	13.77	0.482
0.75	0.482	12.59	0.01400	1.83	4.85	-
0.74	0.481	9.12	0.01057	1.95	17.31	0.0579

Table 52. Comments.

It is seen from the table that, in the absence of potassium ion, the rate of the iodate-thiosulphate reaction is given by:

$$-\frac{d[S_2O_3^{2-}]}{dt} = 3.8 \times 10^{14} \times 10^{-1.01\ F(I)}\ [S_2O_3^{2-}]_T^2\ [H^+]^2\ [IO_3^-]$$

$$M.\ min^{-1}$$

and is independent of the amount of sodium ion present. The rate constant was taken to be the mean of k_5 values under conditions where $[K^+]$ is negligible.

The presence of potassium ion is seen to have a catalytic effect, and it is expected that, under such circumstances, at least two mechanisms may be operative. One of these will be the uncatalysed reaction, the rate of which (Ro) is given by the equation above. The rate of the potassium ion catalysed reaction(s) will then be given by the difference between the observed rate (Robs) and the uncatalysed rate calculated for the particular set of conditions in the run in question. The difference in rates will be denoted by R_K. Table 53 lists values of Ro, Robs and R_K for kinetics experiments at various potassium ion concentrations

It is required to fit the kinetics results to a rate expression involving potassium ion together with the other experimental variables. The first possibility which comes to mind is an expression similar to that derived for the uncatalysed rate but modified by an additional concentration term, first order with respect to $[K^+]$.

Table 54 summarises the calculation used to predict values of the catalysed rate assuming the following rate equation to hold for the process in question:

$$-\frac{d[S_2O_3^{2-}]}{dt} = 160 \times 10^{14} \times 10^{-4.04\,F(I)}\,[S_2O_3^{2-}]_T [H^+]^2\,[IO_3^-]\,[K^+]$$

Table 53.

*Ro	*Robs	*R_K	$[K^+]$
0.59	0.96	0.37	0.098
0.61	1.17	0.57	0.192
0.67	1.41	0.74	0.288
0.61	1.61	1.03	0.385
0.59	1.81	1.30	0.482
0.43	1.95	1.52	0.579

All rates X 10^5 M. min^{-1}

All concentrations M.

Table 54.

$[IO_3^-]$ = 0.0252 M.

$10^{-4.04\,F(I)}$	$10^8\,[H^+]$	$[S_2O_3^{2-}]_T$	$[K^+]$	R_K pred.	R_K exp.
0.0687	6.03	0.01817	0.098	0.33	0.37
0.0579	7.08	0.01606	0.192	0.58	0.57
0.0548	8.32	0.01436	0.288	0.91	0.74
0.0530	8.92	0.01292	0.385	1.09	1.03
0.0527	8.91	0.01168	0.482	1.11	1.30
0.0537	9.12	0.01057	0.579	1.17	1.52

All rates X 10^5 M. min^{-1}

All concentrations M.

Table 54, Comments.

It can be seen that there is some correlation between predicted and experimentally observed values, however the agreement is by no means good. Other and more sophisticated rate expressions may be proposed, however it is considered that the kinetic data is not sufficiently sensitive to distinguish between any such possibilities. It is also considered that the accuracy of the predictions, which are based on the ability to calculate the activity coefficient for a polyvalent electrolyte up to an ionic strength of about 0.8, does not justify a closer correlation than that shown in the table and under such circumstances one ought to be satisfied with similar trends in kinetic data rather than close absolute values.

The rate law originally proposed for the potassium catalysed reaction is therefore quite satisfactory to account for the increase in rate in the presence of K^+.

The specific effects due to the presence of various alkali metal ions occur in the following order of magnitude:

$$Li^+ < Na^+ < K^+ < Cs^+$$

this order also being observed for the tendency of the metal ions to form ion pairs with a particular anion. Potassium ion was found to have a marked effect on the iodate-thiosulphate reaction and it is surprising that no increase in rate accompanied the addition of sodium ion.

It was decided to carry out further experimental work on the effects of the addition of neutral salts to reaction mixtures by extending the range of cations studied to caesium.

The Effect of Added Caesium Nitrate on Rate.

A series of kinetic experiments was carried out as in the previous work on salt effects, caesium nitrate being added in the place of sodium or potassium nitrate. The initial concentration of thiosulphate, iodate and buffer was the same as before but the maximum concentration of added $CsNO_3$ was limited to 0.4 M. by the solubility of $CsIO_3$ which precipitated out at higher concentration.

The experimental data is given in table 55.

Table 55.

$[S_2O_3^{2-}]$ = 0.0252 M.
$[IO_3^-]$ = 0.0252 M.
Temperature = 25.0 ± 0.02°C.
$[H_2PO_4^-]$ = 0.0067 M.
$[HPO_4^{2-}]$ = 0.0333 M.
$[Na^+]$ = 0.142 M.
$[K^+]$ = 0.007 M.

I*	$[CsNO_3]$ M.	pH	$-\frac{d[S_2O_3^{2-}]}{dt} \times 10^5$ M. min^{-1}
0.31	0.100	7.36	1.11
0.41	0.200	7.33	1.44
0.51	0.300	7.30	1.84
0.61	0.400	7.16	1.94

*Calculated from initial reactant concentrations.

It is expected that the most important ion pair in the reaction mixture will be CsL^- where $[L^{2-}]$ will be the sum of $[S_2O_3^{2-}]$ and $[HPO_4^{2-}]$. The value of the dissociation constant for CsL^- is required in order to calculate its concentration.

On theoretical grounds, Davies (51) has calculated a value of - 0.7 for the pK of the ion pair $CsSO_4^-$, corresponding to a dissociation constant of about 0.2 M. If one considers the stability of a particular ion pair to vary as

$$Li^+ < Na^+ < K^+ < Cs^+$$

then this value suggested by Davies is high, since the dissociation constant for KSO_4^- is 0.11 M. and $CsSO_4^-$ is expected to be more stable.

From osmotic coefficient measurements, Chlebek and Littler (52) calculated association constants for the ion pair $CsS_2O_8^-$. Their results are given in table 56 where,

$$Kc = \frac{[CsS_2O_8^-]}{[Cs^+][S_2O_8^{2-}]} \quad M.^{-1}$$

at the ionic strength shown and Ko is the equilibrium constant corrected to zero ionic strength.

Table 56.

I	Kc $M.^{-1}$	Ko $M.^{-1}$
0.106	10.87	27.8
0.116	9.16	24.0
0.201	8.40	24.7
0.197	9.24	27.1
0.201	8.91	26.3

The mean value for Ko represents a dissociation constant of 0.038 M. If we assume that the stability of the ion pair depends only on the charge type of the ligand and the nature of the metal ion, then these values should be applicable for the ion pair $CsS_2O_3^-$. Since the value obtained for $CsS_2O_8^-$ is an experimentally derived result, the lower value is preferred to that suggested by Davies.

The more recently reported investigation (52) was not available at the time when this experimental work was being carried out and in the absence of reliable data it was decided to investigate the stability of the ion pair relevant to this project.

To Determine the Stability Constant for the Ion Pair $CsS_2O_3^-$.

Barium thiosulphate is sparingly soluble in water, its solubility being 0.01135 M. ± 0.2% at 25°C (6). The amount present in solution will be modified in the presence of added anions or cations capable of forming ion pairs with barium or with thiosulphate respectively, such that, at any time, the solubility product, that is, the product of concentration of free barium and thiosulphate ions, will be a constant = 1.638×10^{-5} M.^{2}, under ideal conditions.

This method has been previously utilised to determine the stability constant for the ion pairs $KS_2O_3^-$ and $NaS_2O_3^-$ and it is hoped that by measuring the solubility of barium thiosulphate in the presence of various amounts of CsCl, it may be possible to calculate the stability constant for $CsS_2O_3^-$.

Approximately 2 g. BaS_2O_3 were added to 100 ml. of a solution of CsCl whose concentration was in the range 0.1 - 0.8 M. and which was contained in a 250 ml. reagent bottle. A control experiment was set up in which water was used in place of the caesium ion solutions. The bottles were shaken in a thermostat at 25°C for 24 hours when 25 ml.

aliquots were withdrawn through a cotton wool plug and titrated with standard iodine in the presence of starch as indicator.

The experimental results are shown in table 57.

Table 57.

[CsCl] M.	$[I_2]$ M.	Vol. I_2 ml.	$[S_2O_3^{2-}]$ M.
-	0.01571	18.08	0.01136
0.100	0.01571	29.83	0.01875
0.200	0.01571	38.08	0.02393
0.300	0.03303	21.30	0.02814
0.400	0.03303	24.09	0.03183
0.500	0.03303	26.75	0.03534
0.600	0.03298	29.20	0.03852
0.700	0.03298	31.60	0.04169
0.800	0.03298	33.96	0.04480

The value of 0.01136 M. for the solubility of BaS_2O_3 is very close to 0.01135 M ± 0.2% found by Denney and Monk (6).

