THE KINETICS OF THE OXIDATION OF SOME INORGANIC SPECIES BY PEROXODISULPHATE

by

Salah El Din Mohamed El Amin

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

Bedford College, London
May, 1973

ABSTRACT

The reactions of peroxodisulphate with manganese(II), nitrite and chromium(III) have been studied in the region of 60°C.

In the main introduction a survey is made of published work on the reaction of peroxodisulphate with mainly inorganic substrates.

The oxidation of manganese(II) to manganese(IV) was carried out in sulphate media for most of the kinetic investigation. The reaction was found to be first order with respect to peroxodisulphate and zero order with respect to manganese(II). Despite this, however, the observed first order rate constant is greater than that of the thermal decomposition of peroxodisulphate in the absence of manganese(II). The effect of added salts on the rate of the reaction is negligible though the reaction is sensitive to some impurities, added surface and free radical scavengers which all retard it. The activation energy which is 31.5 kcal/mole is only 2 kcal/mole lower than that for the thermal decomposition of peroxodisulphate alone. A chain mechanism consistent with the observed kinetics is proposed.

The oxidation of nitrite was carried out in phosphate media. The redox reaction is of the second order, being first order with respect to each reactant. Cations catalyze the reaction and the extent of catalysis depends on the nature and concentration of cation. The activation energy for the redox reaction is 14 kcal/mole. E.s.r. spectroscopy did not reveal any stable or detectable free radicals. Reaction mechanisms are proposed.

The peroxodisulphate - chromium(III) reaction was carried out in acid - perchlorate media and acid - sulphate media. The oxidation of chromium(III) to chromium(VI) is faster in the second medium than in the first.

ACKNOWLEDGEMENTS

The author wishes to express his sincere gratitude to his supervisor, Dr. K. E. Howlett for his unfailing help and encouragement during the whole course of this work. He also wishes to thank Professor G. H. Williams for providing a place at Bedford College.

Most of this work was carried out during the tenure of a Fellowship from the United Nations Development Programme - Special Fund. Thanks are also due to the Higher Teacher Training Institute, Omdurman, Sudan and the Sudan Government for leave of absence and partial support.

CONTENTS

CHAPTER I

INTRODUCTION

CHAPTER I

INTRODUCTION

The peroxodisulphate ion is one of the strongest oxidizing agents known in aqueous solution, and the standard redox potential for the reaction

$$S_2O_8^{2-} + 2e = 2SO_4^{2-} \qquad \ldots\ldots \quad [1]$$

is 2.01 volts(1). Many of the reactions involving this ion are very slow at ordinary temperatures but the addition of a catalyst renders the reaction fast enough to be studied kinetically at room temperature(2). The catalyst which has been studied most widely in this respect is the silver(I) ion(3,4,5,6). Some work has also been done on reactions involving the peroxodisulphate ion using copper(II) as catalyst(7,8,9). Other catalysts have also been examined to see if they affect the decomposition of peroxodisulphate(10) because many oxidations by this ion seem commonly to occur as a secondary effect following its decomposition.

Throughout this work we will be using the term peroxodisulphate which is the nomenclature of the International Union of Pure and Applied Chemistry(11) although the terms peroxydisulphate and persulphate are still in wide use.

The Structure of Peroxodisulphate Ion

Mooney and Zachariasen(12) determined the crystal lattice structures of ammonium and caesium peroxodisulphates. They concludded that the peroxodisulphate ion may be pictured as two sulphate groups linked by a bond across a centre of symmetry between two oxygen atoms and that each sulphur atom is tetrahedrally surrounded by four oxygen atoms at a distance of 1.50 Å. The oxygen-oxygen bond length was determined by these authors as 1.31 Å, and both sulphur-oxygen-oxygen interbond angles as 128°.

CHAPTER I

INTRODUCTION

The peroxodisulphate ion is one of the strongest oxidizing agents known in aqueous solution, and the standard redox potential for the reaction

$$S_2O_8^{2-} + 2e = 2SO_4^{2-} \qquad \ldots\ldots \quad [1]$$

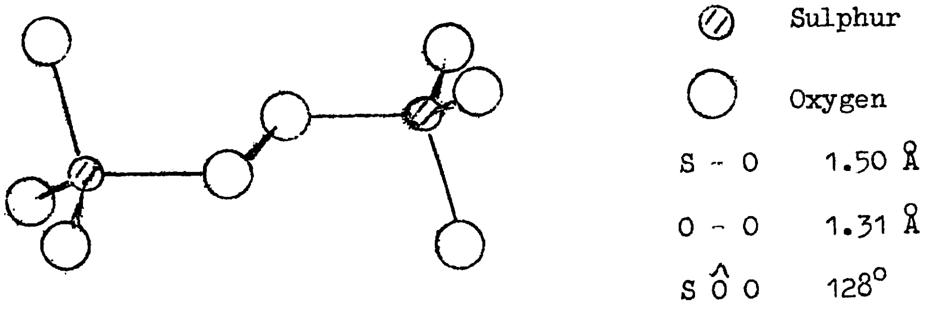
is 2.01 volts(1). Many of the reactions involving this ion are very slow at ordinary temperatures but the addition of a catalyst renders the reaction fast enough to be studied kinetically at room temperature(2). The catalyst which has been studied most widely in this respect is the silver(I) ion(3,4,5,6). Some work has also been done on reactions involving the peroxodisulphate ion using copper(II) as catalyst(7,8,9). Other catalysts have also been examined to see if they affect the decomposition of peroxodisulphate(10) because many oxidations by this ion seem commonly to occur as a secondary effect following its decomposition.

Throughout this work we will be using the term peroxodisulphate which is the nomenclature of the International Union of Pure and Applied Chemistry(11) although the terms peroxydisulphate and persulphate are still in wide use.

The Structure of Peroxodisulphate Ion

Mooney and Zachariasen(12) determined the crystal lattice structures of ammonium and caesium peroxodisulphates. They concludèd that the peroxodisulphate ion may be pictured as two sulphate groups linked by a bond across a centre of symmetry between two oxygen atoms and that each sulphur atom is tetrahedrally surrounded by four oxygen atoms at a distance of 1.50 Å. The oxygen-oxygen bond length was determined by these authors as 1.31 Å, and both sulphur-oxygen-oxygen interbond angles as 128°.

Molar magnetic susceptibilities and infrared absorptions of ammonium and potassium peroxodisulphates also indicate the formula $(SO_4^-)_n$ where n is at least 2(13). The Raman spectra of sodium and ammonium peroxodisulphates were investigated by Simon and Richter(14) and their results confirm the structu



This structure - as will be discussed later - is consistent with many aspects of peroxodisulphate reactions.

Peroxodisulphate is widely used, and has been (and is still being) extensively studied. Its importance lies mainly in its oxidizing property and in its ability to furnish free radicals. It is the latter property which makes the peroxodisulphate ion an important initiator of polymerization of organic molecules(15,16,17) and the industrial importance of this can hardly be over-estimated(18).

The Thermal Decomposition of Peroxodisulphate

House reviewed some aspects of the kinetics and mechanisms of oxidations by the peroxodisulphate ion(2) and covered the literature published prior to 1961. It can be seen from this review and other publications that many of the uncatalyzed reactions involving this ion reach a measurable rate only at or above temperatures where its decomposition becomes significant. Therefore it is logical to assume that peroxodisulphate oxidations often involve species resulting from its decomposition.

