THE KINETICS ~~AND MECHANISM~~ OF SOME REACTIONS INVOLVING ~~Cr(VI)~~ CHROMIUM (VI).

A Thesis Presented for the

Degree of

Doctor of Philosophy

in the

University of London

by

Susan Christmas

Bedford College,
LONDON.

August, 1963.

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

The thesis is concerned with the elucidation of the kinetics and mechanisms for the two analytically important chromic acid oxidations, those of iodide and of ferrous iron.

The introduction reviews past work in this field.

Once a satisfactory procedure for following the reactions had been decided upon, the order of the initial stages of each reaction was determined. Concerning the chromic acid oxidation of iodide, which was examined by titrimetry, the effect of altering the experimental conditions e.g. by changing the ionic strength, dieletric constant and solvent was studied. By measuring rates at various temperatures it became possible to find the activation energy for the reaction. Experiments were also carried out in the attempt to ascertain the intermediate oxidation stage of chromium involved in the reaction, both by studies of induced oxidation and by analysis of the products formed when hydrobenzoin was added to the reaction mixture.

A similar investigation was made of the reaction of Cr(VI) with ferrous iron, using a spectrophotometic technique.

The reactive Cr(VI) species is at least closely allied to $H\,Cr\,O_4^-$. It was therefore important to have

information about the equilibrium

$$H_2O + Cr_2O_7^{2-} \rightleftharpoons 2\ H\ Cr\ O_4^-$$

under the various experimental conditions. This equilibrium constant was measured spectrophotometrically, and the results were considered in relation to the determinations of other workers.

In the last section, following a brief discussion of the equilibria existing in acid chromate solutions, the proposed rate expressions and the rate constants for the expressions are given. For the Cr(VI)/I^- reaction a fairly detailed mechanism is proposed and tested against the kinetic data, but the present work enables one to decide only certain limited aspects of the mechanism of the Cr(VI) oxidation of Fe(11) aq.

The author wishes to thank her supervisor, Dr. K.E. Howlett, for his continued advice and encouragement and Dr. R. Bolton for his sample of hydrobenzoin. She also wishes to express her indebtedness to Professor P.B.D. de la Mare.

The work described in this thesis was carried out during the tenure of a Maintenance Grant from the Department of Scientific and Industrial Research.

CONTENTS.

INTRODUCTION

Chromic acid has been known for many years as a powerful oxidising agent, both in organic and inorganic chemistry, for preparations and analytical work. Comparatively little is known, however, about the mechanism of its reduction (particularly in inorganic reactions) except that it must occur in several stages because the observed overall change is a change in oxidation state of the chromium from 6 to 3 whereas elementary redox steps are recognised to be 1- electron or 2- electron processes. The source of Cr(VI) is usually a dichromate, but the active species in solution might be a single entity or a combination of entities containing Cr(VI). The $HCrO_4^-$ ion has frequently been considered to be the most likely species initiating any oxidation sequence, although the $Cr_2O_7^{2-}$ ion also seems to be a direct participant in some cases.

The equilibrium $H_2O + Cr_2O_7^{2-} \rightleftharpoons 2HCrO_4^-$ is set up rapidly. In the absence of any disturbance the concentrations of these two Cr(VI) species are independent of pH. In the absence of acid however, oxidations using Cr (VI) are extremely slow so that hydrogen ion presumably plays an important part in the mechanism.

One of the best known inorganic chromic acid reactions is the oxidation of iodide. This was first investigated by de Lury (I) by reacting dichromate and iodide in the presence of sulphuric acid at 30°C. He suggested that the reaction was slightly higher than fourth order. The order with respect to each reactant was found by varying its concentration while keeping constant the concentration of the other two. By this way he showed that the reaction was first order with respect to dichromate, 2nd order with respect to hydrogen ion and just over first with respect to iodide. The actual dependence of rate on the iodide concentration was given by the relation: -

$$R = m\left[I^-\right] + n\left[I^-\right]^2$$

De Lury made no attempt to propose any mechanism for the reaction. He did, however, extensive experiments to show the effect of other ions upon the rate and concluded that only Fe^{2+}, Fe^{3+} and possibly Cr^{3+} had any accelerating effect. His results were later interpreted by Bray to suggest the following mechanism: -

$$2I^- + 2H^+ + Cr_2O_7^{2-} = 2IO^- + H_2Cr_2O_5$$

$$I^- + 2H^+ + Cr_2O_7^{2-} = IO^- + 2HCrO_3$$

i.e. two simultaneous reactions. (At this time, quater - and quinque molecular steps were not considered inherently unlikely).

The method used by de Lury to follow the reactions was as follows: - 2 reactants were placed in 1 vessel and the third reactant (usually that present in least quantity) placed in a second container. After attaining the temperature of the thermostat the reactants were mixed and, after a suitable time the reaction was stopped by means of a quencher (in this case a buffer containing sodium acetate with sodium bicarbonate). The extent of the reaction was measured by titrating the liberated iodine with sodium thiosulphate, using starch as the indicator.

Beard and Taylor (II) continued this work and by carrying out the reaction in the presence of a neutral salt were able to show that it was very nearly fifth order. They pointed out that Bronsted had predicted that reactions, such as this, where there appeared to be a non integral order, could be rendered normal (i.e. of integral order) by the addition of sufficient neutral salt to fix the activity coefficients of the ions.

Their experimental procedure was similar to that of de Lury, except that it was always the iodide solution which was added to the other two to initiate the reaction. Every one of their experiments was terminated after twenty minutes by the addition of the quencher, and as before, the iodine was estimated to determine the extent of the reaction. The concentration range investigated was as follows: -

2.021×10^{-4} M $K_2Cr_2O_7$, $71 - 284 \times 10^{-4}$ MKI $181^{-}454 \times 10^{-4}$ M$HClO_4$

A wide range of ionic strength was also covered; the required ionic concentration being obtained by the addition of sodium chloride. Beard and Taylor intended to study this neutral salt effect to see if it could be applied in interpreting this reaction.

A plot of $\sqrt{\mu}$ against log K gave a curve, similar in shape to an activity coefficient curve, and having a minimum value near $\mu = 0.5$. They attempted to interpret the results at some ionic strengths in terms of the Bronsted theory.

From the simplest Debye-Huckel expression: -

$-\log f = Az^2 \sqrt{\mu}$ putting $A = 0.5$

Bronsted developed the following relation: -

$\log K, = \log K + (Z_A Z_B + Z_A Z_C + Z_B Z_C) \sqrt{\mu}$

for a trimolecular reaction. If the reactants are A^+, B^- and C^{--}, when log K is plotted against $\sqrt{\mu}$ a slope of -1 should be obtained. Similarly for a pentamolecular reaction between $(A^+)^2$, $(B^-)^2$, C^{--} the slope should be -2. On Beard and Taylor's graph the curve was possibly tending to be linear at low ionic strength and the slope at this point was about -1.65. This, they said, showed the reaction could occur in two ways, one by a trimolecular mechanism and the other pentamolecular, about two-thirds of the reaction occuring in the latter manner.

$$H^+I^- + Cr_2O_7^{2-} \longrightarrow H.I.Cr_2O_7^{2-} \longrightarrow \text{products}$$

$$2H^+ + 2I^- + Cr_2O_7^{2-} \longrightarrow (H.I.)_2Cr_2O_7^{2-} \longrightarrow \text{products}$$

If there were these two simultaneous reactions occurring it would explain why the overall order was not quite five. It should be pointed out however that the combination of the Debye-Huckel and Bronsted treatments is only really valid at low ionic strength ($< 0.01\ \mu$) and the lowest ionic concentration at which they carried out their reaction was five times greater than this, thus only the sign of the gradient of the $\log K/\sqrt{\mu}$ graph is probably significant. In this present research, experiments were carried out at a very low ionic strength and a more negative slope was obtained for the corresponding plot. Furthermore, since molecularity and reaction order are now distinguished from one another, the above mode of application of the Debye-Huckel and Bronsted theory would not be made today.

Although tentative ideas for mechanism were proposed, none of these workers gave any indication as to the nature of the intermediate compounds or steps of the reaction, partly, probably, because it was not thought to be possible, and partly through ill-developed ideas of the more probable sequences of events in multi-order reactions. Whatever is involved, chromium must at some time exist in an unstable valency state, being either penta- or tetravalent. In some reactions, even divalent chromium may be involved, In considering chromic acid oxidations many facts can be explained by the following assumptions (due mainly to Westheimer): -

(i) The standard oxidising potential of $Cr^{(VI)} - Cr^{(III)}$

is only + 1.36 volts whereas that of $Cr^{(V)} - Cr^{(III)}$ is greater than + 1.75 volts and that of $Cr^{(IV)} - Cr^{(III)}$ may be even higher

(ii) Reducing agents which readily lose one electron will reduce chromic acid to an ion or molecule containing pentavalent chromium. Later stages in the reaction depend on other properties of the reducing agent.

(iii) Quadrivalent chromium is formed during the sequence of reactions which occur when reducing agents losing two electronis are involved.

$Cr^{(VI)} + H_2A \rightarrow Cr^{(IV)} + A$ This may be followed by: -

$Cr^{(VI)} + Cr^{(IV)} \longrightarrow 2Cr^{(V)}$

$Cr^{(V)} + H_2A \longrightarrow Cr^{(III)} + A$

(H_2A = reduced form of reducing agent

A = oxidised form of reducing agent)

(iv) In a mixture of two reducing agents, one of which will preferentially lose one electron, and the other two electrons, there is a combination of the two schemes.

Work on induced oxidation has been closely linked with the determination of these unstable valencies. At low concentrations, the reaction of potassium iodide and chromic acid is very slow. But with the addition of certain reducing agents, the reaction is markedly accelerated. The substances causing this increase in rate are known as "inductors" and they "induce" oxidation under normally unfavourable conditions. The term "induced oxidation" was used by Kessler (III) as early as 1893 when he published a paper tabulating all the then known reactions of this type.

Consider conditions under which the reaction between Fe^{3+} and I^- is slow. When Fe^{2+} is added to iodide under such conditions, in the presence of chromic acid, there is rapid formation of iodine. As normally iodide is not oxidised by either chromic acid or ferric iron very rapidly, there must be formed a more powerful oxidising species. This was first studied by Schonbein in 1858 using comparable experimental conditions for the three following reactions

$$6I^- + 2HCrO_4^- + 14H^+ \xrightarrow{slow} 2Cr^{3+} + 3I_2 + 8H_2O$$

$$2Fe^{3+} \; 2I^- \xrightarrow{slow} 2Fe^{2+} + I_2$$

However: -

$$HCrO_4^- + Fe^{2+} + 2I^- + 7H^+ \xrightarrow{fast} Cr^{3+} + I_2 + Fe^{3+} + 4H_2O$$

and possible steps are: -

$$HCrO_4^- + Fe^{2+} \longrightarrow HCr^{(V)}O_4^{2-} + Fe^{3+}$$

$$HCr^{(V)}O_4^{2-} + 2I^- \longrightarrow I_2 + Cr^{3+}$$

$$Fe^{3+} + I^- \longrightarrow Fe^{2+} + \tfrac{1}{2}I_2$$

Benson (IV) also studied this reaction and showed that the addition of Fe^{3+} retarded the reaction. She proposed the "ferroidion theory" by which she attempted to explain how the ferrous ion caused the increase in rate. She stated that the iodide and ferrous ions combined together to form FeI_2 which was acted upon by $HCrO_4^-$, and was more reactive than I^- by itself.

$$K_2Cr_2O_7 + 2FeI_2 + 7H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 2I_2 + 7H_2O + Fe_2(SO_4)_3$$

This would explain too, why generally two molecules of iodide are used to one of ferrous iron.

In considering chromic acid oxidations where an inductor is used the induction factor

i.e $\dfrac{\text{Number of equivalents reducing agent oxidised}}{\text{Number of equivalents inductor oxidised}}$

has been found to be 2 or 0.5 in the limit. This means that of the three oxidation equivalents supplied by the chromium (VI) either one or two are used by the inductor. This stoichiometry suggests $Cr^{(IV)}$ or $Cr^{(V)}$ as the intermediate valency state. In the case of the induced oxidation of iodide by ferrous iron the induction number was found to be 2, suggesting that the intermediate valency state is $Cr^{(V)}$. Westheimer (V) gave as possible steps the following: -

$$Cr^{(VI)} + Fe^{2+} \longrightarrow Cr^{(V)} + Fe^{3+}$$

$$Cr^{(V)} + I^- \longrightarrow Cr^{(III)} + IO^-$$

$$2H^+ + I^- + IO^- \longrightarrow I_2 + H_2O$$

The reversibility of the first step would account for the Fe^{3+} retardation effects.

Other workers in this field were Manchot and Wilhelms (VI) who also showed that the induction number was 2 and also that chromous compounds had the same effect on reactions as did ferrous compounds. Other entities having an inducing effect are cerrous and manganous compounds.

To calculate the induction factor, the ferrous ion concentration must be determined at the exact end ofthe reaction and this is not always convenient. A better method for deducing the nature of the intermediate valencies of chromium was that devised by Slack and Waters (VII) in the Chromic acid oxidation of organic compounds. Hydrobenzoin was added to the reaction mixture and the oxidation products identified. If equimolecular proportions of benzaldehyde and benzoic acid were formed, then $Cr^{(IV)}$ is the active intermediate, but if only benzaldehyde is found to be present, then this suggests $Cr^{(V)}$. This was applied to inorganic reactions with satisfactory results.

In conclusion it can be said that induced oxidation is a form of catalysis, although this is not strictly correct because in catalysis the catalyst is recovered unchanged whereas in this case the inductor is consumed. The amount of inductor consumed usually bears a stoichiometric relationship to the amount of product formed. Induced oxidation involving $Cr^{(VI)}$ can be of two types: -

1. Where chromic acid acts as the oxidising agent
2. Where chromic acid acts as the inductor

The reaction between Fe^{2+}, I^- and chromic acid falls into the first category.

Further work on the mechanism has been carried out by Autrey and Edwards (VIII) They found in several similar chromic acid oxidations, the intermediate complex was broken down by general acid catalysis. Edwards developed Beard and Taylor's original two-term rate expression into a four term expression: -

$$\text{Rate} = Ka\left[ICrO_3^-\right] + K_b\left[ICrO_3^-\right]\left[I^-\right] + K_c\left[ICrO_3^-\right]\left[H^+\right] + Kd\left[ICrO_3^-\right]\left[I^-\right]\left[H^+\right]$$

$ICrO_3^-$ is an acid-base intermediate, the concentration of which is given by: -

$$\left[ICrO_3^-\right] = k\left[HCrO_4^-\right]\left[I^-\right]\left[H^+\right]$$

The data of Beard and Taylor was sufficient only to solve three of the constants, but by using: -

$$Ka : Kc = K_b : K_d$$

Edwards has calculated the values for the constants. He postulated the rate determining step was

$$N^- + ICrO_3^- + HA \longrightarrow NI^- + HCrO_3^- + A^-$$

where N is a nucleophilic particle.

As shown there is no agreement as to the mechanism, or the rate expression and one aim of this research was to find a simple rate expression that would fit the data obtained, and also to elucidate the stages of reaction. Some early work was repeated as a confirmation of the earlier results, and to provide a sound working basis. The method of following the reaction was that based on de Lury, the reaction being allowed to proceed over a wide range of times. After equilibrating in a thermostat the iodide solution was then added to the chromic acid and samples were removed at given intervals and run into an acetate/bicarbonate buffer to stop the reaction. The iodine was titrated against 0.01N sodium thiosulphate, using starch as an indicator, or (better) by a polarised electrode (dead stop) potentiometric method (IX) This method is very sensitive and is accurate for dilute solutions.

Very little work has been done on the later stages of the reaction, in strongly acid media or in buffered media. Besides the effect of changing pH, that of altering the dielectric constant (D) was also studied. If the rate determining step occurs between ions of opposite sign, then decreasing D should cause an increase in rate, shown by the relation

$$\ln K = \ln K_0 - \frac{N}{RT}\,\frac{(D-1)}{(2D+1)}\left[\frac{\mu_A^2}{r_A^3} + \frac{\mu_B^2}{r_B^3} - \frac{\mu_{\ddagger}^2}{r_{\ddagger}^3}\right]$$

Where K_0 is the rate at infinite dilution, N is Avogadro's number, r is the radius of an ion (A or B) or of the activated complex ($\ddagger$) and μ is the ~~chemical~~ dipole ~~potential~~ moment.

Further information about the rate determining step can be obtained by the use of D_2O. Any increase in rate when D_2O is used as solvent in place of H_2O shows that the rate determining step does not involve proton transfer. Heavy water shows too, whether the reaction is an example of general or specific acid catalysis, any increase in rate when D_2O is used suggesting specific hydrogen ion catalysis because of formation of more favourable pre-equilibrium conditions.

$$S + D^+_3O \rightleftharpoons SD^+ + D_2O$$

$$S + H^+_3O \rightleftharpoons SH^+ + H_2O$$

where S = substrate and products result from the protonated or deuterated intermediate. Work has yet to be done, too, on whether the oxidation products i.e. iodine and chromic ions, have any effect upon the rate

---

A second reaction was also studied, the chromic acid oxidation of ferrous iron. Owing to difficulties in analysis, very little is known about the reaction:-

$6Fe^{2+} + 14H^{+} + 2Cr\ (VI) \longrightarrow 2Cr^{3+} + 7H_2O + 6Fe^{3+}$

Benson (X) did some preliminary work on this in connection with her work on induced oxidation of iodide ion by chromic acid. She stressed the great difficulty in analysis and eventually managed to determine ferrous iron by a complicated and somewhat questionable method developed from her studies on the previous reaction.

To 500 cc solution (A) containing known amounts of Fe^{3+}, H^{+} and $Cr_2O_7^{2-}$ there was added 100 c.c. solution containing a known amount $FeSO_4$. The time of mixing was noted and after x minutes 100 cc dilute potassium iodide solution were added. The reaction was stopped after a further 4 minutes and the free iodine estimated. A second experiment had to be carried out with the above: - to 500cc solution (B) containing H^{+}, $Cr_2O_7^{2-}$, Fe^{3+}, some Fe^{2+} (part I, which was promptly oxidised) and 100 ml dilute KI, the remainder of Fe^{2+} (part II) was added. After 4 minutes the reaction was again stopped. By plotting iodine liberated against Fe^{2+}(part II), it was possible to find the amount of Fe^{2+} in (A) at the moment of adding KI. Although ingenious, this method was rather clumsy and a simpler procedure has been adopted here for studying the $Cr_2O_7^{2-}/Fe^{2+}$ reaction, involving the formation of a ferrous dipyridyl complex. A sample of reaction mixture was removed after a given time and shaken with anion exchange resin to remove the dichromate rapidly. This stopped the reaction and also prevented dichromate from interfering in the analysis. The solution was filtered through glass wool into dipyridyl solution and then made up to a known volume. The colour formed was measured spectrophotometrically. This method appeared to be satisfactory and enabled many runs to be made.

Benson did show that ferric iron had a retarding effect upon the reaction and gave the following rate expression: -

$$\text{Rate} = \frac{K\,[Fe^{2+}]^{2}\,[H^{+}]^{2}\,[Cr]^{1.6}}{[Fe^{3+}]}$$

If an "old" solution of an Fe^{3+} salt was added, the retarding effect was lessened, and this was shown by Gortner (XI) to be due to the hydrolysis of Fe^{3+}: -

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+$$

Later in 1940, Stefanovski (XII) further investigated this reaction and followed the reaction by a flow method by measuring electrical conductivities at various points along a tube at 11° - 26°C. The concentrations used in this work were very low, the dichromate and ferrous ions being in the range $1 \times 10^{-3} - 5 \times 10^{-3}$M and hydrogen ion in the range $3 \times 10^{-3} - 1 \times 10^{-2}$M; but at higher concentrations the reaction was too fast to follow. His results agreed with Benson to some extent, but he decided that it was ferrous ion, not ferric, which retarded the reaction due to some "buffer action" He proposed that the velocity of the reaction was expressed by: -

$$\frac{-d\left[Fe^{2+}\right]}{dt} = K\left[Cr(VI)\right]\left[H^{+}\right]^{2}\left[Fe^{2+}\right]^{2}$$

He concluded that the reaction occured in consecutive steps, but his kinetic investigations were not sufficient to decide upon the mechanism.

It is suprising that very little (if any) work has been done in buffered media. As hydrogen ions (a reactant) is apparently formed during the reaction, a constant pH is important. The part played by hydrogen ion is very interesting as the reaction can proceed fairly well in the absence of any deliberately added initial acid. Presumably some of the H^{+} formed must come from the hydrolysis of ferric ions. No work has apparently been done either at low ionic strength in the range where the Bronsted expression holds. This would probably give further information regarding the initial stages of the reaction.

Since the experimental work for this reaction was completed, another paper has been published (XIII) the author, J.H. Espenson, has suggested the following rate expression: -

$$\frac{-d\left[Fe^{2+}\right]}{dt} = K\frac{\left[Fe^{2+}\right]^{2}\left[HCrO_4^{-}\right]\left[H^{+}\right]^{3}}{\left[Fe^{3+}\right]}$$

He proposed that the retarding effect of the ferric ions was due to the formation of a ferric - chromate complex of the type $FeCrO_4^+$. Evidence is also given in this present work for the formation of just such a complex.

REACTION BETWEEN CHROMIC ACID AND IODIDE IONS

SECTION I

1. TO ESTABLISH A METHOD FOR FOLLOWING THE REACTION

This reaction was conveniently followed by determining the concentration of iodine formed after a given time by titration with sodium thiosulphate, using either the depolarisation end point (IX) or with starch as an indicator. The reaction was stopped by pipetting the test sample into buffer of about pH 7 - 8. This pH is important as the reaction will not be quenched in an acid medium, but in alkaline solutions iodine will form iodide and hypoiodite, the second of which is unstable.

$$I_2 + 2OH^- \longrightarrow I^- + IO^- + H_2O$$

$$3IO^- = 2I^- + IO_3^-$$

The buffer found most suitable was a sodium acetate/sodium bicarbonate mixture (110 g NaOAc and 10g $NaHCO_3$ per litre) That this did not affect the iodine titre was shown by titrating a standard 25 mls 0.01N iodine solution in the presence of 10 ml of this buffer.

Iodine can be lost during titration by volatilisation or hydrolysis. According to Whitman and Popoff (XIV) the best method of obtaining accurate results is to carry out the titration in the presence of 4% iodide and so prevent hydrolysis.

$$I_2 + H_2O \longrightarrow I^- + HIO + H^+$$

During a normal run there was always at least this amount of unchanged iodide present.

II GENERAL TECHNIQUE ADOPTED

Once the analytical technique was decided upon all kinetic experiments were carried out in a thermostat controlled to ± 0.02°C. Potassium dichromate, together with perchloric acid and any other solutions, apart from potassium iodide were measured into a 250 cc reagent bottle (A) by means of pipettes. Into a second reagent bottle (B) was measured the required amount of potassium iodide. The stoppered vessels were then placed in the thermostat and allowed to reach thermal equilibrium. The reaction was then started by mixing the reactants, this being achieved by pouring (A) into (B) andthen back into (A) again, thus ensuring complete mixing. The start of the reaction was taken when (A) was added to (B).

The total volume of the reaction mixture was sufficient to provide five 50 ml samples during the course of a run. These were withdrawn by a pipette after suitable time intervals and run into the buffer solution. Because of the time interval in emptying the pipette, the time for the sample was taken as that when the pipette had half emptied. The solution was then titrated against sodium thiosulphate.

All the reagents used in these experiments were of "analar" grade and were standardised before use.

III THE EFFECT OF SURFACE UPON RATE OF REACTION

As many ions are readily absorbed on to a glass surface the possibility of complication arising from the occurence of a surface reaction could not be excluded; so it was considered advisable to test at an early stage whether this reaction was in fact affected by the surface of the glass reaction vessel. For this purpose a reagent bottle was packed with glass beads so as to increase the area of glass surface exposed to the solution to about three times that present in the bottle itself. Comparative experiments were made with the packed and unpacked reaction vessels and gave results in good agreement with one another so that this source of complication could be discounted

Table 1

Time (min)	Control Expt. in empty bottle	Expt. in packed bottle
10	1.38 ml	1.40 ml
20	2.30	2.30
30	3.39	3.40

Titration figure is ml 0.01N $Na_2S_2O_3$ required for 50 ml sample

$[K_2Cr_2O_7] = 9.55 \times 10^{-4}M$ $[HClO_4] = 1.97 \times 10^{-2}M$ $[KI] = 2.99 \times 10^{-2}M$

IV EXPOSURE TO LIGHT

The possibility of a photochemcial reaction as well as a purely thermal one was studied by carrying out two parallel experiements. The first reaction was carried out in a brown glass vessel whilst the second was exposed to normal laboratory illumination. There was no difference in the rate between these two experiments, so that in the following experiments photochemical complication could be ignored.

Table II

Time (mins.)	Control Expt.	Expt. in dark brown vessel
5	0.72 ml	0.70 ml
10	1.46	1.46
15	2.04	2.06
20	2.70	2.73
30	3.88	3.88

Titre shows ml 0.01N $Na_2S_2O_3$ required for 50 ml sample.

$[K_2Cr_2O_7] = 9.55 \times 10^{-4}M$ $[HClO_4^-] = 2.01 \times 10^{-2}M$ $[KI] = 2.99 \times 10^{-2}$ M

SECTION II

FACTORS AFFECTING REACTION

The conditions for obtaining reproducible results had now been established. A typical series of results recorded during the course of the reaction is shown in **table (III)**. The general pattern of the reaction curve is also shown by plotting titre per 50 ml sample against time (graph - page 62)

Table III

Reaction in unbuffered solution

$T = 25^{\circ}C$ $\mu = 0.10$

$[Cr_2O_7^{2-}] = 1 \times 10^{-2}M$ $[HClO_4] = 1.2 \times 10^{-2}M$ $[KI] = 3.0 \times 10^{-2}M$

Time (min)	Titre per 50 ml sample	Mol/litre I_2 formed
10	2.89 ml	2.89×10^{-4}
20	4.88	4.88
40	7.17	7.17
60	8.51	8.51
120	10.27	10.27

The fall off in rate can only be due to fall in concentration of reactants or possibly the formation of inhibitory products.

I IONIC STRENGTH

Any solution has deviations from ideality, but in the presence of ions these deviations become apparent even at low concentrations. Bronsted deduced that for a reaction proceding via an activated complex, viz. $A + B \rightleftarrows AB$ + products then the rate constant

$$K = K_o \frac{\gamma_A \gamma_B}{\gamma_{AB}} \qquad (1)$$

Ko is the rate constant when the activity factor is unity i.e. usually at infinite dilution. This equation has an important application when one or more of the reactants are ions. According to the Debye-Huckel theory, the relation between the activity coefficient and ionic strength is given by: -

$$-\ln \gamma_i = \frac{Z_i^2 \alpha \sqrt{\mu}}{1 + \beta a_i \sqrt{\mu}} - C_i \mu \qquad (2)$$

μ is the ionic strength

a_i is the distance of closest approach of another ion to the $_i$th ion

α, β and C are constants

By combining the two above equations it is possible to show that: -

$$\ln K = \ln K_o + \frac{2Z_A Z_B \alpha \sqrt{\mu}}{1 + \beta a \sqrt{\mu}} + (C_A + C_B - C_{AB}) \mu \qquad (3)$$

which at very low ionic strength approximates to: -

$$\ln K = \ln K_o + 2Z_AZ_B \alpha \sqrt{\mu} \qquad (4)$$

$$\simeq \log K_o + Z_AZ_B \sqrt{\mu} \quad \text{at } 25^\circ\text{C in water}$$

This equation predicts a linear relationship if log K is plotted against $\sqrt{\mu}$, with a slope proportional to the product Z_AZ_B

Firstly a series of experiments were carried out in which the ionic strength was varied from 0.036 up to 2. In these experiments potassium dichromate and iodide had to be replaced by the corresponding sodium salt because potassium perchlorate is not sufficiently soluble to allow high concentrations to be reached in solutions containing these two ions. As usual the reaction mixture had a volume of 250 cc and had concentrations of 2×10^{-2}M NaI, 2×10^{-3}M $Na_2Cr_2O_7$ and 1×10^{-2}M $HClO_4$ 50 ml samples were removed at 5 minutes intervals and the iodine estimated in the usual manner. $NaClO_4$ was used to make up the ionic strength.

Although this range of ionic strength was too high for the Debye-Huckel law to hold, it was the region studied by Beard and Taylor. Similar results were obtained to these two workers i.e. up to ionic strength of about 0.5 there was a steady decrease in rate, but above this the rate began to increase again (see graph 1) By applying equation (4) and plotting log initial rate against $\sqrt{\mu}$, the slope obtained was about - 1.6, thus agreeing with earlier results. Note that log initial rate can replace log K here because all reactions involve the same concentrations of reactants.

However this work was extended to regions of low ionic strength. Using 4 x 10^{-3} MKI, 2 x 10^{-3}M $K_2Cr_2O_7$ and 4 x 10^{-3}M $HClO_4$ it was possible to reach $\mu = 0.014$ and with the results so obtained it was found that the slope was now about -2 (see graph 2), which suggests either that the rate determining step is between two ions of opposite charge, one of which is doubly charged and the other singly charged, or that the factor -2 is partly due to the charges on the ions in the rate determining step and partly due to preequilibria involving ions.

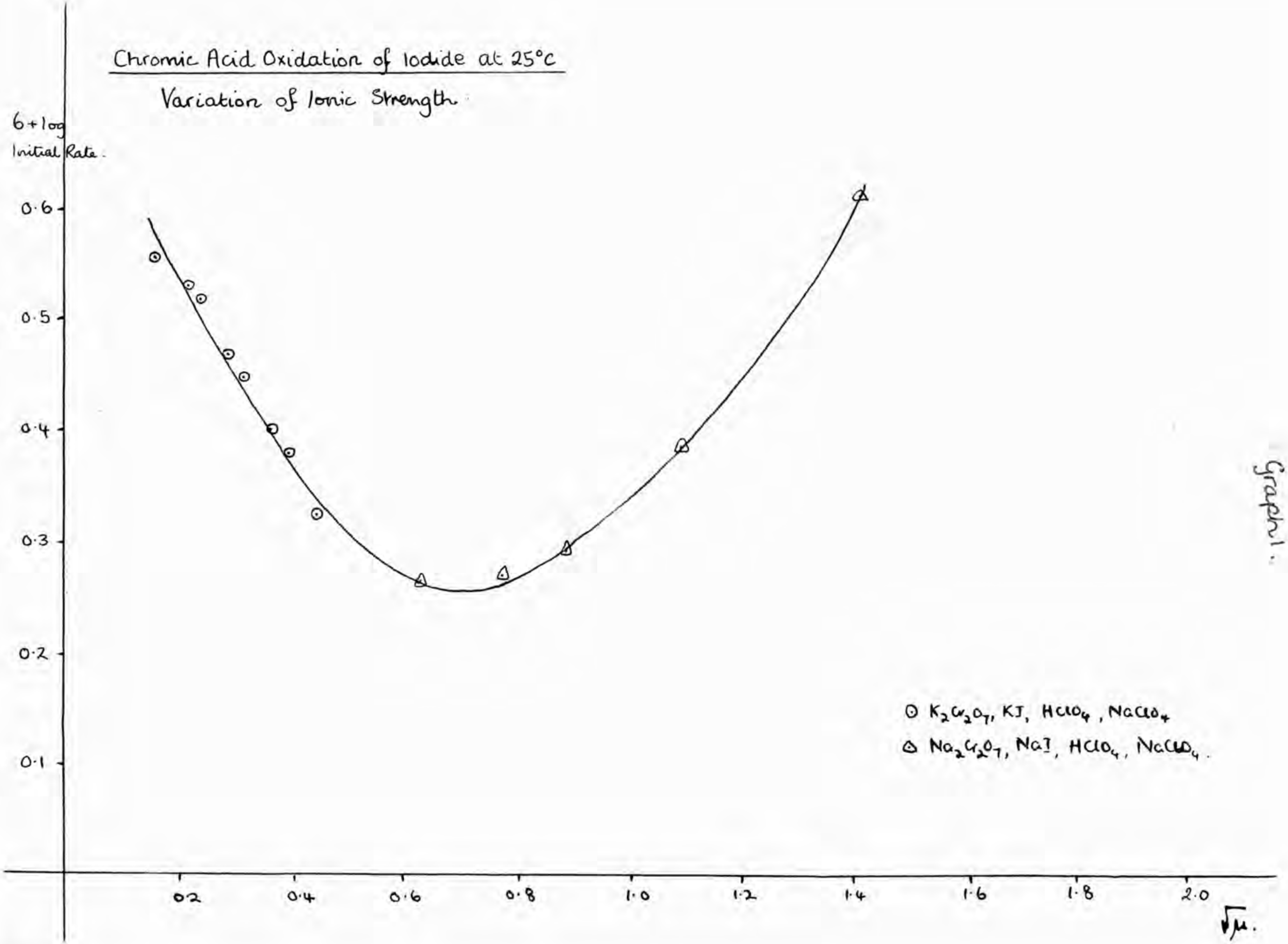
Table (IV) Showing change in initial rate with μ

μ	Init. Rate (moles I_2 formed/l/min x 10^5)
0.036	0.365
0.040	0.335
0.05	0.330
0.075	0.310
0.10	0.27
0.125	0.25
0.150	0.23
0.20	0.22
0.4	0.18
0.6	0.18

(cont) ....