The following equilibria are expected to be of importance in mixtures of barium thiosulphate and caesium chloride, and are shown with their respective equilibrium concentrations:

$$\begin{array}{lcccccl}
BaS_2O_3\ (s) & \rightleftharpoons & Ba^{++} & + & S_2O_3^{\ 2-} & & \ldots\ldots\ (i)\\
 & & (a-x-z) & & (a-x-y) & & \\
BaS_2O_3\ (aq) & \rightleftharpoons & Ba^{++} & + & S_2O_3^{\ 2-} & & \ldots\ldots\ (ii)\\
x & & (a-x-z) & & (a-x-y) & & \\
CsS_2O_3^{\ -} & \rightleftharpoons & Cs^{+} & + & S_2O_3^{\ 2-} & & \ldots\ldots\ (iii)\\
y & & (b-y-w) & & (a-x-y) & & \\
BaCl^{+} & \rightleftharpoons & Ba^{++} & + & Cl^{-} & & \ldots\ldots\ (iv)\\
z & & (a-x-z) & & (b-z-w) & & \\
CsCl & \rightleftharpoons & Cs^{+} & + & Cl^{-} & & \ldots\ldots\ (v)\\
w & & (b-y-w) & & (b-z-w) & &
\end{array}$$

where "a" represents the measured thiosulphate concentration; "b", the amount of caesium chloride added and "w", "x", "y" and "z" refer to the equilibrium concentrations of the ion pairs CsCl, BaS_2O_3, $CsS_2O_3^{\ -}$ and $BaCl^+$ respectively.

The solubility of barium thiosulphate in the absence of any additives is governed by equilibria (i) and (ii), the product $[Ba^{++}][S_2O_3^{\ 2-}]$ in the first being the solubility product, whilst the equilibrium constant in the second is the dissociation constant for the ion pair BaS_2O_3.

Both equilibria involve the formation of an uncharged species from two oppositely charged divalent ions and it is expected that the variation of the constants, Ksp and Ka for (i) and (ii) respectively, with ionic strength will be the same,

$$Ksp = (a - x - z)(a - x - y)$$

$$Ka = \frac{(a - x - z)(a - x - y)}{x}$$

Hence, $$x = \frac{Ksp}{Ka}$$

and this value will be independent of ionic strength or the presence of any added ions.

Two values are available for the dissociation constant of BaS_2O_3. According to Denney and Monk, who calculated the extent of ion pair formation from conductance measurements, the dissociation constant for BaS_2O_3 is 0.0047 M. and they calculated a corresponding value for the solubility product of 1.638×10^{-5} $M.^2$ According to Davies and Wyatt (53), however, the value of the stability constant, which was derived from measurements of the solubility of barium iodate in solutions of sodium thiosulphate, is a somewhat higher value of 0.0061 M.

Both sets of data seem equally reliable and it was decided to carry out two separate calculations incorporating first one and then the other of the two possible equilibrium constants. The higher value (0.0061 M.) was used to calculate the solubility product of barium thiosulphate in the manner described by Denney and Monk, with a result of 1.784×10^{-5} $M.^2$

The two possibilities give values of x as 0.003485 M. and 0.002925 M.

The remaining three equilibria have to be considered simultaneously with one other ((i) or (ii)) to obtain values of w, x, z and the equilibrium constant for (iii).

There has been considerable controversy about the value of the dissociation constant for the ion pair CsCl. From e.m.f. measurements Harned and Schupp (54) obtained a value of 1.1 ± 0.25 M. This is somewhat lower than 3.2 which Davies (55) obtained from conductivities, and 2.0 suggested by Wicke and Eigen (56). Gimblett and Monk (57) calculated a value of 2.85 M. from the data of Robinson and Stokes (58) for experimentally derived mean ionic activity coefficients of

CsCl. The latter result is reasonably close to that proposed by Davies and its value will be used for subsequent calculations.

The dissociation constant for $BaCl^+$ is reported as 1.35 M. (36).

Some simplification of the system is required since the solution of the four simultaneous equations involving the equilibria (iii), (iv), (v) and (i) or (ii), and their respective equilibrium constants is a difficult task.

Considering equilibrium (v), that is the dissociation of the ion pair CsCl. Table 57 shows that, on raising the Cs^+ concentration from 0 to 0.8 M., there is an increase in $[S_2O_3^{2-}]$, measured iodimetrically, by 0.0334 M., that is not more than some 4% of caesium will be ion paired with thiosulphate. Hence equilibrium (iii) will not give rise to an appreciable depletion of Cs^+. Ba^{++} increases by the same amount as $S_2C_3^{2-}$, but the percentage chloride removed in process (iv) is estimated to be much less than the percentage of Cs^+ removed by (iii), since the dissociation constant of the former is some 40 times greater than that which has been reported for a system analogous to process (iii). It may be estimated that about 10% of Cs^+ and Cl^- are effectively lost through ion pairing by equilibrium (v) at the highest concentration, and this constitutes the greatest contribution which, to a first approximation, may be considered on its own.

If the initial concentration of CsCl used is b, and at equilibrium an amount w is ion paired, then for a real system:

$$\frac{(b - w)^2}{w} = 2.85 \text{ X } 10^{1.01\ F(I)}$$

The ionic strength can only be calculated from the experimentally measured concentrations, that is assuming that $[S_2O_3^{2-}]$, determined iodimetrically, is free and is equal to $[Ba^{++}]$, and also $[Cs^+]$ and $[Cl^-]$ are equal to $[CsCl]$ used in the preparation of reaction mixtures.

Although the "true" ionic strength will be considerably lower when equilibrium concentrations are considered, the uncertainty in the stability constant for CsCl and the uncertainty in the calculation of activity coefficients at high ionic strengths make any need for improving the values futile.

Table 58 gives the amount of CsCl present in reaction mixtures for the experiments listed in table 57.

Table 58.

I	$[CsCl]_o$ b, M.	$[CsCl]_{ion\ pair}$ w, M.
0.18	0.100	0.002
0.30	0.200	0.007
0.41	0.300	0.014
0.53	0.400	0.024
0.64	0.500	0.036
0.75	0.600	0.051
0.87	0.700	0.069
0.98	0.800	0.088

The table shows that, although the loss due to ion pairing is small at lower concentration the discrepancy exceeds 10% at the highest concentration of caesium chloride.

The rest of the calculation for the stability constant of $CsS_2O_3^-$ is relatively straightforward. There is now sufficient data to evaluate z in equilibrium (iv) from

$$\frac{(a - x - z)(b - z - w)}{z} = 1.35 \times 10^{2.02\,F(I)}$$

where a is the measured thiosulphate concentration, I, b and w being obtained from table 58. The value of z may then be used in equilibrium (i)

$$(a - x - z)(a - x - y) = Ksp \times 10^{4.04\,F(I)}$$

to calculate y which, when inserted into equation (iii), gives the stability constant for the ion pair $CsS_2O_3^-$.

$$Ko = \frac{(b - y - w)(a - x - y)}{y \times 10^{2.02\,F(I)}}$$

A better ionic strength value may be calculated from

$$I = 4a - 4x - 2z - 2y + b - w$$

A short computer program was written to carry out the last set of calculations for z, y, Ko and I, this calculation being repeated twice each time with improved values of I to yield successive approximations towards a final value of Ko. The final iteration returned the value of I put in. It was considered that the inclusion in this iterative calculation of the equilibrium for the formation of CsCl was not justified on grounds of the uncertainty of the stability constant. A listing of the computer program (written in Fortran) is given in table 59 and table 60 shows the results of the calculation assuming the two values of x corresponding to the possible dissociation constants for BaS_2O_3. The respective solubility products (Ksp) were also fed in as data. In the latter table all concentrations are in M. K is defined as $K = [Cs^+][S_2O_3^{2-}]/[CsS_2O_3^-]$ M. and Ko is the value corrected to zero ionic strength.

Table 59.

```
      REAL K,KS,KSP,KEQ,I,II,KO
      WRITE(1,4)
      DO 1 L=1,2
      READ(2,6) X,KSP
      WRITE(1,5) X
      DO 1 N=1,8
      READ(2,2)A,B,W,I
      DO 10 M=1,3
      FI=(SQRT(I)/(1+SQRT(I)))-0.2*I
      K=1.35*(10**(2.02*FI))
      AMX=A-X
      BMW=B-W
      SUM=AMX+BMW+K
      Z=(SUM-SQRT(SUM*SUM-4*AMX*BMW))/2
      KS=KSP*(10**(4.04*FI))
      Y=A-X-(KS/(A-X-Z))
      KEQ=(B-Y-W)*(A-X-Y)/Y
      KO=KEQ/(10**(2.02*FI))
      II=4*A-4*X-2*Z-2*Y+B-W
10    I=II
1     WRITE(1,3) B,A,I,Z,Y,KEQ,KO
      CALL EXIT
2     FORMAT(F6.5,F2.1,F4.3,F3.2)
3     FORMAT(F8.3,F9.5,F7.3,F10.6,F9.5,F7.3,F8.4)
4     FORMAT(////,13X,41HCALCULATION OF THE STABILITY CONSTANT FOR
     1         , 23X,20HCAESIUM THIOSULPHATE)
5     FORMAT(//,9X,35H(RESULT OF FINAL ITERATION FOR X = F8.6,1H)
     1         //,3X, 6H[CSCL]2X,6H[THIO]4X,1HI8X,1HZ8X,1HY7X,1HK6X,2HKO)
6     FORMAT(2E9.3)
      END
```

Table 60.