Peroxodisulphate decomposes according to the following stoicheiometries(2)

(a) in alkaline or neutral solution

$$S_2O_8^{2-} + H_2O = 2HSO_4^- + \tfrac{1}{2}O_2 \quad \ldots\ldots \quad [2]$$

(b) in dilute acid solution

$$S_2O_8^{2-} + 2H_2O = 2HSO_4^- + H_2O_2 \quad \ldots\ldots \quad [3]$$

(c) in strong acid solution

$$S_2O_8^{2-} + H_2O = H_2SO_5 + SO_4^{2-} \quad \ldots\ldots \quad [4]$$

Bartlett and Cotman(19) studied the decomposition of potassium peroxodisulphate in aqueous solution and in aqueous solutions of methanol at a temperature of 79.8°C and at pH 8. They found that the decomposition is first order in aqueous solution and that the addition of methanol (1 mole/l) increases the rate (up to 25 fold) and changes the order towards 3/2. They proposed two mechanisms to account for the observed kinetics, both having as their rate determining step the symmetrical rupture of the O-O bond of the peroxodisulphate ion to give two sulphate ion-radicals.

The proposals are:

(a) a non-chain mechanism comprising the following steps:

$$S_2O_8^{2-} \xrightarrow{k_5} 2SO_4^- \quad \ldots\ldots \quad [5]$$

$$SO_4^- + H_2O \xrightarrow{k_6} HSO_4^- + OH \quad \ldots\ldots \quad [6]$$

$$2OH \xrightarrow{k_7} H_2O + \tfrac{1}{2}O_2 \quad \ldots\ldots \quad [7]$$

(b) a chain mechanism comprising steps [5] and [6] above plus steps [8] and [9]:

$$S_2O_8^{2-} \xrightarrow{k_5} 2SO_4^- \qquad \ldots\ldots [5]$$

$$SO_4^- + H_2O \xrightarrow{k_6} HSO_4^- + OH \qquad \ldots\ldots [6]$$

$$OH + S_2O_8^{2-} \xrightarrow{k_8} HSO_4^- + SO_4^- + \tfrac{1}{2}O_2 \qquad \ldots\ldots [8]$$

$$OH + SO_4^- \xrightarrow{k_9} HSO_4^- + \tfrac{1}{2}O_2 \qquad \ldots\ldots [9]$$

where equation [9] is regarded by the authors as the chain terminating step.

It can be argued, however, that oxygen atoms rather than molecules are formed in steps [8] and [9] and that a further step [10] is the chain-terminating step:

$$O + O \xrightarrow{\text{solvent}} O_2 \qquad \ldots\ldots [10]$$

Moreover there is a possibility that two OH radicals can come together as suggested by step [7] and again eventually lead to the formation of oxygen molecules as in [10]. There is also the possibility of O and OH radicals colliding to give HO_2 as another possible intermediate:

$$O + OH \longrightarrow HO_2 \qquad \ldots\ldots [11]$$

which eventually leads to the overall reactions

$$HO_2 + OH \longrightarrow O_2 + H_2O \qquad \ldots\ldots [12]$$

$$HO_2 + SO_4^- \longrightarrow O_2 + HSO_4^- \qquad \ldots\ldots [13]$$

In a solvent the collisions O + OH must be of an intermediate frequency to collisions O + O and OH + OH and therefore step [11] is of secondary importance whereas either [10] or [7] is first and the other one third.

Bartlett and Cotman, however, preferred the first non-chain to the chain mechanism because they did not observe any autocatalysis which could be attributed to free radicals produced in the decomposition inducing further decomposition of the ion, although - as will be seen later - the chain mechanism explains the uncatalyzed first order peroxodisulphate reactions more satisfactorily.

The fact that sulphate ion-radicals are produced by the decomposition of peroxodisulphate is well established. In 1947 Smith and Campbell(20) reported that when peroxodisulphate labelled with sulphur-35 is used to initiate the polymerization of styrene in a soap emulsion, polymer fragments containing radioactive sulphur can be separated.

Riesebos and Aten(21) kept solutions of pH 1, 7 and 10 containing potassium sulphate labelled with sulphur-35 and inactive potassium peroxodisulphate at room temperature for a week and observed no exchange of sulphur not even when the solution of pH 10 was boiled. Similar results were obtained by Eager and McCallum(22) and Elkeles and Brosset(23). These results suggest that mechanisms involving steps like

$$S_2O_8^{2-} \rightleftharpoons SO_4 + SO_4^{2-} \qquad \ldots\ldots \quad [14]$$

$$SO_4 + SO_4^{2-} \longrightarrow 2SO_4^{-} \qquad \ldots\ldots \quad [15]$$

as proposed by some authors(24) or

$$S_2O_8^{2-} \rightleftharpoons 2SO_4^{-} \qquad \ldots\ldots \quad [16]$$

$$SO_4^{-} + SO_4^{-} \longrightarrow SO_4^{2-} + SO_4 \qquad \ldots\ldots \quad [17]$$

suggested by others(25) are incorrect.

Kolthoff and Miller(26) made an extensive investigation of the thermal decomposition of peroxodisulphate in aqueous solution at 50°C. They observed that the reaction

(a) is first order in peroxodisulphate

(b) is catalyzed by hydrogen ion

(c) has a rate constant which is independent of ionic strength when the solution is neutral or alkaline but that there is a negative salt effect when the solution is acidic.

Moreover they investigated the source of oxygen liberated in the thermal decomposition of peroxodisulphate using water enriched with oxygen-18. In neutral or alkaline solutions the source of oxygen is water, whereas in acid solutions its origin is peroxodisulphate. To account for all these results the authors proposed two mechanisms for the decomposition of peroxodisulphate - one of which is uncatalyzed and another which is catalyzed by hydrogen ion according to the following rate law:

$$-\frac{d[S_2O_8^{2-}]}{dt} = k[S_2O_8^{2-}] + k_H[H^+][S_2O_8^{2-}] \qquad \ldots\ldots \quad [18]$$

where k is the first order rate constant for the uncatalyzed path and k_H is the second order rate constant for the hydrogen ion dependent path.

For the k path Kolthoff and Miller accepted the non-chain scheme of Bartlett and Cotman(19) which is in agreement with the kinetics and the results of the tracer experiments. For the hydrogen ion catalyzed path they proposed the following mechanism in which the rate determining step is a bimolecular association of a hydrogen ion and a peroxodisulphate ion to form $HS_2O_8^-$ followed by the unsymmetrical rupture of the O-O bond, this heterolysis being due to the associated hydrogen ion:

$$S_2O_8^{2-} + H^+ \longrightarrow HS_2O_8^- \longrightarrow SO_4 + HSO_4^- \qquad \ldots\ldots \quad [19]$$

$$SO_4 \longrightarrow SO_3 + \tfrac{1}{2}O_2 \qquad \ldots\ldots \quad [20]$$

$$SO_3 + H_2O \longrightarrow H_2SO_4 \qquad \ldots\ldots \quad [21]$$

Here again the formation of oxygen molecules in a mechanistic step can be questioned and the production of oxygen atoms which eventually turn up as oxygen molecules should be considered instead of equation [20].