Table(IV) cont.

μ	Init. Rate (moles I_2 formed/l/min x 10^5)
0.8	0.19
1.2	0.23
2.0	0.43



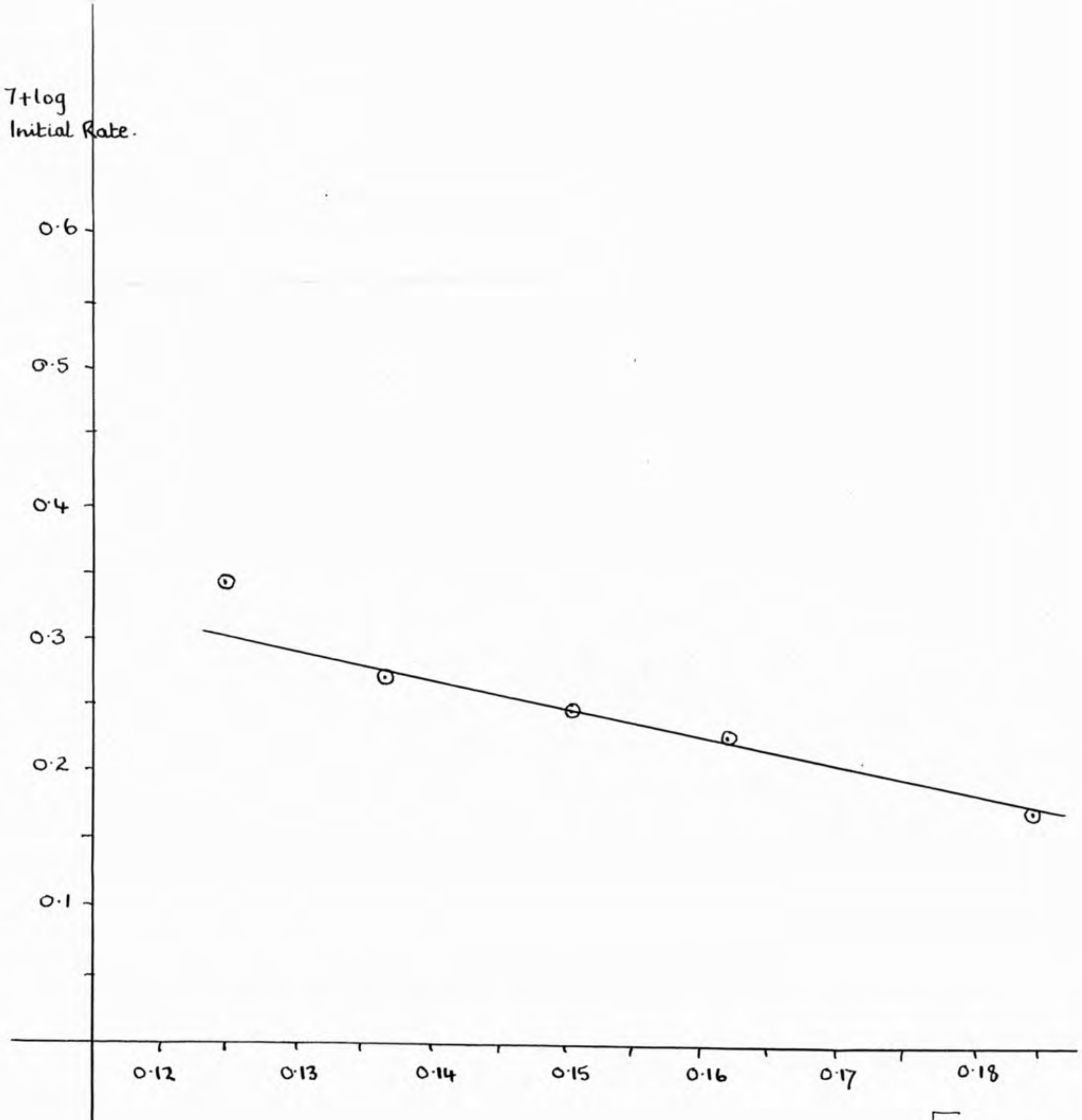
Chromic Acid Oxidation of Iodide at 25°C

Variation of Ionic Strength

Graph 1.

Variation of Initial Rate with Ionic Strength - at low concⁿ

Graph 2.



II CONCENTRATION RATIO OF REACTANTS VARIED

Over a range of temperature and concentration, at constant ionic strength the reaction was found to be initially fifth order. The order with respect to each reactant was found by plotting log initial rate against log concentration i.e. from the equation: -

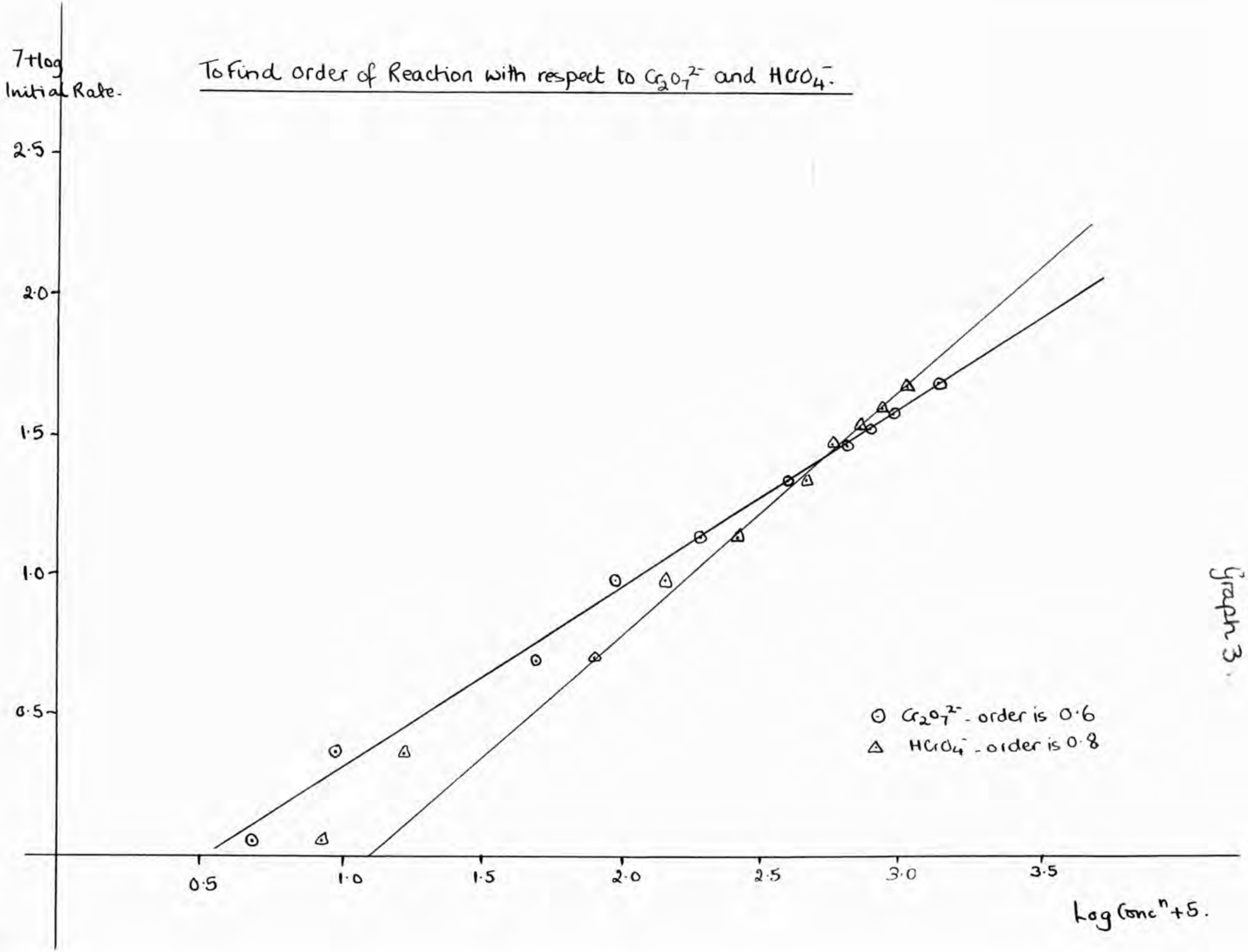
$$\log\left(-\frac{dc}{dt}\right) = \log K + n \log C$$

Table (V)

Reactions carried out at $T = 25^{\circ}C$ and $\mu = 0.93$

(A) varying $[Cr_2O_7^{2-}]$ $[I^-] = 2.99 \times 10^{-2}M$ $[H^+] = 1.22 \times 10^{-2}M$

$[Cr_2O_7^{2-}] \times 10^3$	$[HCrO_4^-] \times 10^3$	Initial Rate (moles I_2 formed/lite/min) $\times 10^6$	
0.049	0.091	0.9	
0.099	0.181	2.3	
0.50	0.847	5.0	
0.99	1.58	9.0	
1.98	2.87	13.0	
4.00	4.97	23.0	
6.00	6.68	28.5	
8.00	8.15	35	
10.10	9.52	40	
13.97	11.70	49	(graph 3.)



To Find order of Reaction with respect to $Cr_2O_7^{2-}$ and $HCrO_4^-$.

Graph 3.

(B) Varying $[I^-]$, $[H^+] = 1.2 \times 10^{-2}M$ $[Cr_2O_7^{2-}] = 9.87 \times 10^{-5}M$

$[I^-] \times 10^2$	Initial Rate $\times 10^6$ (moles I_2 formed/litre/min)	
0.995	0.2	
1.98	0.8	
3.0	2.3	
4.0	3.6	
6.0	5.6	(graph 4)

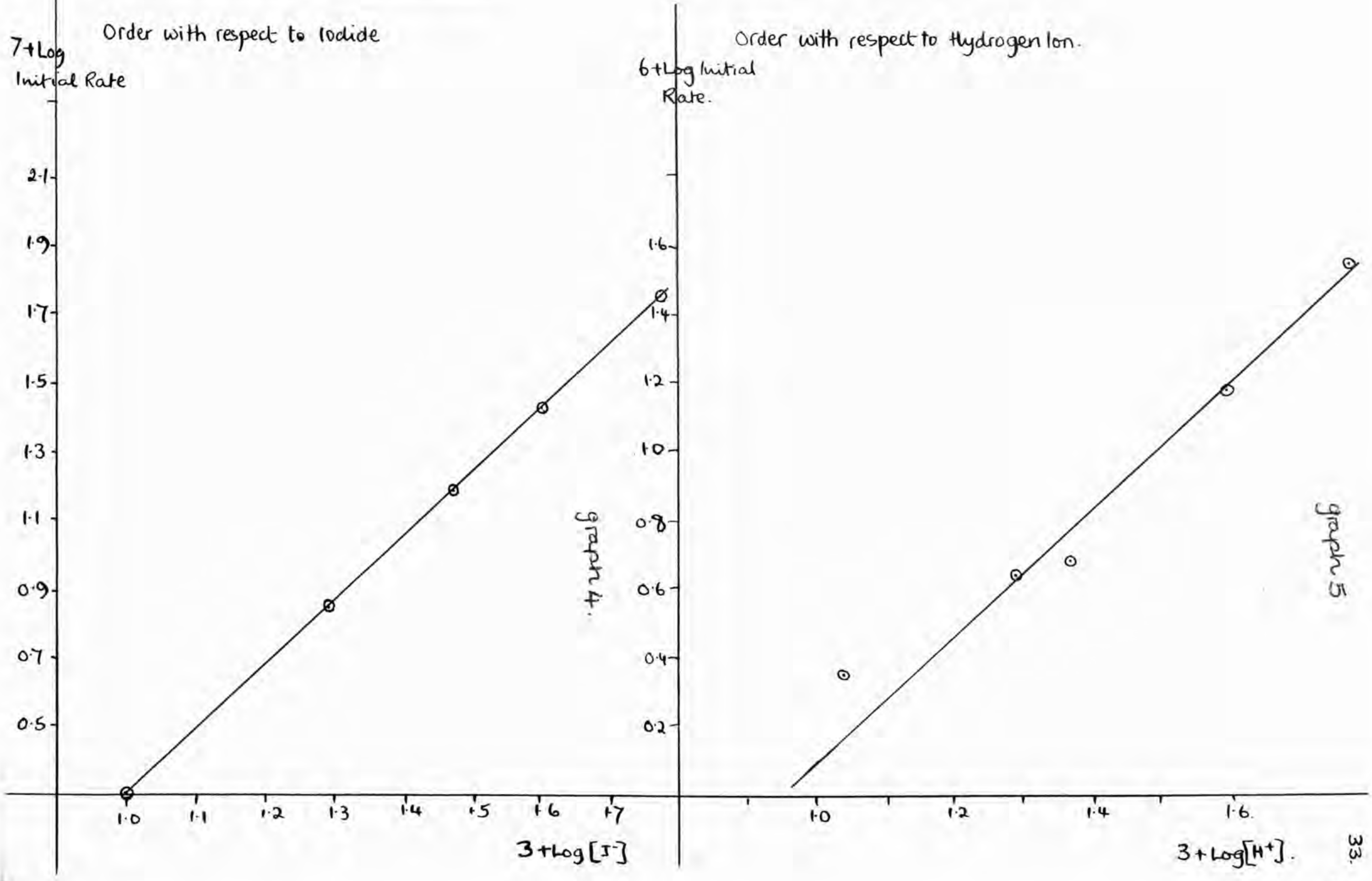
(C) Varying $[H^+]$, $[I^-] = 3.0 \times 10^{-2}M$ $[Cr_2O_7^{2-}] = 9.87 \times 10^{-5}M$

$[H^+] \times 10^2M$	Initial Rate $\times 10^6$ (moles I_2 formed/l/min)	
0.62	1.1	
1.22	2.3	
1.86	4.06	
2.39	4.70	
4.00	14.10	
6.00	32.70	(graph 5)

$[HCrO_4^-]$ is calculated as shown in the section (p.118).

These tables and graphs in fact only indicate approximately integral orders of reaction with respect to each reagent. However if the reactants are considered to be $HCrO_4^-$, I^- and H_3O^+ and allowance is made for loss of hydrogen ion in the formation of H_2CrO_4, then the initial rates give concordant values for a 5th order rate constant. The only reservation on this is concerned with very slow reactions, particularly those involving low concentrations of $HCrO_4^-$. This point is taken up in the next section.

Chromic Acid Oxidation of Iodide.



Order with respect to Iodide

Order with respect to Hydrogen Ion.

III THE EFFECT OF OXYGEN

It appears that slow reactions, particularly those at low dichromate concentrations the reactions were faster than they should have been when compared to experiments done with relatively high dichromate concentration. To see if this might be due to aerial oxidation, a series of comparative experiments were carried out.

Oxygen was bubbled through the solution during the course of reaction, all the reactants having been previously saturated with oxygen before mixing. This was done over a wide range of dichromate concentrations, the acid and iodide concentrations being kept constant, the results were compared to a series of controls in which the same concentrations of reactants had been used, but in which the oxygen had been omitted. The graph(6) shows that the affect is only noticeable at low dichromate concentrations.At higher concentrations the rate of reaction is much faster, consequently masking the oxygen effect.

Table (VI)

$[K_2Cr_2O_7] \times 10^3$M	Control Initial Rate $\times 10^5$	Oxygenated Expt. Initial Rate $\times 10^5$
0.05	0.2	0.24
0.10	0.35	0.40
0.20	0.545	0.55
1.00	1.795	0.89
3.00	3.82	3.91
16.30	12.52	12.52

The initial rate was measured in terms of moles I_2 formed/litre/min.

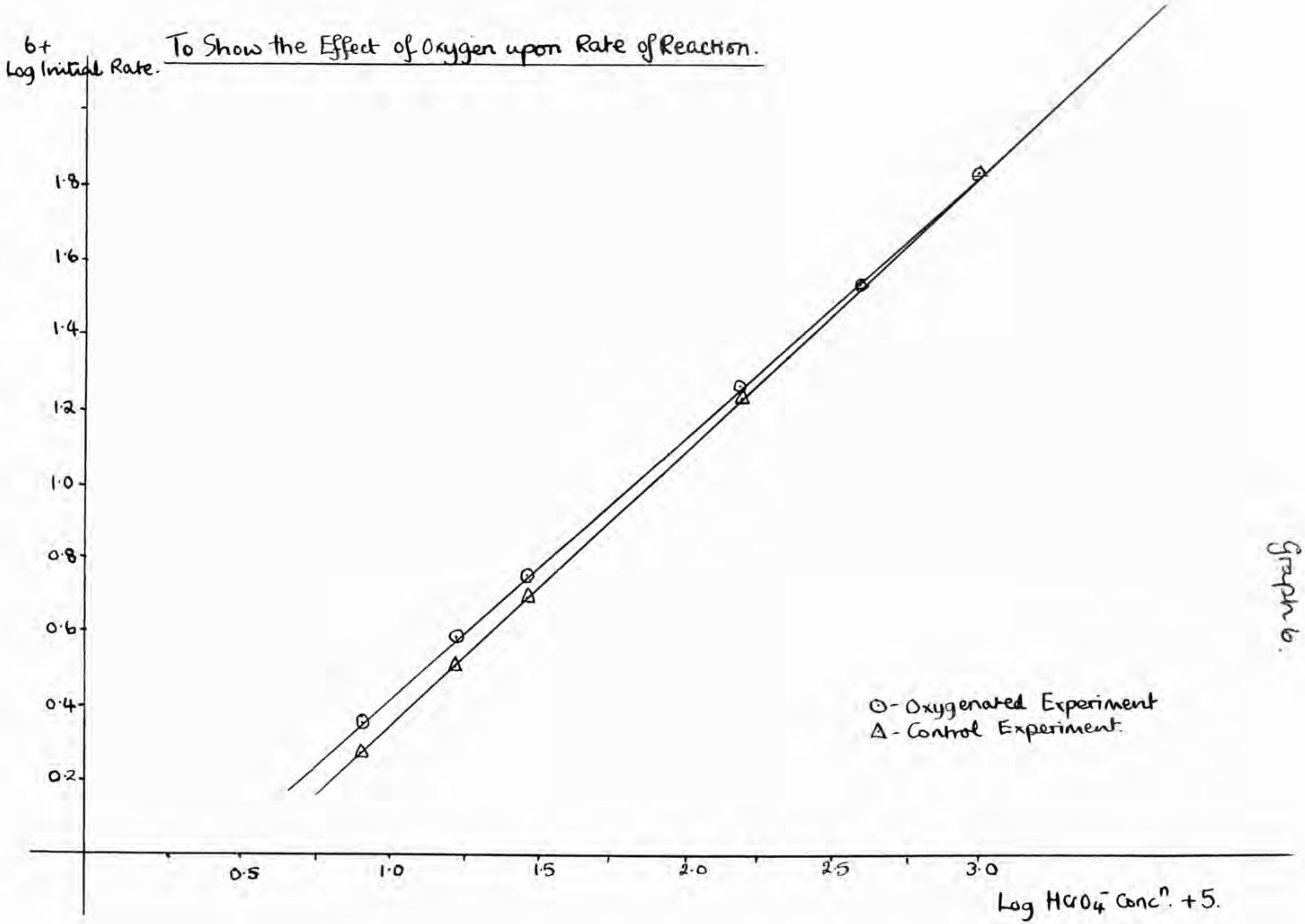
$T = 25^{\circ}C$ $\mu = 0.10$

$[H^+] = 2 \times 10^{-2}M$ $[I^-] = 3 \times 10^{-2}M$

Because of this aerial oxidation occurring all later experiments were carried out with a dichromate concentration greater than $2 \times 10^{-3}M$

Graph 6.

To Show the Effect of Oxygen upon Rate of Reaction.



IV EFFECT OF SOLVENT

As ions in solution are solvated the nature of the solvent will play a part in the reaction. When ions of opposite sign come together there is a lowering of the net charge, and as solvation depends upon the charge on the ion, with decreased charge there is decreased solvation. With ions of the same sign, however, the transition state will be highly charged and more solvent molecules will be required for solvation than for the separate ions. This leads to decrease in entropy in forming the transition state. The relationship between electrostatic free energy (ΔF_{el}) and the dielectric constant (D) is given by: -

$$\Delta F_{el} = \frac{Z_A Z_B e^2}{D r_{+}}$$

This can be developed into: -

$$\ln K = \ln K_o - \frac{N Z_A Z_B e^2}{D R T r_{+}}$$

K_o being the specific rate constant in a medium of infinite dielectric constant. This equation predicts a linear plot of log K against $^1/D$, with a positive slope if the charges are of opposite sign.

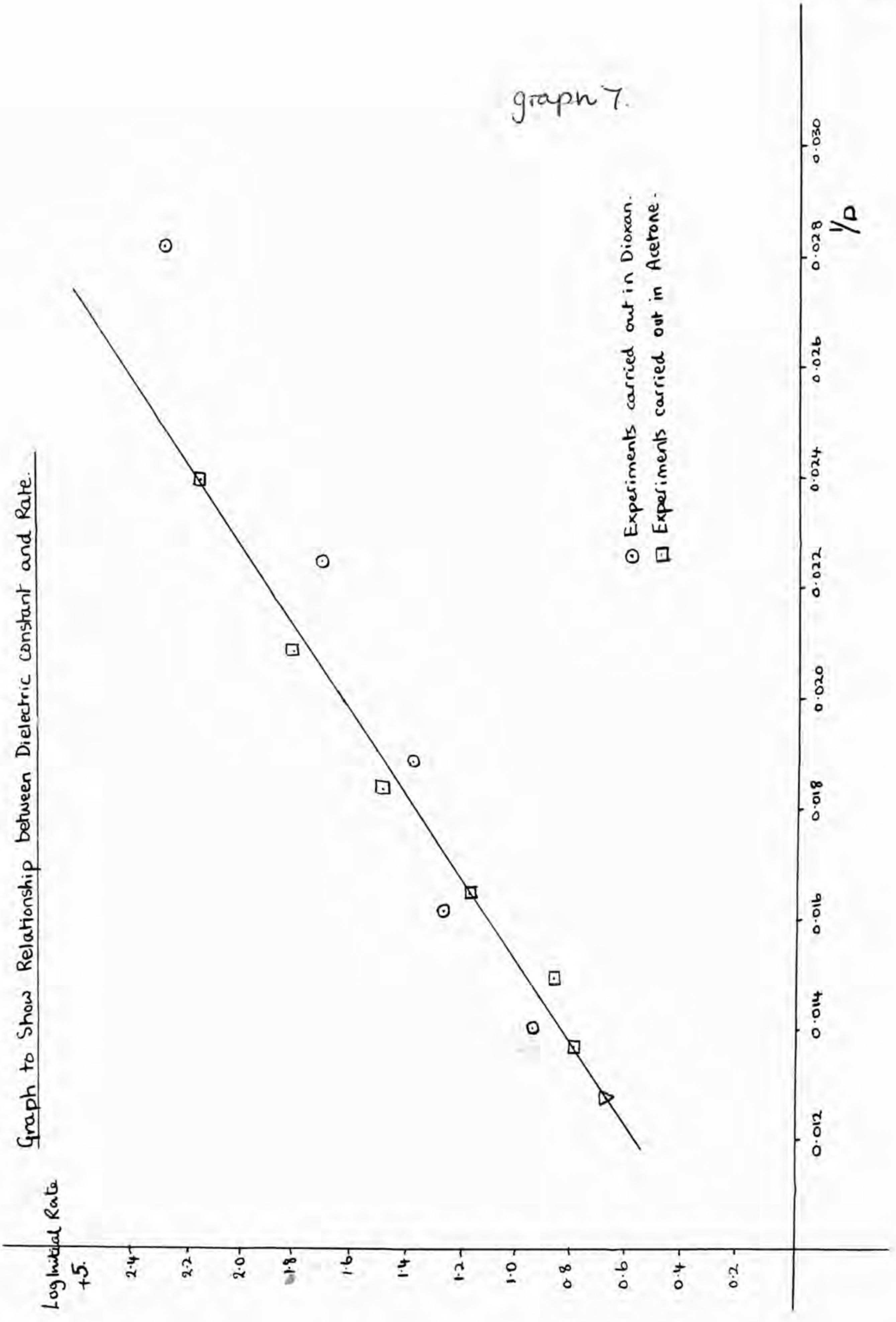
A series of experiments was carried out in two different solvents, the dielectric constant being varied by the addition of various amounts of "analar" dioxan and acetone (see Appendix p. 151-2) In both cases the rate increased as the dielectric constant decreased, showing that the complex in the transition state was of lower net charge than the reactants i.e. ions of opposite sign were coming together.

Table V11

D	Acetone Init. Rate(Moles I_2 ×2 /l/min x 10^4)	Dioxan Init. Rate (Moles I_2 /l/min x 10^4 ×2.
78.5	1.13	1.13
73.0	1.49	
71.2		2.2
67	1.87	
62		4.75
54	7.80	6.25
48.2	17.00	
44		13.75
35.6		20.50

These experiments were carried out at 25°C and were 2×10^{-2} M with respect to iodide and acid, and 2×10^{-3} M with respect to dichromate concentration. The reaction was followed in the usual manner. i.e. by removing 10 ml samples at given intervals and titrating it against 0.01N sodium thiosulphate.

Owing to presence of peroxides in the dioxan, which caused immediate oxidation of iodide, the solvent had to be purified (see appendix p.151)



Graph to Show Relationship between Dielectric constant and Rate.

graph 7.

V EFFECT OF D_2O

If, in the reaction, there is specific hydrogen ion catalysis, the rate is generally increased in D_2O because of the formation of more favourable pre-equilibrium conditions. Supposing that the reaction involved $HCro_4^-$, or any protonated species derived from it e.g. H_2CrO_4 or the superacid $H_3CrO_4^+$ then the equilibria

$$H_2O + Cr_2O_7^{2-} \rightleftharpoons 2HCrO_4^- \qquad A$$

$$H_3O^+ + HCrO_4^- \rightleftharpoons H_2O + H_2CrO_4 \qquad B$$

$$H_3O^+ + H_2CrO_4 \rightleftharpoons H_2O + H_3CrO_4 \qquad C$$

will be affected by the substitution of deuterium for hydrogen. The affect on A is not clear, but B and C, involving competition for the H^+ or D^+ would have higher equilibrium constants in D_2O than in H_2O. Thus if H_2CrO_4 or $H_3CrO_4^+$ is an effective reagent the reaction will be faster in D_2O, Since these equilibria will presumably lower $\left[Cr_2O_7^{2-}\right]$ in D_2O, relative to H_2O, the reaction should be slightly slower (if the effect is perceptible) in D_2O.

Owing to the small amount of D_2O available, the experiments had to be carried out in small volumes. A stock solution of chromic acid was made up by adding standard perchloric acid, from a burette, to a known weight of sodium dichromate to make 50 ml solution. 2 mls of this stock solution were added to 50ml. of iodide in D_2O. 10ml samples were then removed at timed intervals and analysed for iodine. By comparison with a control experiment, carried out in a similar manner by replacing D_2O with water, it was found that the rate had increased 2 - 3 times (graph 8). Thus we have good evidence here for the acid catalysis and for the probable participation of a protonated acid chromate species as a reactant.

Table V111

A.

Time (mins)	D_2O (moles I_2/l)	Control (moles I_2/l)
5	2.13×10^{-4}	0.62×10^{-4}
10	3.00	1.19
15	3.22	1.53
20	3.34	1.94
25	3.40	2.19

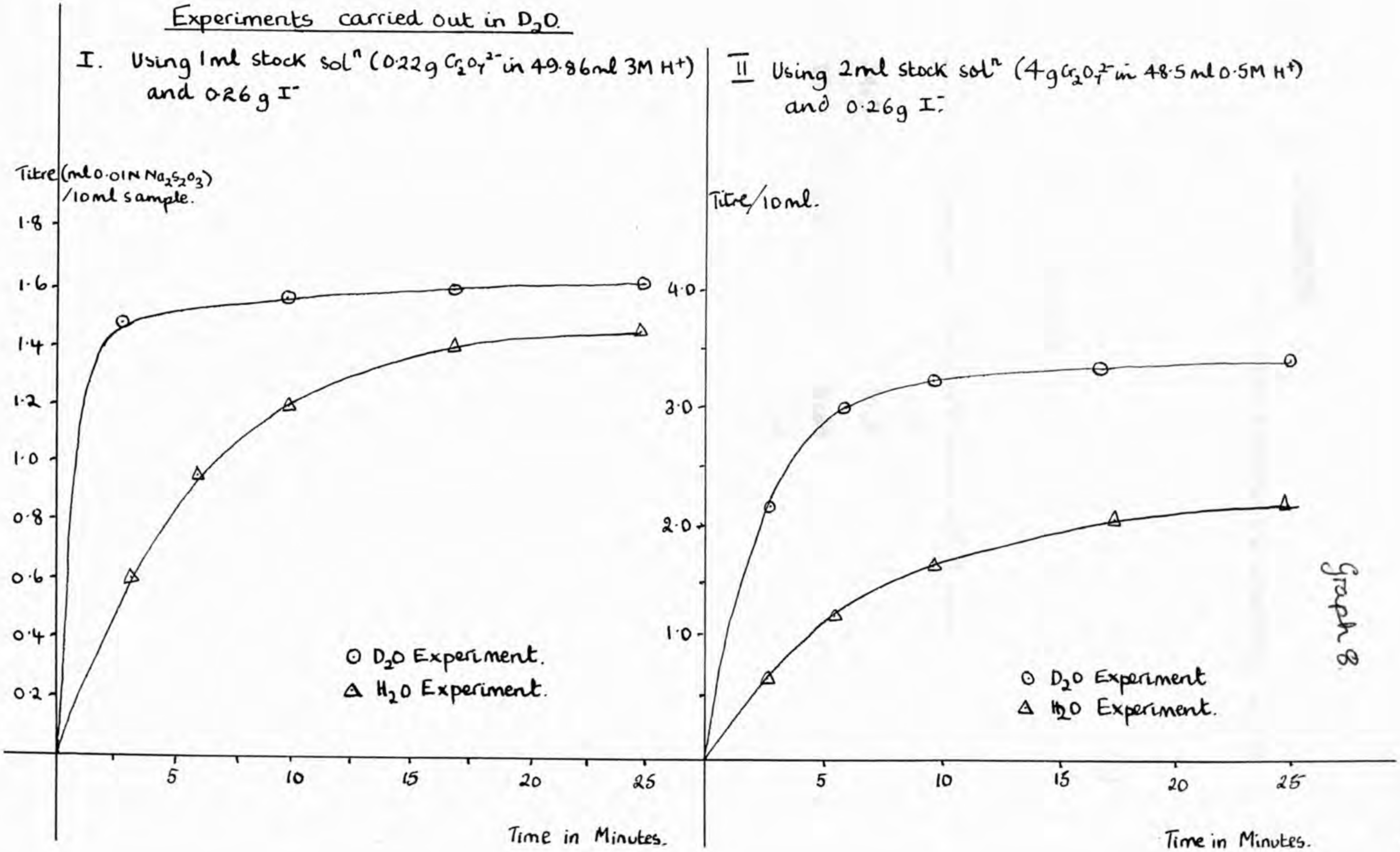
$\left[Cr_2O_7^{2-}\right] = 1.05 \times 10^{-2} M$ $\left[H^+\right] = 1.87 \times 10^{-2} M$ $\left[I^-\right] = 3.01 \times 10^{-2} M$

B.

Time (mins)	D_2O (moles I_2/l)	Control (moles I_2/l)
5	3.0×10^{-4}	0.61×10^{-4}
10	3.18	0.97
15	3.18	1.21
20	3.20	1.39
25	3.24	1.47

$\left[Cr_2O_7^{2-}\right] = 2.93 \times 10^{-4} M$ $\left[H^+\right] = 5.9 \times 10^{-2} M$ $\left[I^-\right] = 3.08 \times 10^{-2} M$

Experiments carried out in D_2O.



I. Using 1ml stock sol^n ($0{\cdot}22g\ Cr_2O_7^{2-}$ in 49·86ml 3M H^+) and 0·26g I^-

II Using 2ml stock sol^n ($4g\ Cr_2O_7^{2-}$ in 48·5ml 0·5M H^+) and 0·26g I^-.

Graph 8.