CALCULATION OF THE STABILITY CONSTANT FOR CAESIUM THIOSULPHATE

(RESULT OF FINAL ITERATION FOR X = 0.003485)

[CSCL]	[THIO]	I	Z	Y	K	KO
0.100	0.01875	0.150	0.000338	0.00410	0.255	0.0801
0.200	0.02393	0.255	0.000746	0.00868	0.249	0.0663
0.300	0.02814	0.356	0.001211	0.01300	0.244	0.0599
0.400	0.03183	0.451	0.001732	0.01717	0.233	0.0547
0.500	0.03534	0.543	0.002326	0.02139	0.216	0.0498
0.600	0.03852	0.632	0.002975	0.02533	0.200	0.0460
0.700	0.04169	0.717	0.003703	0.02930	0.182	0.0422
0.800	0.04480	0.801	0.004517	0.03320	0.165	0.0368

(RESULT OF FINAL ITERATION FOR X = 0.002925)

[CSCL]	[THIO]	I	Z	Y	K	KO
0.100	0.01875	0.152	0.000349	0.00397	0.280	0.0875
0.200	0.02393	0.258	0.000764	0.00846	0.273	0.0724
0.300	0.02814	0.358	0.001236	0.01276	0.266	0.0651
0.400	0.03183	0.454	0.001765	0.01695	0.253	0.0593
0.500	0.03534	0.546	0.002366	0.02121	0.233	0.0538
0.600	0.03852	0.634	0.003023	0.02519	0.216	0.0496
0.700	0.04169	0.720	0.003757	0.02921	0.196	0.0454
0.800	0.04430	0.804	0.004580	0.03316	0.178	0.0417

Table 60. Comments.

The final column in the table lists values for the stability constant of $CsS_2O_3^-$. Although at either of the two x values tried there is some 50% variation of the constant over the range of ionic strength 0.15 - 0.80, the order of magnitude of the result for Ko is the same as that for the dissociation constant for $CsS_2O_8^-$ (0.034 M.) (52). When one considers that the final value has depended on a knowledge of the equilibrium constants for four processes, in each case there being an activity coefficient term with its inherent error, the agreement between values is quite reasonable. The chief source of deviation is attributed to possible doubt regarding the equilibrium constants, reported in literature, which have been of importance in this calculation. The stability constant for $BaCl^+$, which was used, for example, is based on a single reported value. No improvement in Ko, however, was evident for realistic values of the latter, when the constant in question was varied between 0.05 and 2.0 M. The method of computing the results has made few serious assumptions, however, the solution of such a problem is more suited to analog computation rather than digital.

The analog computer would permit a much freer alteration of the reaction parameters so that values for say the various dissociation constants may be tried, and since the system is completely dynamic, there will be an instant indication of their effect on Ko. Digital computers may be adapted to analog problems by suitable programming and, at the time of writing, the "PACTOLUS" method is being applied to an IBM 1130 computer for the solution of the problem discussed in this text. Information regarding the application of this method of programming is being obtained from the relevant operation manual (59).

Considering the wide range of values found for the dissociation constant of $CsS_2O_3^-$ it would not be correct to take a mean value. Since, however, the results are close to the reported dissociation constant for $CsS_2O_8^-$, which was determined by a more direct technique than was used in the present investigation, the value of 0.038 M. was considered to be quite adequate for $CsS_2O_3^-$ and was applied in the subsequent calculation. The value predicted by Davies (51) for $CsSO_4^-$ is rejected in view of our result being near that for $CsS_2O_8^-$.

Turning now to consider the kinetic data. Two ion pairing equilibria will compete in solution,

$$NaL^- \rightleftharpoons Na^+ + L^{2-}$$

$$CsL^- \rightleftharpoons Cs^+ + L^{2-}$$

with dissociation constants, corrected to zero ionic strength, of 0.21 and 0.038 M. for sodium and caesium ion respectively. Although there is a large difference between the two stability constants, it is not possible to say that $[NaL^-]$ will be negligible compared to $[CsL^-]$ and the two processes have to be considered simultaneously. The calculation of ion pair concentrations has to be carried out by method (b) described on page 176 where, in this case $[Cs^+]$ replaces $[K^+]$. Equations (ii) and (iii) on page 177 thus become,

$$y = b - x - \frac{K_{Na} \quad x}{a - x} \qquad \ldots\ldots (a)$$

and

$$x = b - y - \frac{K_{Cs} \quad y}{c - y} \qquad \ldots\ldots (b)$$

where "a", "b" and "c" denote initial concentrations of

Na^+, L^{2-} and Cs^+ respectively and "x" and "y" refer to the equilibrium concentration of the ion pairs NaL^- and CsL^- respectively. The values of the relevant dissociation constants under real conditions are denoted by K_{Na} and K_{Cs}. A first approximation for the ionic strength was calculated from the initial reactant concentrations.

In the calculations for experiments involving sodium and potassium ions as the only cations, a method of successive approximations was used to solve the two equations ((i) and (ii) on page 177) simultaneously. In this case a graphical method was tried as a possible alternative. The functions (a) and (b) were plotted over a suitable range of x and y values using the same axes, the coordinates of the intercept of the two graphs being the solution to the simultaneous equations. Graph 18 shows that the graphs are, in fact, straight lines over the range of values plotted, as illustrated by the first calculation for the data in table 61, which also shows the solutions for the remaining three reaction mixtures. The graphs shown are typical of those plotted in these calculations.

As before the "true" thiosulphate ion concentration $[S_2O_3^{2-}]_T$ was calculated from $[L^{2-}]_T$ by simple proportion and the results for x and y were used to calculate an improved value for the ionic strength (I_T) which was used in the subsequent calculations.

Graph 18.

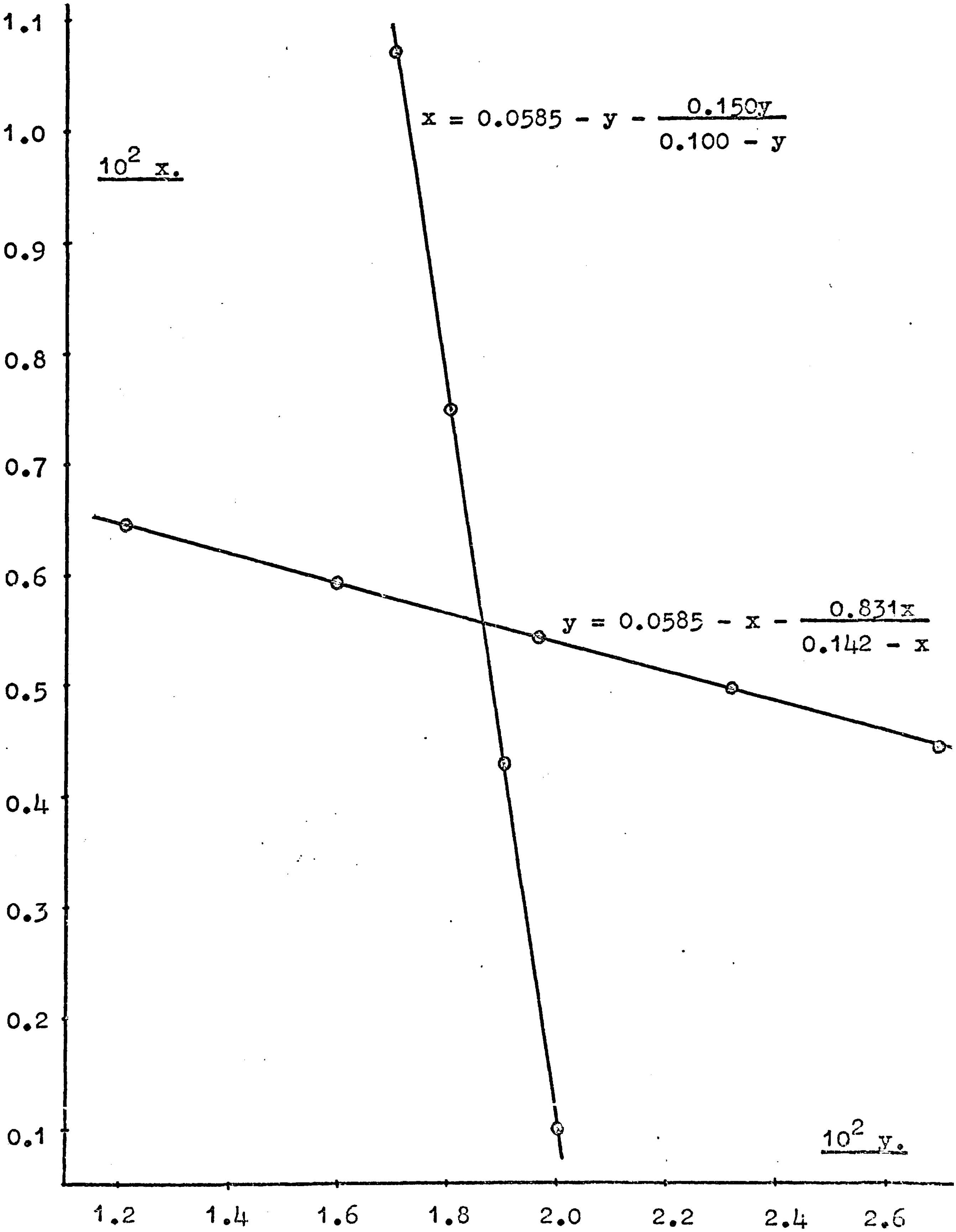

10^2 x.
10^2 y.
$x = 0.0585 - y - \frac{0.150y}{0.100 - y}$
$y = 0.0585 - x - \frac{0.831x}{0.142 - x}$
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
1.2
1.4
1.6
1.8
2.0
2.2
2.4
2.6

Table 61.