These authors also suggested that in strong acid (2 - 5 M $HClO_4$) reaction [22] occurs

$$SO_4 + H_2O \longrightarrow H_2SO_5 \qquad \ldots\ldots \quad [22]$$

Equation [20] explains the fact that oxygen in this path originates from peroxodisulphate. However, Bawn and Margerison(6) who studied the decomposition of peroxodisulphate in the presence of the radical scavenger diphenylpicrylhydrazyl (DPPH) found the rate of disappearance of DPPH to be independent of pH in the pH range 3 - 7 which suggested to them that either SO_4 radicals were not present or that if they exist in the system then they do not show the normal reactivity associated with free radicals. It may be argued, however, that the k_H path of Kolthoff and Miller assumes importance only at pH values lower than 3, so that the results of Bawn and Margerison are not in disagreement with those of Kolthoff and Miller.

Fronaeus and Ostman(27), see as the rate determining step of the uncatalyzed decomposition of peroxodisulphate the bimolecular reaction

$$S_2O_8^{2-} + H_2O \longrightarrow SO_4^- + OH + HSO_4^- \qquad \ldots\ldots \quad [23]$$

rather than the unimolecular homolytic scission of the O-O bond (equation [5]) as suggested by Bartlett and Cotman and accepted by Kolthoff and Miller and many other workers in this field. These authors arrived at this conclusion through their study of the cerium(III)-peroxodisulphate reaction in perchloric acid-sodium perchlorate media. They found that the following rate law holds for the reaction

$$\frac{d[Ce(IV)]}{dt} = \frac{k\alpha\,[Ce(III)][S_2O_8^{2-}]}{1 + \alpha\,[Ce(III)]} \qquad \ldots\ldots \quad [24]$$

where α and k are constants and the value of k is found to be the same as that of k in equation [18] of Kolthoff and Miller. When sodium sulphate is used as part of the ionic medium and when the concentration of cerium(III) is higher than 0.1 m mole/l the value of α was found to be so high that the rate tends towards a maximum value

$$\frac{d[Ce(IV)]}{dt} = k[S_2O_8^{2-}] \qquad \ldots\ldots \quad [25]$$

They concluded that:

(a) cerium(III) is oxidized only by intermediates formed in the uncatalyzed path of the peroxodisulphate decomposition;

(b) if the rate determining step is that suggested by Bartlett and Cotman (equation [5]) and if only sulphate ion radicals oxidize cerium(III) then the maximum rate should be $2k[S_2O_8^{2-}]$ and not $k[S_2O_8^{2-}]$, which suggests that only one sulphate ion-radical is produced in the rate determining step proving that equation [23] and not [5] is the correct representation of the rate determining step.

These authors made another study of the same reaction, this time following it by measuring the rate of evolution of oxygen gas[(28)]. The rate of evolution of oxygen is found to remain constant while cerium(III) is present but as the cerium(III) becomes exhausted, the rate of oxygen evolution rises to that produced by peroxodisulphate alone in the same medium. This indicates that (a) the rate of formation of cerium(IV) is independent of cerium(III) concentration and that (b) the oxidizing radicals are effectively captured as was assumed in their earlier work. Moreover when the rates of evolution of oxygen in presence and absence of cerium(III) are plotted against hydrogen ion concentration, two straight lines parallel to each other are obtained. This result shows - indirectly - that the rate of oxidation of cerium(III) is independent of hydrogen ion concentration which again indicates that cerium(III) is oxidized only by intermediates formed in the uncatalyzed path of peroxodisulphate decomposition. The intercepts of the two lines at zero hydrogen ion concentration show that the rate of evolution of oxygen in presence of cerium(III) is half the value in its absence. These findings suggest that only one sulphate ion radical which is the only intermediate that oxidizes cerium(III) is formed by the decomposition of one peroxodisulphate ion.

The above conclusions, however, contradict the results obtained by Kolthoff and coworkers(17) who studied the rate of initiation of emulsion polymerization of styrene using potassium peroxodisulphate labelled with sulphur-35 in an effort to measure the rate of production of sulphate ion radicals. They found that the rate of initiation (from combined sulphur-35 counts) corresponds to 6 - 7 x 10^{12} radicals/ml/sec while the rate of thermal decomposition of peroxodisulphate at the same temperature, (from their own work and that of others) corresponds to 8.4 - 8.8 x 10^{12} radicals/ml/sec assuming that two radicals are produced per decomposition (equation [5]). They therefore concluded that the two rates are equal - within the limits of experimental error - and that equation [5] of Bartlett and Cotman in which one peroxodisulphate ion decomposes to give two sulphate ion-radicals, is correct.

It looks as though more work involving direct measurement as far as possible is needed before the controversy can be resolved. Fortunately both mechanisms agree in that (a) there is an O-O bond rupture in the rate determining step which (b) produces sulphate ion radicals and in that (c) hydroxyl radicals are produced, either in the first rate determining step or in a subsequent step. These three features are important in interpreting many peroxodisulphate reactions.

First Order Uncatalyzed Oxidations

The first order uncatalyzed oxidations by peroxodisulphate ion have some general characteristic features:

(i) They are very slow at room temperature and become reasonably measurable only above 50°C.

(ii) The rate of any reaction is usually independent of the concentration of the reducing agent and despite this;

(iii) first order rate constants vary with varying substrates and in all cases these rate constants are higher than the k value for the thermal decomposition of peroxodisulphate alone.

(iv) Reproducibility of results is quite difficult to obtain and reactions are quite sensitive to the presence of trace impurities.

(v) Catalytic effects of heavy metal ions especially silver(I) and copper(II) are quite large, although in the presence of a catalyst the reaction is only pseudo-first order at constant catalyst concentration.

(vi) Many of these reactions are inhibited by free radical scavengers like allyl acetate.

(vii) Activation energies are relatively high (usually greater than 25 kcal/mole).

Examples of first order peroxodisulphate reactions exhibiting these characteristics are the oxidations of arsenious acid(7), hydrogen peroxide under certain conditions (see p. 25) and oxalate(2,9). Because of the slowness of these reactions under easily accessible conditions not many have yet been investigated.

All reactions belonging to this class have as their rate determining step the rupture of the O-O bond in the peroxodisulphate ion and this probably accounts for the slowness of these reactions and their relatively high activation energies. To account for all the characteristics of these reactions a chain mechanism similar to that proposed by House(2) may be appropriate. Let us assume that equation [5] of Bartlett and Cotman is the rate determining step in the oxidation of a reducing agent R which produces an intermediate I which in turn eventually turns into product P. This implies that the mechanism is designed to fit reactions involving reducing agents which undergo at least a two electron oxidation, as of course is so in the examples quoted. I for example could involve As(IV).

$$S_2O_8^{2-} \xrightarrow{k_5} 2SO_4^- \quad \text{slow} \qquad \text{......} \quad [5]$$

$$SO_4^- + H_2O \xrightarrow{k_6} HSO_4^- + OH \qquad \text{......} \quad [6]$$

$$OH + R \xrightarrow{k_{26}} I + OH^- \qquad \text{......} \quad [26]$$

$$I + S_2O_8^{2-} \xrightarrow{k_{27}} SO_4^{2-} + SO_4^- + P \qquad \text{......} \quad [27]$$

$$I + SO_4^- \xrightarrow{k_{28}} SO_4^{2-} + P \qquad \text{......} \quad [28]$$