VI VARIATION OF TEMPERATURE

The rate of reaction varies with temperature according to the Arrhenius' equation

$$k = Ae^{-E/RT}$$

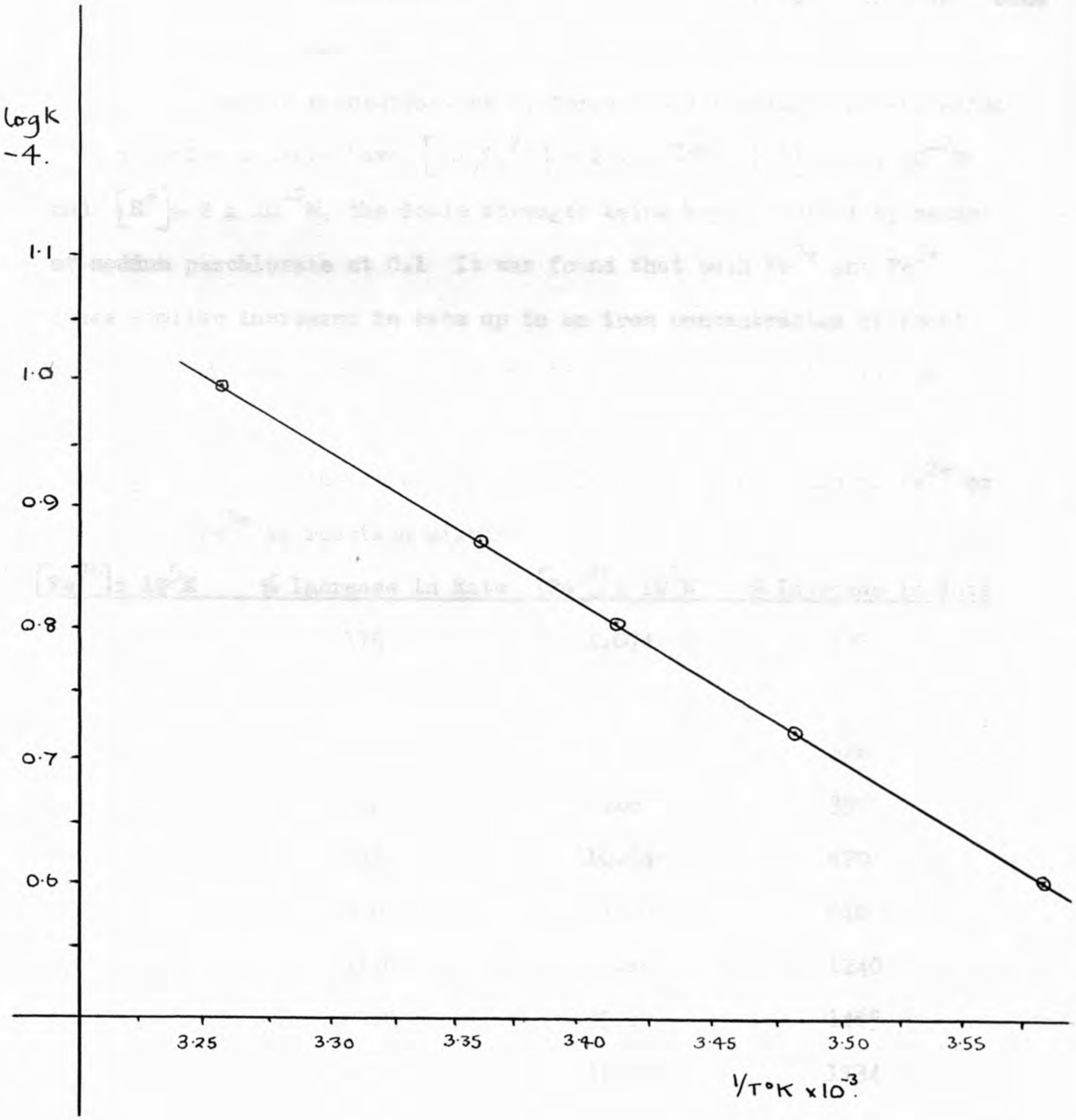
By plotting $^{I}/T^{o}$ against log K, the energy of activation (E) was found to be 5.4 Kcal / [illegible] mole.

Table IX

$T^{o}C$	K (moles $^{-4}$ 1 ^{4} mins $^{-1}$)
6.3	4.06×10^{4}
14.5	5.36
20	6.48
25	7.52
34.5	10.12

Chromic Acid Oxidation of Iodide - showing relation between rate of reaction (K) and temperature.

graph 9.



SECTION 3

FURTHER EXPERIMENTS:

1. ADDITION OF IRON

a) Earlier work had shown that addition of ferrous and ferric ions to the reaction mixture caused an appreciable increase in rate. Some of this work was repeated.

Various concentrations of ferrous and ferric iron were added to a reaction mixture have $[Cr_2O_7^{2-}] = 2 \times 10^{-3}M$ $[I^-] = 2 \times 10^{-2}M$ and $[H^+] = 2 \times 10^{-2}M$, the ionic strength being kept constant by means of sodium perchlorate at 0.1 It was found that both Fe^{2+} and Fe^{3+} cause similar increases in rate up to an iron concentration of about $1 \times 10^{-4}M$, but above this the ferric iron seemed more effective in causing oxidation. (see graph 10)

Table X - Showing the effect upon initial rate by addition of Fe^{2+} or Fe^{3+} to reaction mixture

$[Fe^{2+}] \times 10^5 M$	% Increase in Rate	$[Fe^{3+}] \times 10^5 M$	% Increase in Rate
2.12	178	1.074	125
3.18	236	3.58	275
4.24	305	5.37	326
8.48	520	7.16	390
12.70	763	10.64	620
21.20	930	17.90	910
29.70	1140	28.64	1240
42.40	1260	35.80	1465
63.60	1270	42.96	1734

b) Induction by Iron: -

Before a complete mechanism could be proposed, it was necessary to have an idea of the intermediate valency state(s) of chromium during the course of reaction. By methods of induced oxidation it had previously been suggested (VI) that the main intermediate involved Cr(V) It was therefore decided to check this conclusion.

The induction factor can be defined as the ratio of the number equivalents of reducing agent oxidised to the number equivalents of inductor used. A ratio of 0.5 or 2 can be obtained suggesting intermediate valencies of either Cr(V) or Cr(IV).

To find the induction factor, the concentration of iodide (the reducing agent) and ferrous iron (the inductor) must be known at the end of the reaction. Iodide is found simply by determining the iodine formed. The analysis of iron however presented more problems as in the standard titrimetric methods the dichromate present interferes. Eventually the colorimetric determination of Fe^{2+} by dipyridyl was decided upon.

A known concentration of Fe^{2+} was added to the reaction mixture and samples were removed at intervals. Once the quenched samplehad been titrated with sodium thiosulphate, and the iodide removed, dipyridyl was added and the solution made up to a known volume. The red colour was permitted to stand for 1 hour to allow complete development of the complex before the optical density was measured.

It was necessary to calculate the ratio at the exact end of the reaction, otherwise extraordinary values were obtained.

i) If ferrous iron was in excess of the iodide, then when the iodide is exhausted, the $HCrO_4^-$ present will still oxidise the Fe^{2+}, causing a high value for the induction factor.

ii) If the iodide is in excess then there will still be oxidation of this by $HCrO_4^-$ after the Fe^{2+} has been used, thus giving a low value.

Below are given tables showing how the values of induction numbers vary throughout an experiment, The completion of the reaction is seen by the titre remaining constant.

Table XI

$[I^-] = 4 \times 10^{-2}$M $[Cr_2O_7^{2-}] = 2 \times 10^{4}$M $[Fe^{2+}] = 6.18 \times 10^{-4}$M

Time (mins)	$[I^-]$ used x 10^4M	$[Fe^{2+}]$ used x 10^4M	Induction Factor
12	6	2.38	2.52
13	6.3	2.48	2.53
14	6.42	2.62	2.51
15	6.51	2.75	2.36
16	6.58	2.80	2.35
18	6.67	3.06	2.18
19	6.69	3.18	2.09
20	6.70	3.38	1.98
21	6.70	3.40	1.97

Table XII

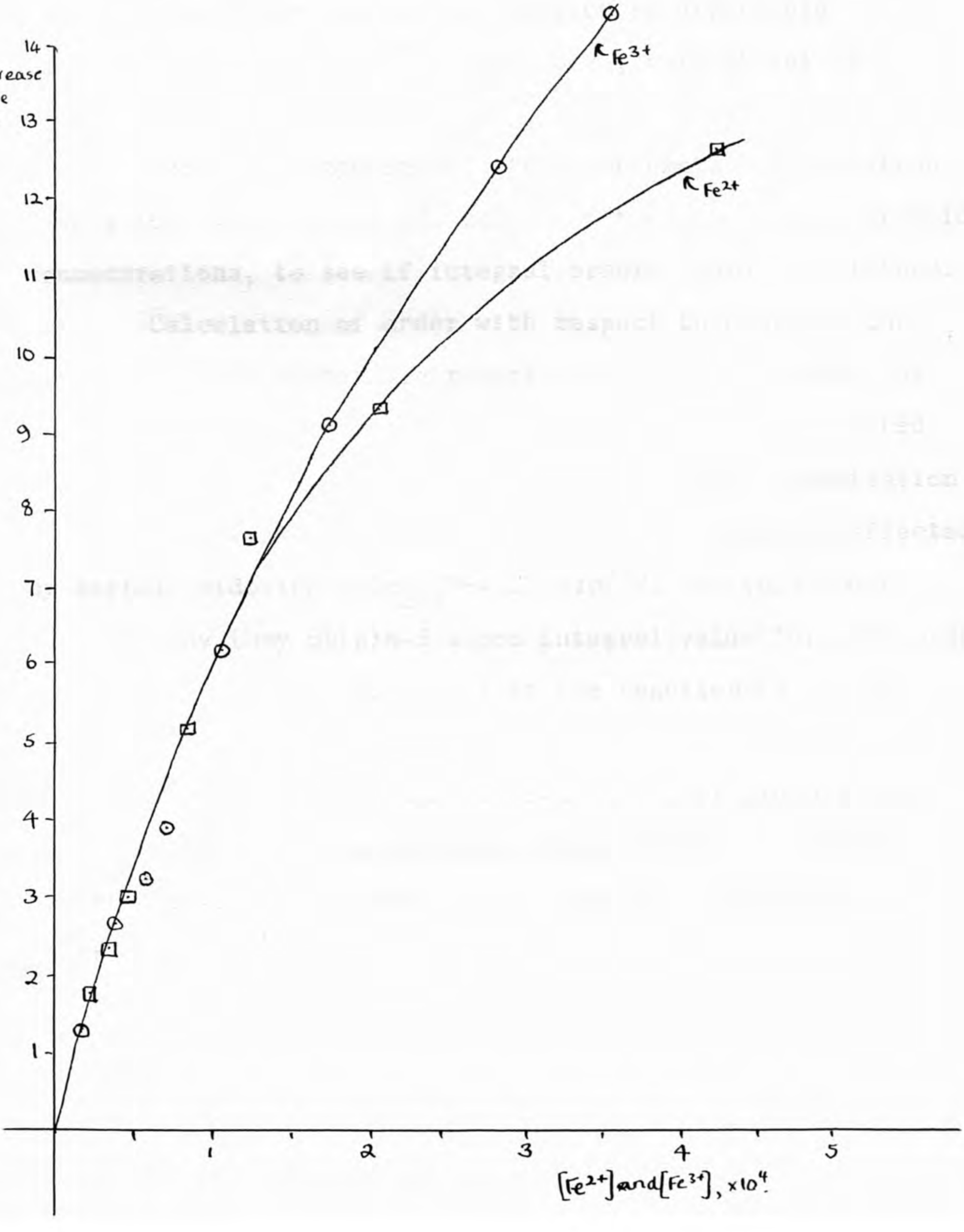
$[K_2Cr_2O_7] = 2 \times 10^{-4}M$ $[H^+] = 2 \times 10^{-2}M$ $[I^-] = 1 \times 10^{-2}M$

Time (mins)	$[I^-]$ used $\times 10^4$	$[Fe^{2+}]$ used $\times 10^4$	Induction Factor
5	7.7	4.8	1.81
10	9.0	4.0	2.25
20	9.0	3.95	2.30
41	9.2	3.90	2.33
60	9.0	3.80	2.37

These results do suggest an intermediate valency of 5, but not very convincingly. Experiments were carried out later (page 69) which were more conclusive.

Showing % Increase in Initial Rate on the Addition of Fe^{2+} and Fe^{3+}.

graph 10.



II EFFECT OF CARRYING OUT REACTIONS WITH HIGHER DICHROMATE CONCENTRATIONS

At low dichromate concentrations oxidation is slow, and as shown previously,(page 34) there is a certain amount of aerial oxidation of iodide. However at dichromate concentrations of 2×10^{-3}M, and above, this effect is negligible.

Series of experiments with dichromate concentration of 2×10^{-3} were performed, varying either the iodide or acid concentrations, to see if integral orders could be obtained.

Calculation of order with respect to hydrogen ion shows that with higher dichromate concentration, the order is much more closely two. Beard and Taylor(II) determined the order with respect to acid at a dichromate concentration at which the reaction would be very slow and greatly affected by aerial oxidation ($Cr_2O_7^{2-} = 2 \times 10^{-4}$M) and this would explain why they obtained a non integral value for the order.

The new results show that the reaction is closely second order with respect to both H^+ and I^-, and the possibility of two simultaneous reactions, as proposed by Beard and Taylor, is eliminated. These results and those reported earlier for lower Cr(VI) concentrations are plotted in figs(11,12).

Table XIII

A. Order with respect to iodide

$[H^+] = 1.2 \times 10^{-2}M$ (a) $2 \times 10^{-2}M$ (b)

$[Cr_2O_7^{2-}] = 1.0 \times 10^{-3}M$ (a) $2 \times 10^{-3}M$ (b)

$[I^-] \times 10^2M$	Initial Rate (a)	Initial Rate (b)
1	0.05	0.415
2	0.525	1.45
3	0.714	6.70
4	1.46	8.92
6.0	6.80	-

Initial Rate measured as moles I_2/litre/min x 10^3

B. Order with respect to H^+

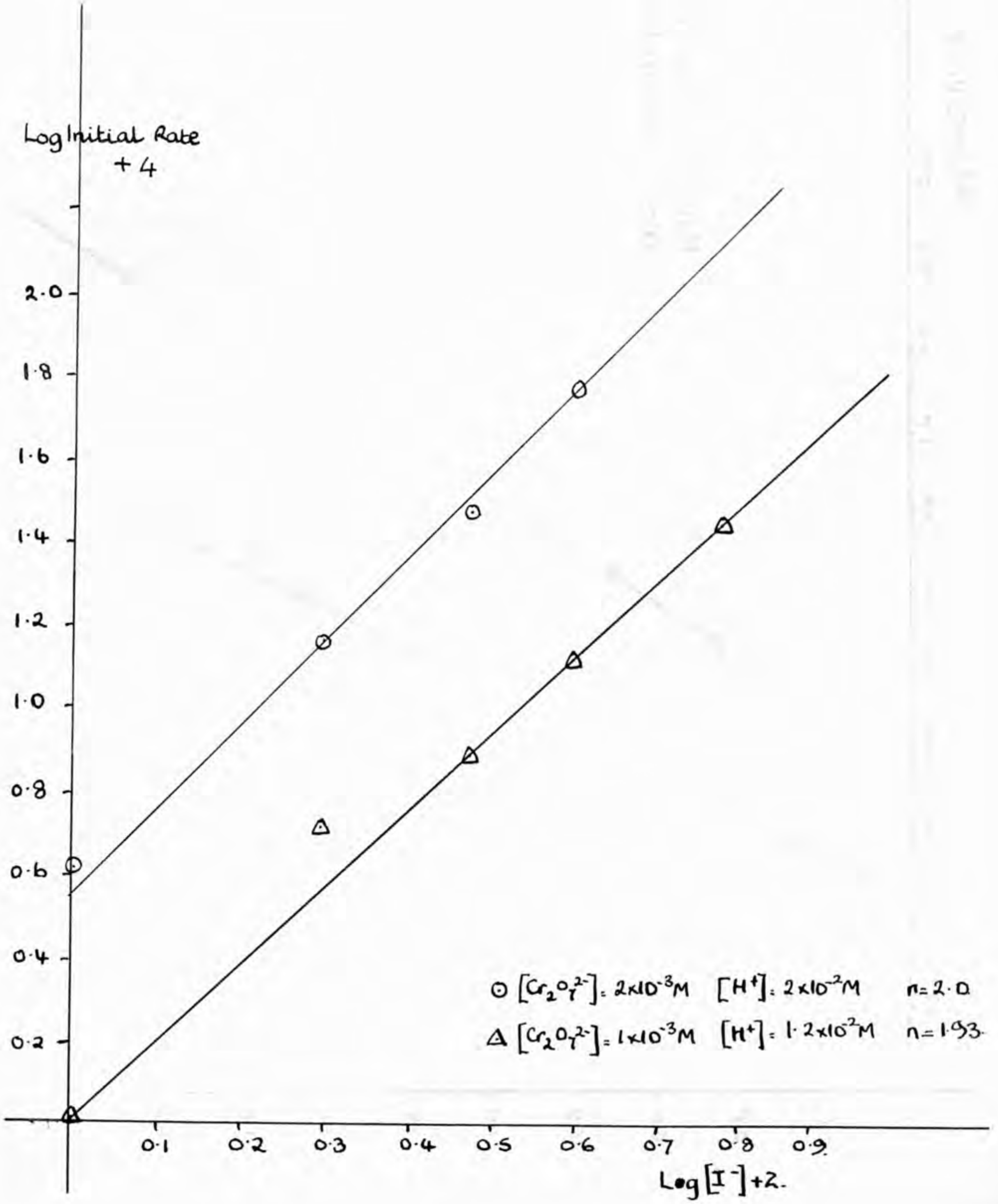
$[I^-] = 3.0 \times 10^{-2}M$ (a) and (b)

$[Cr_2O_7^{2-}] = 1.0 \times 10^{-4}M$ (a) $2 \times 10^{-3}M$ (b)

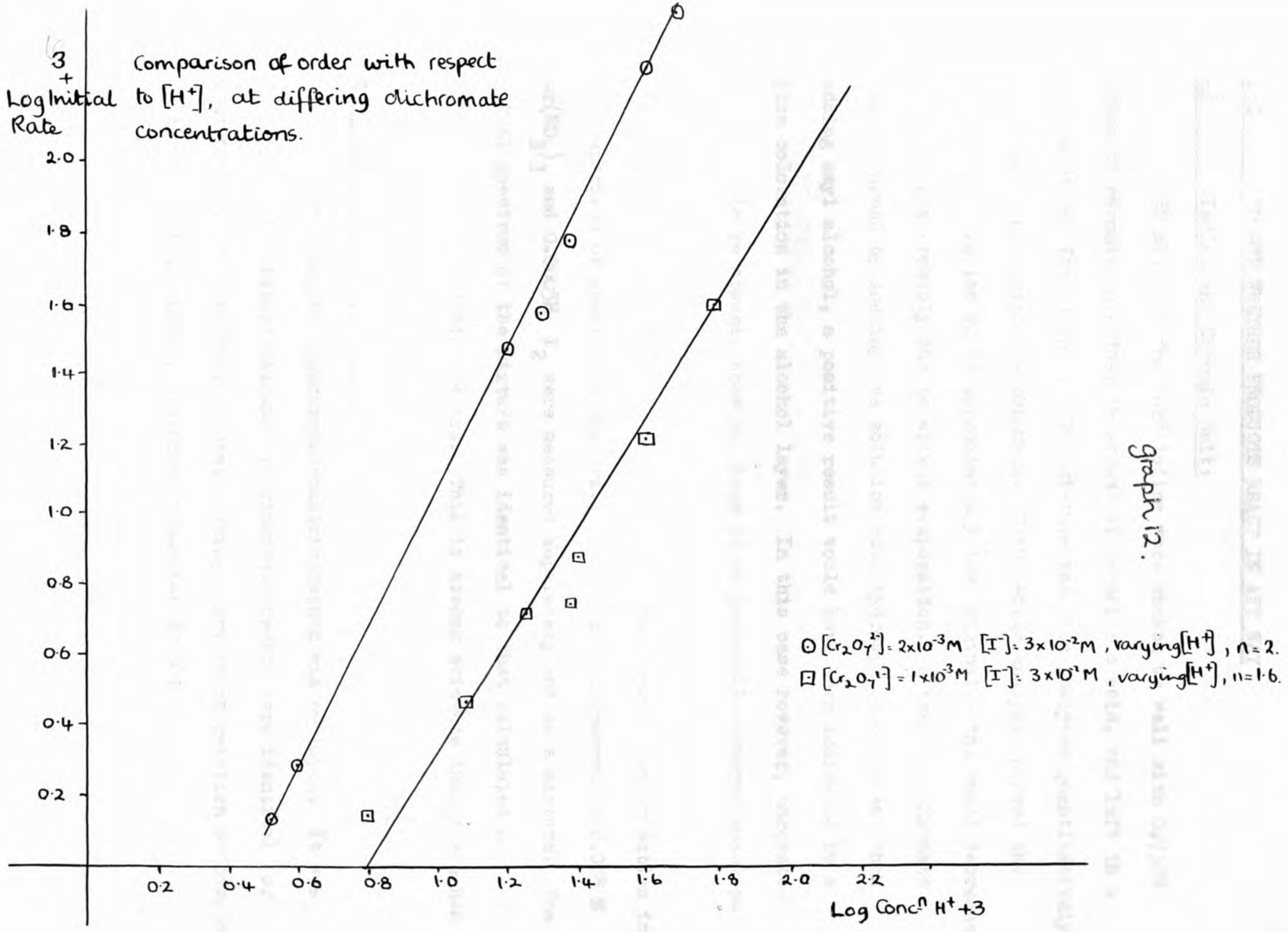
$[H^+] \times 10^2M$	Initial Rate (a)	Initial Rate (b)
0.4		1.53
0.6	0.87	
1.2	5.40	
1.6		23.00
1.8	7.78	
2.0		29.50
2.4	8.00	
2.5		47.90
4.0	13.20	145.0
4.95		220
6.00	31.60	

Initial Rate measured as Moles I_2/litre//min x 10^3

Determination of the Order with respect to I^- at differing Dichromate Concentrations. graph 11.



Graph 12.



Comparison of order with respect to [H⁺], at differing dichromate concentrations.

III TO SEE WHETHER PRODUCTS REACT IN ANY WAY

a) Iodine and Chromic Salt:

50 mls 0.1N "analar" iodine were shaken up well with 0.7309 grams of chromic chloride, in excess of perchloric acid, and left in a stoppered jar for 24 hours. The mixture was then analysed quantitatively for iodine and tested for chromate. Titrimetric analysis showed the iodineconcentration to be approximately the original - the small decrease in titre was probably due to slight evaporation. A test for chromate was performed by shaking the solution with hydrogen peroxide and then adding amyl alcohol, a positive result would have been indicated by a blue coloration in the alcohol layer. In this case however, chromate was found to be absent, showing there is no detectable reverse reaction between iodine and chromic ions.

A more accurate way of testing whether there is any reaction is by comparison of absorption spectra. The absorption spectra of 0.005 M $Cr(NO_3)_3$ and 0.0005M I_2 were measured separately and as a mixture. The actual spectrum of the mixture was identical to that calculated as the sum of the separate spectra. This is strong evidence that there has not been any interaction of iodine and chromic salts.

b) Chromic and Chromate Ions

Once again a spectrophotometric method was employed. It was found that the theoretical and experimental spectra were identical for a mixture of Cr^{3+} and Cr(VI) ions, showing there is no reaction or complex formation between these two species (see table XIV)

Table XIV

Cr^{3+} / Cr(VI) mixture being 5 ml 2 x 10^{-4}M $Cr_2O_7^{2-}$
5 ml 1 x 10^{-2}M Cr^{3+}

mμ.	[Cr(VI)]= 1 x 10^{-4}M	[Cr^{3+}]= 5 x 10^{-3}M	Theoretical O.D	Actual O.D.
550	.007	0.091	0.098	0.086
540	.007	.080	0.087	0.086
530	.007	.072	0.079	0.079
520	.007	.065	.072	.069
510	0.007	.065	.072	.073
500	.007	.072	.079	.081
490	.013	.070	.083	.091
480	.019	.083	.101	.104
470	.026	.091	.127	.126
460	.034	.109	.143	.150
450	.039	.126	.165	.170
440	.044	.142	.196	.199
430	.045	.162	.207	.220
420	.047	.176	.223	.239
4.0	0.058	.189	.247	.254
400	.090	.186	.276	.289
390	.144	.193	.337	.338
380	.174	.206	.380	.400
370	.239	.215	.444	.483
360	.289	.238	.527	.546

continued.....

continued......

mμ	$[Cr(VI)] = 1 \times 10^{-4}M$	$[Cr^{3+}] = 5 \times 10^{-3}M$	Theoretical O.D	Actual O.D.
350	.310	.262	.572	.592
340	.277	.282	.559	.585
330	.210	.312	.522	.534
320	.138	.330	.468	.500
310	.124	.353	.477	.522
300	.172	.400	.572	.615
290	.238	.440	.678	.719
280	.273	.500	.773	.838
270	.327	.585	.912	.970
260	.368	.760	1.128	1.144
250	.369	1.006	1.375	1.395

IV REACTIONS CARRIED OUT OVER A LONG PERIOD OF TIME

In order to see whether a proposed rate expression held over a wide range of the reaction, several series of experiments were performed where the reaction was allowed to approach completion. Typical results obtained have been plotted in the usual manner.

Table XV

20°C $[H^+] = 1.6 \times 10^{-2}M$ $[I^-] = 3.0 \times 10^{-2}M$ $[Cr_2O_7^{2-}] = 2 \times 10^{-3}M$

Time (mins)	Moles I_2/litre x 10^3
5	0.075
10	0.13
15	0.192
20	0.243
60	0.610
90	0.759
120	0.900
180	1.052
240	1.150
300	1.198

Over a wide range of temperature, ionic strength and concentration, the following rate expression held for initial rates: -

$$\text{Rate} = k \left[HCrO_4^-\right] \left[I^-\right]^2 \left[H^+\right]^2$$

The rate of reaction always falls below this calculated form as reaction proceeds. Since we have shown that the reaction does not go measurably to an equilibrium this could mean either that the rate expression is incomplete or possibly that the concentration of reactants were not as calculated.

Analysis of Reaction Mixture

Samples of reaction mixture were analysed at intervals for iodide, iodine, dichromate and hydrogen ion concentration. The acid concentration was found easily by measuring pH at intervals throughout the reaction.

Table XVI

$[I^-] = 3.0 \times 10^{-2}M$ $[H^+] = 1.2 \times 10^{-4}M$ $[Cr_2O_7^{2-}] = 1.2 \times 10^{-2}M$ u =

$\mu = 0.092$

Time (mins)	H^+ found (M)	H^+ calculated (M)
2.5	0.0118	0.0116
10	0.0107	0.0106
20	0.0098	0.0099
40	0.0085	0.0086

In later stages of reaction the hydrogen ion concentration did seem to fall faster than calculated.

Dichromate was estimated gravimetrically as barium chromate. 100 ml. of reaction mixture was quenched after about 90 minutes and diluted with 100 ml of water after the solution had been made neutral. A 10% solution of barium acetate was then added. The precipitate was filtered off on a weighed sintered glass crucible. For the reaction mixture of initial concentrations $1 \times 10^{-2}M$ $Cr_2O_7^{2-}$, $3 \times 10^{-2}M$ I^-, and $2 \times 10^{-2}M$ H^+, after 90 minutes the dichromate concentration was found to be 9.4×10^{-3} in exact agreement with expectation.

Analysis of iodide was carried out in the following manner. Samples of reaction mixture were removed at given intervals and run into acetate buffer. Besides quenching the reaction, the buffer also brought the solution to the pH necessary for precipation of $BaCrO_4$. The iodine present was reconverted to iodide with thiosulphate. To the boiling reaction mixture was added a slight excess of barium chloride to precipitate the dichromate, this was found to be necessary as the dichromate interferes later. The yellow barium chromate was filtered off and conc. HCl and a little chloroform were added to the filtrate which was titrated against potassium iodate. This method will thus detect whether iodine is present as any species other than iodide and what is effectively molecular iodine, and since iodine has been determined by the thiosulphate titration, iodide is also determined.

Table XVII

$[I^-] = 3 \times 10^{-2}M$ $[H^+] = 2.0 \times 10^{-2}M$ $[Cr_2O_7^{2-}] = 1 \times 10^{-2}M$ 25^0C $\mu = 0.1$

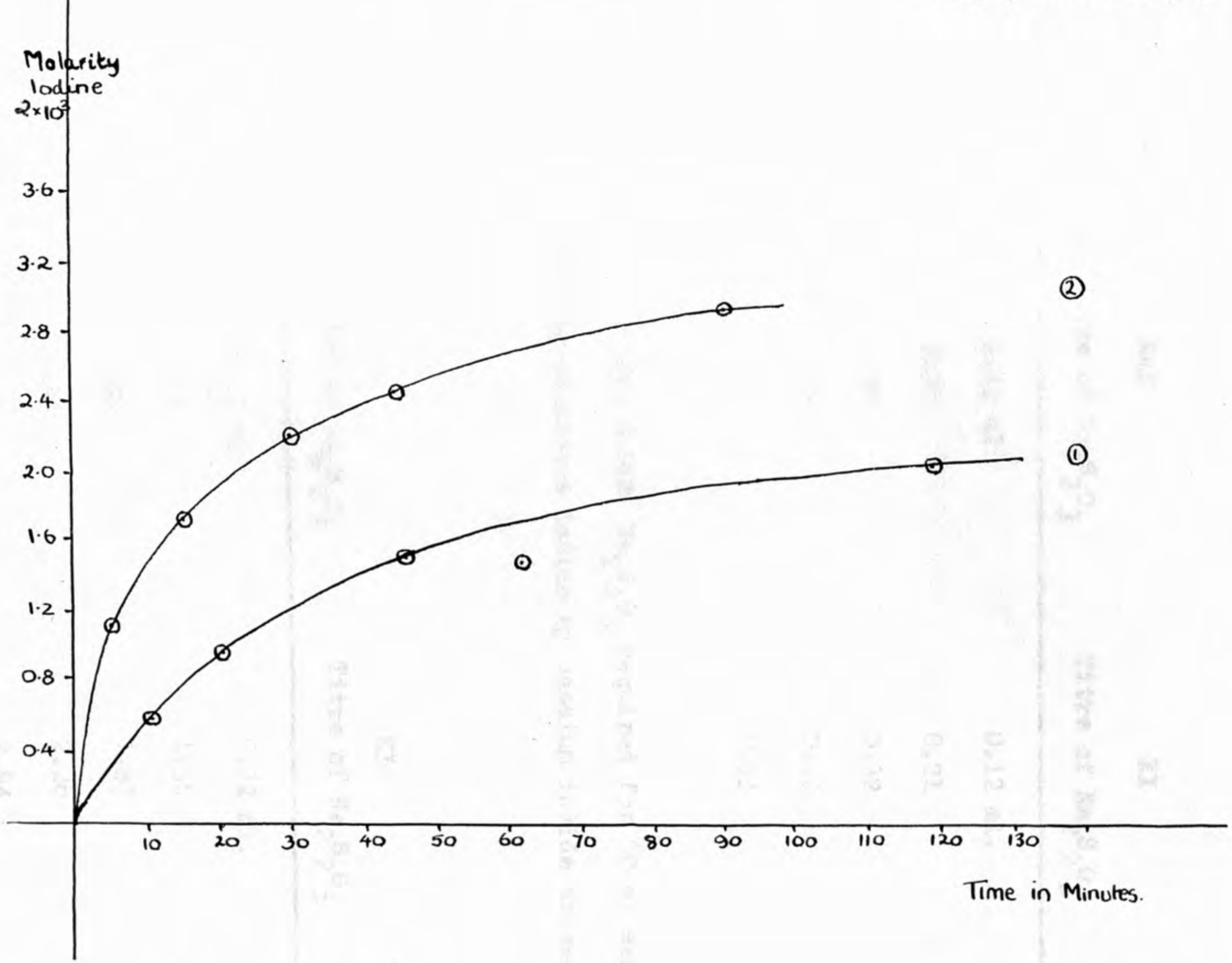
Time (mins)	$[I^-]$ calc.	$[I^-]$ found
5	0.0291	0.0290
15	0.0281	0.0290
30	0.0275	0.0280
45	0.0272	0.0275
90	0.0271	0.0270

This is reasonable experimental agreement, showing that all the iodine is in one or other of these two forms. Thus for a considerable extent of reaction during which the rate is falling appreciably below that indicated by the initial kinetics, theconcentrations of reactants are truly found to be those calculated from the starting conditions and the stoichiometric chemical equation.

Reaction followed over a period of Time 25°C $\mu = 0{\cdot}10$.

① $[H^+] = 1{\cdot}2 \times 10^{-2}M$ $[I^-] = 3 \times 10^{-2}M$ $[Cr_2O_7^{2-}] = 1 \times 10^{-3}M$.