$[L^{2-}]$ = 0.0585 M; $[Na^{+}]$ = 0.142 M.

I	K_{Na}	K_{Cs}	$[Cs^{+}]$	$10^{3}x$	$10^{3}y$	10^{3} x $[L^{2-}]_T$	10^{3} x $[S_2O_3^{2-}]_T$	I_T
0.31	0.831	0.150	0.100	5.64	18.58	34.28	14.77	0.26
0.41	0.881	0.159	0.200	4.09	28.26	26.15	11.26	0.34
0.51	0.907	0.164	0.300	3.23	34.17	21.10	9.09	0.43
0.61	0.915	0.166	0.400	2.67	38.26	17.57	7.57	0.53

All concentrations and equilibrium constants are in M.

If the total observed rate in the presence of caesium ion is made up of an "uncatalysed" rate and a Cs^{+} catalysed rate, denoted by Ro and R_{Cs} respectively, then the rate for the catalysed process will be the difference between the total rate (R_{obs}) and that calculated for the step where only sodium ion is present. The latter is predicted by the equation,

$$-\frac{d[S_2O_3^{2-}]}{dt} = 3.8 \times 10^{14} \times 10^{-1.01\,F(I)}\,[S_2O_3^{2-}]^2\,[H^{+}]^2\,[IO_3^{-}]$$

M.

Table 62 gives the calculation of the catalysed rate at various caesium ion concentrations.

Table 62.

$[IO_3^-]$ = 0.0252 M.

I_T	$10^{-1.01}$ F(I)	$[S_2O_3^{2-}]_T$	$10^8[H^+]$	Ro	R_{obs}	R_{Cs}	$[Cs^+]_T$
0.26	0.515	0.01477	6.09	0.40	1.11	0.71	0.081
0.34	0.497	0.01126	6.62	0.27	1.44	1.17	0.172
0.43	0.486	0.00909	7.19	0.20	1.84	1.64	0.266
0.53	0.480	0.00757	9.98	0.26	1.94	1.68	0.362

All concentrations are in M.
All rates are X 10^5 M. min^{-1}.

If a rate equation for the caesium catalysed step is proposed to be of the same order as that for the potassium catalysed reaction discussed previously, with $[Cs^+]$ replacing $[K^+]$, then,

$$-\frac{d[S_2O_3^{2-}]}{dt} = k_6 \times 10^{-4.04} F(I) \; [S_2O_3^{2-}]^2 \; [H^+]^2 \; [IO_3^-][Cs^+]$$

for which values of k_6 are calculated in table 63.

Table 63.

$[IO_3^-]$ = 0.0252 M.

R_{Cs}	$10^{-4.04}$ F(I)	$[S_2O_3^{2-}]_T$	$10^8[H^+]$	$[Cs^+]_T$	$10^{-14}k_6$
0.71	0.0701	0.01477	6.09	0.081	613
1.17	0.0612	0.01126	6.62	0.172	794
1.64	0.0559	0.00909	7.19	0.266	1025
1.68	0.0532	0.00757	9.98	0.362	607

All concentrations are in M. The units of k_6 are $M.^{-5}$ min^{-1}.
All rates are X 10^5 M. min^{-1}.

If the third value (1025 X 10^{14}) for the rate constant k_6 (table 62) is ignored owing to it being relatively high, the mean of the remaining three values is 670 X 10^{14} $M.^{-5}$ min^{-1} as compared with 160 X 10^{14} $M.^{-5}$ min^{-1} for the potassium catalysed reaction. The fifth order rate constant for the uncatalysed reaction is 3.8 X 10^{14} $M.^{-4}$ min^{-1} which is unaffected by the presence of sodium ion.

The Effect of Temperature of the Rate of Reaction.

The rate of reaction was measured at a variety of temperatures, all other conditions being kept the same. Reaction mixtures were prepared containing only sodium ion as cation and the process which was measured was predominantly the one which is not catalysed by cations.

The energy of activation for the reaction was calculated from the Arrhenius relationship,

$$k = A e^{-E/RT}$$

a plot of $\log_{10}$initial rate vs. $1/T^{o}K$ giving a slope of $E/2.303\ R$, when initial rates refer to experiments carried out under identical conditions of concentration.

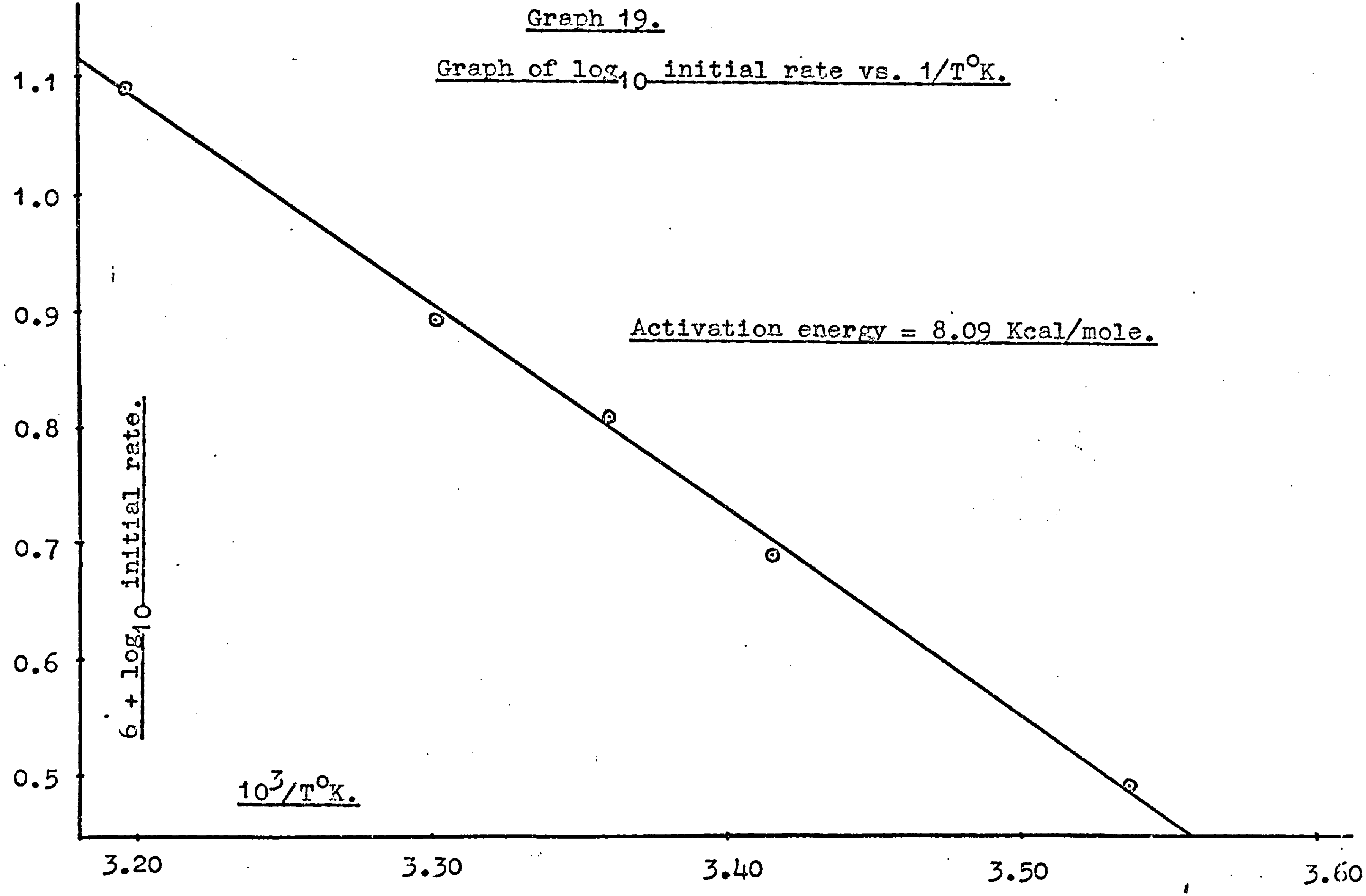
Table 64.