Application of the steady state approximation to this mechanism (see Chapter II) leads to the rate law

$$\frac{-d[S_2O_8^{2-}]}{dt} \cong \left(k_5 + \sqrt{\frac{k_5 k_6 k_{27}}{k_{28}}} \right) [S_2O_8^{2-}] \qquad \text{......} \quad [29]$$

which is similar to

$$\frac{-d[S_2O_8^{2-}]}{dt} = k_{obs}[S_2O_8^{2-}] \qquad \text{......} \quad [30]$$

where

$$k_{obs} = k_5 + \sqrt{\frac{k_5 k_6 k_{27}}{k_{28}}} \qquad \text{......} \quad [31]$$

is the observed first order rate constant. It is clear from equation [29] that the rate expression does not involve [R] but that the presence of R increases the value of the first order rate constant k_5 of the thermal decomposition of peroxodisulphate by $\sqrt{\frac{k_5 k_6 k_{27}}{k_{28}}}$ and the magnitude of this term depends on k_{27} and k_{28} which are dependent upon the nature of I which is produced from R.

Second Order Reactions

Second order reactions involving peroxodisulphate ion are much faster than the corresponding first order reactions$^{(2,29)}$ and some of them are so fast that a flow system is needed in order to investigate the kinetics$^{(30)}$. The activation energies are less than 15 kcal/mole $^{(cf.29)}$. In reactions of this class the O-O bond is broken after the rate determining step which is usually formulated as the bimolecular reaction involving peroxodisulphate ion and the reducing agent, e.g.

$$X^{n+} + S_2O_8^{2-} \longrightarrow [XS_2O_8]^{n-2} \longrightarrow \text{Products} \qquad \ldots\ldots \ [32]$$

$$X^{m-} + S_2O_8^{2-} + M^{+} \longrightarrow [XMS_2O_8]^{(m+1)-} \longrightarrow \text{Products} \qquad \ldots\ldots \ [33]$$

where X^{n+} or X^{m-} is the reducing agent and M^+ in equation [33] is a cation present in the reaction medium. Examples of equation [32] are the oxidations of chromium(II)(30) and some iron(II) complexes(31) while the oxidation of iodide ion is an example of equation [33].

The presence of the cation as part of the activated complex modifies the distribution of electrons within the peroxodisulphate ion and weakens the O-O bond making its rupture easier as will be discussed in Chapter III and the fact that oxidations by peroxodisulphate are accompanied by the rupture of the O-O bond has been confirmed by tracer experiments(32). A brief discussion of some examples of this class of second order reactions follows.

I. Copper(I) oxidation

Chaltykian and Beileryan(33) studied the oxidation of copper(I) chloride. The second order reaction was found to be retarded by increased chloride ion concentration. Moreover they found that the diammine complex $[Cu(NH_3)_2]^+$ reacts virtually instantaneously and that, in presence of copper(I), peroxodisulphate does not oxidize ammonia. The stoicheiometry of the reaction is given by equation [34]

$$2Cu^{+} + S_2O_8^{2-} = 2SO_4^{2-} + 2Cu^{2+} \qquad \ldots\ldots \ [34]$$

and the proposed mechanism is

$Cu^{+} + S_2O_8^{2-} = CuS_2O_8^{-}$ slow ...... [35]

$CuS_2O_8^{-} = Cu^{2+} + SO_4^{2-} + SO_4^{-}$ ...... [36]

$SO_4^{-} + Cu^{+} = Cu^{2+} + SO_4^{2-}$ ...... [37]

Possible side reactions are

$SO_4^{-} + H_2O = HSO_4^{-} + OH$ ...... [6]

$OH + Cu^{+} = Cu^{2+} + OH^{-}$ ...... [38]

$OH^{-} + H^{+} = H_2O$ (assumed elsewhere) ...... [39]

The retarding effect of increased chloride ion concentration may be due to the formation of a chloro complex or complexes which have an adverse Coulombic effect on the rate determining step [35].

II. Iron(II) oxidation

The oxidation of iron(II) and its complexes by peroxodisulphate has been the subject of many papers (29,37,35,36). The stoicheiometry of the reaction is

$2Fe^{2+} + S_2O_8^{2-} = 2Fe^{3+} + 2SO_4^{2-}$ ...... [40]

Irvine(31) studied the oxidation of some complexes of iron(II) (and of ruthenium(II)) in order to establish the importance of standard free energy change as a factor in determining the rate of a redox reaction(37). He found that the rate of the reaction increases as the difference in standard redox potential between the peroxodisulphate and complex ion couples increases. He also found that equation [41] holds for the rate constant

$\log k_o = -6.4 + 7.0\,\Delta E^o$ ...... [41]

where k_o is the second order rate constant in l/mole/sec. at zero ionic strength and ΔE^o is the difference in standard redox potential between the two couples ($SO_4^{2-}/S_2O_8^{2-}$, Fe^{2+}/Fe^{3+}). Since the free energy change (ΔG^o) for the reaction represented by the stoicheiometric equation [40] in which Fe^{2+} represents the iron(II) complex is

$$\Delta G^o \;=\; 2F\left\{E^o(SO_4^{2-}/S_2O_8^{2-}) - E^o(Fe^{2+}/Fe^{3+})\right\} \;=\; 2F\Delta E^o \quad \ldots\ldots \quad [42]$$

the linear relationship between the logarithm of the rate constant and the standard free energy change is established.

Burgess and Prince(36) studied the effect of substituents in the ligand when tris-1,10-phenanthroline iron(II) and tris-bipyridyl iron(II) are oxidized by peroxodisulphate ion. The nature of the substituent was found to affect the value of the rate constant (and the activation energy). More powerful electron withdrawing substituents like nitro- and chloro-groups tend to lower the value of k (and increase the value of E) relative to the values found with unsubstituted ligands, whereas electron repelling substituents have a similar effect in the opposite direction. They also found that there is a linear relationship between the energy of activation and log A (and hence a relationship with the entropy of activation).

The mechanism of the oxidation of iron(II) complexes may be represented by

$$Fe^{2+} + S_2O_8^{2-} \longrightarrow Fe^{3+} + SO_4^{-} + SO_4^{2-} \quad \text{slow} \quad \ldots\ldots \quad [43]$$

$$Fe^{2+} + SO_4^{-} \longrightarrow Fe^{3+} + SO_4^{2-} \quad \text{fast} \quad \ldots\ldots \quad [44]$$

III. Thiosulphate oxidation

This reaction was first investigated by King and Steinbach(38). They found that the reaction is first order in peroxodisulphate and almost independent of thiosulphate concentration. They also found that the reaction is very sensitive to impurities, and that reproducibility is quite difficult to obtain. They reported that the reaction is catalyzed to a large extent by copper(II) and to a less extent by iron(II) while silver(I) was found to have little effect. Sorum and Edwards(39) re-investigated this reaction and found that (a) results are reproducible only if identical solutions prepared using the same batch of distilled water are used and that (b) there are large specific salt effects. Like their predecessors they reported that the reaction is first order in peroxodisulphate and zero order with respect to thiosulphate. They proposed a chain mechanism. However, Patat and Proelss(8) studied this reaction using carefully purified starting materials, especially the solvent water. They observed that the reaction follows second order kinetics under these conditions, being first order with respect to each reactant - a fact which has been confirmed by another group of workers(40). When Patat and Proelss replaced double distilled water with ordinary distilled water they found that the order with respect to thiosulphate varies between zero and one as was observed by the previous workers. This they explained as being due to the superimposition of a heavy metal ion catalyzed reaction on the uncatalyzed reaction because they found that traces of copper or iron alter the kinetics completely.