② $[H^+] = 2{\cdot}0 \times 10^{-2}M$ $[I^-] = 3 \times 10^{-2}M$ $[Cr_2O_7^{2-}] = 1 \times 10^{-3}M$.



graph 13.

V EFFECT OF VARYING "INERT" CATION AND AMION

Experiments were carried out using KI, NaI, and CsI as the source of iodide. The comparison of sodium and potassium iodide was carried out at $\mu = 0.2$, using reaction mixtures of 2×10^{-2}M I^-, 2×10^{-3}M $K_2Cr_2O_7$, 1×10^{-2}M $HClO_4$ at 25°C. There was no difference in the rate.

Table XVIII

Time (mins)	NaI Titre of $Na_2S_2O_3$	KI Titre of $Na_2S_2O_3$
5	0.12 ml	0.12 ml.
10	0.22	0.21
15	0.33	0.32
20	0.43	0.42
25	0.54	0.53

Titration figure is mls. 0.01N $Na_2S_2O_3$ required for 50 ml sample

Similarly replacing potassium iodide by caesium iodide showed no change

Table XIX

Time (mins)	CsI Titre of $Na_2S_2O_3$	KI Titre of $Na_2S_2O_3$
5	0.73 ml	0.72 ml.
10	1.34	1.36
15	1.87	1.87
20	2.27	2.28
25	2.83	2.84

Reaction mixture is 2×10^{-2} MI$^-$, 2×10^{-3}M $K_2Cr_2O_7$, 2×10^{-2}M $HClO_4$

$\mu = 0.1$ T = 25°

Titration figure is mls. 0.01N $Na_2S_2O_3$ required for 50ml sample

Having shown that varying the size of cation has no effect upon rate, it was then decided to try the effect of amions. Earlier experiments had suggested that bromide, chloride and perchlorate did not produce different rates. Further experiments were carried out in perchloric acid, with the addition of F^-, NO_3^-, Cl^-, and ClO_4^-. Results showed that again reaction mixtures containing ClO_4^- and Cl^- reacted at similar rates, but nitrate was slightly inhibitory. At moderately high F^- concentrations, the reaction was strongly inhibited, and precipitations occured. This was not further investigated, but could be important, analytically.

As all the above amions were univalent, sulphate ions were also added to see whether the charge on the ion was important. Results showed that this was not so, suggesting that there is no ion association during the reaction.

Table XX - Comparing Br^-, ClO_4^-, and Cl^-, added to reaction mixture as HX and NaX

Acid	Conc$^{\underline{n}}$	Initial Rate	Conc$^{\underline{n}}$	Initial Rate
HBr	.0597M	3.8×10^{-5}	.006M	1.0×10^{-5}
HCl	.0597	3.8	.006	1.0
$HClO_4$	.0597	3.7	.006	1.0

Reaction mixture: $[I^-] = 3 \times 10^{-2}M$, $[Cr_2O_7^{2-}] = 1 \times 10^{-4}M$ $\mu = 0.0935$

$T = 25^{o}C$

Initial Rate measured as moles I_2 formed / litre / min.

Table XXI - Comparing F^-, NO_3^-, Cl^-, and ClO_4^-

$25^{o}C$ $[Cr_2O_7^{2-}] = 9.95 \times 10^{-4}M$, $[H^+] = 3.9 \times 10^{-2}M$ $[I^-] = 2.997 \times 10^{-2}M$

$[X^-] = 1.99 \times 10^{-2}M$ $\mu = 0.10$

Time (mins)	ClO_4^-	Cl^-	NO_3^-	F^-
5	4.37 ml.	4.36 ml	4.43 ml	2.27 ml.
10	7.75	7.74	7.21	4.63
15	10.02	10.34	9.69	6.30
20	12.20	12.19	10.61	7.51
25	13.50	13.35	11.92	8.45

Titration figures given show mls 0.01N $Na_2S_2O_3$ required for 50 ml sample

Table XXII - Showing inhibition by F^-

$\mu = 0.2$ $[I^-] = 2.997 \times 10^{-2}M$ $[Cr_2O_7^{2-}] = 9.98 \times 10^{-4}M$ $[H^+] = 3.9 \times 10^{-2}M$

$[X^-] = 1.28 \times 10^{-1}M$

Time (mins)	ClO_4^-	F^-
5	3.90 ml.	0.09 ml
10	6.59	0.10
15	8.85	0.13
20	10.56	0.15
25	11.15	0.16

Titration figures given show mls 0.01N $Na_2S_2O_3$ required for 50 ml sample

Table XXIII - Comparing SO_4^{2-} and ClO_4^-

$[H^+] = 2 \times 10^{-2}M$ $[I^-] = 2 \times 10^{-2}M$ $[Cr_2O_7^{2-}] = 2 \times 10^{-3}M$

$T = 25^\circ C$ $\mu = 0.1$

Time (Mins)	ClO_4^-	SO_4^{--}
5	0.69 ml	0.70 ml
10	1.35	1.30
15	1.98	1.91
20	2.52	2.50
25	2.95	2.95

Titration figures given show mls. 0.01 $Na_2S_2O_3$ required for 50 ml sample

VI SPECTOPHOTOMETRIC EXPERIMENTS

Experiments were carried out to see if it were possible to follow the oxidation of iodide, either by measuring the decrease in the dichromate concentration or by determining the iodine formed, using spectrophotometric methods. Absorption spectra were obtained of a 0.0005M solution of iodine and an 0.001M dichromate solution. The results obtained showed that both absorbed in the same region and it would therefore be impossible to follow the reaction in this way.

Table XXIV

mμ.	EI_2	$EK_2Cr_2O_7$
420	520	471
410	606	505
400	798	902
390	1168	1439
380	1600	1740
370	2040	2390
360	2460	2890
350	2580	3100
340	2440	2770

Measurements of optical density were carried out using a 1 cm silica cell, using a unicam S.P. 500 spectrophotometer.

During the course of reaction there must be formed some intermediate involving chromium in an unstable valency state and it was hoped to try and detect the presence of such an intermediate. According to Bailey and Symons (XV) chromium (V) shows a broad absorption peak at 625 $m\mu$ with a relatively low molar extinction coefficient of 250 It might therefore be possible to show traces of this valency of chromium by taking recordings at 625 $m\mu$ throughout the reaction 3 mls of a reaction mixture of 1×10^{-3} M $K_2Cr_2O_7$, 2×10^{-2}M KI and 1.24×10^{-1}M $HClO_4$ were placed into a 1 cm cell, within a thermostatted cell compartment of the S.P. 500. Excess thiosulphate, previously shown to have no absorption over the range to be investigated, was added to remove iodine. There was no absorption, however at 625 $m\mu$ probably due to the Cr(V) species being very short lived. We can only conclude that there is no large build up of Cr(V) during the reaction.

VII DETERMINATION OF THE INTERMEDIATE VALENCY STATES OF CHROMIUM

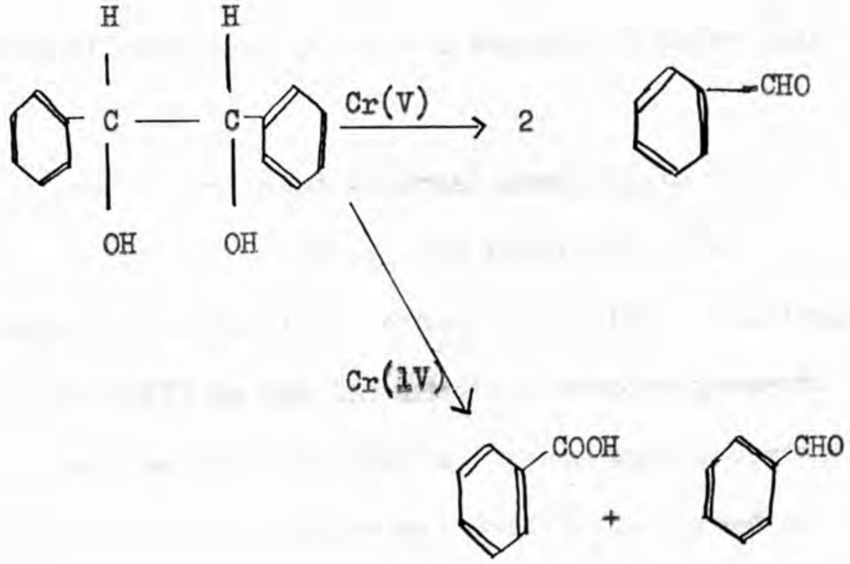
In course of reduction from a dichromate to a chromic salt, chromium must pass through an intermediate valency state of either five or four. Both pentavalent and quadrivalent chromium are unstable and disproportionate in aqueous solution

$3Cr(V) \longrightarrow 2Cr(VI) + Cr(111)$

$3Cr(1V) \rightarrow 2Cr(111) + Cr(VI)$

Through the study of chromic acid oxidations of organic substances, Slack and Waters (VII) devised a method to find the valency of Cr in an intermediate. When hydrobenzoin is added to the reaction mixture, possible oxidation products are benzaldehyde and benzoic acid, the proportions of each formed depending upon the number transferred to the acid chromate.

Reaction mixture +



This had only previously been applied to organic reactions and it was decided to follow the same procedure in our investigation.

Concentrated solutions of potassium dichromate, potassium iodide and perchloric acid were prepared. To the strong chromic acid mixture was added about 10 grams hydrobenzoin followed by the potassium iodide. After about 30 minutes, the iodine was removed by means of thiosulphate and the resulting solution shaken vigorously with ether. The ethereal layer was then separated off and concentrated by evaporation. This was then analysed for benzaldehyde and benzoic acid by V.P.C. methods.

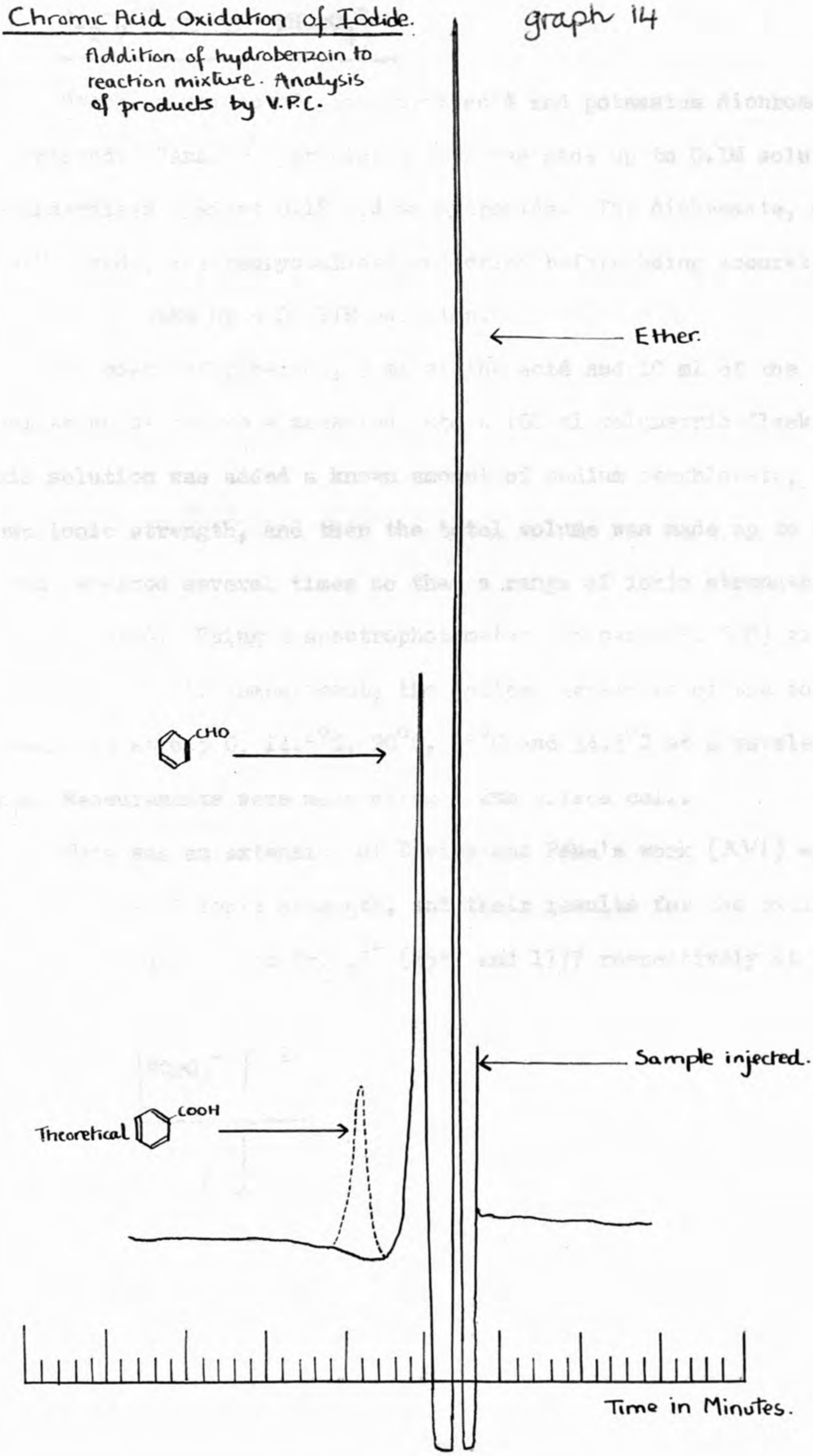
The apparatus used was a Griffin V.P.C. apparatus (mark II) the chromatographic separation being achieved by using a six foot 25% silicone 60/80 celite column at 170°C. With control experiments It was found that benzaldehyde gave a peak after 3 minutes and an equimolecular quantity of benzoic acid gave a shorter, broader peak at $7\frac{1}{2}$ minutes.

Injection of the concentrated ethereal sample into the column produced a large peak at 3 minutes, but nothing further, showing that only benzaldehyde had been formed during the oxidation. Hence it would seem that Cr(V) is the intermediate species present. It must of course be admitted that the result depends upon competitive processes. These experiments only prove that Cr(IV) (if formed at all) is very rapidly removed by the reaction sequence, so that negligible oxidation of the hydrobenzoin by Cr(IV) is observed.

Chromic Acid Oxidation of Iodide.

Addition of hydrobenzoin to reaction mixture. Analysis of products by V.P.C.

graph 14



VIII EXPERIMENTAL DETERMINATION OF EQUILIBRIUM CONSTANT FOR $Cr_2O_7^{2-} \rightleftharpoons 2HCrO_4^-$

Stock solutions of perchloric acid and potassium dichromate were prepared. "Analar" perchloric acid was made up to 0.1M solution and standardised against 0.1N sodium hydroxide. The dichromate, also "analar" grade, was recrystallised and dried before being accurately weighed out to make up a 0.011M solution.

By means of pipettes, 5 ml of the acid and 10 ml of the dichromate solutions were measured into a 100 ml volumetric flask. To this solution was added a known amount of sodium perchlorate, to give a known ionic strength, and then the total volume was made up to 100 ml. This was repeated several times so that a range of ionic strength, could be covered. Using a spectrophotometer (unicam S.P. 500) with a thermostatted cell compartment, the optical densities of the solutions were measured at 6.5°C, 14.5°C, 20°C, 25°C and 34.5°C at a wavelength of 404 mµ. Measurements were made using a 2mm silica cell.

This was an extension of Davies and Prue's work (XVI) over a greater range of ionic strength, and their results for the extinction coefficients of $HCrO_4^-$ and $Cr_2O_7^{2-}$ (258 and 1777 respectively at 404 mµ) were used.

$$K_c = \frac{\left[HCrO_4^-\right]^2}{\left[Cr_2O_7^{2-}\right]}$$

If m = molarity $Cr_2O_7^{2-}$ put in

then m_1 = equilibrium molarity $Cr_2O_7^{2-}$

m_2 = equilibrium molarity $HCrO_4^-$

$m = m_1 + m_2/2$

$\equiv m\,(1 - \alpha) + \alpha m$

$$K_c = \frac{(2\alpha m)^2}{(1 - \alpha)\, m}$$

$$= \frac{4\alpha^2 m}{1 - \alpha}$$

Using the previously found t values for $HCrO_4^-$ and $Cr_2O_7^{2-}$

$$\alpha = \frac{1777 - \epsilon}{1261}$$

$$(\epsilon_{\text{measured}} = \epsilon_1 (1 - \alpha) + 2\alpha\epsilon_2)$$

As the extinction coefficient of the 0.0011M solution of $K_2Cr_2O_7$ at 404 mμ agreed exactly with that found by the two above workers, it was not necessary to correct theoptical density formed throughout these series of experiments. A typical series of results is shown in the following table.

Table XXV

μ	$O.D._{404}$	ϵ_{404}	α	$4\alpha^2m/(1-\alpha)$
.0083	0.160	727	.833	0.0183
.015	0.161	731	.830	0.0178
.050	0.163	740	.822	0.0167
.100	0.170	772	.797	0.0138
.300	0.174	790	.784	0.0125
.600	0.187	849	.736	0.009
.900	0.190	863	.725	0.0084
1.50	0.198	899	.692	0.0068
3.00	0.209	949	657	0.0055

These are the results taken at 14.5°C . Also given are tables showing how the experimentally found K' values agree with those calculated from

$$pK' = pK + \frac{2A\sqrt{\mu}}{1+\sqrt{\mu}} - x\mu \quad \text{(x being equal to 0.3)}$$

see page (120)

Table XXVI - Comparison of Calculated and Experimental K' Values At Various Temperatures

6.5°C

μ	K' Exp.	K'calc.
0.0083	0.0173	0.0151
0.015	0.0158	0.0142
0.05	0.0140	0.0122
0.10	0.0114	0.0109
0.30	0.0104	0.0084
0.600	0.0088	0.0072
0.900	0.0070	0.0067
1.50	0.0056	0.0058
3.00	0.0041	0.0048

14.5°C

μ	K' exp.	K' calc.
0.0083	0.0183	0.0189
0.015	0.0178	0.0178
0.05	0.0167	0.0152
0.10	0.0138	0.0136
0.30	0.0125	0.0108
0.60	0.009	0.009
0.90	0.0084	0.0083
1.50	0.0068	0.0067
3.00	0.0055	0.0056

20°C

μ	K' Exp.	K' calc.
0.0083	-	0.022
0.015	0.0208	0.0203
0.05	0.0173	0.0173
0.10	0.0152	0.0154
0.30	0.0142	0.0124
0.600	0.0106	0.0102
0.900	0.0075	0.0094
1.500	0.0067	0.0081
3.00	0.0058	0.0067

34.5°C

μ	K' Exp.	K' calc.
0.0083	-	0.0304
0.015	0.029	0.0287
0.05	0.023	0.0240
0.10	0.021	0.0216
0.30	0.0189	0.0170
0.60	0.0167	0.0141
0.90	0.0131	0.0129
1.50	0.0088	0.0111
3.00	0.0075	0.0091

25°C

μ	K' Exp.	K' calc.
0.0083	0.0268	0.0247
0.015	0.0240	0.0238
0.05	0.0202	0.0198
0.10	0.0184	0.0182
0.30	0.0150	0.0140
0.60	0.0130	0.0116
0.90	0.0108	0.0107
1.50	-	0.0088
3.00	-	0.0076

Note Davies and Prue (XVI) find K = 0.030

Tong and King (XVII) find K = 0.028, they also find

K' = 0.127 at $\mu = 0.25$, and K = 0.080 at $\mu = 1.0$

Sasaki (XVIII) finds K' = 0.0065 at $\mu = 3.0$

Although not in exact agreement, there is a similar trend in the K' values, whether calculated or found experimentally, suggesting that

$$pK' = pK + \frac{2A\sqrt{\mu}}{1+\sqrt{\mu}} - 0.3\ \mu$$

is valid over the temperature and ionic strength range investigated.

On the calculations it has been assumed that the ~~optical~~ extinction ~~densities~~ coefficients of $HCrO_4^-$ and $Cr_2O_7^{2-}$ are invariant with ionic strength and temperature.

Chapter III

THE REACTION BETWEEN CHROMIC ACID AND FERROUS IRON

SECTION I (1) To Establish a Method for following the Reaction

Several difficulties were encountered, due mainly to: -

i) The reaction being fast, so that very dilute solutions had to be employed.

ii) Dichromate infering with the standard methods of analysis of Fe^{2+}

Methods Attempted

A Analysis of Fe^{2+} by $KMnO_4$

As the potassium dichromate present in the reaction mixture interfered, it had first to be removed. This was done by precipitation with lead nitrate. The precipitate was filtered off and the filtrate was treated with potassium permanganate. Owing to the dilution used the end point was rather hard to detect and consequently inconsistent results were obtained.

Table XXVII

Reaction mixture of 0.012 MFe^{2+}, 0.01 MH^+, 0.001 $MCr_2O_7^{2-}$

Titrations were carried out using 10 ml. samples of reaction mixture and 0.002M $KMnO_4$.

Time (mins)	Titre (ml)
0.33	6.01
1	6.08
4.75	6.14
10	6.14
15	6.08
∞	6.00 (calculated)

Obviously the reaction is far too fast to follow, but if more dilute solutions are employed, volumetric analysis becomes very inaccurate.

B. Analysis of Fe^{3+} by KCNS

This is a colorimetric method, a red solution being formed when ferric iron is in the presence of potassium thiocyanate. The true nature of the entity responsible for the red colour is not absolutely clear, and many suggestions have been put forward. A growing body of evidence suggests that the main contributor is $(FeCNS)^{2+}$ (XIX)

A standard concentration/optical density curve was prepared as follows. A solution of ferric ammonium sulphate in hydrochloric acid was prepared so that 1ml solution contained 0.1 mg iron. 2 - 4 ml 4M hydrochloric acid were added to 5 ml 4M potassium thiocyanate and slightly diluted with water. A known volume of the ferric solution was then added and the total volume made up to 50 ml. The intensity of the red colour so formed was read off immediately in a 1 cm silica cell using a Unicam S.P. 500 at 480 mμ as the colour fades on standing. In all the experiments the blank was a solution of 5 ml. potassium thiocyanate solution in 50 ml aqueous solution

Table XXVIII

mg Fe^{3+}/ 50 ml.	O.D (Corrected for Blank)
0	0
0.05	0.159
0.10	0.330
0.15	0.494
0.20	0.660
0.25	0.835
0.30	1.034
0.35	1.172
0.40	1.359

However this method too was found to be unsatisfactory as the analysis must be carried out in strong acid in order to suppress the hydrolysis.

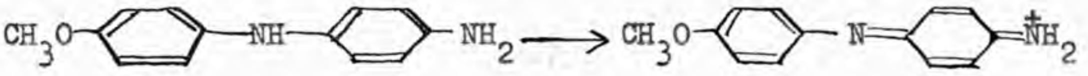
$$Fe^{3+} + 3H_2O \rightleftharpoons Fe(OH)_3 + 3H^+$$

Although the reaction has been quenched by considerable dilution, as soon as the acidic thiocyanate is added, the reaction proceeds immediately to completion.

C. Analysis of Fe^{3+} by E.D.T.A. titration using variamine blue as the indicator

The end point in an E.D.T.A. titration may sometimes be detected by changes in redox potential, hence by the use of appropriate indicators such as variamine blue B, it is possible to titrate ferric iron in a mixture of ferric and ferrous iron. In titrating with E.D.T.A., it is the former that disappears first. As soon as an amount of complexing agent equivalent to Fe^{3+} concentration has been added, pFe^{3+} increases abruptly and there is a sudden decrease in redox potential. The jump in redox potential will always be obtained even if no ferrous salt is added since the extremely small amount Fe^{2+} needed is always present in ferric salt.

Visible detection of redox change is made with variamine blue B



(a) (b)

The almost colourless leuco form of the base (a) passes upon oxidation into the strongly coloured indamine (b). When titrating ferric iron at pH3, and the colourless hydrochloride of the leuco base is added, oxidation to the blue complex (b) occurs with the formation of an equivalent amount of Fe^{2+} At the end point of the E.D.T.A. titration, the small amount offerrous iron formed when the indicator was introduced is also transformed into the Fe^{3+} E.D.T.A. complex, whereupon the blue indamine is reduced back to the leuco base.

20 ml reaction mixture were made neutral to congo Red by addition of ammonia. A few drops of the redox indicator were added and the whole titrated against E.D.T.A. Unfortunately although the method promised well, a clear end point could not be obtained. This was thought originally due to the presence of Cr(VI) and Cr(III), but even

the removal of these did not improve the clarity of the end point.

Table XXIX

Reaction Mixture of $1.2 \times 10^{-4}M\ H^+$, $8 \times 10^{-4}M\ Fe^{2+}$, $1 \times 10^{-4}M\ Cr_2O_7^{\ 2-}$

$\mu = 0.005$

Indicator: - 1% base in water.

Time (mins)	Titre (ml 0.001M EDTA/10 ml sample)
0.5	0.11
2.5	0.22
5	2.75
10	2.05
15	1.69

D. Attempt to follow the Reaction by change in pH

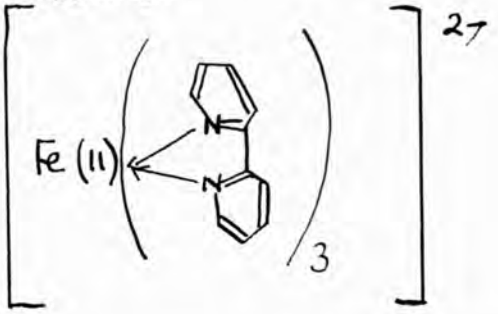
This was unsatisfactory because: -

i) If the reaction is carried out in a large excess of acid any small change in pH would be virtually impossible to detect.

ii) The pH fell during reaction (see later)

E. Colorimetric Analysis of Fe^{2+}

This method depends upon the formation of a red complex with α - α' dipyridyl



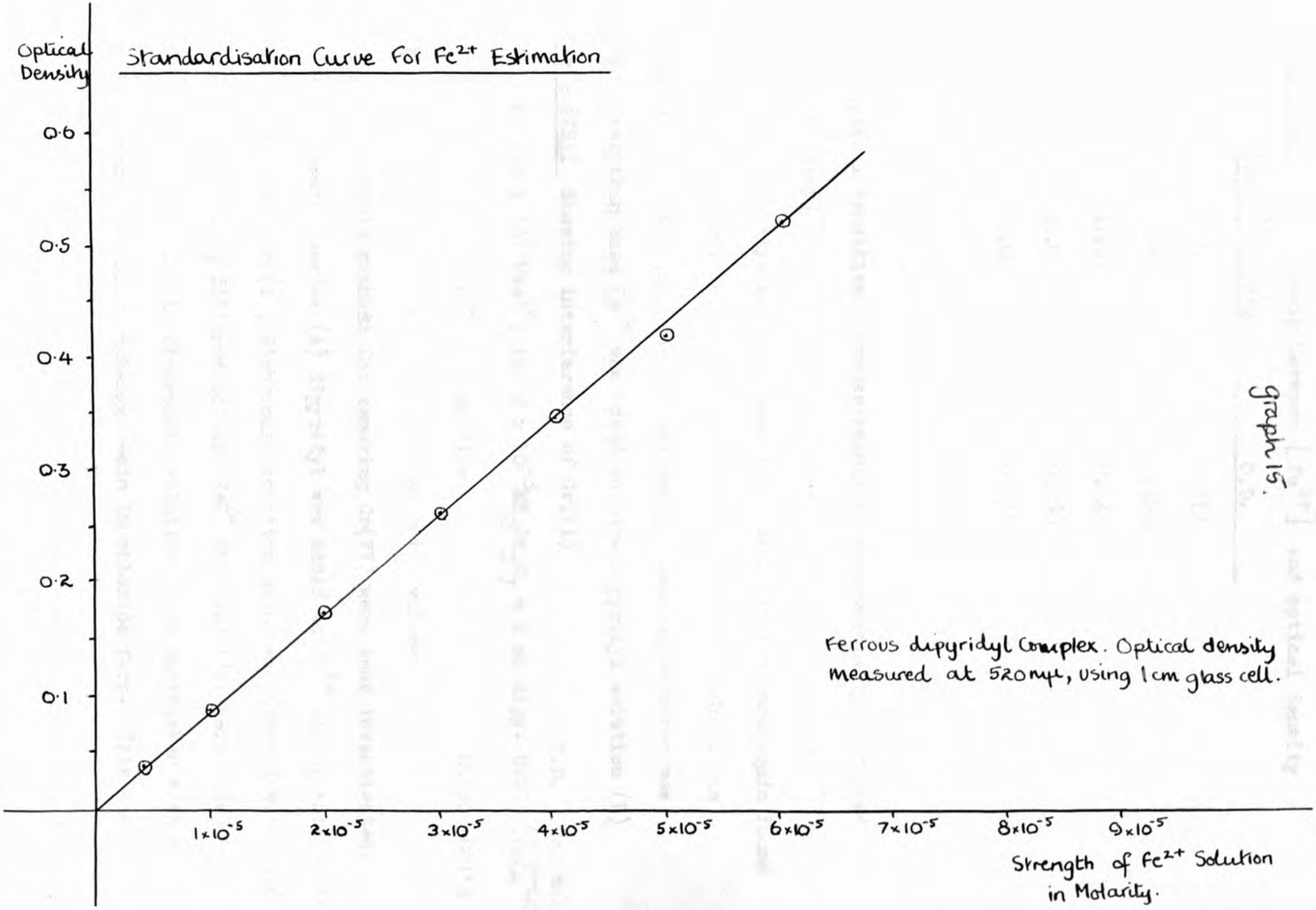
The wavelength at which maximum absorption occurs was found for the red complex and all later readings were made at this wavelength (520 mμ).

Table XXX Showing Wavelength at which Maximum Absorption Occurs for a Solution 6.2×10^{-4} M in Water

mμ	Transmission %	mμ	Transmission %
625	97.5	515	0.78
605	84.2	510	0.71
590	72.5	500	0.90
560	25.0	490	1.18
540	2.50	480	1.80
530	0.65	420	8.40
525	0.65		
522	0.59		
520	0.51		
519	0.60		

A standard optical density / concentration curve was prepared by adding 2 ml stock dipyridyl solution to a known quantity of Fe^{2+} and diluting to 50 ml. This was repeated over a range of iron concentrations. The red solution was then left for about an hour before being measured on a Unicam S.P. 500 or S.P. 600 at 520 mμ in a 1 cm silica cell.

graph 15.



Standardisation Curve For Fe^{2+} Estimation

Ferrous dipyridyl Complex. Optical density measured at 520 mμ, using 1 cm glass cell.

Table XXXI Relationship between $[Fe^{2+}]$ and optical density

$[Fe^{2+}] \times 10^5$M	O.D.
6.07	0.518
5.06	0.421
4.04	0.348
3.03	0.260
2.02	0.173
1.01	0.083
0.404	0.040

(The optical densities of these solutions were virtually unaltered 24 hours alter)

In analysis of the reaction mixture it was once again found that Cr(VI) interfered. If Fe^{2+} solution was added to Cr(VI) in dipyridyl solution (A), the optical density reading obtained was much lower than when Fe^{2+} was added to pure dipyridyl solution (B)

Table XXXII Showing interference of Cr(VI)

	O.D.	Cal.mol. of orig.
(A) 1 ml 1.6×10^{-3}MFe^{2+}, 1ml 4×10^{-3}M$K_2Cr_2O_7$ + 1 ml dipy.	0.207	.0006
(B) 1 ml 1.6×10^{-3}MFe^{2+}, + 1 ml dipy	0.540	.00158

(Both (A) and (B) were made up to 25 ml total volume)

Simple methods for removing Cr(VI) were thus investigated. In the following series (A) dipyridyl was added to Fe^{2+} alone, this is the control series. In (B), dichromate solution alone was treated with lead nitrate, the $PbCrO_4$ filtered off and Fe^{2+} and dipyridyl were added to the filtrate. In (C) dichromate solution alone was shaken with a small quantity of anion exchange resin in chloride form. This was then filtered through glass wool and treated as in (B). The following results indicate that the interfering chromate was effectively removed by (B) and (C). Since (C) was much the simpler and more rapid method it was adopted.

Table XXXIII

	Sample	Fe^{2+} Molarity Found	Fe^{2+} Molarity Theoretical
i)	A	.000368	.00038
	B	.00036	.00038
	C	.00036	.00038
ii)	A	.00073	.00074
	B	.00074	.00074
	C	.00074	.00074

Besides eliminating a source of interference in the analysis, removal of Cr(VI) ions

i) Stopped the reaction

ii) Removed the yellow colour which might have some absorption at 520mμ and hence interfere with the optical measurements.