$[S_2O_3^{2-}]$ = 0.0252 M. $[Na^+]$ = 0.142 M.

$[IO_3^-]$ 0.0252 M. pH = 7.44

$T^{o}C$	$10^3/T^{o}K$	$-\frac{d[S_2O_3^{2-}]}{dt} \times 10^5$ M. min^{-1}	6 + $\log_{10}$ init. rate
10.0	3.534	0.31	0.491
20.0	3.413	0.41	0.690
25.0	3.358	0.64	0.806
30.0	3.300	0.78	0.892
40.0	3.195	1.23	1.090

See graph 19.



Graph 19.

Graph of $\log_{10}$ initial rate vs. $1/T^oK$.

SECTION VI.

THE REACTION BETWEEN HALATE AND THIOSULPHATE IONS.

DISCUSSION.

GENERAL DISCUSSION.

The Bromate-Thiosulphate Reaction.

The experimental kinetic data has been used to show that the oxidation of thiosulphate by bromate ion is of first order with respect to bromate, thiosulphate and hydrogen ions. In addition, the process exhibits general acid catalysis in which the third order rate constant is related to the concentration of $H_2PO_4^-$ by

$$k_3 = k_3' (1 + 20 [H_2PO_4^-])$$

The overall observable reaction may thus be broken down into possible rate laws for two concurrent reactions, that is,

$$\text{(a)} \quad \text{Rate} = k \, [BrO_3^-][H^+][S_2O_3^{2-}]$$

$$\text{(b)} \quad \text{Rate} = k' \, [BrO_3^-][H^+][S_2O_3^{2-}][H_2PO_4^-]$$

however, it must be remembered that no experimental work was carried out to confirm that the order with respect to bromate and thiosulphate was still unity for the catalysed reaction.

It is apparent from the data presented by Edwards (1) that most oxidations involving bromate are of second order with respect to hydrogen ion, as is the exchange of oxygen between the anion and water. The intermediate BrO_2^+ or its hydrated form has been proposed by several workers, arising from a two stage protonation of bromate followed by elimination of water,

$$H^+ + BrO_3^- \rightleftharpoons HBrO_3$$

$$H^+ + HBrO_3 \rightleftharpoons H_2BrO_3^+$$

$$H_2BrO_3^+ \rightleftharpoons H_2O + BrO_2^+$$

and presumably the reactivity of bromate towards anionic reducing agents lies in the mutual attraction of the latter to the positively charged intermediate.

Oxygen exchange between BrO_3^- and H_2O, which obeys the following rate law:

$$\text{Rate} = k\,[BrO_3^-][H^+]^2\,[H_2O]$$

and the oxidation of, say, halide ion by bromate, whose rate law is the same as that for water with the exception that the term $[H_2O]$ is replaced by X^- ($X^- = Cl^-, Br^-, I^-$), is thus considered to go by the same route.

In their discussion of the bromate-iodide reaction, Barton and Wright (60) argued against BrO_2^+ existing as a common intermediate in the above mentioned processes. They considered that the rate of reaction of BrO_2^+ or, more likely, the hydrated form, with water,

$$H_2O^* + H_2BrO_3^+ \longrightarrow H_2O + H_2BrO_3^{*+}$$

would constitute the fastest possible reaction of the intermediate, so all other reactions of this type will be slower. This is contrary to observations since even the rate constant for the bromate-chloride reaction, which is the slowest of its type, is many times faster than exchange.

On the other hand, the reaction between BrO_2^+ and X^- would be fairly fast and under some conditions the formation of BrO_2^+ by fission of the Br-O bond could be expected to be rate determining, giving a rate law

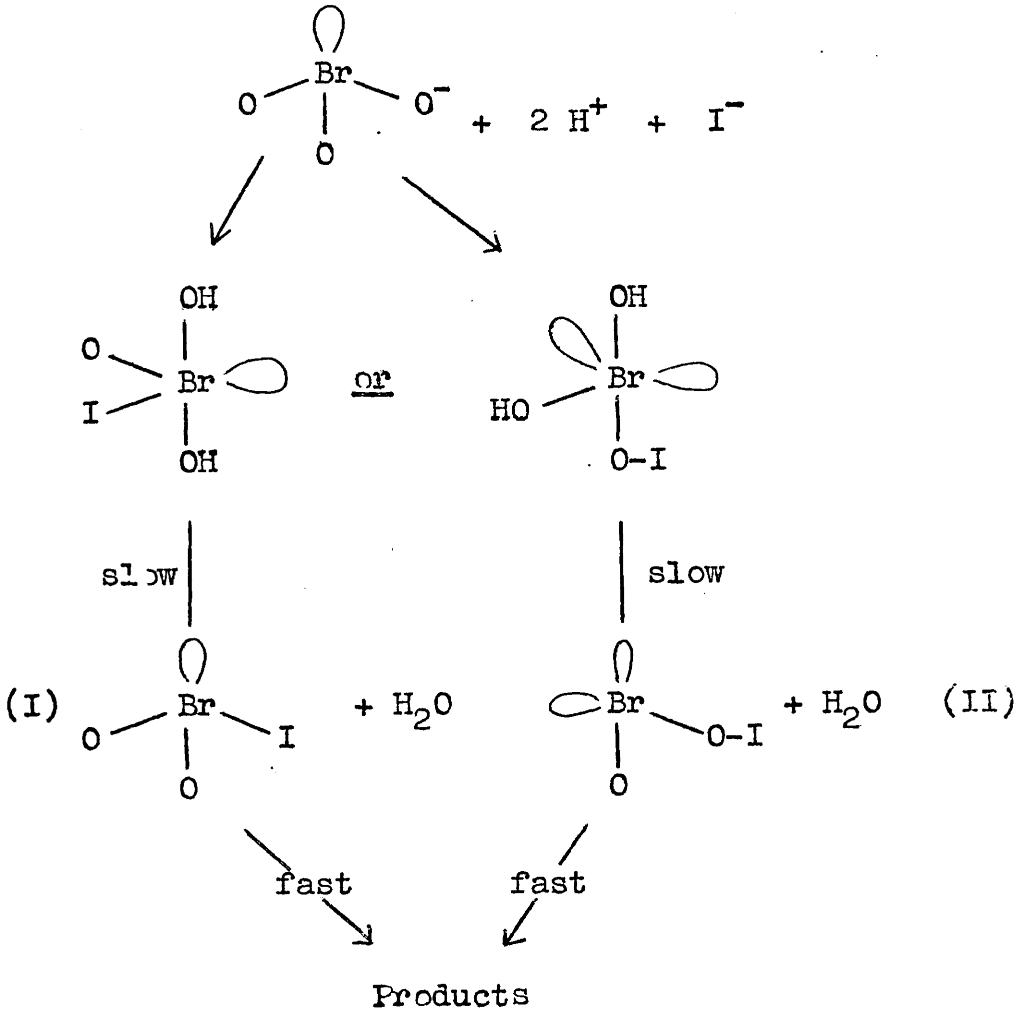
$$\text{Rate} = k\,[H^+]^2\,[BrO_3^-]$$

which is never observed. It is of interest that some oxidations involving nitric acid are described by,

$$\text{Rate} = k\,[H^+]^2\,[NO_3^-]$$

which is of zero order with respect to reducing agent. In the last case the existence of the species NO_2^+ has been postulated.

Barton and Wright found it difficult to explain the observed general base catalysis for the bromate-iodide reaction in terms of a reactive intermediate BrO_2^+. A single reaction step in which all the reactants come together followed by subsequent rate determining elimination of water was thought most likely:



where the reaction scheme shows the possible structures for the intermediates, that is, either the iodide ion is bonded directly to the central bromine atom or by means of an oxygen-iodine bond. No preference for either of the two structures was given.

It was assumed that the activated complex (I or II) would react rapidly with iodide as follows:

$$IBrO_2 + I^- \longrightarrow I_2 + BrO_2^-$$

$$2.H^+ + BrO_2^- + 2\,I^- \longrightarrow I_2 + BrO^- + H_2O$$

$$2\,H^+ + BrO^- + 2\,I^- \longrightarrow I_2 + Br^- + H_2O$$

the intermediates BrO_2^- and BrO^- being well known in aqueous solution.

The catalysed part of the bromate-thiosulphate reaction may be explained in terms of the possible mechanisms involving second order dependence on hydrogen ion concentration.