IV. Iodide ion oxidation

The iodide peroxodisulphate reaction has already gained an analytical importance for the determination of peroxodisulphate(41). The kinetics of the reaction have been extensively studied especially in regard to the salt effect, an effect which will be discussed in Chapter III(2,42,43). The reaction is second order, being first order with respect to each reactant. It is also relatively rapid and very sensitive to added salts. The rate of the reaction is dependent on the nature and concentration of any cation(s) present rather than on the ionic strength(42,43,44).

Silver(I) Catalyzed Reactions

As mentioned earlier the addition of a catalyst renders most of the slow peroxodisulphate reactions fast enough to be studied at room temperature. The catalyst which has been most widely used is silver(I) ion. Almost all of the silver(I) catalyzed reactions are first order with respect to peroxodisulphate, first order in silver(I) and zero order with respect to the reducing agent. The value of the second order rate constant (k_2) is similar for different reducing agents under similar conditions. These reactions obey the rate law

$$\frac{-d[S_2O_8^{2-}]}{dt} = k_2[S_2O_8^{2-}][Ag^+] \qquad \text{......} \quad [45]$$

Therefore all these reactions seem to have a common rate determining step. Examples of these silver(I) catalyzed oxidations are those of chromium(III)(3), manganese(II), hydrazine(45) and cerium(III)(4).

The first worker to investigate the mechanism of silver(I) catalysis of peroxodisulphate reactions was Yost(3) who studied the silver(I) catalyzed oxidation of chromium(III). He observed that when peroxodisulphate and silver(I) solutions are mixed in the absence of the reducing agent a black precipitate is formed immediately and that this precipitate has powerful oxidizing properties. His analysis of the precipitate led him to the conclusion that it is an oxide of silver(III). Therefore he proposed that in the silver(I) catalyzed oxidation of chromium(III) by peroxodisulphate the active intermediate is silver(III) which is formed according to the equation

$$S_2O_8^{2-} + Ag^+ \longrightarrow Ag^{3+} + 2SO_4^{2-} \qquad \ldots\ldots \quad [46]$$

which is the rate determining step and which is followed by the reaction of silver(III) with the reducing agent leading eventually to the oxidation products and the reduction of silver(III) to silver(I). The theory that silver(III) is the active intermediate in silver(I) catalyzed peroxodisulphate oxidations remained unchallenged for a long time(2,35).

As early as 1930, however, Morgan and Burstall(46) reported that, when bis-bipyridyl silver(I) is added to a cold aqueous solution of peroxodisulphate, the bis-bipyridyl silver(II) ion is formed. It was also observed by Malaguti(5) that both silver(I) and bis-bipyridyl silver(I) catalyze the hydrogen peroxide-peroxodisulphate reaction to the same extent. These two separate observations suggest that silver(II) rather than silver(III) may be the intermediate in this class of peroxodisulphate reactions. In 1968 Miller(47) reported the results of a study of the kinetics of the peroxodisulphate oxidation of bisbipyridyl silver(I) and of ethylenebis-biguanide (enbig) silver(I) ions - the enbig ligand being one of the few that can form a stable complex with silver(III). He found that the formation of bis-bipyridyl silver(II) complex is a second order reaction which is first order with respect to each of the two reactants, while the enbig complex of silver(III) is formed by two consecutive reactions each being first order in both reagents. Thus Miller concluded that the peroxodisulphate-silver(I) reaction involves a one-electron process, a finding which is in accordance with the empirical rules postulated by Higginson and Marshall(48). The mechanism for the formation of the silver(II) complex is given as

(a) $\mathrm{Ag(dipy)_2^{+} + S_2O_8^{2-} \longrightarrow Ag(dipy)_2^{2+} + X}$ slow ...... [47]

$\mathrm{Ag(dipy)_2^{+} + X \longrightarrow Ag(dipy)_2^{2+} + X^{-}}$ fast ...... [48]

where X is presumably $\mathrm{SO_4^{-}}$.

The mechanism put forward for the formation of Ag(III) complex is

(b) $\mathrm{Ag(enbig)^{+} + S_2O_8^{2-} \longrightarrow Ag(enbig)^{2+} + X}$ ...... [49]

$\mathrm{Ag(enbig)^{2+} + S_2O_8^{2-} \longrightarrow Ag(enbig)^{3+} + X}$ ...... [50]

where X may be $\mathrm{S_2O_8^{3-}}$ or $\mathrm{(SO_4^{2-} + SO_4^{-})}$, but in mechanism(b) X does not react with silver complexes but probably oxidizes water, whereas in (a) X reacts with a silver complex.

From this discussion the consensus of opinion is that the silver(I) catalyzed reactions involving peroxodisulphate ion take place according to the following generalized mechanism in which R is a reducing agent and P is the product or products of its oxidation

$\mathrm{Ag^{+} + S_2O_8^{2-} \longrightarrow Ag^{2+} + SO_4^{-} + SO_4^{2-}}$ slow ...... [51]

$\mathrm{Ag^{+} + SO_4^{-} \longrightarrow Ag^{2+} + SO_4^{2-}}$ fast ...... [52]

$\mathrm{Ag^{2+} + R \longrightarrow Ag^{+} + P}$ fast ...... [53]

and in which the active intermediate formally contains silver(II) and not silver(III).

Other Reactions

Not all peroxodisulphate reactions can be categorized under one of the three types discussed above. Many have uncertain orders or orders (especially with respect to reducing agent) that do not assume simple values, but vary according to conditions. The case of cerium(III) has already been discussed. Other examples are:

I. Oxidation of hydrogen peroxide

Hydrogen peroxide reacts with peroxodisulphate according to the stoicheiometric equation

$$H_2O_2 + S_2O_8^{2-} = O_2 + 2HSO_4^- \qquad \ldots\ldots [54]$$

Tsao and Wilmarth(49) gave the following rate law for the reaction at 30°C

$$\frac{-d[S_2O_8^{2-}]}{dt} = [S_2O_8^{2-}]\left\{\frac{9.5\text{x}10^6}{[H_2O_2]} + \frac{7.6\text{x}10^7[S_2O_8^{2-}]}{[H_2O_2]} + 2.9\text{x}10^{10}[S_2O_8^{2-}] + 7.9\text{x}10^8\right\}^{-\frac{1}{2}} \qquad \ldots\ldots [55]$$

(in which the units of rate are mole/l/sec) and which approaches the limiting forms shown below, under the respective conditions.