2. GENERAL TECHNIQUE ADOPTED

A suitable method for Fe^{2+} analysis having now been established, the reaction could now be studied. The solutions were placed in the thermostat. Potassium dichromate, perchloric acid and any other necessary materials, made up to a total volume of 100 ml, were placed in a 250 ml reagent bottle (A) and 100 ml ferrous sulphate solution were placed in a similar vessel (B). After thermal equilibrium, the solutions were mixed by carefully pouring (B) into (A), and then back into (B). At timed intervals samples were withdrawn by pipette into a flask containing amion exchange resin, and were well shaken before being filtered through glass wool into a 25ml (or 50 ml) volumetric flask containing 1 ml (or 2 ml) stock dipyridyl solution. After the necessary dilution, the solutions were left for one hour before the optical density was measured on a Unicam S.P. 500 or S.P 600, both spectrophotometers giving identical readings.

For very fast reactions the method was adapted slightly. The reaction vessel used in this case was a small round bottomed flask with an indented division in the bottom, thus giving two sepearate compartments. 2 ml chromic acid were measured into one compartment and 2 ml ferrous solution into the other. After thermal equilibrium the solutions were mixed by shaking the flask. The reaction was stopped by adding to the reaction vessel a quantity of the resin, and then the analysis was continued in the usual manner. By this method it was possible to obtain reasonably reproducible results at 3 seconds, although, of course, only 1 reading could be obtained from each experiment.

All the reagents used were of "analar" grade. The stock dipyridyl solution was 0.025 M $\alpha - \alpha'$ dipyridyl and 0.05M $HClO_4$. The resins used in order to stop the reaction were: -

a) Amberlite IRA 400 (Cl^-) resin

b) Deacidite FF (SRA 65) Cl^- form

Table XXXIV Showing Change in $[Fe^{2+}]$, during a typical run at 25°C and $\mu = 0.005$

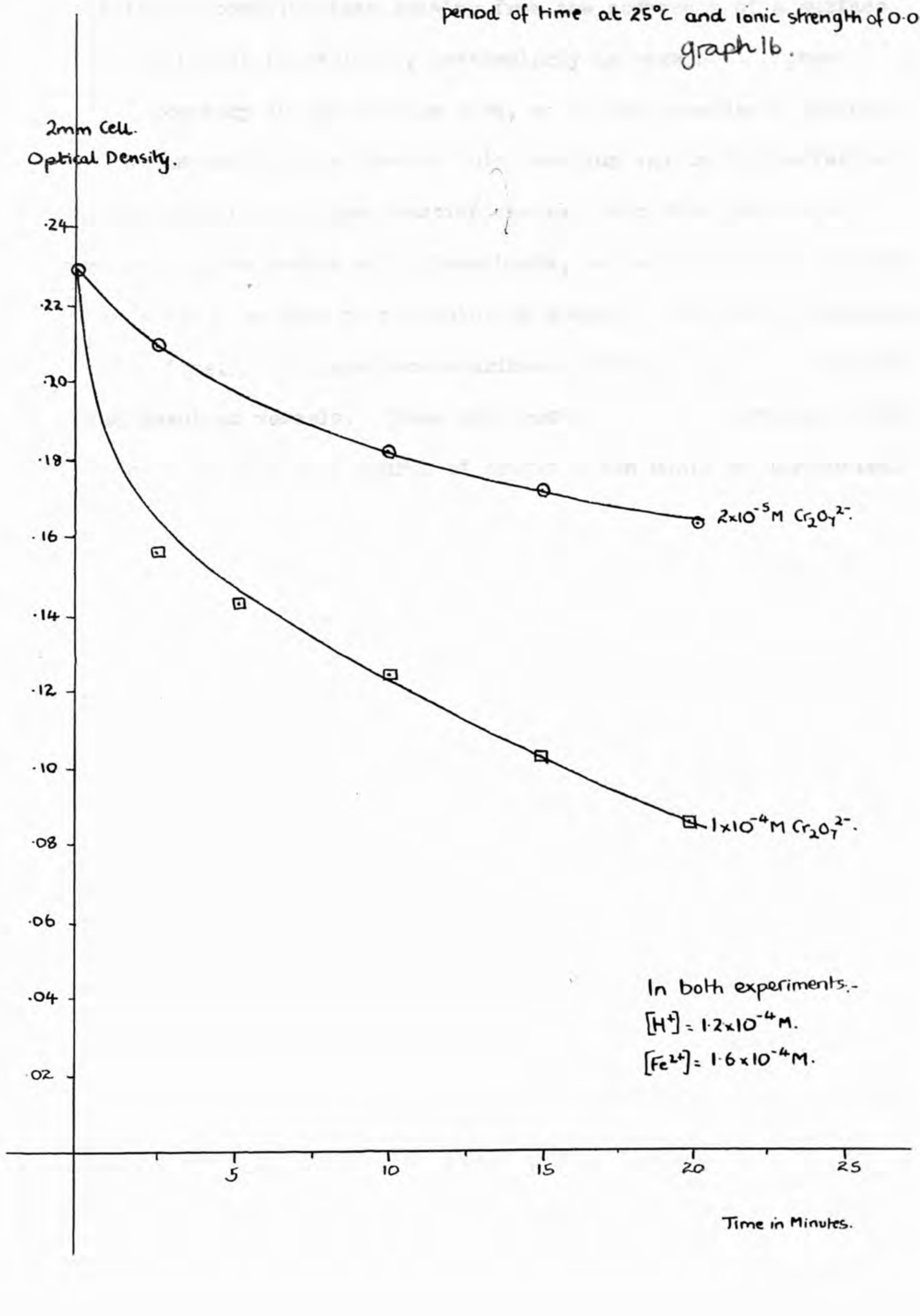
Reaction Mixture of 1.35×10^{-4}M Fe^{2+}, 2.5×10^{-5}M$Cr_2O_7^{2-}$, 9×10^{-4}MH^+

Time (mins)	$[Fe^{2+}] \times 10^4$M
0	1.35
0.25	1.33
0.50	1.31
1	1.29
3	1.20
6	1.05
10	0.90
15	0.81

Chromic Acid Oxidation of Ferrous Iron.

Two typical reactions followed over a short period of time at 25°C and ionic strength of 0·005.

graph 16.



In both experiments.-
$[H^+] = 1{\cdot}2\times10^{-4}$M.
$[Fe^{2+}] = 1{\cdot}6\times10^{-4}$M.

3. THE EFFECT OF SURFACE UPON THE REACTION

As many ions are absorbed readily on a glass surface, the possibility of complications arising from the ocdurence of a surface reaction could not be excluded, particularly in view of the great dilution necessary in the kinetic work, so it was considered advisable to test at an early stage whether this reaction was in fact affected by the surface of the glass reaction vessel. For this purpose a reagent bottle was packed with glass beads, so as to increase the area of glass surface exposed to the solution several times that present in the bottle itself. Comparative experiments were made with packed and unpacked reaction vessels. These gave results in good agreement with one another, so that this source of complication could be discounted.

Table XXXV.

A. Reaction Mixture $[Cr_2O_7^{2-}] = 2 \times 10^{-5}M$ $[H+] = 1.2 \times 10^{-4}M$
$[Fe^{2+}] = 1.6 \times 10^{-4}M$

Time (mins)	Control $[Fe^{2+}] \times 10^4M$	Increased S.A. $[Fe^{2+}] \times 10^4M$
2.5	1.53	1.56
5	1.34	1.31
10	1.26	1.27
15	1.25	1.24
20	1.19	1.17
25	1.17	1.13

B. Reaction Mixture $[Cr_2O_7^{2-}] = 1 \times 10^{-4}M$ $[H^+] = 1.2 \times 10^{-4}M$
$[Fe^{2+}] = 1.6 \times 10^{-4}M$

Time (mins)	Control $[Fe^{2+}] \times 10^4M$	Increased S.A. $[Fe^{2+}] \times 10^4M$
2.5	1.09	1.10
5	1.03	1.01
10	0.90	0.87
15	0.75	0.73
20	0.62	0.63
25	0.57	0.55

4. Effect of Exposure to Light.

The possibility of a photochemical reaction, as well as a purely thermal one, was studied by carrying out two parallel experiments. In the first, the reaction vessel was exposed to normal laboratory illumination, whilst in the second, the reaction was carried out in a brown glass vessel. There was no difference in reaction rate, so that in later experiments, photochemical complications could also be ignored.

Table XXXVI.

A. Reaction Mixture $[Cr_2O_7^{2-}] = 2 \times 10^{-5}M$ $[H^+] = 1.2 \times 10^{-4}M$
$[Fe^{2+}] = 1.6 \times 10^{-4}M$

Time (mins)	Control $[Fe^{2+}] \times 10^4 M$	Dark Expt. $[Fe^{2+}] \times 10^4$
2.5	1.53	1.53
5	1.34	1.30
10	1.26	1.27
15	1.25	1.24
20	1.19	1.19
25	1.17	1.16

B. Reaction Mixture $[Cr_2O_7^{2-}] = 1 \times 10^{-4}M$ $[H^+] = 1.2 \times 10^{-4}M$
$[Fe^{2+}] = 1.6 \times 10^{-4}M$

Time (mins)	Control $[Fe^{2+}] \times 10^4 M$	Dark Expt. $[Fe^{2+}] \times 10^4$
2.5	1.09	1.10
5	1.03	1.06
10	0.90	0.92
15	0.75	0.73
20	0.62	0.62
25	0.57	0.58

SECTION 2.

Factors Affecting the Reaction.

The conditions for obtaining reproducible results had now been established. A typical series of results recorded during the course of the reaction are shown below. The general pattern of the reaction curve is obtained by plotting $[Fe^{2+}]$ remaining against time.

Table XXXVII.

Reaction Mixture $[Cr_2O_7^{2-}] = 2 \times 10^{-5}M$ $[Fe^{2+}] = 1.6 \times 10^{-4}M$

$[H^+] = 2.4 \times 10^{-4}M$

$T = 25^oC.$ $\mu = 0.005.$

Time (mins)	$[Fe^{2+}] \times 10^4 M$
2.5	1.45
5	1.36
10	1.22
15	1.14
20	1.11
25	1.06

This reaction has a very high initial rate. The fall off in rate is due either to the decreasing concentration of reactants as a reaction of high order proceeds, or possibly due to the formation of inhibitory products. Factors having an affect upon the rate were now examined.

1. Concentration Ratio of the Reactants Varied.

Over a range of temperature and concentration, at constant ionic strength, the reaction is found to be fifth order. The following results show that the reaction between chromic acid and ferrous iron is first order with respect to hydrogen ion and second order with respect to each of the other two reactants. Using:-

$$-\frac{dc}{dt} = Kc$$

$$\log\left(-\frac{dc}{dt}\right) = \log K + n\log c.$$

therefore plotting log K against log concentration reactant should giv e the order with respect to the reactant being investigated. In practice initial rates were used for this purpose in order to eliminate any affects arising later in the reaction mechanism. The initial rate $\left(\frac{dc}{dt}\right)$ was found from the $[Fe^{2+}]$ /time graph by measuring the slope of the curve at zero time.

The rate slows down as reaction proceeds mainly due to reactants being used up. This can be demonstrated quite simply by adding to the spent reaction mixture that reactant originally present in the react quantity. It will be found that there is a sudden acceleration in rate.

Table XXXVIII - Showing increase in initial rate with increased reaction concentration.

I. Varying $[Fe^{2+}]$

$[Cr_2O_7^{2-}] = 2 \times 10^{-5}$M $[H^+] = 1.2 \times 10^{-4}$M T = 25°C.
$\mu = 0.006$

$[Fe^{2+}] \times 10^4$M	Initial Rate (moles $Fe^{2+} \times 10^4$ mins^{-1})
0.38	0.003
0.71	0.004
1.66	0.056
2.95	0.079
3.50	0.155
4.80	0.295
6.60	0.488
7.05	0.56

graph 18

II. Varying $[H^+]$

$[Cr_2O_7^{2-}] = 2 \times 10^{-5}$M $[Fe^{2+}] = 1.6 \times 10^{-4}$M T = 25°C
$\mu = 0.005$

$[H^+] \times 10^4$M	Initial Rate (moles $Fe^{2+} \times 10^4$ mins^{-1})
1.2	0.056
2.4	0.104
3.6	0.166
6.0	0.180
7.2	0.224
9.0	0.260
18.0	0.700
36.0	1.54

graph 17

III. Varying [Dichromate]

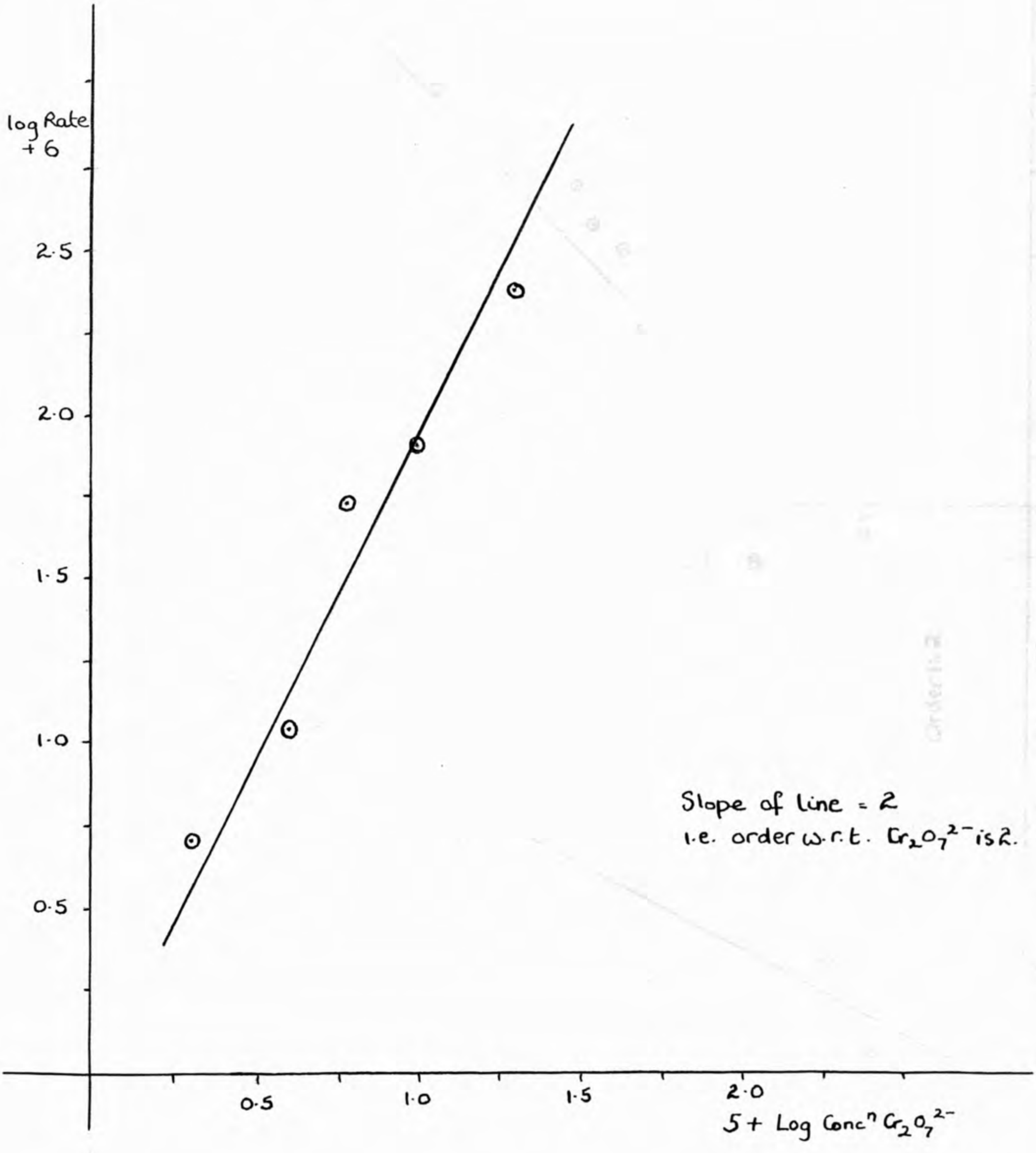
$[H^+] = 1.2 \times 10^{-4}$M $[Fe^{2+}] = 1.6 \times 10^{-4}$M T = 25°C
$\mu = 0.005$

$[Cr_2O_7^{2-}] \times 10^4$M	Initial Rate (moles $Fe^{2+} \times 10^4$mins^{-1})
0.2	0.054
0.4	0.128
0.6	0.56
1.0	0.87
2.0	1.74

graph 16.

To Find Order with respect to Dichromate- 25°C.

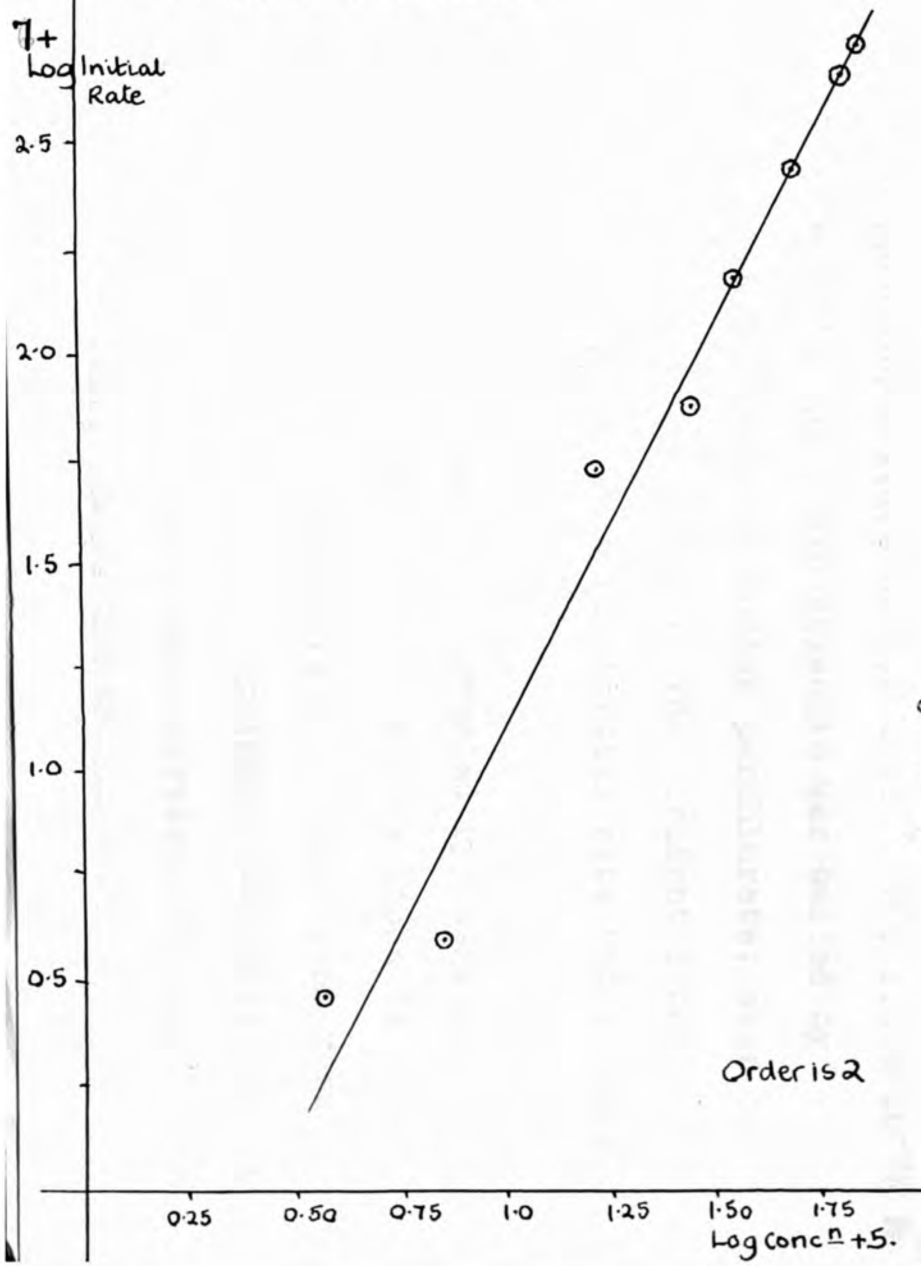
graph 17.



Slope of line = 2
i.e. order w.r.t. $Cr_2O_7^{2-}$ is 2.

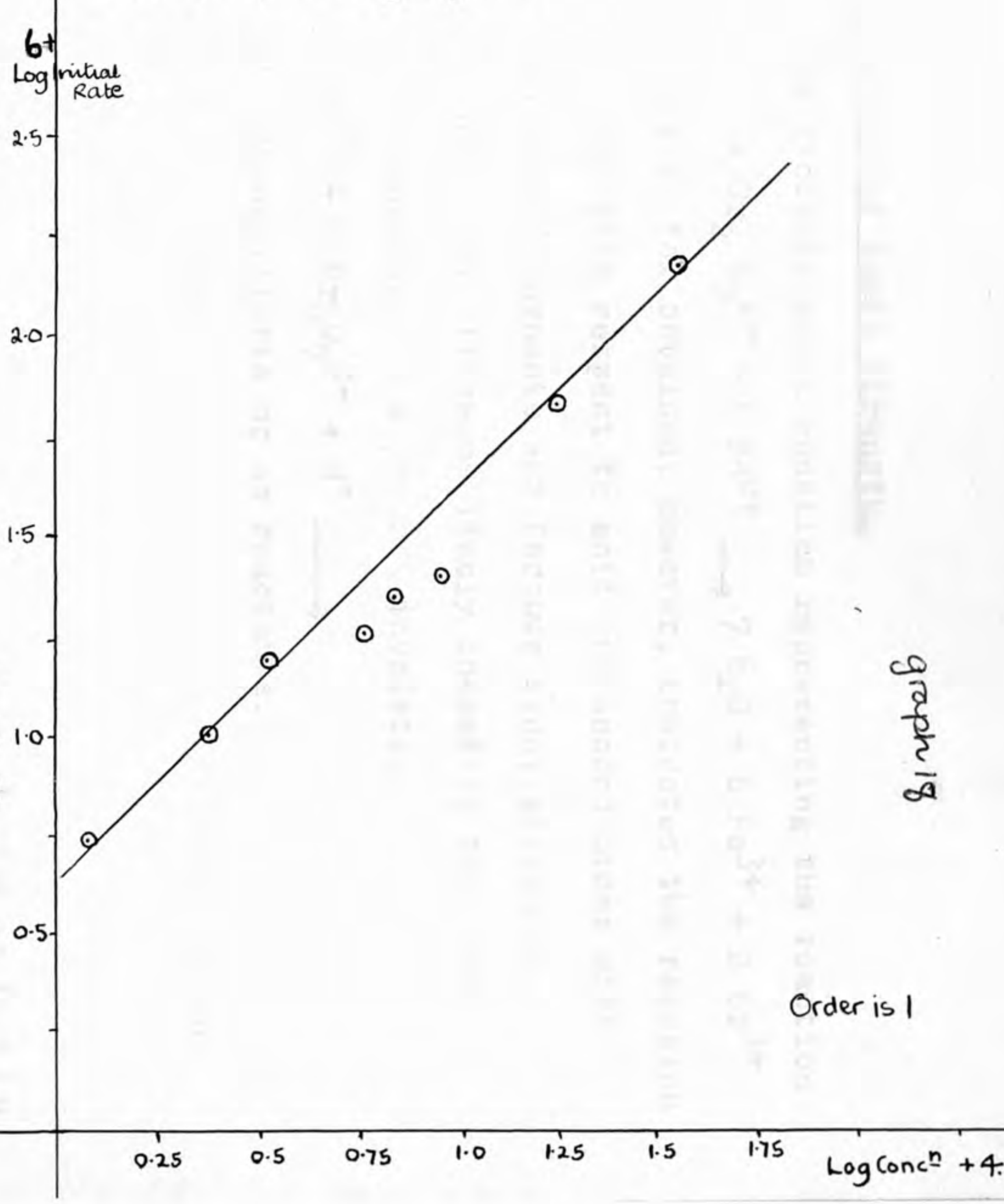
To Find the Order of Reaction:-

1. With respect to ferrous Iron.



graph 19

2. With respect to hydrogen ion.



graph 18

2. Variation of Ionic Strength.

The stoichiometric equation representing the reaction is - $14\ H^+ + Cr_2\ O_7^{2-} + 6\ Fe^{2+} \longrightarrow 7\ H_2O + 6\ Fe^{3+} + 2\ Cr^{3+}$ the evidence so far obtained, however, indicates the reaction is first order with respect to acid and second order with respect to both dichromate and ferrous iron, giving an overall order of 5. It seems likely therefore that the rate determining step is a process involving:-

$$2\ Fe^{2+} + 2\ Cr_2O_7^{2-} + H^+ \longrightarrow \ldots\ldots$$

either in pre-equilibria or as reactants.

Further information can be obtained by application of the Debye-Huckel theory. The equation

$$\ln K = \ln K_o + Z_A\ Z_B\ \alpha\sqrt{\mu}$$

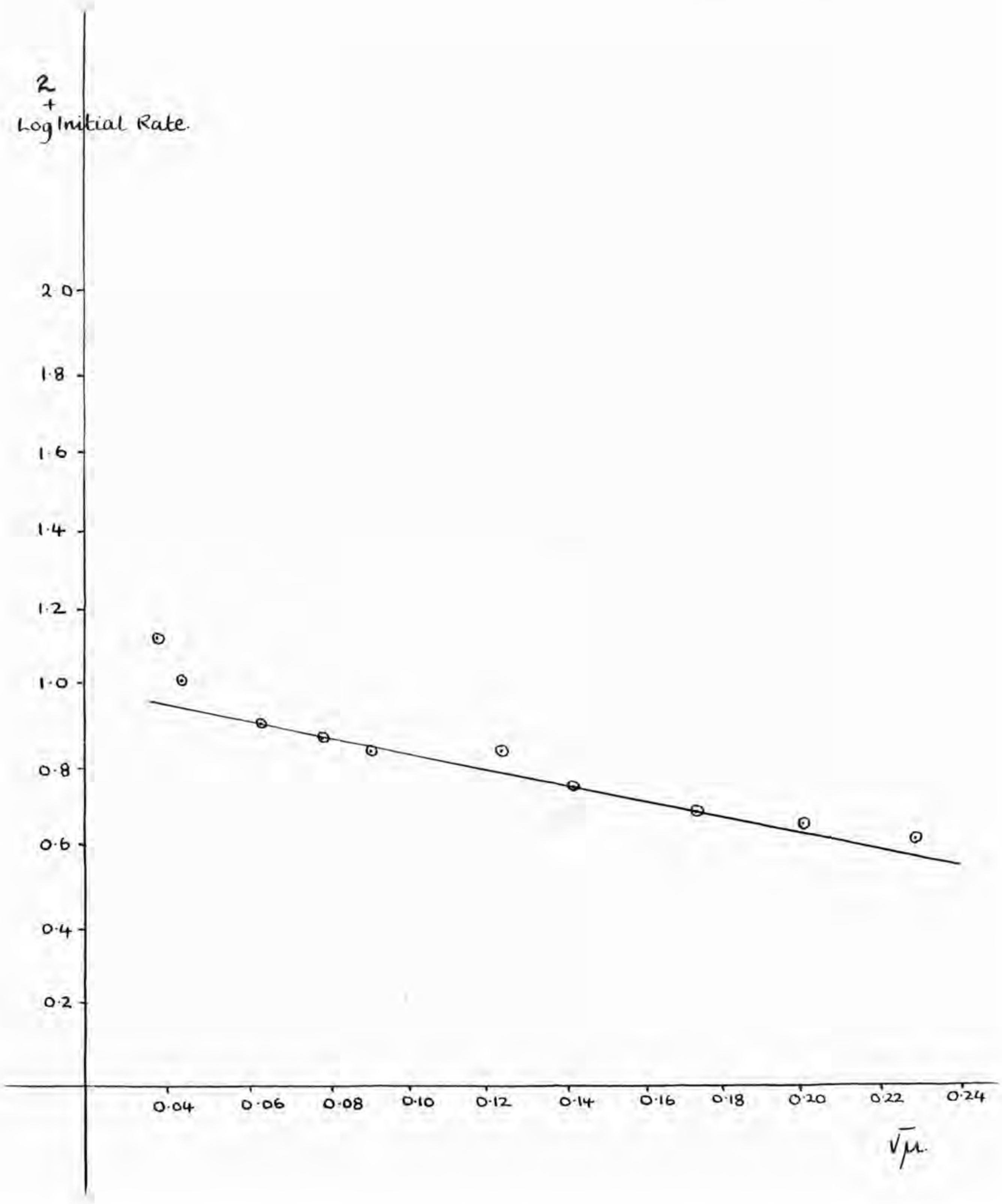
predicts a linear relationship if log K is plotted against $\sqrt{\mu}$.

Using a reaction mixture of 1.2×10^{-4}M H^+, 1.6×10^{-4}M Fe^{2+} and 1×10^{-4}M $Cr_2O_7^{2-}$, the ionic strength was varied by using varying concentrations of sodium perchlorate, over quite a considerable range at 25°C. The straight line obtained by plotting $\sqrt{\mu}$ against log initial rate had a slope of -2. (see graph 19)

The ionic strength was mostly varied by means of Na ClO_4, although at very high ionic concentrations it was found that sodium chloride often gave more consistent results. In most experiments, because of this primary salt effect, the ionic strength had to be fixed by the addition of the required amount of a neutral salt, always the sodium salt of the acid present.

Variation of Initial Rate with Ionic Strength.

graph 20.



3. The Effect of Oxygen.

As the presence of additional oxygen caused an increase in rate in the $Cr(VI)/I^-$ reaction when dilute solutions were used, experiments were carried out on the $Cr(VI)/Fe^{2+}$ reaction to see if there was any similar effect. Two comparable experiments were carried out. One, the control experiment was done under normal conditions and the other, having the reactants well saturated with oxygen before mixing and oxygen continually bubbled through the solution during reaction time. As the results below show, there was no difference in rate.

Table XXXIX.

Time (mins)	Control $[Fe^{2+}] \times 10^4 M$	Oxygenated Expt. $[Fe^{2+}] \times 10^4 M$
2.5	1.53	1.53
5	1.34	1.31
10	1.26	1.25
15	1.25	1.21
20	1.19	1.19
25	1.17	1.17

Reaction Mixture $[Cr_2O_7^{2-}] = 2 \times 10^{-5}M$ $[H^+] = 1.2 \times 10^{-4}M$

$[Fe^{2+}] = 1.6 \times 10^{-4}M$

$\mu = 0.005$ $T = 25^{\circ}C.$

4. The Effect of Temperature

The rate of reaction varies with temperature according to the Arrhenius Equation:-

$$K = A e^{-E/RT}$$

In the chromic acid oxidation of iron, the rate increases with increasing temperature, and the energy of activation for the reaction was found to be I5.43 Kcal/ gram mole.