One such possibility is as follows:

$$H^+ + BrO_3^- \rightleftharpoons HBrO_3$$

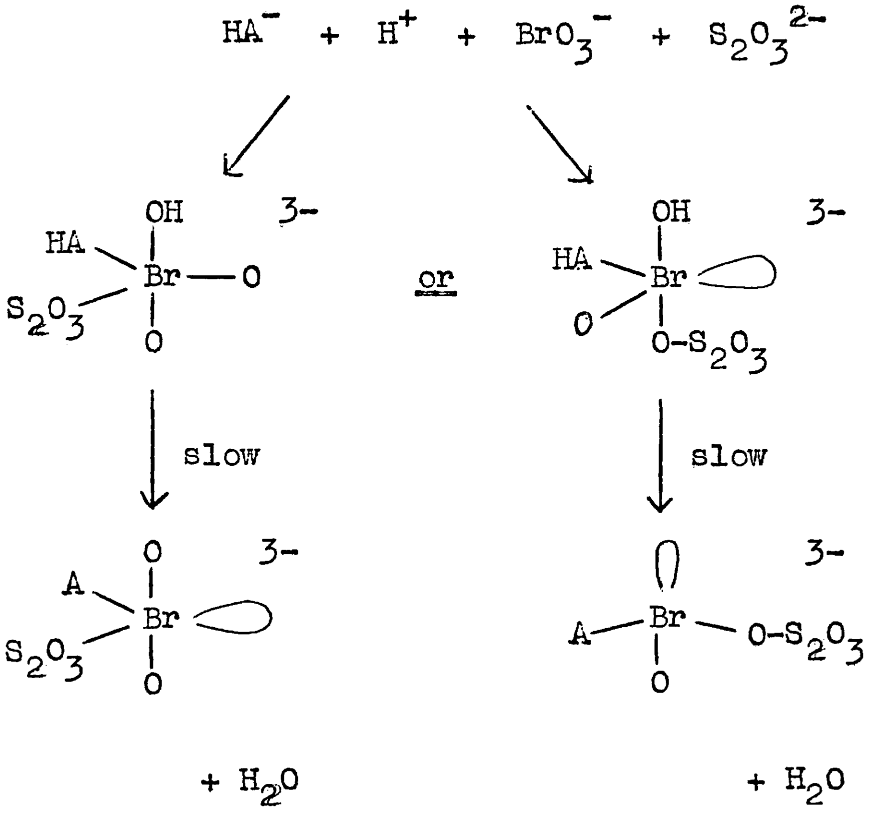
$$HA^- + HBrO_3 = H_2BrO_3^+ + A^{2-}$$

$$H_2BrO_3^+ + S_2O_3^{2-} \xrightarrow{slow} (BrO_2.S_2O_3)^- + H_2O$$

$$(BrO_2.S_2O_3)^- \xrightarrow{fast} \text{products}$$

This mechanism presupposes the existence of the intermediate $BrO_2^+(H_2O)$. The necessity for involving the acid in this scheme may be explained as follows. The kinetics of oxidation by bromate have previously been followed under conditions of fairly high acid concentration, for example, 0.1 M. HCl in the case of the bromate-sulphite reaction (61) and up to pH 4 in the study of the bromate-iodide reaction. In the case of the bromate-thiosulphate reaction a pH of 6 - 7 produced a conveniently measurable rate but representing a hydrogen ion concentration at least 100 times lower than that in the previous investigations. This could well make the straightforward second protonation equilibrium a very unlikely situation and the alternative shown above becomes observable owing to the relatively high acid concentration (up to 0.7 M.).

If the proposals of Barton and Wright are accepted then one may consider the reactants to be in equilibrium with a complex as follows:



where the reaction scheme shows two possible structures for the intermediate analogous to those suggested for the bromate-iodide reaction.

An alternative mechanism which does not involve the acid HA^- in the initial pre-equilibrium may be valid. Under these conditions the attack of HA^- on the complex is shown to be rate determining.

$$H^+ + BrO_3^- + S_2O_3^{2-} \rightleftharpoons (HBrO_3.S_2O_3)^{2-}$$

$$(HBrO_3.S_2O_3)^{2-} + HA^- \overset{\text{slow}}{\rightleftharpoons} (BrO_2.S_2O_3)^- + A^{2-} + H_2O$$

The last mechanism predicts the existence of an activated complex with a much smaller negative charge than has been proposed in the other reaction schemes, possibly making the formation of such an intermediate energetically more favourable.

Whichever of the possible mechanisms is considered as most suitable, whether it is by way of BrO_2^+ or by way of a single step complex formation, the activated complex will essentially be the same, that is, it will contain the species $(BrO_2.S_2O_3)^-$, with or without an anion A^{2-}. In a manner analogous to that suggested for the bromate-iodide reaction it is proposed that subsequent reactions of the complex are fast involving well known intermediates such as BrO_2^- and BrO^-, i.e:

$$(BrO_2.S_2O_3)^- + S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + BrO_2^-$$

$$2\,H^+ + BrO_2^- + 2\,S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + BrO^- + H_2O$$

$$2\,H^+ + BrO^- + 2\,S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + Br^- + H_2O$$

assuming that the stoicheiometry of the reaction is

$$6\,H^+ + BrO_3^- + 6\,S_2O_3^{2-} \longrightarrow 3\,S_4O_6^{2-} + Br^- + 3\,H_2O$$

Under the conditions of pH and "acid" concentration the contribution of the catalysed rate to the overall rate was approximately half. The remaining contribution was from the uncatalysed process, which was of first order with respect to each of the reactants, bromate, thiosulphate and hydrogen ion.

The formation of a complex $(HBrO_3.S_2O_3)^{2-}$ as described above cannot be rate determining since any reaction schemes involving this species have required a subsequent slow step which gave rise to a reaction of similar rate to that under discussion. If the complex specified above is involved in the rate determining step it must undergo some spontaneous change which will be primarily responsible for reaction.

The only possibilities for such a change are

$$\text{(a)}\quad (HBrO_3.S_2O_3)^{2-} \xrightarrow{\text{slow}} HBrO_3^{2-} + S_2O_3^{0}$$

$$HBrO_3^{2-} + H^+ \xrightarrow{\text{fast}} H_2BrO_3^-$$

$$H_2BrO_3^- \xrightarrow{\text{fast}} BrO_2^- + H_2O$$

$$\text{(b)}\quad (HBrO_3.S_2O_3)^{2-} \xrightarrow{\text{slow}} (BrO_2.S_2O_3)^- + OH^-$$

$$OH^- + H^+ \xrightarrow{\text{fast}} H_2O$$

In (a) the product $S_2O_3^{0}$ may react with thiosulphate ions to form tetrathionate or, if it has the properties of disulphur trioxide it may react with water to form some sulphate. It is also possible that some sulphide ion may be produced at the same time and it is interesting to note that during kinetics experiments, mixtures of bromate and thiosulphate, invariably smelt strongly of H_2S.

In the case of (b) the complex $(BrO_2.S_2O_3)^-$ is again proposed, the terminating processes involving this species having been previously described.

Further kinetic work is clearly required on the bromate-thiosulphate reaction and an investigation of the products would be highly desirable. As the available information stands it is impossible to propose an unambiguous mechanism.

The Iodate-Thiosulphate Reaction.

The kinetics of the iodate-thiosulphate reaction show that it is of first order with respect to iodate, second order with respect to thiosulphate and second order with respect to hydrogen ion. Although the rate of reaction was unaffected by the presence of sodium ion, both potassium and caesium ions were found to be very effective catalysts. The ratio of sixth order rate constants, given by:

$$k_6 = \frac{\text{Rate}}{[S_2O_3^{2-}]^2\,[H^+]^2\,[IO_3^-]\,[M^+]}$$

$$(\text{where } [M^+] = [K^+] \text{ or } [Cs^+])$$

was $k_{Cs}/k_K \sim 4$.

It was assumed that the rate equation for the catalysed reaction was of the same general type as that for the uncatalysed process although no experimental data is available to confirm the order with respect to thiosulphate and iodate under these conditions. The dependence of rate on $[H^+]$, however, was measured at high potassium ion concentration where the reaction was predominantly the cation catalysed one.

The salt effects on the reaction in the absence of caesium or potassium ion were consistent with the reactants being in equilibrium with a trivalent activated complex as follows:

$$2\,S_2O_3^{2-} + 2\,H^+ + IO_3^- \rightleftharpoons (\text{complex})^{3-}$$

and the activation energy for the reaction was found to be 9.08 Kcal/mole.

In a manner analogous to that of bromate oxidations, the intermediate species in iodate oxidations is generally accepted as being IO_2^+. In this case the exchange with water follows a different rate law,

$$\text{Rate} = k\,[H^+][IO_3^-]$$

(other than at high acid concentrations) from that normally observed in oxidation reactions where,

$$\text{Rate} = k\,[H^+]^2\,[IO_3^-]\,[\text{Red}]^n$$

($[\text{Red}]^n$ refers to an n th. order dependence on the reducing agent)

and the arguments against the existence of BrO_2^+ in the bromate-iodide system are not valid in the case of iodate.