(i) $[S_2O_8^{2-}] = 0.001 - 0.025$ mole/l; $[H_2O_2] = 0.001 - 0.005$ mole/l

$$\frac{-d[S_2O_8^{2-}]}{dt} = k_{(i)}[S_2O_8^{2-}][H_2O_2]^{\frac{1}{2}} \qquad \ldots\ldots [56]$$

(ii) $[S_2O_8^{2-}] = 0.002 - 0.010$ mole/l; $[H_2O_2] = 0.025$ mole/l

$$\frac{-d[S_2O_8^{2-}]}{dt} = k_{(ii)}[S_2O_8^{2-}] \qquad \ldots\ldots [57]$$

(iii) $[S_2O_8^{2-}] = 0.100 - 0.250$ mole/l; $[H_2O_2] = 1.00$ mole/l

$$\frac{-d[S_2O_8^{2-}]}{dt} = k_{(iii)}[S_2O_8^{2-}]^{\frac{1}{2}} \qquad \ldots\ldots [58]$$

The authors give the following overall mechanism for the reaction:

$$S_2O_8^{2-} \longrightarrow 2SO_4^- \qquad \ldots\ldots [5]$$

$$SO_4^- + H_2O \longrightarrow H^+ + SO_4^{2-} + OH \qquad \ldots\ldots [6]$$

$$OH + H_2O_2 \longrightarrow H_2O + HO_2 \qquad \ldots\ldots [59]$$

$$HO_2 + S_2O_8^{2-} \longrightarrow O_2 + HSO_4^- + SO_4^- \qquad \ldots\ldots [60]$$

$$HO_2 + H_2O_2 \longrightarrow O_2 + H_2O + OH \qquad \ldots\ldots [61]$$

and they consider the following four reactions as the most important chain terminating steps.

$$HO_2 + OH \longrightarrow O_2 + H_2O \qquad \ldots\ldots [12]$$

$$SO_4^- + OH \longrightarrow HSO_5^- \qquad \ldots\ldots [62]$$

$$HO_2 + SO_4^- \longrightarrow O_2 + HSO_4^- \qquad \ldots\ldots [13]$$

$$SO_4^- + SO_4^- \longrightarrow S_2O_8^{2-} \qquad \ldots\ldots [63]$$

II. Oxidation of antimony(III)

The antimony(III)-peroxodisulphate reaction is another one of the rare reactions in which the order with respect to peroxodisulphate is other than unity. The rate law is reported to be$^{(51)}$

$$\frac{-d[S_2O_8^{2-}]}{dt} = k[Sb(III)]^{\frac{1}{2}} [S_2O_8^{2-}]^{\frac{1}{2}} \qquad \ldots\ldots [64]$$

The reaction is independent of hydrogen ion concentration in the range 0.005 - 0.08 mole/l, and the mechanism proposed is:

$$S_2O_8^{2-} \longrightarrow 2SO_4^{-} \qquad \ldots\ldots \quad [5]$$

$$Sb(III) + SO_4^{-} \longrightarrow Sb(IV) + SO_4^{2-} \qquad \ldots\ldots \quad [65]$$

$$S_2O_8^{2-} + Sb(IV) \longrightarrow Sb(IV) + SO_4^{2-} + SO_4^{-} \qquad \ldots\ldots \quad [65]$$

$$Sb(IV) + SO_4^{-} \longrightarrow Sb(V) + SO_4^{2-} \qquad \ldots\ldots \quad [67]$$

It may be noted that this set of one-electron oxidation steps does not fall into the category of two-electron processes postulated as virtually invariable for non-transitional/non-transitional element redox processes(48).

Although much work has been done on peroxodisulphate reactions and many aspects have been conclusively studied still there is disagreement between different groups of workers in other aspects of these reactions and many results, especially of the thermal decomposition of peroxodisulphate are far from conclusive(2,51,52). The author, therefore, thinks that there is still scope for more work in this field.

CHAPTER II

THE OXIDATION OF MANGANESE(II)

CHAPTER II

INTRODUCTION

The silver(I) catalyzed reaction between peroxodisulphate and manganese(II) was studied by Dekker et al(45) as well as by Gupta and Ghosh(53). Both groups of workers reported that the uncatalyzed reaction (at 25° or 35°C) is very slow and therefore they did not study it. In fact it seems that the kinetics of this reaction have not been studied at all as far as our survey of literature could prove.

Dekker and his co-workers followed the silver ion catalyzed reaction by filtering off the product, manganese dioxide, from the sample and estimating peroxodisulphate by treating it with excess of standard iron(II) solution and determining the reacted iron(II). However, Gupta and Ghosh preferred to avoid both the process of filtration and the use of iron(II) which is subject to atmospheric oxidation. They analyzed for the product manganese dioxide and estimated peroxodisulphate indirectly. The sample to be analyzed was added to a volume of standard oxalic acid to which hydrochloric acid was added in order to quench the reaction by precipitating the silver ions as silver chloride. The excess oxalic acid was then titrated against standard permanganate solution. From the amount of manganese dioxide formed the concentration of peroxodisulphate was calculated.

The results of the two studies, however, were not very different.

In this part of the present work an attempt is made to study the uncatalyzed reaction between peroxodisulphate and manganese(II).

EXPERIMENTAL

Preliminary Work

A series of experiments was planned and carried out to see if

(1) The uncatalyzed reaction between manganese(II) and peroxodisulphate was measurable under any conditions and if so under what conditions it would reasonably be followed.

(2) A direct method of estimating peroxodisulphate could be found.

I. When equal volumes of A.R. manganese(II) sulphate and A.R. ammonium peroxodisulphate solutions - each approximately 0.2 mole/l - were mixed at 60°C, the solution was turbid within two minutes and a precipitate - probably manganese dioxide - started to form within ten minutes.

II. A mixture which was 0.05 mole/l in manganese(II) sulphate and 0.04 mole/l in ammonium peroxodisulphate was maintained at 60°C. The initial pH of the solution - as measured with a Pye-Dynakap pH-meter was 3.62.

The same changes as in I above were observed but within thirty minutes.

These two tests suggested that manganese(II) and peroxodisulphate react at 60°C and that the reaction is 'apparently' fast enough to study kinetically. Therefore further preliminary work was pursued in order to analyze the precipitate, to find suitable conditions of temperature and reactant concentration and a method of analysis for following the reaction.

III. Analysis of the Precipitate

A mixture of ammonium peroxodisulphate and manganese(II) sulphate which was approximately 0.1 mole/l in each was thermostatted at 60°C for about seven hours. The solution was then filtered and the residue washed several times with distilled water. The precipitate was then left overnight in an oven at 110°C. It was cooled in a desiccator and then tested qualitatively and quantitatively.

A - Qualitative tests:

1. A sample of the precipitate was treated with a mixture of A.R. nitric acid, A.R. sulphuric acid and A.R. potassium periodate (see p. 47). The precipitate reacted forming a purple solution. The spectrum of the resulting solution was scanned in a Unicam SP.800 spectrophotometer. The spectrum (Fig. 1) was identical to that of an authentic sample of permanganate solution (Fig. 7).

2. When a sample of the precipitate was treated with hydrogen peroxide and dilute hydrochloric acid oxygen gas was evolved. The resulting solution gave no precipitate or even turbidity with barium chloride solution.

3. When the precipitate was treated with chromium(III) perchlorate solution and sulphuric acid, the precipitate dissolved. When the resulting solution was treated with diphenylcarbazide it gave a positive test for chromate.