Table XL

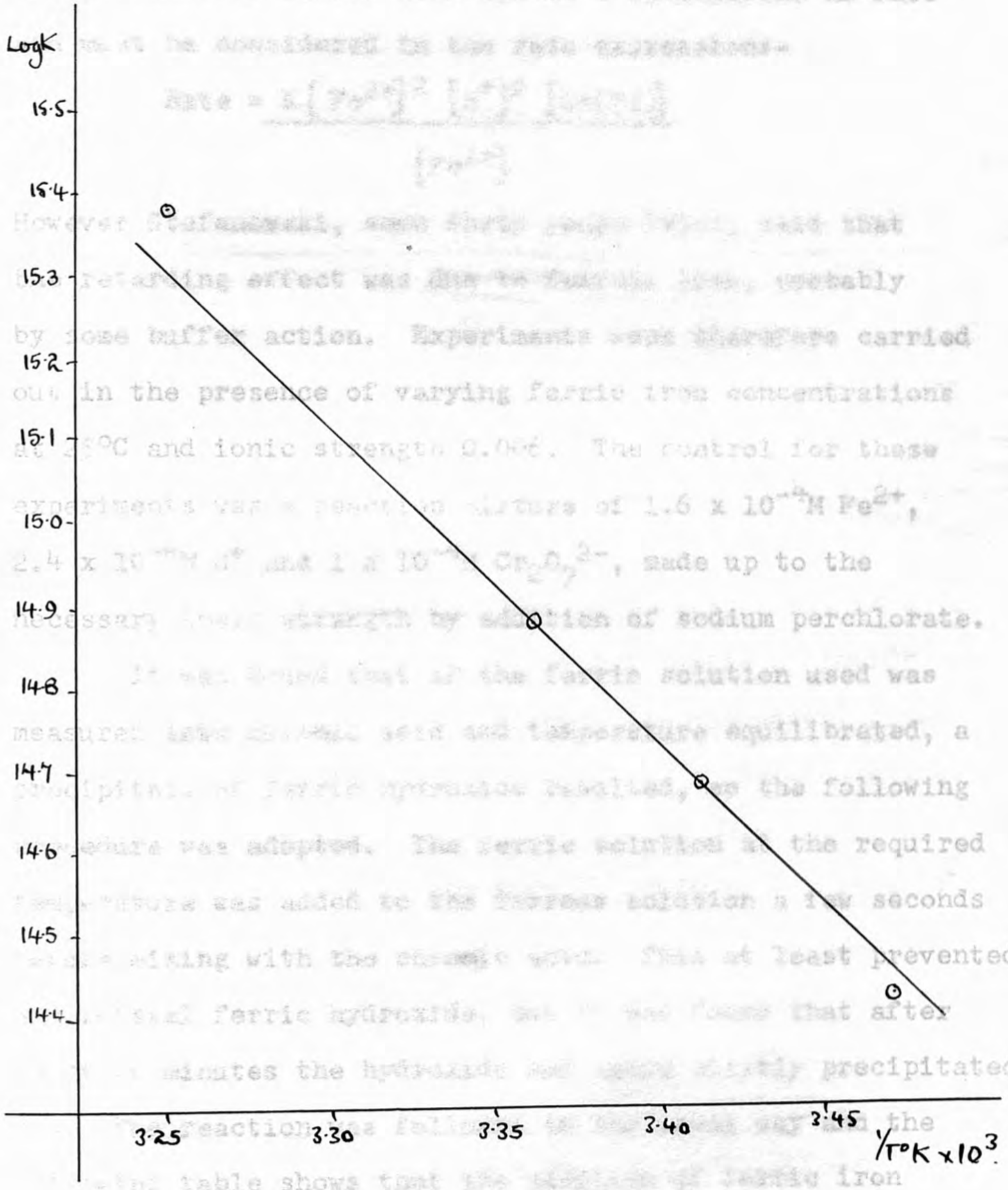
K(1^{4} moles^{-4} mins^{-1})	Temp.° C
2.39 x IO^{I5}	35
0.8I	25
0.48	20
0.27	14.5

Variation of Rate(K) with Temperature - graph 21

$$\text{Log } K = \frac{-E}{RT} + \text{Constant}$$

$$E = \frac{0.39 \times 4.575}{0.12 \times 10^3}$$

$$= 15.43 \text{ Kcal/gram mole.}$$



5. Effect of Adding Products to the Reaction Mixture.

A. Ferric Ions.

There seems to be some doubt as to the action of ferric salts upon the reaction. According to Benson, the presence of ferric iron causes a retardation in rate and must be considered in the rate expression:-

$$\text{Rate} = \frac{K\left[Fe^{2+}\right]^2 \left[H^+\right]^2 \left[Cr(VI)\right]}{\left[Fe^{3+}\right]}$$

However Stefanovski, some forty years later, said that the retarding effect was due to ferrous iron, probably by some buffer action. Experiments were therefore carried out in the presence of varying ferric iron concentrations at 25°C and ionic strength 0.006. The control for these experiments was a reaction mixture of 1.6×10^{-4}M Fe^{2+}, 2.4×10^{-4}M H^+ and 1×10^{-4}M $Cr_2O_7^{2-}$, made up to the necessary ionic strength by addition of sodium perchlorate.

It was found that if the ferric solution used was measured into chromic acid and temperature equilibrated, a precipitate of ferric hydroxide resulted, so the following procedure was adopted. The ferric solution at the required temperature was added to the ferrous solution a few seconds before mixing with the chromic acid. This at least prevented any initial ferric hydroxide, but it was found that after about 20 minutes the hydroxide had again visibly precipitated out. The reaction was followed in the usual way and the following table shows that the addition of ferric iron appears to have no effect upon the rate, even changing the concentration four times. This is somewhat surprising because if $Fe(OH)_3$ is formed, and it apparently is, the H^+ concentration is increased and this should accelerate reaction slightly. As will be seen later, we think the lack of effect is due to an approximate cancelling of opposing effects.

Table XLI.

Time (mins)	Control Expt.	1.1×10^{-4}M Fe^{3+}	2.2×10^{-4}M Fe^{3+}	4.3×10^{-4}M Fe^{3+}
0	1.69	1.69	1.69	1.69
1	1.29	1.31	1.30	1.34
3	1.24	1.14	1.18	1.16
6	1.09	1.09	1.11	1.11
10	0.98	0.98	1.00	1.00
15	0.84	0.90	0.86	0.84
20	0.75	0.80	0.76	0.80
25	0.68	0.68	0.68	0.68

Figures given on the table are $[Fe^{2+}] \times 10^{-4}$M.

A series of experiments was then carried out in a buffered medium; this would prevent the ferric hydroxide from precipitating out and so prevent the consequent rise in$[H^+]$. The buffer used was a mixture of N sodium acetate and N hydrochloric acid, having an initial pH of 2.9, but an effective pH of 3.4 in the reaction mixture. 5 ml of this buffer were added to 1 ml 0.01 M $K_2 Cr_2 O_7$. The ionic strength was adjusted to 0.048 with Nacl. Before diluting this solution to 100 ml, a known quantity Fe^{3+} was added. Having been temperature equilib~~e~~rated, this solution was mixed with further 100 ml solutions containing 1 ml 0.016 M Fe^{2+}.

Samples were removed at intervals and the ferrous iron estimated as previously. This was repeated several times using different amounts of ferric iron.

In a buffered medium, the addition of ferric ions does lower the reaction rate. Thus the "null" effect in the previous set of experiments was due to retardation by Fe^{3+} coupled with acceleration due to H_3O^+ ions being produced. A typical series of results is shown in the following table.

Table XLII.

Time (mins)	Control	$1 x 10^{-5}$M Fe^{3+}	$5 x 10^{-5}$M Fe^{3+}	$2.5 x 10^{-4}$M Fe^{3+}	$5 x 10^{-4}$M Fe^{3+}
0	$7.85 x 10^{-5}$	$7.85 x 10^{-5}$	$7.85 x 10^{-5}$	$7.85 x 10^{-5}$	$7.85 x 10^{-5}$
1	6.12	6.33	6.62	7.60	7.73
3	5.15	5.40	5.85	7.29	7.44
6	4.25	4.38	5.30	6.90	7.12
10	3.83	4.28	4.70	6.28	6.70
15	3.48	3.78	4.29	5.98	6.44
20	3.20	3.38	4.00	5.45	6.00

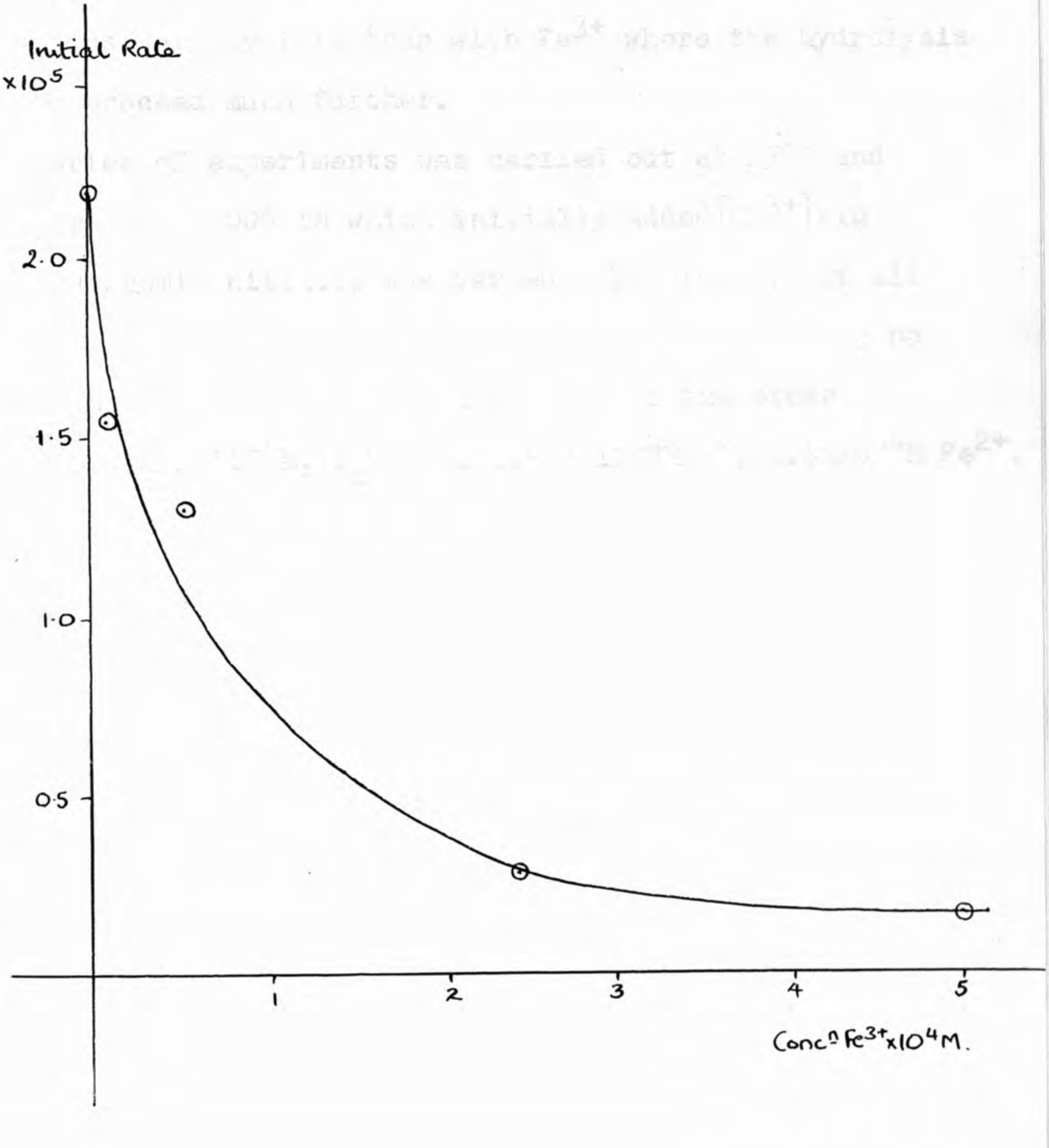
Table shows $[Fe^{2+}] x 10^{-5}$M

Reaction mixture := $[Cr_2O_7^{2-}] = 1 \times 10^{-4}$M, $[Fe^{2+}] = 1 \cdot 6 \times 10^{-4}$ pH = 3·4 $\mu = 0 \cdot 048$

Ferric ions may have their retarding effect due to combination with dichromate. It was noted that on the addition of ferric iron to dichromate, a deep golden yellow colour resulted. Both the ultra-violet and visible spectrun of this complex show detectable differences from the summed spectra of the components, e.g. there is a strongly absorbing peak at 360 ,mμ. The spectrum also showed almost complete absence of a peak at 250 mμ where ferric iron absorbs strongly. (see page 116)

To Show that the presence of Fe^{3+} has a retarding effect upon reaction rate.

graph 22.



6. Chromic Ions.

As ferric ions produced no effect, in the unbuffered reaction, upon the rate it seemed reasonable to expect that chromic ions also would have no retarding or accelerating effects upon the reaction. Slight hydrolysis occurs,

$$Cr^{3+} + 2\,H_2O \longrightarrow (Cr\,O\,H)^{2+} + H^{2+} + H_3O^{+}$$

giving increase in hydrogen ion concentration, but the effect is considerably less than with Fe^{3+} where the hydrolysis is known to proceed much further.

A series of experiments was carried out at 25°C and at ionic strength 0.006 in which initially added $[Cr^{3+}]$ (in the form of chromic nitrate) was varied. The results of all those experiments were compared to the control containing no added Cr^{3+}, but having the same quantities of the other reactants i.e. 1×10^{-4}M, $K_2Cr_2O_7$, 2.4×10^{-4}M H^+, 1.6×10^{-4}M Fe^{2+}.

Table XLIII - Showing comparative Rates of Reaction.

Time (mins)	Control	1 x 10^{-4} Cr^{3+}	2 x 10^{-4} Cr^{3+}	3 x 10^{-4}M Cr^{3+}	4 x 10^{-4}M Cr^{3+}	5 x 10^{-4}M Cr^{3+}
0	1.69x10^{-4}	1.69 x 10^{-4}	1.69 x 10^{-4}	1.69 x 10^{-4}	1.69 x 10^{-4}	1.69x10^{-4}
1	1.29	1.24	1.20	1.11	1.20	1.17
3	1.24	1.11	1.09	1.00	1.05	1.00
6	1.09	1.01	0.94	0.90	0.89	0.84
10	0.98	0.85	0.75	0.77	0.75	0.70
15	0.84	0.76	0.65	0.65	0.58	0.55
20	0.75	0.63	0.54	0.55	0.50	0.47
25	0.68	0.55	-	0.45	0.43	0.40

Table shows decrease in $[Fe^{2+}]$ x 10^{4}M

Reaction Mixture = 1×10^{-4}M $K_2Cr_2O_7$, $2{\cdot}4 \times 10^{-4}$M H^+, $1{\cdot}6 \times 10^{-4}$M Fe^{2+}

Two comments should be made here. The acceleration is presumably due to hydrolysis of Cr^{3+}, yielding hydrogen ion. Secondly the amount of acceleration is relatively small considering the concentration of Cr^{3+} which builds up during our normal kinetic runs in which there is no deliberate initial addition of Cr^{3+}.

SECTION 3.

Further Investigations into the Reaction.

1. Measurement of pH through the reaction.

When preliminary experiments were being carried out, it was found impossible to follow the reaction by pH methods as the hydrogen ion concentration increased during the course of the reaction. The pH change during a typical reaction is recorded below (Table XLIV). Measurements were made using a Doran pH meter, standardised over the pH range investigated by means of buffers of known pH. Measurements were made using a glass electrode, with calomel as the reference electrode. Before use, the glass electrode was soaked in HCl for at least 24 hours.

The reactants were mixed into a wide necked vessel, clamped in the thermostat~~e~~, and the electrodes were then carefully lowered into the reaction mixture. Readings could now be easily taken at any moment.

Table XLIV.

Reaction Mixture $[Cr_2O_7^{2-}] = 1x10^{-4}M$ $[H^+] = 1.2x10^{-4}M$ $[Fe^{2+}] = 1.6x10^{-4}M$
$T = 25^{\circ}C$ $\mu = 0.005$.

Time (mins)	pH
0.5	3.85
1	3.85
2	3.78
3	3.74
5	3.63
10	3.58
12	3.49
16	3.43
20	3.36
24	3.35

This result is obtained despite the fact that hydrogen ion is written stoichiometrically as a reactant. Clearly a product (Fe^{3+}) undergoes hydrolysis and produces more hydrogen ion than is consumed in the main reaction.

The pH could quite easily be kept constant, however, by means of buffers. These buffers were prepared by mixing N sodium acetate with N hydrochloric acid in differing proportions. However the effective pH depends upon the solution conditions so the pH was measured when 10 ml buffer were added to the reactants.

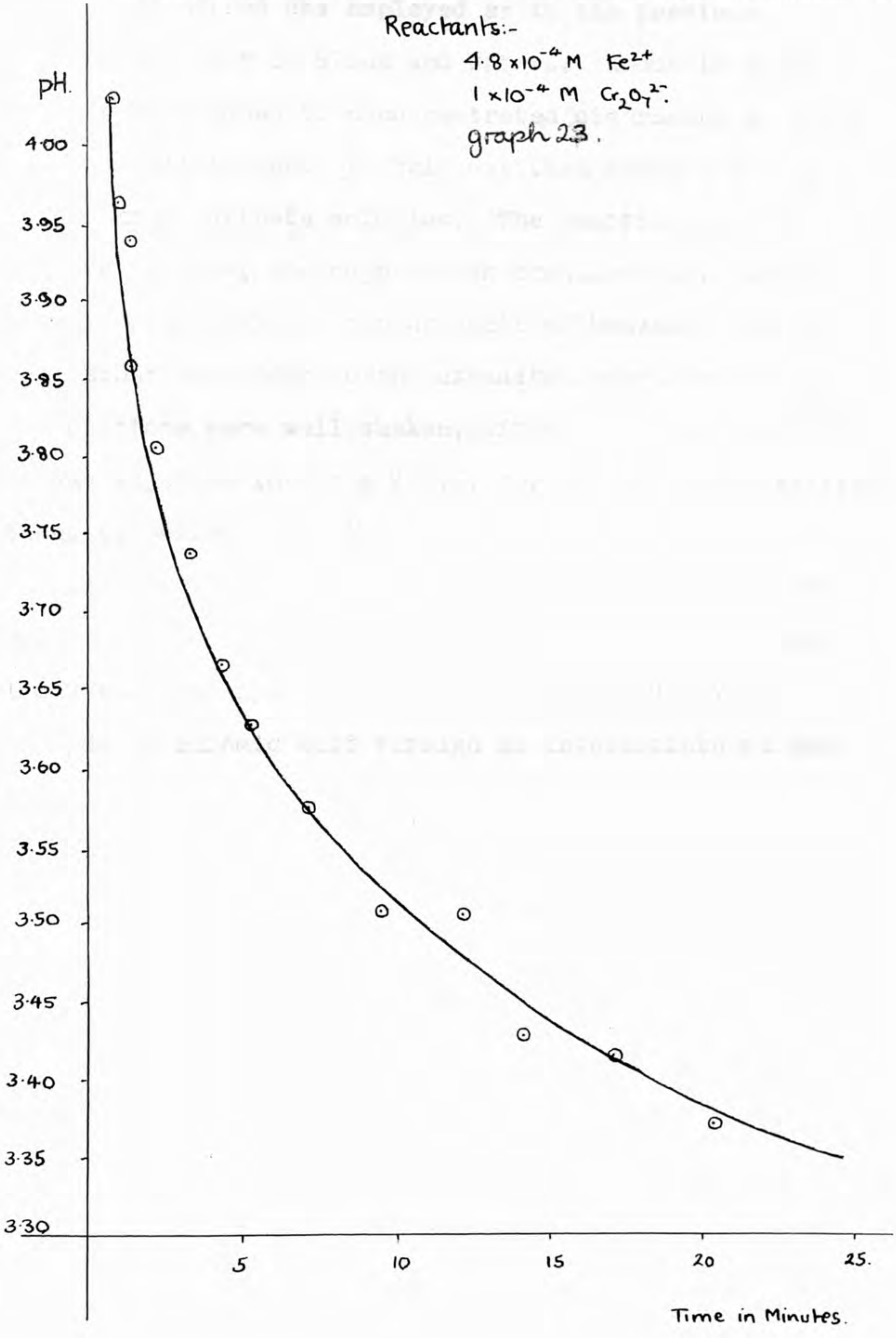
Table XLV - showing constancy of pH using buffer.

Reaction Mixture: $[Fe^{2+}] = 1.6 \times 10^{-4}M$ $[Cr_2O_7^{2-}] = 1 \times 10^{-4}M$
$[H^+] = 1.2 \times 10^{-4}M$ $\mu = 0.025$ $T = 25°C$.

Time(mins)	pH
0.25	2.55
1.5	2.55
4.5	2.53
10	2.53
15	2.54
25	2.54

The buffer used was prepared by using 50 ml N NaOAc and 55 ml N HCl, which was diluted to 250 ml, giving a nominal pH of 1.71. 10 ml of this solution were added to the reactants, giving a final pH of 2.55. In these buffered reactions, the reaction is slowed because hydrogen ion concentration is prevented from rising.

Variation in pH during the Chromic Acid Oxidation of Ferrous Ions



II. Determination of Intermediate Valency.

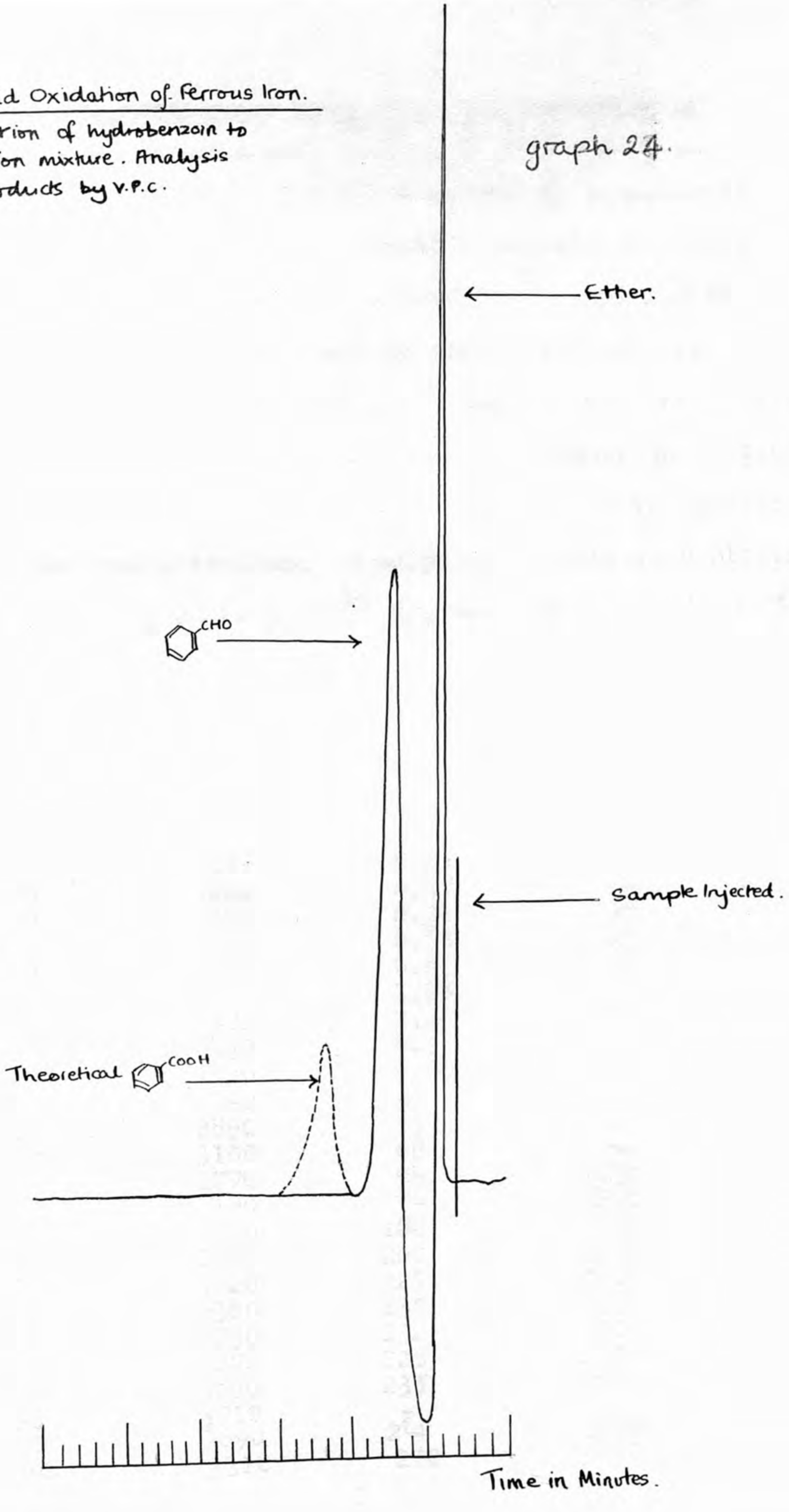
The same method was employed as in the previous reaction, namely that of Slack and Waters. About 10 grams hydrobenzoin were added to a concentrated dichromate solution in acid, and well shaken. To this was then added a strong ferrous ammonium sulphate solution. The reaction was left for about 20 minutes, although shaken occasionally. Almost immediately after mixing a strong smell of benzaldehyde was noticed. Ether was added to the exhausted reaction mixture and the solutions were well shaken, after which the ethereal extract was injected into the V.P.C. apparatus, having similar conditions as before (page 70)

A large peak was obtained after 3 minutes; this was the benzaldehyde. No further peaks occurred and so it was concluded that the hydrobenzoin was oxidised purely to benzaldehyde by chromic acid through an intermediate valency of five.

Chromic Acid Oxidation of Ferrous Iron.

Addition of hydrobenzoin to reaction mixture. Analysis of products by V.P.C.

graph 24.



III. Spectrophotometric Studies on the Oxidation of Fe^{2+} by $H\,Cr\,O_4^-$

In this reaction the whole series of experiments were followed by a spectrophotometric method, but it was hoped to be able to develop a direct reading method by allowing the reaction to occur in the silica cell in the appropriate thermostatted compartment. The most simple way in which to do this is to follow the change in optical density due either to formation of products or to decrease in reactant concentration. Absorption spectra were obtained for Fe^{3+}, $K_2\,Cr_2\,O_7$ (2×10^{-4}M $Cr_2\,O_7^{2-}$ in 2×10^{-4}M $H\,Cl\,O_4$) and Fe^{2+}.

Table XLVI.

Mμ	E $K_2Cr_2O_7$(in H^+)	E Fe^{2+}	E Fe^{3+}
500	74	0.16	12
490	129	0.24	8
470	262	0.27	12
450	390	0.34	15
430	449	0.56	19
420	515	0.81	26
410	582	1.25	35
400	902	2.25	58
390	1439	4.5	107
380	1740	9.00	196
370	2390	26	354
360	2890	43	610
350	3100	68	940
340	2770	94	1530
330	2100	154	1850
320	1380	178	2190
310	1240	200	2570
300	1720	225	2810
290	2380	230	2950
280	2730	232	3000
270	3270	228	2950
260	3680	235	2910
258	3710	-	-
250	3690	248	3130
240	3310	270	3480

As both dichromate and ferric ions absorb strongly over the same region it is virtually impossible to follow the reaction by direct optical density methods.

An attempt was made to detect an intermediate species and various reaction mixtures were prepared.

1) 5×10^{-5}M $K_2Cr_2O_7$ and 5×10^{-4}M Fe^{2+}

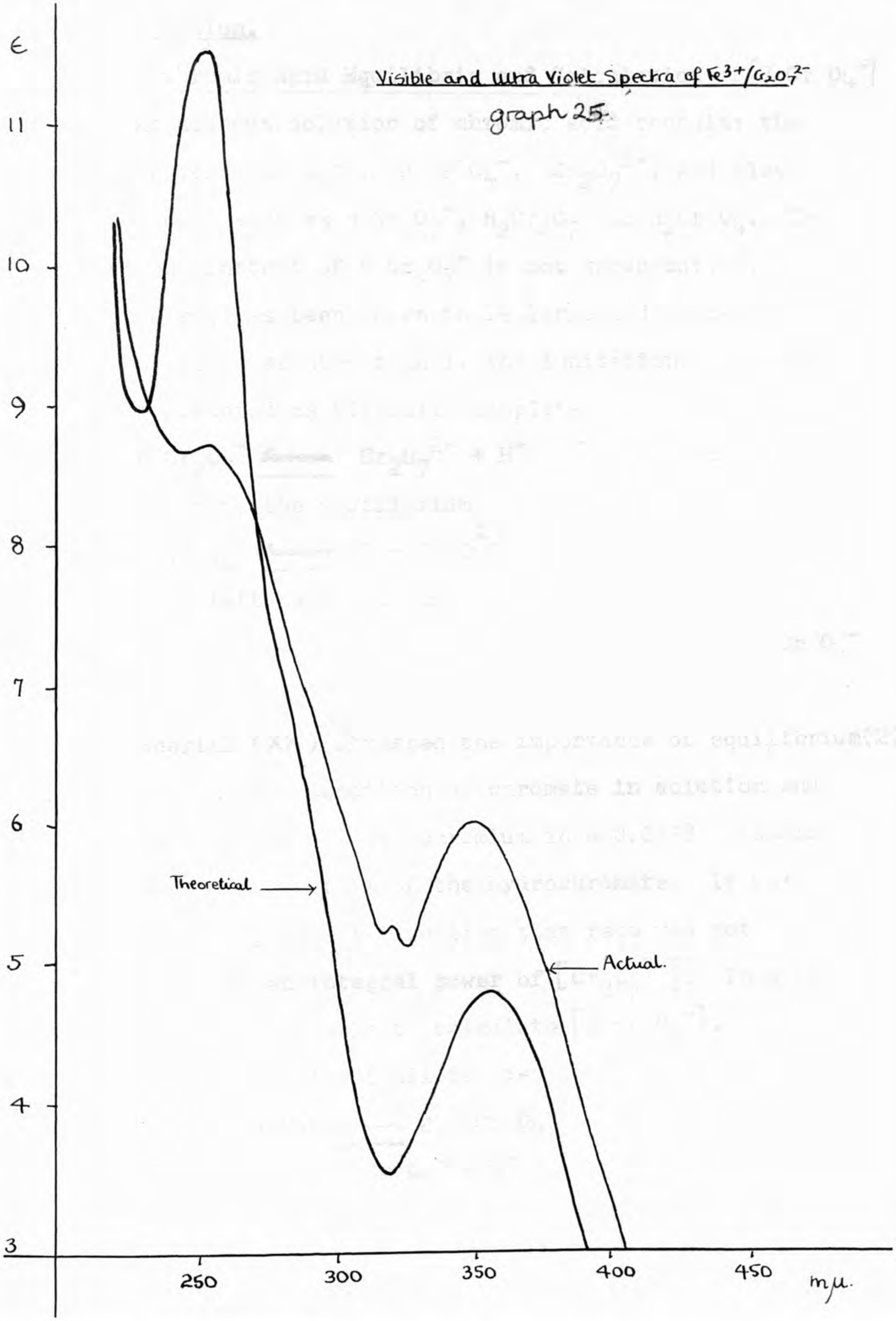
2) 5×10^{-4}M Fe^{3+} and 5×10^{-4}M Fe^{2+}.

Table XLVII.

mμ	$K_2Cr_2O_7/Fe^{2+}$ O.D.	Fe^{3+}/Fe^{2+} O.D.
500	0.016	0.026
480	0.04	0.031
460	0.059	0.038
440	0.076	0.044
420	0.117	0.060
410	0.142	0.072
400	0.176	0.083
390	0.228	0.103
380	0.283	0.123
370	0.349	0.141
360	0.411	0.165
350	0.484	0.187
340	0.538	0.207
330	0.601	0.220
320	0.685	0.241
310	0.760	0.276
300	0.835	0.290
290	0.860	0.293
280	0.882	0.293
270	0.920	0.293
260	0.945	0.301

The spectrum of the ferrous–ferric system is similar to the individual iron types, for example the usual shoulder at 250–300 mμ is present. There is no new, or shifted peak. The spectrum of the $Cr_2O_7^{2-}/Fe^{2+}$ mixture is not that obtained by summing those of the two separate solutions – it is more intense. The explanation of this is that the dichromate and ferrous ions have reacted together to form some ferric iron, and this is the absorption seen. Unfortunately none of these experiments can give any indication of the existence of an intermediate.

To see if there was any combination between ferric ions and dichromate ions, the visible and ultra-violet spectrum was obtained of a 10 ml solution, containing 5 ml 2 x 10^{-4}M $Cr_2O_7^{2-}$ and 5 ml 2 x 10^{-3}M Fe^{3+}. This was compared to the theoretical spectrum obtained by summing the spectra of a 1 x 10^{-4}M $Cr_2O_7^{2-}$ solution and 1 x 10^{-3}M Fe^{3+} solution. As can be seen from the graph(25) there is stronger absorption at 350 mμ, presumably due to a new chromium species, and a diminished absorption at 250 mμ. This is presumably because the ferric ions (which give this strong band) have been "mopped up" by combination with the dichromate ions.



Visible and Ultra Violet Spectra of $Fe^{3+}/Cr_2O_7^{2-}$

graph 25.

IV. Discussion.

I. Chromic Acid Equilibria and Calculation of $[HCrO_4^-]$

An aqueous solution of chromic acid contains the following ions CrO_4^{2-}, $HCrO_4^-$, $Cr_2O_7^{2-}$, and also other species such as $HCr_2O_7^-$, $H_2Cr_2O_7$ and H_2CrO_4. The ionisation constant of $HCr_2O_7^-$ is not known but, by careful work, has been shown to be large and hence in solutions at pH greater than 1, the ionisation of $HCr_2O_7^-$ may be considered as virtually complete.

$$HCr_2O_7^- \rightleftharpoons Cr_2O_7^{2-} + H^+ \qquad (1)$$

consequently as the equilibrium

$$HCrO_4^- \rightleftharpoons H^+ + CrO_4^{2-} \qquad (2)$$

lies to the left hand side in acid solution, the only chromium (VI) ions present in large quantities are $HCrO_4^-$ and $Cr_2O_7^{2-}$.

Sherill (XX) stressed the importance of equilibrium(2) in determining the condition of chromate in solution and showed that nearly all the chromium in a 0.0338 atomic solution was in the form of the hydrochromate. It was shown in the experimental section that rate was not proportional to an integral power of $[Cr_2O_7^{2-}]$. Thus it was necessary to be able to calculate $[HCrO_4^-]$.