According to Edwards (1) the oxidation of thiosulphate by iodate is best described by the following scheme:

$$IO_3^- + H^+ \rightleftharpoons HIO_3$$

$$HIO_3 + H^+ \rightleftharpoons H_2IO_3^+$$

$$H_2IO_3^+ + S_2O_3^{2-} \rightleftharpoons (IO_2.S_2O_3)^- + H_2O$$

$$(IO_2.S_2O_3)^- + S_2O_3^{2-} \xrightarrow{\text{slow}} IO_2^- + S_4O_6^{2-}$$

however, Barton and Wright would prefer to write:

$$IO_3^- + 2\,H^+ + S_2O_3^{2-} \rightleftharpoons (H_2IO_3.S_2O_3)^-$$

$$\downarrow$$

$$(IO_2.S_2O_3)^- + H_2O$$

$$(IO_2.S_2O_3)^- + S_2O_3^{2-} \xrightarrow{\text{slow}} IO_2^- + S_4O_6^{2-}$$

by analogy with the iodate-iodide reaction (47) where the authors avoided the inclusion of free IO_2^+ or its hydrated form.

Two structures may be proposed for the iodate-thiosulphate intermediate complexes; one where thiosulphate will be bonded directly to a central iodine atom and one where the bonding will occur through oxygen on iodate.

The possible involvement of cation may now be considered. The metal ion will form ion pairs with some kinetically important anions so as to either make a process energetically more favourable by reducing say the mutual electrostatic repulsion between reactants or by making an intermediate more stable so that it may have a greater chance of an encounter which will take it past the stage of an activated complex. The possible participation of potassium or caesium ions can be in two places, either by forming ion pairs with the singly charged $(IO_2.S_2O_3)^-$ or by stabilising the activated complex formed during the reaction of the latter intermediate with thiosulphate when the species of interest will have a triple negative charge. In either of the two situations the rate of the catalysed reaction will depend on the concentrations, $[MIO_2.S_2O_3]$ or $[MIO_2.S_2O_3.S_2O_3^{2-}]$ and since the amounts of the species formed from caesium or from potassium ions will depend on the relevant stability constants, the rates of reaction should be related to the dissociation constants for the ion pairs.

There is much variation in reported values for dissociation constants for ion pairs between singly charged anions and cations. Stability constants for the nitrates of the three cations of interest have been reported as 3.9, 1.4 and 1.0 M. for Na^+, K^+ and Cs^+ respectively (36) the values being corrected to zero ionic strength. These data predict that the cation catalytic effect would give rise to a value of 1.4 for the ratio of sixth order rate constants

k_{Cs}/k_K, as compared with approximately 4.0 observed experimentally.

There are no reliable data on the dissociation constants of ion pairs of sodium, potassium and caesium with trivalent anions. Some work has been carried out on systems involving ferricyanide ion, by measuring the solubility of $Co(NH_3)_6.Fe(CN)_6$ in solutions of alkali metal nitrates (62), however the conditions of high MNO_3 ($\sim$ 3.0 M.) concentration lead one to speculate as to the significance of the results under normal conditions. It is not understood whether the values of 0.48, 2.0 and 3.3 M. for the stability constants of $MFe(CN)_6^{2-}$, where $M^+ = Na^+$, K^+ and Cs^+ respectively, were corrected to zero ionic strength; however they predict the reverse order of stabilities for the ion pairs to that normally expected. For comparison, a previously reported value for the dissociation constant of $KFe(CN)_6^{2-}$ is 0.08 M. (36), this value being fairly reproducible amongst the other workers contributing to this reference.

The dissociation constants for ion pairs between the singly charged species suggest that the kinetic role of potassium and of caesium is not to form the complex $(MIO_2.S_2O_3)$ but perhaps to assist in stabilising the activated complex formed during the rate determining step. There is insufficient data, however, to enable this conclusion to be drawn.

The absence of any kinetic effect in the presence of sodium cannot be explained in terms of the above arguments since, in all the systems referred to in this thesis, the ratio of equilibrium constants for ion pairs containing sodium or potassium (K_{Na}/K_K) is rarely greater than 2 or 3, and in the light of the large potassium ion effect it would be expected for sodium to have at least some catalytic power. If a reaction intermediate is indeed IO_2^+ or a related cation, then it is possible that nitrate may form sufficiently stable ion pairs, $IO_2.NO_3$, so as to reduce the concentration of the active species, thereby reducing the rate accordingly. It may only be presumed that in the case of $NaNO_3$ there is a balance of the catalytic and retarding effects resulting in no observable change. If this were the case, the net result for potassium and caesium effects would be left virtually unchanged.

The last explanation is by no means satisfactory and cannot be substantiated with experimental data. Further work on the iodate-thiosulphate reaction is clearly required, especially in the field of salt effects.

SECTION VII.

THE REACTION BETWEEN HALATE AND THIOSULPHATE IONS.

CONCLUSION.

CONCLUSION.

The Bromate-Thiosulphate Reaction.

The rate law for the bromate-thiosulphate reaction was confirmed to be of first order with respect to bromate, thiosulphate and hydrogen ion, and the process was catalysed by the presence of the "acid", $H_2PO_4^-$.

The catalysed reaction was explained in terms of the kinetics generally observable during the bromate oxidation of many anionic reducing agents (e.g. I^-, Cl^-, SO_3^{2-}) where the reaction is of second order with respect to H^+, however, there was some ambiguity as regards the point at which the acid becomes involved.

An intermediate complex $(BrO_2...S_2O_3)^-$ was proposed in accordance with Edwards (1).

The uncatalysed reaction, first order with respect to hydrogen ion, was considered to go by way of an intermediate $(HBrO_3.S_2O_3)^{2-}$ which decomposed either to give a species $S_2O_3^o$ yielding sulphate as a possible hydrolysis product or by way of the intermediate suggested for the catalysed reaction, by elimination of OH^-.

Continuation and terminating processes involve more well known anions such as BrO_2^- and BrO^-.

The Iodate-Thiosulphate Reaction.

The kinetics of the iodate-thiosulphate reaction were shown to be the same as reported by the previous workers, namely, first order with respect to iodate and second order with respect to thiosulphate and to hydrogen ions. Cation catalysis by potassium and caesium was found, however sodium had apparently no effect.

The rate law in the absence of cation was explained in terms of a rate determining step involving the species $(S_2O_3.IO_2)^-$ and $S_2O_3^{2-}$.

$$(S_2O_3.IO_2)^- + S_2O_3^{2-} \longrightarrow IO_2^- + S_4O_6^{2-}$$

the formation of the intermediate anion occurring by way of the iodyl cation IO_2^+ (analogous to BrO_2^+ proposed for bromate oxidations) or via a two step mechanism where IO_3^-, $S_2O_3^{2-}$ and 2 H^+ react to form a complex which will subsequently eliminate water.

It was impossible to explain the cation catalysis in terms of the dissociation constants of appropriate ion pairs owing to the lack of reported information regarding their values.

Terminating processes are fast and analogous to those proposed for the bromate oxidation of thiosulphate, the intermediates in this case being IO_2^- and IO^-.

The ground covered in this investigation of the bromate and iodate oxidations of thiosulphate is clearly only preliminary and considerable kinetic information is still to be obtained. Further experimental work is considered essential on both systems possibly extending the range of halate ions covered to chlorate which may react under conditions of pH where thiosulphate is stable.

APPENDICES.

Appendix I.

Preparation of Potassium Dithionate.

About 25 g. of potassium acetate were dissolved in water and warmed with 15 g. sodium dithionate. The solution was filtered hot through a fluted filter paper and then alcohol was added at 40° until a precipitate formed. The mixture was cooled to 0° and the solid filtered, dissolved in water and the dithionate precipitated with alcohol. The solid was filtered, washed and dried in a vacuum oven at 50 - 60°.

Preparation of Potassium Tetrathionate.

About 50 g. sodium thiosulphate ($5\ H_2O$) were ground up in a mortar with a little water. About 25 g. of iodine were added with stirring until the mixture contained excess iodine. After leaving to stand for 10 minutes, methylated spirits was added and the resulting solid was filtered on a Buchner funnel. The solid was washed with alcohol and then dissolved in a small amount of water and filtered. About 30 g. of potassium acetate were added to the solution, followed by alcohol when the acetate had dissolved. After cooling the mixture in ice the precipitated $K_2S_4O_6$ was filtered and washed with alcohol. It was recrystallised by dissolving in the least quantity of water, filtering through a fluted filter paper and adding alcohol at 40° until crystals began to appear. The mixture was cooled slowly to 0°. The solid was filtered, washed with a mixture of 1:1 water and alcohol and finally with alcohol. The potassium tetrathionate was dried at 60° in a vacuum oven.

Appendix II.