Conclusions: The first of the three tests above indicates that the precipitate contains manganese, while the second and third show that the precipitate is or contains manganese dioxide. Moreover the barium chloride test on the solution in the second test indicates the absence of sulphate in the precipitate showing that the precipitate is not an addition product of a manganese oxide and sulphate unlike the case when peroxodisulphate and silver(I) react(3).

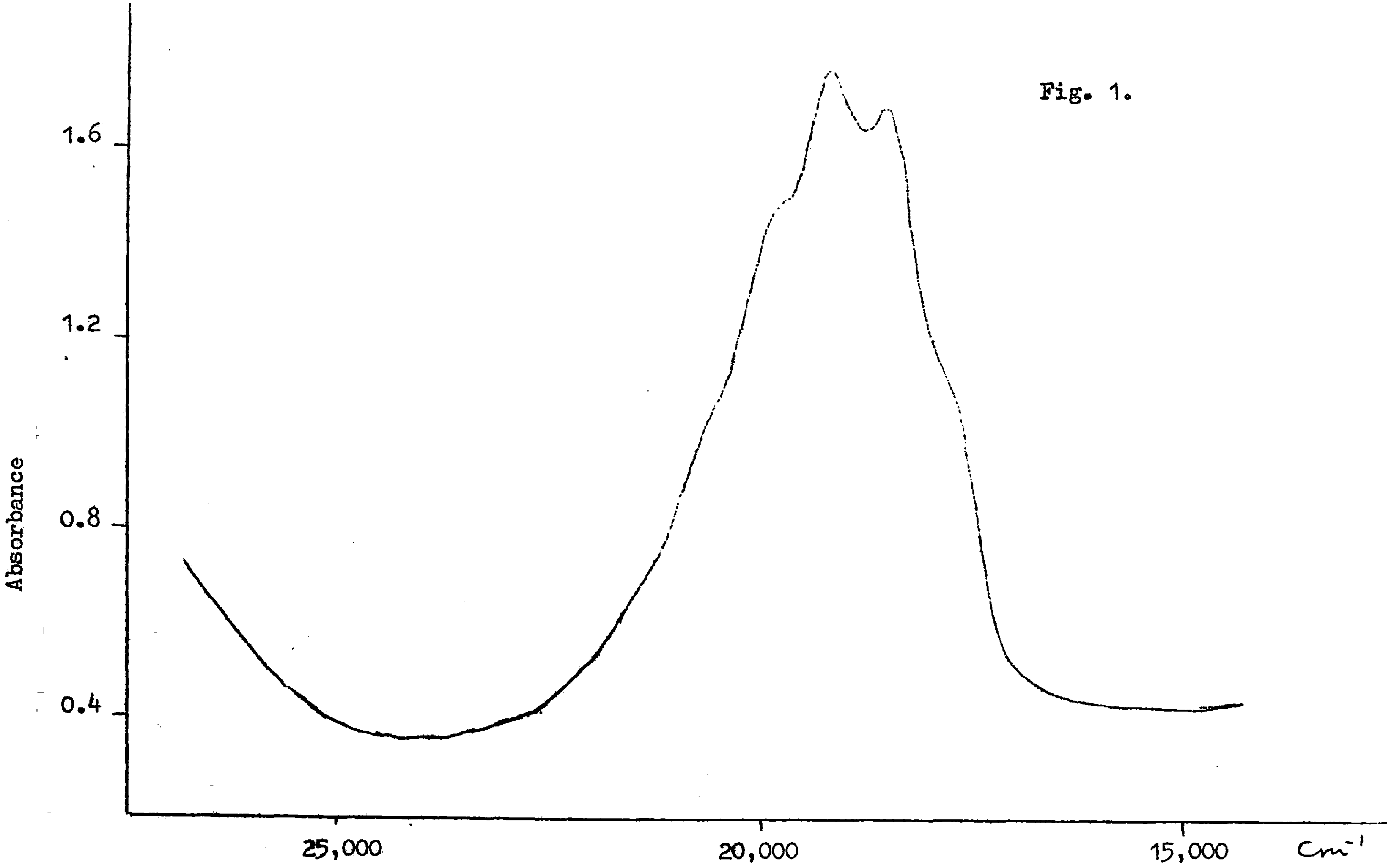


Fig. 1.

B - Quantitative analysis:

Manganese dioxide - precipitated from solutions - is a non-stoicheiometric compound usually of the form $MnO_2.xH_2O^{(54)}$. Any attempt to remove the water completely (which is virtually impossible), leads to the decomposition of the compound, as precipitated manganese dioxide decomposes at temperatures as low as 200°C(55). Despite all this, however, an attempt was made to analyze the precipitate which has been dried at 110°C.

A sample was weighed into an iodine flask. An excess of potassium iodide together with 2 ml of dilute sulphuric acid and water to dissolve the iodide were added and the flask was stoppered. A similar flask containing similar amounts of potassium iodide, acid and water was also stoppered and left to stand beside the flask containing the sample to act as a blank which will account for atmospheric oxidation of the iodide. The liberated iodine was titrated against standard sodium thiosulphate solution.

The results give manganese dioxide as 74.83% which may mean that the precipitate is $MnO_2.xH_2O$ where $1 < x < 2$.

IV. Analytical Methods for Following the Reaction

The kinetics of the reaction were investigated using two methods of analysis. In the early stages of the work the reaction was followed by estimating peroxodisulphate and in later stages, and for most of the work, by estimating manganese(II).

(A) Estimation of peroxodisulphate : Many of the reducing agents used for the estimation of peroxodisulphate e.g. iron(II) and iodide react with manganese dioxide, which is a product of the reaction.

Therefore the dissolution of manganese dioxide in excess oxalic acid followed by the iodometric estimation of peroxodisulphate was contemplated.

To see if the presence of oxalic acid will affect the iodometric determination of peroxodisulphate 5 ml of approximately 0.10 mole/l ammonium peroxodisulphate was added to each of the following:

(i) 10 ml 40% potassium iodide solution,

(ii) 10 ml 40% potassium iodide + 10 ml 0.4 mole/l oxalic acid,

(iii) 10 ml 40% KI + 10 ml 0.4 mole/l oxalic acid + 6 ml bicarbonate buffer.

(iv) 10 ml 40 KI + 6 ml bicarbonate buffer.

In each case the resulting iodine was titrated against approximately 0.10 mole/l sodium thiosulphate using a 50 ml grade A burette (Table 1(a)) and against approximately 0.15 mole/l sodium thiosulphate using a 10 ml semi-micro burette (Table 1(b)).

A look at this table shows that peroxodisulphate can be estimated iodometrically in presence of oxalic acid, an excess of which can be used to reduce the manganese dioxide before the iodide is added.

Table 1

Mixture	Titre ml (a)	Titre ml (b)
i	10.62	7.10
ii	10.58	7.10
iii	10.58	6.98
iv	10.57	7.06

Manganese(II), however, cannot interfere in presence of iodide ion because the manganese(II) - peroxodisulphate reaction is quite insignificant at room temperature in comparison to the iodide-peroxodisulphate reaction.

(B) Estimation of Manganese(II) : In most of the work the reaction was followed by estimating manganese(II) spectrophotometrically as will be described.

Experimental Details

I. Chemicals

All the chemicals used in this part of the work were Analar Grade. The two reactants were manganese(II) sulphate and ammonium peroxodisulphate.