Considering the equilibria:-

$$Cr_2O_7^{2-} + H_2O \rightleftharpoons 2\,HCrO_4^-$$

$$H_2CrO_4 \rightleftharpoons HCrO_4^- + H^+$$

the equilibrium constants are as follows:-

$$K_1 = [H\,Cr\,O_4^-]^2 \Big/ [Cr_2O_7^{2-}]$$

$$K_2 = [H\,Cr\,O_4^-][H^+] \Big/ [H_2Cr\,O_4]$$

i.e. $$[H_2Cr\,O_4] = \frac{[H\,Cr\,O_4^-][H^+]}{K_2}$$

The molarity (M) of the total Cr(VI) (put in as $K_2Cr_2O_7$) can be expressed as

$$M = [Cr_2O_7^{2-}] + \frac{[H\,Cr\,O_4^-]}{2} + \frac{[H_2Cr\,O_4]}{2}$$

$$[H\,Cr\,O_4^-]^2 = K_1 \left\{ M - \frac{[H\,Cr\,O_4^-]}{2} - \frac{[H\,Cr\,O_4^-][H^+]}{2\,K_2} \right\}$$

Since $H_2Cr\,O_4$ is a small correction, the hydrogen ion concentration variation in the calculation of $[H_2Cr\,O_4]$ is neglected.

i.e. $$[H\,Cr\,O_4^-]^2 + [H\,Cr\,O_4^-]\left\{\frac{K_1}{2} + \frac{K_1[H^+]}{2K_2}\right\} - K_1M = 0.$$

$$[H\,Cr\,O_4^-] = -\left(\frac{K_1}{4} + \frac{K_1\,[H^+]}{4\,K_2}\right) + \sqrt{\frac{K_1^{\,2}}{16} + \frac{K_1^{\,2}[H^+]}{8\,K_2} + \frac{K_1^{\,2}[H^+]^2}{16\,K_2} + K_1M.}$$

$$= K_1\left\{\sqrt{\frac{1}{16} + \frac{[H^+]}{8K_2} + \frac{[H^+]^2}{16K_2} + \frac{M}{K_1}} - \frac{1}{4} - \frac{[H^+]}{0.8}\right\}$$

If $K_2 = 0.2$, unchanging with ionic strength ,then

$$[H\,Cr\,O_4^-] = K_1\left\{\sqrt{\frac{1}{16} + \frac{[H^+]}{1.6} + \frac{[H^+]^2}{0.64} + \frac{M}{K_1}} - \frac{1}{4} - \frac{[H^+]}{0.8}\right\}$$

Neuss and Rieman(XXI) in 1934 found K_1, at 25°C by means of glass electrode studies, to have a value of 0.023. By application of the Debye-Huckel equation they were able to correct for ionic strength thus:-

$$pK = pK^1 - \frac{\sqrt{\mu}}{1+0.7\sqrt{\mu}}$$

Neuss and Rieman also found $K_2 = 0.2$.
Further measurements were made of acid chromate equilibria by Davies and Prue (XVI) in 1955 by spectrophotometric methods, the value of K being found at 20°C and 25°C.

$$K_{20} = 0.026$$

$$K_{25} = 0.030$$

To correct for ionic strength they supposed that

$$pK^1 = pK + \frac{2A\sqrt{\mu}}{1+\sqrt{\mu}}$$

Tong and King (XVII) have also reported spectrophotometric determinations of pK^1 up to about $\mu = 1$, and Sasaki (XVIII) has measured pK^1 spectrophorometrically and potentiometrically at $\mu = 3$. Although there is approximate concordance between comparable results, the agreement is not perfect and all but a single result reported in the literature refer to 25°C.
We have therefore (i) determined spectrophotometrically pK^1 over a range of ionic strength and temperature (see experimental section) and (ii) investigated the possibility of obtaining an equation correlating pK^1 measurements at any temperature.
Tong and King also did this for their measurements. Davies (XXII) recently modified his earlier empirical rate expression for calculating activity coefficients in aqueous solutions. Thus he writes $- -\log f_{\pm} = 0.5 Z_A Z_B \left\{ \frac{\sqrt{\mu}}{1+\sqrt{\mu}} - 0.3\,\mu \right\}$

This would imply that for $Cr_2O_7^{2-} + H_2O \rightleftharpoons 2\,H\,Cr\,O_4^-$

$$pK^1 = pK + \frac{\sqrt{\mu}}{1+\sqrt{\mu}} - 0.3\,\mu.$$

However Davies' equation is only reckoned to be reasonable up to $\mu = 0.1$ and we were interested in a wider range of applicability.

A possible way of achieving our aim is as follows. The mean ionic activity coefficient for $K_2Cr\,O_4$ is known over a wide range of concentrations. If we put these measured values into an equation of the form -

$$-\log f_{\pm} = 0.5\ Z_A\ Z_B \left\{ \frac{\sqrt{\mu}}{1 + \sqrt{\mu}} - x\mu \right\},$$

x can be found at any ionic strength. These values of can then be used in place of Davies factor of 0.3. The relationship between x and μ is shown in graph (p. 122). The use of this equation in conjunction with Davies and Prue's value for pK (i.e. $pK^1_{\mu \to 0}$) yields the results in table (XLIX). A similar treatment is compared with our own measurements for pK^1 in table (XXVI). These are not claimed to be of great accuracy, but do indicate the consistency of the treatment.

By extending Davies and Prue's values for K and using known A values, it was then possible to find K^1 over a range of temperature. The extended K values are shown in the following table.

Table XLVIII.

Temperature °C	A	K_T	
25	0.5115	0.030	from Davies & Prue
20	0.5070	0.026	
34.5	0.5209	0.037	By extrapolation of the above measurements
14.5	0.5025	0.023	
6.3	0.4961	0.018	

By using the data overleaf the following K^1 values were obtained.

Table XLIX.

Temperature °C.	Ionic Strength	K^1
34.5	0.1	0.022
25	0.1	0.0181
20	0.1	0.0154
14.5	0.1	0.0136
6.3	0.1	0.0109

II. Calculation of Rate Constant.

Table (L) showing rate constants calculated assuming rate is first order in either $Cr_2O_7^{2-}$ or $H\,Cr\,O_4^-$

Experiments at 25°C $\mu = 0.10$

$$[H^+] = 1.2 \times 10^{-2}M \quad [I^-] = 3 \times 10^{-2}M.$$

$$K_A = \text{Initial Rate}/\ [Cr_2O_7^{2-}]\,[H^+]^2\ [I^-]^2$$

$$K_B = \text{Initial Rate}/\ [H\,Cr\,O_4^-]\,[H^+]^2\ [I^-]^2$$

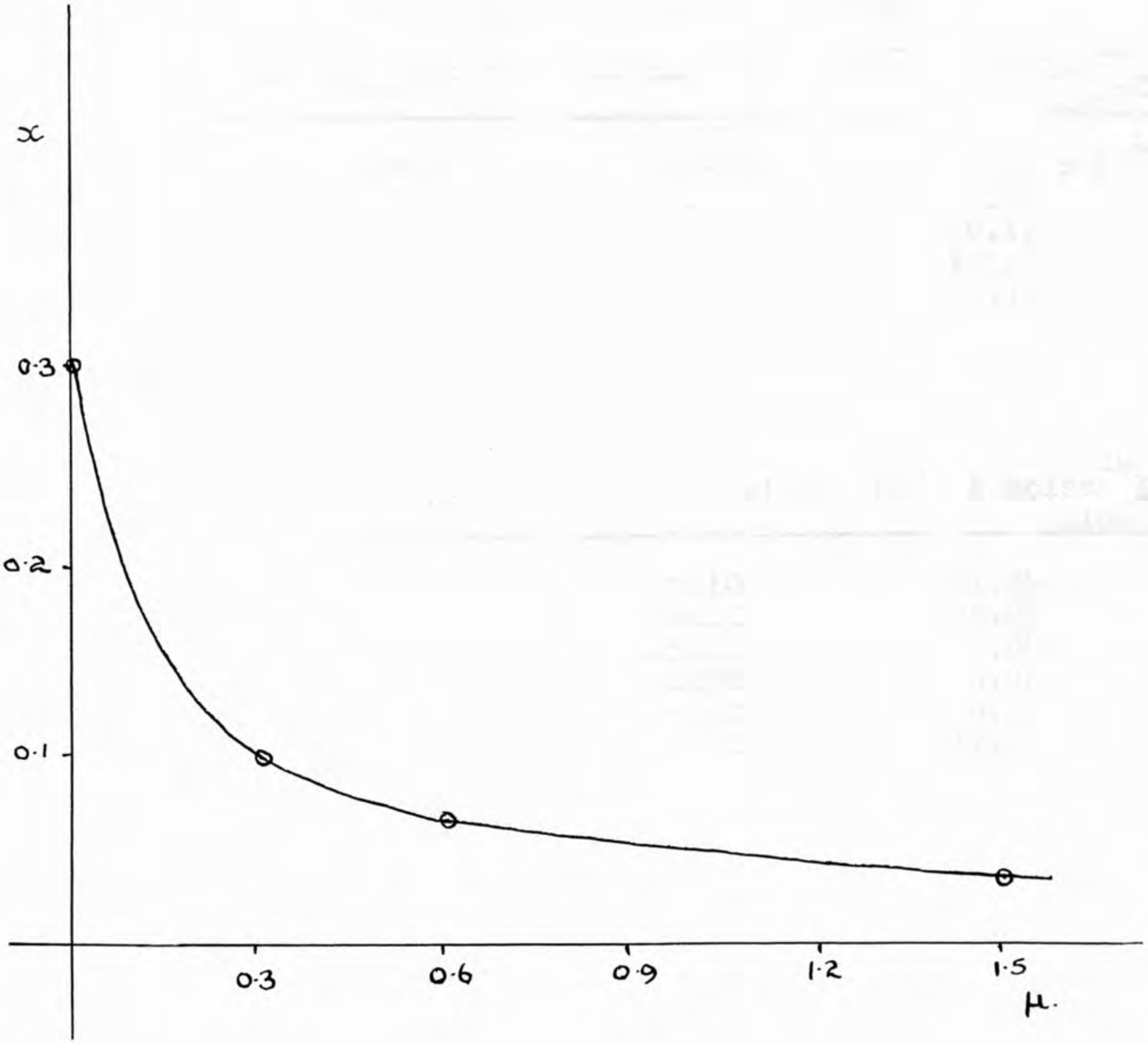
$[Cr_2O_7^{2-}]\ x10^3M$	$[H\,CrO_4^-]\,x10^3M$	$K_A\,l^4\,moles^{-4}mins^{-1}$	$K_B\,l^4\,moles^{-4}\,mins^{-1}$
1.98	2.87	$11.41x10^4$	7.74×10^4
4.00	4.97	9.22	7.82
6.00	6.68	7.76	7.54
7.992	8.15	7.98	7.40
10.05	9.52	6.20	7.44
13.97	11.75	5.14	7.40

Graph to Show Relationship between μ and x.

as used in the following:-

$$pK_\mu = pK + \frac{2A\sqrt{\mu}}{1+\sqrt{\mu}} - x\mu.$$

graph 26



I T A. Calculation of K from initial Rates.

34.5°C. $\mu = 0.1$

A. $[H^+] = 1.97 \times 10^{-2}M$ $[H\,Cr\,O_4^-] = 2.928 \times 10^{-3}M$

$[I^-] \times 10^2M$	Initial Rate($\times 10^{-5}$) moles/1/min.	k $moles^{-4} l^4 mins^1$
1.00	1.156	10.16×10^4
2.00	4.60	10.12
3.00	10.36	10.12
4.00	18.44	10.16

B. $[I^-] = 3.0 \times 10^{-2}$ $[Cr_2O_7^{2-}] = 2 \times 10^{-3}M$

$[H^+] \times 10^{-2}M$	$[H\,Cr\,O_4^-] \times 10^{-3}M$	Initial Rate $\times 10^{-5}$	K $moles^{-4} l^4 mins^{-1}$
0.4	3.06	0.420	9.84×10^4
1.0	3.02	2.64	10.00
1.6	2.97	6.76	10.12
2.0	2.93	10.36	10.12
2.4	2.887	14.80	10.16
4.0	2.737	40.50	10.52
4.95	2.684	58.00	10.08

C. $[I^-] = 3 \times 10^{-2}M$ $[H^+] = 2 \times 10^{-2}M$

$[Cr_2O_7^{2-}] \times 10^{-3}M$	$[HCrO_4^-] \times 10^3M$	Initial Rate $\times 10^{-5}$	K $moles^{-4} l^4 mins^{-1}$
0.8	1.296	5.10	11.04×10^4
3.0	4.604	14.20	8.92
5.96	6.901	25.20	10.88
8.94	10.76	30.80	8.92
11.9	13.64	39.20	9.24
16.4	15.01	49.20	11.24

25°C. $\mu = 0.1$ Table LII

A. $[H^+] = 2.0 \times 10^{-2}$M $[Cr_2O_7^{2-}] = 2 \times 10^{-3}$M $[HCrO_4^-] = 2.79 \times 10^{-3}$M

$[I^-] \times 10^2$M	Initial Rate ($\times 10^{-5}$) I_2 moles/l/min	K moles^{-4}l^{4}mins^{-1}
1.00	0.83	7.64×10^4
2.00	3.3	7.60
3.00	7.6	7.76
4.00	12.6	7.24

B. $[I^-] = 3 \times 10^{-2}$M $[Cr_2O_7^{2-}] = 2 \times 10^{-3}$M

$[H^+] \times 10^2$M	$[HCrO_4^-] \times 10^3$M	Initial Rate moles I_2 formed/ l/min $\times 10^{-5}$	K moles^{-4}l^{4}mins^{-1}
0.4	3.168	0.31	7.00×10^4
1.0	3.034	1.90	6.96
1.6	2.853	4.54	7.08
2.0	2.797	6.76	7.76
2.4	2.786	9.56	6.80
4.0	2.623	29.80	8.08
4.95	2.576	42.60	7.68

C. $[I^-] = 2.997 \times 10^{-2}$M $[H^+] = 1.20 \times 10^{-2}$M

$[Cr_2O_7^{2-}] \times 10^3$M	$[HCrO_4^-] \times 10^3$M	Initial Rate moles I_2 formed/ l/min $\times 10^{-5}$	K moles^{-4}l^{4}mins^{-1}
↑ 0.50	0.8638	1.0	8.52×10^4
* 0.99	1.598	2.0	9.84
1.98	2.865	2.7	7.52
4.0	4.944	4.8	7.88
6.0	6.630	6.1	7.60
8.0	8.126	7.2	7.44
10.10	9.478	8.0	7.24
13.97	11.714	9.88	7.48

↑ * aerial oxidation occurring.

20°C. $\mu = 0.10$ Table LIII

A $[H^+] = 2.0 \times 10^{-2}$M $[Cr_2O_7^{2-}] = 2 \times 10^{-3}$M

$[H\,CrO_4^-]$ 2.723×10^{-3}M

$I^- \times 10^2$M	Initial Rate moles I_2 formed/1/min. $\times 10^{+5}$	K moles^{-4} 1^4 mins^{-1}
1.0	0.67	6.36×10^4
2.0	2.64	6.24
3.0	6.00	6.32
4.0	10.60	6.28

B $[I^-] = 3 \times 10^{-2}$M $[Cr_2O_7^{2-}] = 2.0 \times 10^{-3}$

$[H^+] \times 10^2$	$[H\,CrO_4^-] \times 10^{-3}$	Initial Rate moles I_2formed/1/min. $\times 10^5$	K moles^{-4} 1^4 mins^{-1}
0.40	2.876	0.26	6.48×10^4
1.00	2.799	1.08	4.36
1.6	2.754	4.04	6.52
2.0	2.723	6.00	6.32
2.4	2.694	8.92	6.56
4.0	2.581	26	7.16
4.95	2.514	35.6	6.28

C $[I^-] = 3 \times 10^{-2}$M $[H^+] = 1.2 \times 10^{-2}$M

$[Cr_2O_7^{2-}] \times 10^3$	$[H\,CrO_4^-] \times 10^3$	Initial Rate Moles I_2 formed/1/min. $\times 10^5$	K moles^{-4} 1^4 mins^{-1}
1.1	1.706	1.52	7.00×10^4
2.2	3.003	2.34	6.28
4.02	4.73	3.32	5.68
6.02	6.312	4.60	6.00
8.03	7.665	5.80	6.32
10.03	8.877	7.00	6.80
14.06	11.03	8.80	6.12

14.5°C $\mu = 0.1$ Table LIV.

A $[H^+] = 2.0 \times 10^{-2}M$ $[Cr_2O_7^{2-}] = 2 \times 10^{-3}M$

$[H\ Cr\ O_4^-] = 2.679\ M$

$[I^-] \times 10^2M$	Initial Rate moles I_2 formed/l /min. x 10^5	K $moles^{-4}\ l^4\ mins^{-1}$
1.0	0.48	4.60×10^4
2.0	2.24	5.40
3.0	4.96	5.32
4.0	9.26	5.52

B $[I^-] = 3.0 \times 10^{-2}M$ $[Cr_2O_7^{2-}] = 2.0 \times 10^{-3}M$

$[H^+] \times 10^2M$	$[H\ Cr\ O_4^-] \times 10^3M$	Initial Rate	k $Moles^{-4}\ l^4\ min^{-1}$
0.40	2.802	0.201	5.16×10^4
1.0	2.751	1.292	5.32
1.6	2.706	3.3	5.44
2.0	2.679	4.96	5.32
2.4	2.651	7.26	5.36
4.0	2.543	1.93	5.36

C $[I^-] = 3.003 \times 10^{-2}M$ $[H^+] = 1.2 \times 10^{-2}M$

$[Cr_2O_7^{2-}] \times 10^3M$	$[H\ CrO_4^-] \times 10^3M$	Initial Rate moles I_2 formed/ l/min. x 10^5	K($moles^{-4}\ l^4\ mins^{-1}$)
0.55	0.9194	0.648	5.32×10^4
1.1	1.681	1.1	5.12
2.2	2.944	1.86	5.04
6.0	5.511	3.48	5.12
8.0	7.434	4.52	5.76
10.04	8.624	5.20	5.12
14.04	10.69	6.78	5.40

6.5°C μ = 0.10 Table LV.

A $[H^+]$ = 2.0 x 10^{-2}M $[Cr_2O_7^{2-}]$ = 2 x 10^{-3}M

$[H\ Cr\ O_4^-]$ = 2.576 x 10^{-3}M.

$[I^-]$ x 10^2M	Initial Rate moles I_2 formed/ l/min x 10^5	K(moles^{-4}l^4 mins^{-1})
1.0	0.40	3.996 x 10^4
2.0	1.72	4.32
3.0	3.82	4.24
4.0	6.50	4.04

B $[I^-]$ = 3 x 10^{-2}M $[Cr_2O_7^{2-}]$ = 2.0 x 10^{-3}M

$[H^+]$x 10^2M	$[H\ Cr\ O_4^-]$x10^3M	Initial Rate moles I_2formed/ l/min x 10^5	K (moles^{-4}min^{-1} l^4)
1.0	2.623	1.0	4.32 x 10^4
1.6	2.592	2.4	4.12
2.0	2.572	3.82	4.24
2.4	2.553	5.2	4.04
4.0	2.453	15.8	4.60

C $[I^-]$ = 3 x 10^{-2}M $[H^+]$ = 1.2 x 10^{-2}M

$[Cr_2O_7^{2-}]$x10^3M	$[H\ CrO_4^-]$x10^3M	Initial Rate I_2 moles/l/ min x 10^5	K(moles^{-4}l^4 mins^{-1})
0.5	0.8265	0.46	4.28 x 10^4
1.1	1.634	0.90	4.32
2.2	2.827	1.488	4.12
4.01	4.383	2.356	4.28
6.01	5.79	3.036	4.24
8.01	7.00	3.40	4.00
10.04	8.096	4.00	4.16
14.00	9.99	5.00	4.28

Suggested Mechanism for the Chromic Acid Oxidation of Iodide and calculation of the rate constant.

It has been established experimentally that the initial rate is given by the expression -

$$\text{Rate} = K\left[H\,Cr\,O_4^-\right]\left[I^-\right]^2\left[H^+\right]^2$$

but as reaction proceeds, the rate falls off considerably. This suggests that the products may be interfering in the reaction. However it has been shown that removal of $H\,Cr\,O_4^-$ by Cr(III) is quite insufficient to account for the retardation. cf also King (XXIII, XXIV) and similarly iodide is not removed by Cr(III), but there is some evidence that iodine may be involved.

Neglecting H_3O^+, the right basic Kinetics can be obtained by a mechanism of the following type:-

$$Cr(VI) + I^- \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} \text{complex} \qquad \text{equilibrium maintained}$$

$$\text{Complex} + I^- \underset{K_{-2}}{\overset{K_2}{\rightleftharpoons}} I_2 + Cr(IV)$$

$$Cr(IV) + Cr(VI) \xrightarrow[K_3]{} 2\,Cr(V)$$

$$Cr(V) + I^- \xrightarrow[k_4]{} I\,O^- + Cr(III)$$

$$2H_3O^+ + I\,O^- + I^- \xrightarrow[k_5]{} 3H_2O + I_2$$

) relatively fast and irreversible. Both Cr(IV) and Cr(V) have to be postulated intermediates. Our other evidence suggests that k_4 is smaller than k_2 and k_3 so that - $[Cr(V)] > [Cr(IV)]$

$$\text{Rate} = d\left[I_2\right]/dt = k_2\left[\text{complex}\right]\left[I^-\right] + 2\,k_3\left[Cr(VI)\right]\left[Cr(IV)\right] - k_{-2}\left[I_2\right]\left[Cr(IV)\right]$$

$$\text{Now:-}\quad \frac{[\text{complex}]}{[\text{Cr(VI)}]\,[\text{I}^-]} = \frac{k_1}{k_{-1}} = K_1$$

$$\text{or}\quad [\text{complex}] = K_1\,[\text{Cr(VI)}]\,[\text{I}^-]$$

$$\text{Also}\quad \frac{d\,[\text{Cr(IV)}]}{dt} = k_2\,[\text{complex}]\,[\text{I}^-] - k_{-2}\,[\text{Cr(IV)}]\,[\text{I}_2] - k_3\,[\text{Cr (IV)}]\,[\text{Cr(VI)}]$$

This can be set = 0 in steady state.

$$\text{or}\quad [\text{Cr(IV)}] = \frac{k_2K_1\,[\text{Cr(VI)}]\,[\text{I}^-]^2}{k_{-2}\,[\text{I}_2] + k_3\,[\text{Cr(VI)}]}$$

Therefore Rate =

$$k_2K_1\,[\text{Cr(VI)}]\,[\text{I}^-]^2 + \frac{2k_2k_3K_1\,[\text{Cr(VI)}]^2[\text{I}^-]^2}{k_{-2}\,[\text{I}_2] + k_3\,[\text{Cr(VI)}]} - \overset{\textcircled{1}}{\frac{k_2k_{-2}K_1\,[\text{Cr(VI)}][\text{I}^-]^2[\text{I}_2]}{k_{-2}\,[\text{I}_2] + k_3\,[\text{Cr(VI)}]}}$$

At zero time, the final term is zero, and $k_{-2}\,[I_2]$ in the second term is zero whence:

$$\text{Initial Rate} = 3\,k_2K_1\,[\text{Cr(VI)}]\,[\text{I}^-]^2$$

which, neglecting acid concentration, is experimentally observed.

The dependance of rate upon $[H_3O^+]^2$ can be accounted for if equilibria involving H_3O^+ are assumed to be set up before the rate determining step. Such a possible arrangement would be:-

$$\text{Cr}_2\,\text{O}_7^{2-} + \text{H}_2\text{O} \rightleftharpoons 2\text{H Cr O}_4^- \qquad (A) \quad k_A$$

$$\text{H Cr O}_4^- + \text{H}_3\text{O} \rightleftharpoons \text{H}_2\,\text{Cr O}_4 \qquad (B) \quad k_B$$

$$\text{H}_2\,\text{Cr O}_4 + \text{H}_3\text{O}^+ \rightleftharpoons \text{H}_3\,\text{Cr O}_4^+ \qquad (C) \quad k_C$$

(A) has already been shown to be an experimental requirement. If equilibria (B) and (C) yield little of the products, then there will be little disturbance of each equilibrium by successive protonations and each subsequent species will be proportional in concentration to $H\,Cr\,O_4^-$. In fact:-

$$\left[H_3\,Cr\,O_4^+\right] = k_B\,k_C\left[H\,Cr\,O_4^-\right]\left[H_3O^+\right]^2$$

Thus if the superacid $H_3\,Cr\,O_4^+$ is the effective Cr(VI) reagent, then the rate = $k\left[H\,Cr\,O_4^-\right]\left[H_3O^+\right]^2\left[I^-\right]^2$, the experimentally found rate expression. It does not matter that Cr(VI) may be different species at different points in the mechanisim, if all are proportional to one another.

Once the reaction begins, the iodine concentration begins to rise and one term involving $[I_2]$ will become important first.

Suppose the rate expression (1) is rewritten as:-

$$\text{Rate} = k_2K_1\,[Cr(VI)][I^-]^2 + \frac{k_2K_1[Cr(VI)][I^-]^2}{k_{-2}[I_2] + k_3[Cr(VI)]}\left(2k_3[Cr(VI)] - k_{-2}[I_2]\right)$$

Early on in the reaction $k_3\,[Cr(VI)] > k_{-2}\,[I_2]$ so that the initial rate form is regained.

Later however

$$k_{-2}\,[I_2] > k_3\,[Cr(VI)]$$

this must be so if the mechanisim is to account for the retardation.

If $k_{-2}\,[I_2] \gg k_3\,[Cr(VI)]$

the rate = $k_2\,K_1\,[Cr(VI)]\,[I^-]^2 - k_2K_1[Cr(VI)]\,[I^-]^2 = 0$

Thus the actual rate must involve the whole of the rate expression given above.

Another equilibrium has also to be considered:-

$$I^- + I_2 \rightleftharpoons I_3^-$$

as it drastically reduces iodine and iodide concentrations. If I_3^- was inactive this equilibrium could be very important. When $[I^-]$ is 3×10^{-2}M and $[I_2]$ is 5×10^{-4}M - 2×10^{-3}M, i.e. approximately the measured range of reaction, then at equilibrium the iodine is virtually a constant fraction of the total iodine produced (in this case ca.5%). If the iodide concentration is changed, of course the fraction changes slightly. But throughout most runs the iodine concentration could be taken as a constant fraction of the total iodine produced, hence this fraction is conveniently included in k_{-2}. The amount of iodide lost this way is insignificant except in the late stages of the reaction.

<u>Evaluation of Rate Constants.</u>

By putting rate expression over a common denominator:-

Rate =

$$\frac{k_2K_1[Cr(VI)][I^-]^2[H^+]^2\left(k_{-2}[I_2] + k_3[Cr(VI)] + 2k_3[Cr(VI)] - k_{-2}[I_2]\right)}{k_{-2}[I_2] + k_3[Cr(VI)]}$$

$$= \frac{3k_2K_1\,k_3\,[Cr(VI)]^2\,[I^-]^2\,[H^+]^2}{k_{-2}[I_2] + k_3[Cr(VI)]}$$

$$= \frac{k_{initial}\,k''\,[Cr(VI)]^2\,[I^-]^2\,[H^+]^2}{k_{-2}[I_2] + k_3[Cr(VI)]}$$

The Cr(VI) species involved is (at least proportional to) $H\,Cr\,O_4^-$, and as some acid is involved in its formation, a corrected value for $[H_3O^+]$ has to be employed.

$[H^+]_{eff} = [H^+]_{initial} - [H_2\,Cr\,O_4]$ and using the first known dissociation constant of $H_2Cr\,O_4$

$$[H_2\,Cr\,O_4] = 5[H^+]_{initial} \times [H\,Cr\,O_4^-]$$

The most convenient method of calculating the rate constant of the back reaction is by an integral method.

By writing:-

$$[Cr(VI)]_o = a$$
$$[I^-]_o = b$$
$$[H^+]_o = c$$
$$\text{Total } [I_2] = x/2 \quad \text{i.e. } [I^-] \text{ lost} = x$$

then:

$$\text{Rate} = \frac{dx}{dt} = \frac{k_i\, k''\,(a - x/3)^2\,(b - x)^2(c - 7x/3)^2}{k'x/2 + k''(a - x/3)}$$

$$\int dt = \int \left\{ \frac{k'x/2 + k''\,(a - x/3)}{k_i\, k''(a - x/3)^2\,(b - x)^2\,(c - 7x/3)^2} \right\} dx$$

$$\text{or} \quad kt = \int \left\{ \frac{x/2 + k''(a - x/3)}{(a - x/3)^2\,(b - x)^2\,(c - 7x/3)^2} \right\} dx \qquad 2.$$

The equation is finally solved by numerical integration and application of Simpson's Rule. k is the rate constant found from the initial rate measurements. The true value of k''' is taken as that which when substituted in (2) gives the nearest representation of the reaction curve to the experimentally found results.

A typical set of calculations obtained by this method is given overleaf. The calculation takes a particular set of experimental conditions, assumes the experimental initial rate constant, and then attempts to calculate the experimental results for various values of k'''. A rough value is soon obvious, the final stages of this successive approximation are shown to indicate the sensitivity of the calculated result to the assumed value for K'''. As it can be seen a value of 0.08 for K''' gives a very similar curve to the experimental results.

Table (LVI)

$[Cr_2O_7^{2-}] = 6 \times 10^{-3}M$ $[I^-] = 3 \times 10^{-2}M$ $[H^+] = 1.2\times10^{-2}M$ $k_{init} = 8\times10^4$, i.e. $K = k_{init}$ $k''' = 4\times10^3$. $(K''' = 0.05)$

T = 25° = 0.10

1 x	$(a - x/3)$	$(b - x)$	$(c - 7x/3)$	$x/2 + k'''(a - x/3)$	Integrand	Application of Simpsons Rule	kt	Time (Mins)	Experimental Times
0	6.677×10^{-3}	30×10^{-3}	12×10^{-3}	0.334	5.78×10^7				
0.1×10^{-3}	6.647	29.90	11.77	0.382	6.98				
0.2	6.617	29.80	11.53	0.431	8.34	42.04×10^7	14.01×10^3	3.50	3.30
0.3	6.577	29.70	11.30	0.479	9.83				
0.4	6.544	29.60	11.07	0.527	11.45	101.15	33.72	8.43	7.80
0.5	6.510	29.50	10.83	0.576	13.29				
0.6	6.477	29.40	10.60	0.624	16.29	181.99	60.67	15.17	13.60
0.7	6.444	29.30	10.37	0.672	17.51				
0.8	6.410	29.20	10.13	0.721	20.01	288.27	96.09	24.02	20.78
0.9	6.377	29.10	9.90	0.769	22.79				
1.0	6.344	29.00	9.67	0.817	25.79	425.23	141.74	35.43	29.60
2						$k_{init} = 8\times10^4$, i.e. $K = k_{init}$		$k''' = 6.4\times10^3$.	$(K''' = 0.08)$
				0.534	9.24×10^7				
				0.582	10.60	63.84×10^7	21.28×10^3	3.33	3.30
				0.629	12.22				
				0.676	13.91				
				0.724	15.70	147.40	49.13	7.68	7.80
				0.771	17.84				
				0.818	21.31	255.77	85.26	13.30	13.60
				0.866	22.62				
				0.913	25.31	392.87	130.96	20.45	20.78
				0.960	28.40				
				1.008	31.83	563.61	187.87	29.35	29.60

$[Cr_2O_7^{2-}] = 6\times10^{-3}M$ $[I^-] = 3\times10^{-2}M$ $[H^+] = 1.2\times10^{-2}M$.

1. $K_{init} \neq 8\times10^4$ $k''' = 0.05$ $k_{init} k''' = 4\times10^3$

2. $k''' = 0.08$ $k_{init} k''' = 6.4\times10^3$

This same expression held over a wide range of temperature and ionic strength. Varying temperature besides causing a change in $k_{initial}$, also caused variation in k'''. Below are given some results at differing temperatures. The $k_{initial}$ is that found from the initial rate experiments.