Main Program for Polynomial Regression.

```
   DIMENSION X(75),DI(10),D(6),B(2),E(2),SB(2),T(2),XBAR(3),
  1         STD(3),SUMSQ(3),ISAVE(3),ANS(10),PP(25)
   INTEGER FINISH
   DATA FINISH/4HLAST/
 1 READ 7,TAB,N,NEXT
   PRINT 8,TAB
   M=2
   L=N*M
   DO 2 I=1,N
   J=L+I
 2 READ 9,X(I),X(J)
   CALL GDATA(N,M,X,XBAR,STD,D,SUMSQ)
   MM=M+1
   DO 3 I=1,M
   ISAVE(I)=I
   CALL ORDER(MM,D,MM,I,ISAVE,DI,E)
   CALL MINV(DI,I,DET,B,T)
 3 CALL MULTR(N,I,XBAR,STD,SUMSQ,DI,E,ISAVE,B,SB,T,ANS)
   PRINT 10,ANS(1),B(1),SB(1),B(2),SB(2)
   PRINT 11
   DO 5 I=1,N
   SUM=0.0
   AA=1.0
   DO 4 J=1,M
   AA=AA*X(I)
 4 SUM=SUM+B(J)*AA
 5 PP(I)=SUM+ANS(1)
   DO 6 I=1,N
   J=L+I
   DIFF=X(J)-PP(I)
 6 PRINT 12,X(I),X(J),PP(I),DIFF
   IF(NEXT.NE.FINISH)GOTO1
   STOP
 7 FORMAT(2I2,A4)
 8 FORMAT(1H1//,37X,7HTABLE  I2,1H.//,
  1             21X,42HPOLYNOMIAL REGRESSION. TO FIT KINETIC DATA/,
  2             31X,22HTO QUADRATIC RATE LAW.15/)
 9 FORMAT(F7.6,33X,F9.8)
10 FORMAT(16X,26HCOEFFICIENTS OF REGRESSION///,
  1        20X,4HA = E10.4,//,
  2        20X,4HB = E10.4,7H  +OR- E10.4,//,
  3        20X,4HC = E10.4,7H  +OR- E10.4,4/)
11 FORMAT(16X,18HTABLE OF RESIDUALS///,
  1        22X,7H[TETRA]7X,4HRATE6X,9HPREDICTED5X,8HRESIDUAL//)
12 FORMAT(16X,4(3X,E10.3))
   END
```

For method, see reference 37.

Appendix III.

Preparation of Phosphate Buffers for the Study of Hydrogen Ion Dependences.

(a) Iodate-Thiosulphate Reaction.

25 ml. 1.000 M. KOH
x ml. 1.000 M. KH_2PO_4
1.000 M. KNO_3 to make 250 ml.

x (ml.)	Approx pH
27.0	7.6
27.6	7.5
28.2	7.4
29.0	7.3
30.0	7.2
31.2	7.1

(b) Bromate-Thiosulphate Reaction.

Stock solutions:

A : 0.3 M. K_2SO_4
0.3 M. KH_2PO_4

B : 0.3 M. KNO_3
0.3 M. K_2HPO_4

A (ml.)	B (ml.)	pH (reaction)
100	60	6.41
100	80	6.53
100	100	6.63
100	40	6.22
60	120	6.95
50	150	7.14

BIBLIOGRAPHY.

Bibliography.

1. J. O. Edwards. Chem. Revs. 1952, 50, 455.
2. O. Foss and A. Hordvik. Acta Chem. Scand. 1957, 11, 1443.
3. Masao Atoji and R. E. Rundle.
   J. Chem. Phys. 1958, 29, 1306.
4. S. C. Abrahams. Quart. Revs. 1956, 10, 407.
5. F. M. Page. J. Chem. Soc. 1953, 1719.
6. T. O. Denney and C. B. Monk.
   Trans. Faraday Soc. 1951, 47, 992.
7. C. W. Davies. J. Chem. Soc. 1938, 2093.
8. I. L. Jenkins and C. B. Monk.
   J. Amer. Chem. Soc. 1950, 72, 2695.
9. N. V. Sidgwick. The Chemical Elements and their Compounds, Clarendon Press, Oxford 1950. Page 919.
10. M. I. Stubbins. Thesis (Univ. of Lond.) 1966.
11. K. Sandved. Kgl. Norske Vidensk. Selsk. Forhandlinger Bd. II.
12. K. Sandved and J. B. Holte.
    Tidsskr. Kjemi Bergvsen. 1940, 20, 106.
13. J. M. Batstone. Thesis (Univ. of Lond.) 1957.
14. A. V. Harcourt and W. Esson.
    Proc. Roy. Soc. 1866, 15, 262.
15. Y. Abdul Majid and K. E. Howlett.
    J. Chem. Soc. (A), 1968, 679.
16. O. Foss. Acta Chem. Scand. 1950, 4, 866.
17. O. Foss and I. Kringlebotn.
    Acta Chem. Scand. 1961, 15, 1608.
18. C. J. Battaglia and W. J. Miller.
    Photgr. Sci. Eng. 1968, 12, 46.
19. J. H. Swinehart. J. Inorg. Nucl. Chem. 1967, 29, 2313.
20. M. Spiro and M. L. S. M. Barreira. Private communication.

21. E. Chaffee and J. O. Edwards.

Progress in Inorganic Chemistry, Vol. 13, Interscience Publishers, 1970, Page 205.

22. R. Reider. J. Phys. Chem. 1930, 34, 2111.

23. W. M. Latimer and J. H. Hildebrand.

Reference Book of Inorganic Chemistry. Third Edition. Macmillan 1951, Page 262.

24. F. M. Page. Trans. Faraday Soc. 1953, 49, 635.

25. D. P. Ames and J. E. Willard.

J. Amer. Chem. Soc. 1951, 73, 165.

26. V. A. Lunenok-Burmakina and I. F. D'yakova.

Ukrain. Khim. Zhur. 1957, 23, 303.

27. A. D. Awtrey and R. E. Connick.

J. Amer. Chem. Soc. 1951, 73, 1341.

28. V. Gold. pH Measurements. Methuen, London 1956. Page 37.

29. V. Gold and B. M. Lowe.

J. Chem. Soc. (A), 1968, 1923.

30. P. Salomaa, R. Hakala, S. Vesala and T. Aalto.

Acta Chem. Scand. 1969, 23, 2116.

31. G. N. Lewis, A. R. Olson and W. Maroney.

J. Amer. Chem. Soc. 1933, 55, 4731.

32. J. Wyman, Jr., and E. N. Ingalls.

J. Amer. Chem. Soc. 1938, 60, 1182.

33. P. Salomaa and V. Aalto.

Acta Chem. Scand. 1966, 20, 2035.

34. P. Salomaa. Acta Chem. Scand. 1969, 23, 2095.

35. P. Salomaa, A. Vesala and S. Vesala.

Acta Chem. Scand. 1969, 23, 2107.

36. Stability Constants. Special Publication No. 17. The Chemical Society, London 1964.

37. System/360, Scientific Subroutine Package, (360A-CM-03X) Version III. Programmers Manual. I.B.M. 1968.

38. A. Indelli. J. Phys. Chem. 1961, 65, 972.

39. A. Giacomelli. Gazz. Chim. Ital. 1970, 100, 414

40. R. H. Dinegar, R. H. Smellie and V. K. La Mer.
J. Amer. Chem. Soc. 1951, 73, 2050.

41. R. E. Davis. J. Amer. Chem. Soc. 1958, 80, 3565.

42. V. Agarwala, C. E. Rees and H. G. Thode.
Can. J. Chem. 1965, 43, 2802.

43. W. A. Pryor and U. Tonellato.
J. Amer. Chem. Soc. 1967, 89, 3379, 6391.

44. F. A. Cotton and G. Wilkinson.
Advanced Inorganic Chemistry. 2 nd. Edition.
Interscience Publishers, 1966, Page 540.

45. K. B. Wiberg, H. Maltz and M. Okano.
Inorg. Chem. 1968, 7, 830; and references cited.

46. A. I. Vogel. A Text Book of Quantitative Inorganic
Analysis. 3 rd. Edition. Longmans 1961,
Page 67.

47. A. F. M. Barton and G. A. Wright.
J. Chem. Soc. (A), 1968, 2096.

48. C. K. Rule and V. K. La Mer.
J. Amer. Chem. Soc. 1938, 60, 1974.

49. R. A. Dwek, Z. Luz, S. Peller and M. Shporor.
J. Amer. Chem. Soc. 1971, 93, 77.

50. A. O. McDougal and F. A. Long.
J. Phys. Chem. 1962, 66, 429.

51. C. W. Davies. Ion Association. Butterworths 1962,
Page 47.

52. R. W. Chlebek and M. W. Lister.
Can. J. Chem. 1971, 49, 2943.

53. C. W. Davies and P. A. H. Wyatt.
Trans. Faraday. Soc. 1949, 45, 770.

54. H. S. Harned and O. E. Schupp.
J. Amer. Chem. Soc. 1930, 52, 3892.

55. C. W. Davies. Trans. Faraday Soc. 1927, 23, 351.

56. Wicke and Eigen. Z. Electrochem. 1953, 57, 319.

57. F. G. R. Gimblett and C. B. Monk.

Trans. Faraday Soc. 1954, 50, 965.

58. R. A. Robinson and R. H. Stokes.

Trans. Faraday Soc. 1949, 45, 612.

59. 1130 Continuous System Modeling Program. Program Description and Operations Manual. (1130-CX-13X) Third Edition. I.B.M. 1969.

60. A. F. M. Barton and G. A. Wright.

J. Chem. Soc. (A), 1968, 1747.

61. J. Halperin and H. Taube.

J. Amer. Chem. Soc. 1952, 74, 375.

62. Yu. I. Rutkovskii and V. E. Mironov.

Zh. Neorg. Khim. 1967, 12, 3287.