Table (LVII)

A. 14.5°C. $\mu = 0.1$

$[Cr_2O_7^{2-}] = 2 \times 10^{-3}M$ $[H^+] = 1.6 \times 10^{-2}M$

$[I^-] = 3.0 \times 10^{-2}M$

$k_{init} = 5.4 \times 10^4\ l^4\ moles^{-4}\ mins^{-1}$. $k''' = 0.15$ $x = [I_2]/2$

x (x10^3M)	Experimental time (Mins)	Calculated time (mins)
0.1	3.50	3.25
0.2	7.06	7.06
0.3	11.60	11.49
0.4	16.70	16.64
0.5	22.56	22.56

(graph 28)

B. 6.3°C $\mu = 0.1$

$[I^-] = 4 \times 10^{-2}M$ $[Cr_2O_7^{2-}] = 2 \times 10^{-3}$

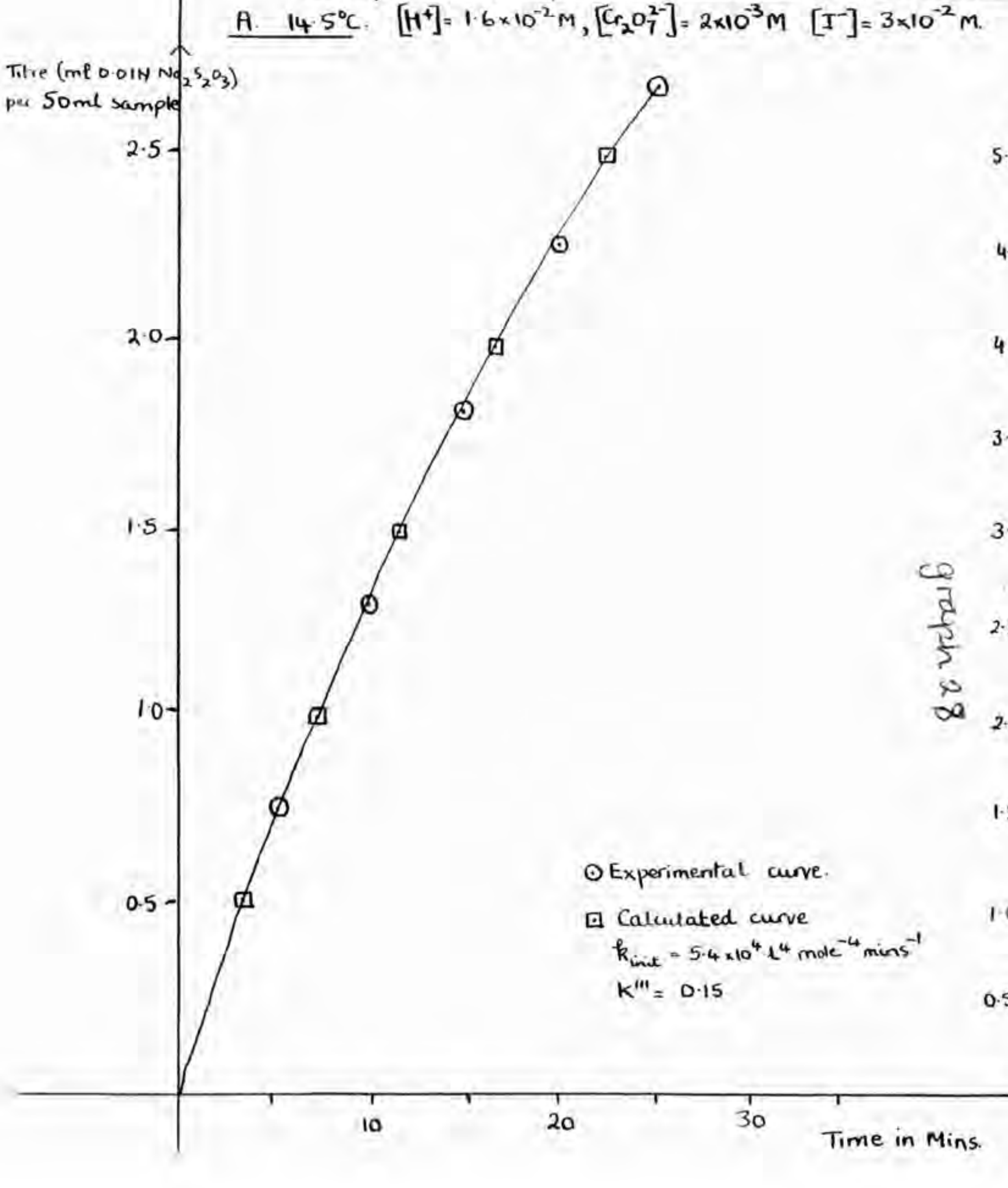
$[H^+] = 2 \times 10^{-2}M$.

$k_{init} = 406 \times 10^4\ l^4\ moles^{-4}\ mins^{-1}$ $k''' = 0.30$

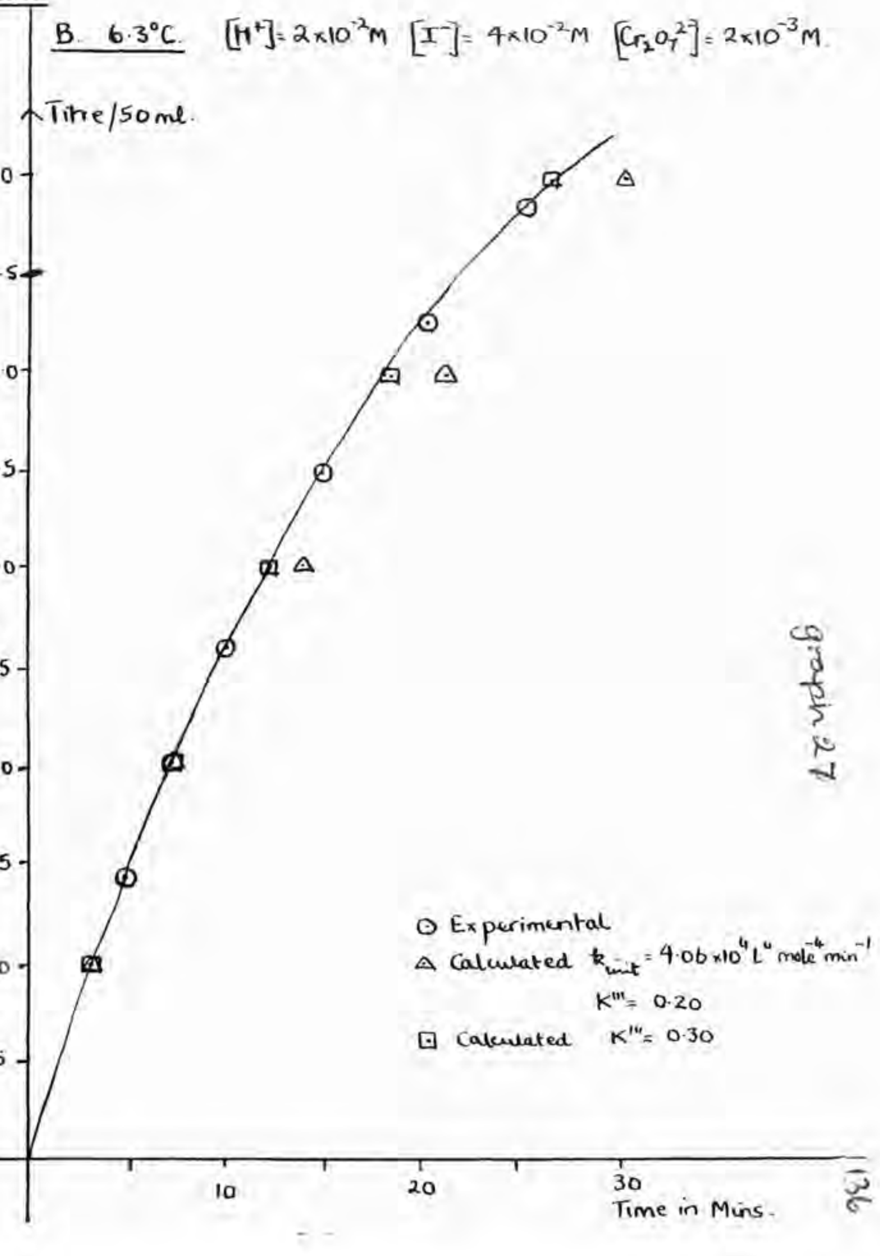
x (x10^3M)	Experimental time (mins)	Calculated time (mins)
0.2	3.37	3.37
0.4	7.55	7.55
0.6	12.65	12.65
0.8	18.82	18.82
1.0	26.29	26.29

(graph 27)

Comparison of Experimental and Calculated Results.


A. 14.5°C. $[H^+] = 1.6\times10^{-2}M$, $[Cr_2O_7^{2-}] = 2\times10^{-3}M$ $[I^-] = 3\times10^{-2}M$.

graph 28


B. 6.3°C. $[H^+] = 2\times10^{-2}M$ $[I^-] = 4\times10^{-2}M$ $[Cr_2O_7^{2-}] = 2\times10^{-3}M$.

graph 27

C. 34.5°C $\mu = 0.1$

$$[Cr_2\,O_7^{2-}] = 6 \times 10^{-3}M \quad [H^+] = 1.2 \times 10^{-2}M$$

$$[I^-] = 3.0 \times 10^{-2}M$$

$k_{init} = 10.88 \times 10^4\ l^4\ moles^{-4}\ mins^{-1}$ $k''' = 0.08$

x (x10^{3}M)	Experimental time (mins)	Calculated time(mins
0.2	2.50	2.30
0.4	3.60	5.34
0.6	9.14	9.14
0.8	14	14
1.0	20	20

It was found that in the later stages of the reaction, the experimental results appeared faster than the calculated. This would be partly due to the dichromate concentration falling rather low and consequently a certain amount of aerial oxidation would then occur. Our approximation would also begin to be suspect.

At varying ionic strength it was found that k''' remained roughly constant at a particular temperature but $k_{init.}$ increased with increasing ionic strength. From the experiments on varying ionic strength (page 24) it was found that k_{init} at $\mu = 1.5$ at 25° C should be $12.10 \times 10^4\ l^4$ $moles^{-4}\ mins^{-1}$.

Table (LVIII)

$T = 25^{o}C \quad \mu = 1.5$

$[Cr_2O_7^{2-}] = 1.003 \times 10^{-2}M \quad [H^+] = 1.2 \times 10^{-2}M \quad [I^-] = 3.0 \times 10^{-2}M$

$k_{init} = 12.10 \times 10^4\ 1^4\ moles^{-4}\ mins^{-1} \quad k''' = 0.10.$

x (x 10^3M)	Experimental time (mins)	Calculated time (mins)
0.2	2.13	2.13
0.4	4.80	4.80
0.6	8.14	8.14
0.8	12.20	12.28
1.0	17.00	17.40

graph 29

Table (LIX)

Showing variation of k_{init} and K''' with temperature at $\mu = 0.10$

Temp°C	k_{init} $moles^{-4}1^4\ mins^{-1}$	k'''
34.5	10.88×10^4	0.08
25	7.7	0.08
20	6.48	0.10
14.5	5.4	0.15
6.3	4.06	0.30

Table (LX)

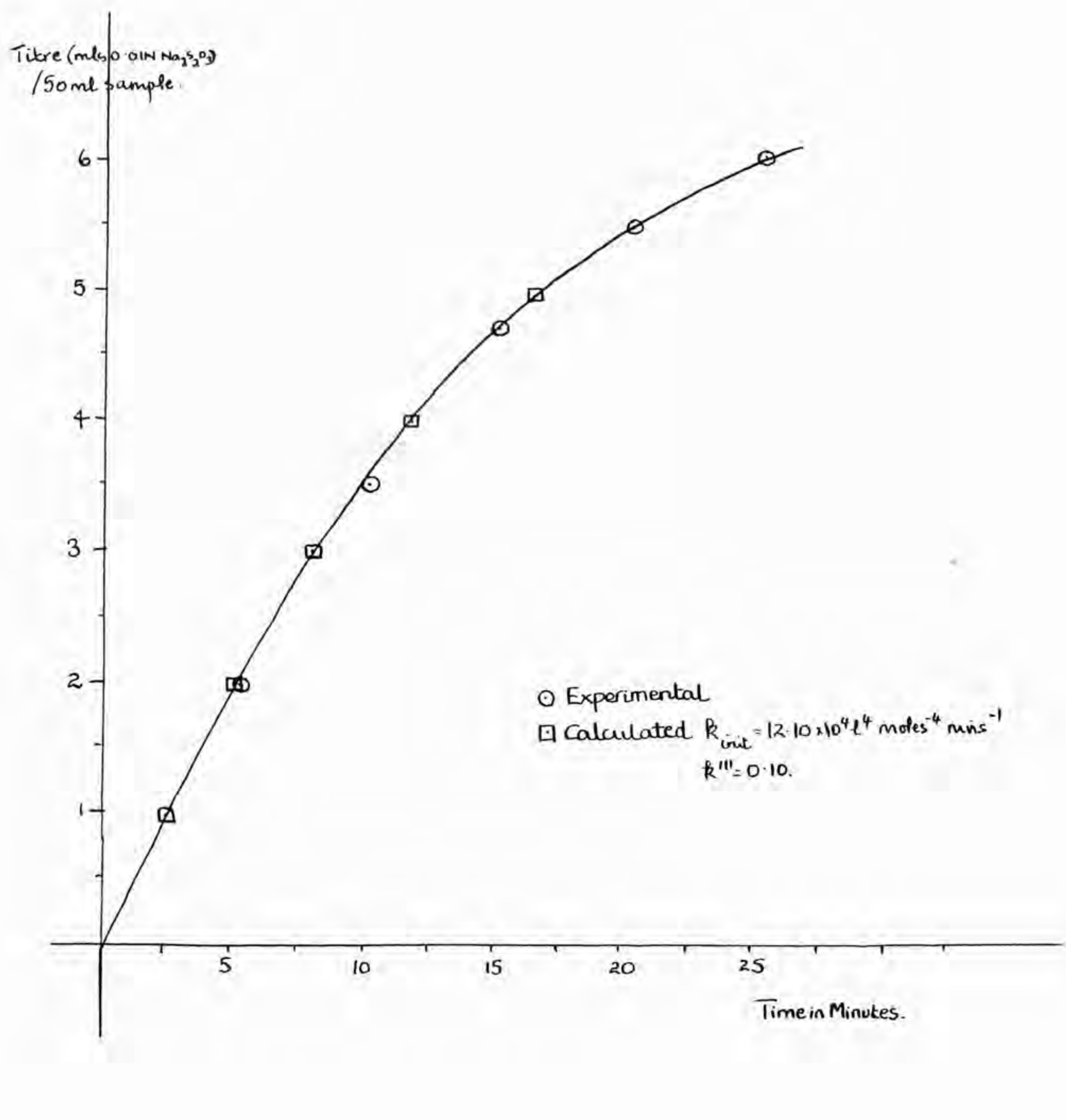
Showing change in k_{init} with μ.

μ	Temp°C	k_{init} $moles^{-4}1^4\ mins^{-1}$	k'''
0.10	25°	7.7×10^4	0.08
	14.5°	5.4×10^4	0.15
1.5	25°	12.10×10^4	0.08
	14.5°	8.00×10^4	0.15

Comparison of Calculated and Experimental Results.

High Ionic Strength (μ=1·5), T=25°C

$[Cr_2O_7^{2-}]$ = 1·003×10^{-2}M, $[H^+]$=1·2×10^{-2}M, $[I^-]$= 3·0×10^{-2}M. graph 29



Note that k''' is a ratio of rate constants(not a simple constant), thus k''' need not rise with temperature k''' is furthermore a pure number, being the ratio of two second order constants.

There does appear to be a check on the interpretation because the numerical integration yields $kt = k_{init} k''' t$ whence k_{init} can be deduced not only as previously from the initial rate, but also from the best curve which fits the later parts of the reaction.

Reaction between Ferrous Iron and Chromic Acid.

From the investigations on this reaction, three points of interest were noticed.

1) As the reaction proceeded the pH fell. H^+ is one of the reactants, and during the course of reaction it must be formed in quantities large enough to exceed the reaction demand.

2) Early workers had said that Fe^{3+} had a retarding effect. This was only found so in buffered media.

3) Spectrophotometric work suggested the formation of a complex between ferric ions and dichromate ions . Before the rate constant can be calculated, all these factors must be considered.

The stoichiometric equation for the reaction is given by:

$$14H^+ + 6Fe^{2+} + 2\ Cr(VI) \longrightarrow 6Fe^{3+} + 7H_2O + 2\ Cr^{3+}.$$

Ferric iron readily hydrolyses in aqueous solution

$$Fe^{3+}\ aq \longrightarrow Fe(OH)^{2+}\ aq + H^+\ etc.$$

If complete hydrolysis occurs, for every ferric ion three hydrogen ions are formed.

$$\text{Formally } Fe^{3+} + 3H_2O \longrightarrow Fe(OH)_3 + 3H^+.$$

The equilibrium constants for the formation of these hydrolysed species are known to be high. Furthermore we observe a precipitate of ferric hydroxide after long runs.

During the course of reaction 6 Fe^{3+} are formed and thus if complete hydrolysis occurs there will be a net gain of $4H^{+}$. Assuming this, comparison of the observed pH and calculated pH show good agreement.

Table (LXI)

Time (mins)	Observed pH	Observed $H^{+} \times 10^{4}M$	Calculated $H^{+} \times 10^{4}$
0	3.86	1.20	1.2
5	3.76	1.48	1.52
10	3.73	1.59	1.61
15	3.72	1.62	1.65
20	3.71	1.66	1.68

Reaction Mixture =

$[Cr_2O_7^{2-}] = 6 \times 10^{-5}M$ $[H^{+}] = 1.20 \times 10^{-4}M$ $[Fe^{2+}] = 1.6 \times 10^{-4}M$

$T = 25^{\circ}C$ $\mu = 0.005$

Considering the second point of interest, it was found that the addition of Fe^{3+} to the normal reaction mixture produced no retarding effect whatsoever. However a yellow precipitate formed, and the reaction appeared to increase slightly in rate.

Table (LXII)

Reaction Mixture =

$[Fe^{2+}] = 1.6 \times 10^{-4}$ $[Cr_2O_7^{2-}] = 1 \times 10^{-4}M$ $[H^{+}] = 2.4 \times 10^{-4}M$

$T = 25^{\circ}$ $\mu = 0.006$

$[Fe^{3+}] \times 10^{4}M$	Initial Rate (Fe^{3+} MOLES formed/ $\times 10^{5}$)
0	7.4
1.08	7.4
3.24	7.8
4.32	7.9

Obviously the Fe^{3+} ions were being hydrolysed to ferric hydroxide and so could no longer play an effective part in the reaction.

However when Fe^{3+} was added to a buffered reaction mixture at pH 3 4 no precipitation occurred, and there was a marked slowing in the rate. Under these conditions the buffer prevents any H^+ ion formed from Fe^{3+} from having its usual effect and any retardation effect by Fe^{3+} now becomes obvious.

From spectrophotometric experiments it was concluded that there was complex formation between Fe^{3+} and $H\,Cr\,O_4^-$. This was also shown to be so by Espenson (XIII). It is suggested that the complex may be of the nature $Fe\,Cr\,O_4^+$. If there is an unreactive complex formed, then not all the $H\,Cr\,O_4^-$ is available for oxidation purposes, and consequently an effective $[H\,Cr\,O_4^-]$ had to be calculated throughout the reaction.

Several courses are open in the attempt to interpret the retardation of the reaction by ferric iron in a quantitative manner.

First of all we will take it as axiomatic that only free Cr(VI) is an effective oxidising species. It could be assumed that the equilibrium constant for the formation of a ferric - chromate complex is very high, so that, approximately, each ferric ion produced removes one Cr(VI) ion.

Secondly one could determine the relevant equilibrium constant, either spectrophotometrically or from the measured kinetics by using a numerical integration procedure as was done for the iodide reaction. It appears that this latter would be almost prohibitively complex however, since, if the equilibrium is of the form

$$H\,Cr\,O_4^- + Fe^{3+} \rightleftharpoons H^+_{solv} + Fe\,Cr\,O_4^+$$

both H^+ and $H\,Cr\,O_4^-$ are affected by the equilibrium, and apart from this the equation to be integrated already has the form

$$\frac{dx}{dt} = k\left(a - \frac{x}{3}\right)^2 (b - x)^2 \left(c + \frac{2x}{3}\right)$$

where $a = [H\,Cr\,O_4^-]$ $b = [Fe^{2+}]$ $c = [H_3O^+]$

x = fall in Fe^{2+}

However while the interpetation of these results was in progress an abstract appeared of a thesis by Espenson in which the equilibrium constant of the Fe^{3+} - Cr(VI) complex formation reaction is reported to be 1.4 at 0°C.

The use of this constant in conjunction with the results obtained here gives the results shown in the following tables (page 146 et seq.)

The method of resting is as follows:

From the experimentally determined values of $[Fe^{2+}]$:- Firstly, tangents to a concentration/time graph gives rates of reaction (although these cannot be expected to be very accurate); Secondly the fall in $[H_3O^+]$

and $[\mathrm{H\ Cr\ O}\ ^{-}]$ due to the stoichiometric equation can be calculated. A final value for $[\mathrm{H_3O^+}]$ was then guessed (the guess improved with experience) and the concentration of the complex (x) was calculated as

$$\text{Guessed final } [\mathrm{H_3O^+}] \times x = 1.4([\mathrm{H\ Cr\ O_4^-}] - x)([\mathrm{Fe^{2+}}] - x)$$

The actual values of $[\mathrm{H\ Cr\ O_4^-}]$ and $[\mathrm{H_3O^+}]$ could then be determined. If the actual $[\mathrm{H_3O^+}]$ was far from the guessed figure, the calculation was repeated.

Since the rates are obviously approximate, and the equilibrium constant used is appropriate at 0°C. for an equilibrium between somewhat questionable Fe (111) species, one cannot expect great concordance of the finally calculated values for the rate constant of the reaction. However general agreement while the initial concentrations and measured rates vary over a power of 10. would indicate that the treatment is reasonable.

The tables show that only moderate success attends these calculations. The results however are considerably better than if this complex formation is neglected. The kinetic results reported here would clearly be better fitted by using a rather higher value for the equilibrium constant.

Table of Results LXIII.

At 14.5°C.

I. $[Fe^{2+}] = 1.64 \times 10^{-4}M$ $[Cr_2O_7^{2-}] = 4 \times 10^{-5}$ $[H^+] = 5.4 \times 10^{-4}M$ $\mu = 0.005$

t_{min}	$[Fe^{2+}] \times 10^4$	$[H^+] \times 10^4$	$[Fe^{3+}] \times 10^5$	$[H\,Cr\,O_4^-] \times 10^5$	Rate x 10^4	k $moles^{-4} l^4 mins^{-1}$
0	1.64	5.4	0	8	0.28	0.28×10^{15}
2.5	1.24	5.7	4	6.15	0.042	0.13
5	1.11	5.7	5.3	5.58	0.021	0.10
10	0.98	5.7	6.6	5.08	0.014	0.10

II. $[Fe^{2+}] = 1.64 \times 10^{-4}M$ $[Cr_2O_7^{2-}] = 4 \times 10^{-5}M$ $[H^+] = 9.0 \times 10^{-4}$

t_{min}	$[Fe^{2+}] \times 10^4$	$[H^+] \times 10^4$	$[Fe^{3+}] \times 10^5$	$[H\,Cr\,O_4^-] \times 10^5$	Rate x 10^4	k $moles^{-4} l^4 mins^{-1}$
0	1.64	9.0	0	8.0	0.46	0.29×10^{15}
1	1.38	9.13	2.6	6.8	0.16	0.20
2.5	1.20	9.22	4.4	6.1	0.075	0.15
10	0.96	9.36	6.8	5.2	0.027	0.12

III. $[Fe^{2+}] = 2.85 \times 10^{-4}M$ $[H^+] = 1.2 \times 10^{-4}M$ $[Cr_2O_7^{2-}] = 2 \times 10^{-5}$

t_{min}	$[Fe^{2+}] \times 10^4$	$[H^+] \times 10^4$	$[Fe^{3+}] \times 10^5$	$[H\,Cr\,O_4^-] \times 10^5$	Rate x 10^4	k $moles^{-4} l^4 mins^{-1}$
0	2.85	1.2	0	4.0	0.055	0.35×10^{15}
1	2.80	1.2	0.5	3.67	0.044	0.35
2.5	2.74	1.21	1.1	3.30	0.037	0.37
10	2.55	1.28	3.0	2.10	0.021	0.43

At 25°C. LXIV.

$[H^+] = 3.6 \times 10^{-4}$ $[Fe^{2+}] = 1.66 \times 10^{-4}$ $[Cr_2O_7^{2-}] = 2 \times 10^{-5}M$

t_{mins}	$[Fe^{2+}] \times 10^4 M$	$[H^+] \times 10^4 M$	$[Fe^{3+}] \times 10^5 M$	$[H\,Cr\,O_4^-] \times 10^5$	Rate x 10^4	k $moles^{-4} l^4 mins^{-1}$
0	1.66	3.60	0	4.0	0.13	0.82 x 10^{15}
2.5	1.45	3.70	2.1	3.1	0.05	0.67
5	1.36	3.74	3.0	2.7	0.03	0.59
10	1.24	3.82	4.2	2.37	0.018	0.55
20	1.10	3.92	5.6	1.87	0.009	0.54

At 34.5°C. LXV.

I. $[Fe^{2+}] = 4.13 \times 10^{-4}M$ $[H^+] = 1.2 \times 10^{-4}M$ $[Cr_2O_7^{2-}] = 2 \times 10^{-5}M$

t_{mins}	$[Fe^{2+}] \times 10^4$	$[H^+] \times 10^4$	$[Fe^{3+}] \times 10^5$	$[H\,Cr\,O_4^-] \times 10^5$	Rate x 10^4	k
0	4.13	1.20	0	4	0.64	2.0 x 10^{15}
0.5	3.93	1.24	2.0	2.88	0.32	2.0
2.5	3.55	1.45	5.8	1.34	0.115	3.5
5	3.35	1.61	7.8	0.87	0.051	3.7
7.5	3.25	1.68	8.8	0.64	0.028	3.8
10	3.20	1.70	9.3	0.53	0.016	3.3

II $[Fe^{2+}] = 3.24 \times 10^{-4}M$ $[H^+] = 1.2 \times 10^{-4}$ $[Cr_2O_7^{2-}] = 2 \times 10^{-5}M$

t_{mins}	$[Fe^{2+}] \times 10^4$	$[H^+] \times 10^4$	$[Fe^{3+}] \times 10^5$	$[H\,Cr\,O_4^-] \times 10^5$	Rate x 10^4	k
0	3.24	1.20	0	4.0	0.54	2.7 x 10^{15}
0.5	3.10	1.23	1.4	3.18	0.20	1.8
2.5	2.8	1.34	4.4	2.02	0.074	1.7
5	2.68	1.42	5.2	1.64	0.041	1.5
10	2.55	1.51	6.5	1.18	0.020	1.5

At 34.5°C. (Contd)

III. $[Fe^{2+}] = 8.1 \times 10^{-5}M$ $[H^+] = 1.2 \times 10^{-4}M$ $[Cr_2O_7^{2-}] = 2 \times 10^{-5}M$

t_{mins}	$[Fe^{2+}] \times 10^4$	$[H^+] \times 10^4$	$[Fe^{3+}] \times 10^5$	$[H\ Cr\ O_4^-] \times 10^5$	Rate x 10^4	k
0	0.81	1.20	0	4.0	0.04	3.2 x 10^{15}
0.5	0.78	1.21	0.3	3.84	0.035	3.2
2.5	0.74	1.22	0.7	3.57	0.019	2.2
5	0.70	1.22	1.1	3.34	0.013	2.0
15	0.72	1.24	1.9	2.91	0.007	1.8

IV $[Fe^{2+}] = 1.62 \times 10^{-4}M$ $[H^+] = 1.20 \times 10^{-4}M$ $[Cr_2O_7^{2-}] = 4 \times 10^{-5}M$

t_{mins}	$[Fe^{2+}] \times 10^4$	$[H^+] \times 10^4$	$[Fe^{3+}] \times 10^5$	$[H\ Cr\ O_4^-] \times 10^5$	Rate x 10^4	k
0	1.62	1.20	0	8.0	0.36	1.7 x 10^{15}
1	1.40	1.20	2.2	6.4	0.14	1.5
2.5	1.24	1.21	3.8	5.3	0.078	1.5
5	1.11	1.23	5.1	4.7	0.037	1.1
15	0.93	1.30	6.9	3.87	0.010	0.6

The experiments described do enable the retardation by ferric iron to be understood. Earlier workers have usually assumed a reversible first step e.g.

$$Cr(VI) + Fe^{2+} \rightleftharpoons Cr(V) + Fe^{3+}$$

This is no longer a necessity as a retardation step.

It also appears that it has not been reported before that one of the reactants according to the stoichiometric equation (viz H_3O^+) is actually a product of the reaction.

Apart from this the work reported here does not really establish a mechanism for the steps in the oxidation.

APPENDIX.

1. Purification of Dioxan.

This is carried out in order to reduce the peroxide content. 500 ml. analar Dioxan were refluxed with about 20 ml. concentrated hydrochloric acid, in an atmosphere of nitrogen, for about 3 hours. This removed any acetaldehyde which may be present. The cold solution was then treated with potassium hydroxide pellets, with shaking, until some remained undissolved. The rest of the water remaining was removed by keeping dioxan over fresh potassium hydroxide pellets for 24 hours. The filtered dioxan was then refluxed over sodium for 6 - 12 hours i.e. until reaction had ceased and the sodium remained bright. Dioxan was then distilled off from the sodium and stored out of contact with the air.

On keeping, Dioxan develops appreciable quantities of peroxides upon exposure to air. These can be eliminated by refluxing over stannous chloride or by filtration through a column of activated alumina.

II. Table showing Dieletric constant of Water/Dioxan and Water/acetone mixtures. LXVI.

a.

vol % Dioxan in H_2O	D	
0	78.5	
10	71.2	
20	62.2	
30	53.2	
40	44.3	
50	35.6	
60	27.0	(Ref XXV)

b. Weight % acetone in water	D
0	78.5
10	73.0
20	67.0
30	61.0
40	54.6
50	48.2
60	41.8
70	35.7

(Ref XXVI)

III. Preparation of Chromium Perchlorate.

A concentrated solution of chrome alum was prepared and to this was added aqueous ammonia until there was no further precipitate. The chromic hydroxide formed was filtered off, washed with water several times to remove any excess ammonia, and then dissolved in perchloric acid to form a deep green solution. This was evaporated down slightly and allowed to crystallise.

The green needle-shaped deliquescent crystals which formed were chromic perchlorate. Various preparations and crystallisations produce slightly different coloured crystals. This is because the perchlorate forms several hydrates, containing, 3, 5, 6, 9, 10 or 21 molecules of water. Before an accurate standard solution could be prepared the water content had to be determined.

IV. Analysis of Chromium Perchlorate.

Principle.

The chromium was estimated as chromate by persulphate oxidation and titration of the chromium (VI) formed with ferrous ammonium sulphate.

Method.

A known weight of chromic perchlorate was boiled with excess potassium persulphate, a small trace of $AgNO_3$ being added as a catalyst. Any excess persulphate remaining at the end of the oxidation was decomposed by prolonged boiling (if persulphate is not removed, it will interfere with the titration). The now yellow solution was acidified with dilute H_2SO_4 and about 10 drops of N-phenyl anthranilic acid indicator was added before titrating with standard ferrous ammonium sulphate.

$$1 \text{ ml N } Fe^{2+} \text{ solution} \equiv 0.01734 \text{ g } Cr^{3+}$$

It is therefore possible to estimate percentage Cr^{3+} in the sample and hence find the formula weight. The formula weight was found to be 735, suggesting that 21 molecules of water are present per Cr^{3+} atom in the sample of chromic perchlorate.

V. Preparation of Chromic Nitrate $Cr(NO_3)_3 . x H_2O$.

Freshly precipitated chromic hydroxide was dissolved in a slight excess of ntric acid, and evaporated to dryness over a water bath at 100° C.

Analysis of the green crystalline salt formed showed it to be the trihydrate.

BIBLIOGRAPHY

I de Lury J.Phys. Chem I903 7 239

II Beard and Taylor J. Am. Chem. Soc. I929 2 I973

III Kessler Pogg. Ann. I863 II9 "2I8

IV Benson J. Phys. Chem. I903 7 356

V Westheimer Chem. Revs. I949 45 4I9

VI Manchot and Wilhelms O. Ann. I902 325 I25

VII Slack and Waters J. Chem. Soc. I949 596

VIII Autrey and Edwards Chem. Revs. I952 455

IX Evans Analyst I947 72 99 852

X Benson J. Phys. Chem. I903 7 I

XI Gortner J. Phys. Chem. I908 I2 632

XII Stefanovski C. A.35 3I49 (J. Gen. Chem. U.S.S.R. I940 I0 I62I)

XIII Espenson Dissertation Abstracts I962 23 I9I7

XIV Whitman and Popoff J.Am. Chem. Soc. I925 47 2259

XV Bailey and Symons J. Chem. Soc. I957 203

XVI Davies and Prue Trans. Far. Soc. I955 I045

XVII Tong and King J. Am. Chem. Soc. I953 75 6I80

XVIII Sasaki Acta Chem. Scand. I962 I6 7I9

XIX Sidgwick The Chemical Elements and their Compounds Clarendon Press, Oxford.(I950) p.I360

XX Sherrill J. Am. Chem. Soc. I907 29 I64I

XXI Neuss and Rieman J. Am. Chem. Soc. I934 56 2238

XXII Davies J. Chem. Soc. I938 2093

XXIII King and Neptune J. Am. Chem. Soc. I935 77 3I86

XXIV Stability Constants Part II Chem Soc (London)

XXV Frost and Pearson Kinetics and Mechanism (Wiley) 2nd Ed p.I46

XXVI Akerlof J. Am. Chem. Soc. I932 54 4I25