II. Apparatus

The reaction vessels were 100 ml round bottomed Quick-fit flasks. Most of the volumetric glassware was grade A type. The reaction vessels, pipettes and all measuring flasks were cleaned as thoroughly as possible with chromic acid, washed several times with tap water, at least twice with distilled water and then rinsed twice with doubly distilled water (see below). The reaction vessels were dried in the oven while the pipettes were dried by passing air through them.

III. Medium

The reaction medium was water redistilled from alkaline potassium permanganate. It was necessary to use carefully doubly distilled water because it was found that the quality of water has a profound effect on reproducibility (see page 103).

For most of the kinetic runs the reaction mixture was made 0.250 mole/l in potassium sulphate to maintain a fairly constant ionic strength.

IV. Preparation of Solutions

Peroxodisulphate solutions were prepared fresh before each run or runs if done simultaneously or within two days, and under no circumstances were solutions used after more than 48 hours from the time of their preparation. These solutions were prepared by accurately weighing out the amount of ammonium peroxodisulphate required to make the solution. The concentration was also checked - if necessary - iodometrically.

Manganese(II) sulphate solutions were prepared in a similar manner but because this salt tends to lose its water of crystallization its concentration was determined spectrophotometrically (see p. 47). The manganese(II) sulphate solution was also made 0.500 mole/l in potassium sulphate in order to make the reaction mixture 0.250 mole/l in the added salt.

Experimental Procedure

The two reactants were thermostatted separately in a water bath maintained at 60°C. The surface of the bath was covered with polystyrene spheres. After 30 minutes the two reactants were mixed by pipetting equal volumes (25 ml of each) into the reaction vessel using pre-heated pipettes. Zero time for the reaction was taken as the time when the pipette introducing the second reactant, which was always the peroxodisulphate, was half empty. The reaction vessel was then stoppered and vigorously shaken.

At appropriate intervals 5 ml samples were withdrawn and added to 10 ml cold and approximately 0.4 mole/l oxalic acid in an iodine flask (or treated differently for the estimation of manganese(II) as will be described). After the manganese dioxide had dissolved, 5 ml 40% potassium iodide was added and the flask was stoppered and kept in the dark for 30 minutes. The iodine liberated was then titrated against standard sodium thiosulphate solution using a 10 ml semi-micro burette.

For each run the concentration of peroxodisulphate was plotted versus time and the slope of the best straight line through the early points was taken as the initial rate of the reaction.

To determine the order with respect to each reactant, the initial concentration of one was kept constant while that of the other was varied. A plot of log initial rate against log initial concentration - not reproduced here - gave an estimate of the order. Then the initial rate was plotted against the initial concentration to confirm the order (which is first with respect to peroxodisulphate and zero with respect to manganese(II)) and from these the rate constants were calculated.

The choice of a temperature

The reaction was tried at 50°C and 55°C and 60°C. At the former two temperatures it was inconveniently slow but it was reasonably measurable at 60°C. Therefore 60°C was chosen as the temperature at which the reaction was to be studied.

The control of hydrogen ion concentration

No simple way of controlling the pH of the reaction mixture could be found because peroxodisulphate reacts with acetate ion, and phosphate buffer or the addition of an alkali precipitate manganese(II) while the use of phthalate was found to stop the reaction completely. However, the absence of a buffer does not affect the results (see p. 91).

Order with respect to peroxodisulphate

In the following set of kinetic runs the concentration of manganese(II) was held constant at 0.04006 mole/l while that of peroxodisulphate was varied between 0.03000 mole/l and 0.08000 mole/l.

The concentration of peroxodisulphate was determined iodometrically as described earlier. Tables 2 - 7 show the experimental data and Figures 2 - 4 are the $[S_2O_8^{2-}]$/time plots from which the initial rates were calculated. Note that since quite small fractional conversion of peroxodisulphate are observed, a simple graph of $[S_2O_8^{2-}]$ versus time is adequate for the purpose here - especially in view of the order with respect to manganese(II) reported later. Table 8 summarises the variation of initial rate of reaction with initial concentration of peroxodisulphate. When the initial rate is plotted against initial peroxodisulphate concentration (Fig. 5), a straight line passing through the origin is obtained, thus showing that the reaction is first order with respect to peroxodisulphate. The slope of this plot gives the observed pseudo-first order rate constant (k_{obs}) as 3.29×10^{-4} min^{-1}.

The following experimental conditions apply to Tables 2 - 7. All concentration units are mole/l.

$[Mn(II)]_o$ = 0.04006

$[K_2SO_4]$ = 0.250

Temperature = 60.0°C

Table 2

$[S_2O_8^{2-}]_o$ = 0.0300

Time (min)	Titre* (ml)	$10^2[S_2O_8^{2-}]$
0	6.78	2.976
30	6.76	2.967
60	6.74	2.958
90	6.74	2.958
120	6.59	2.892
150	6.52	2.862
180	6.46	2.837
210	6.41	2.813
240	6.32	2.774

Table 3

$[S_2O_8^{2-}]_o$ = 0.0400

Time (min)	Titre* (ml)	$10^2[S_2O_8^{2-}]$
0	8.965	3.935
30	8.980	3.941
60	8.99	3.946
90	-	-
120	8.805	3.865
150	8.73	3.832
180	8.70	3.818
210	8.60	3.775
240	8.42	3.696

Table 4

$[S_2O_8^{2-}]_o$ = 0.05000

Time (min)	Titre* (ml)	$10^2[S_2O_8^{2-}]$
0	11.25	4.938
60	11.25	4.938
90	11.10	4.872
120	11.10	4.872
170	10.97	4.813
210	10.70	4.696
240	10.59	4.646
300	10.38	4.556

Table 5

$[S_2O_8^{2-}]_o$ = 0.08000

Time (min)	Titre** (ml)	$10^2[S_2O_8^{2-}]$
90	6.00	7.632
130	5.97	7.594
150	5.94	7.556
180	5.87	7.467
210	5.82	7.403
240	5.74	7.295
270	5.68	7.225
300	6.63	7.155

* $[Na_2S_2O_3]$ = 0.04389

** $[Na_2S_2O_3]$ = 0.1272

Table 6

$[S_2O_8^{2-}]_o$ = 0.06000

Time (min)	Titre** (ml)	$10^2[S_2O_8^{2-}]$
30	4.69	5.966
60	4.65	5.915
120	4.51	5.737
150	4.49	5.711
180	4.42	5.622
210	4.36	5.546
240	4.34	5.520
270	4.27	5.431
300	4.225	5.374
330	4.175	5.311
360	4.120	5.241
390	4.085	5.196

Table 7

$[S_2O_8^{2-}]_o$ = 0.07000

Time (min)	Titre** (ml)	$10^2[S_2O_8^{2-}]$
30	5.46	6.945
60	5.45	6.932
120	5.36	6.818
150	5.28	6.716
180	5.20	6.614
210	5.14	6.538
240	5.08	6.462
270	5.02	6.385
300	4.98	6.335
330	4.91	6.246
360	4.82	6.131
390	4.78	6.080

** $[Na_2S_2O_3]$ = 0.1272

Table 8

Variation of Initial Rate with Initial Peroxodisulphate concentration.

$[Mn(II)]_o$ = 0.04006 mole/l
$[K_2SO_4]$ = 0.250 mole/l
Temperature = 60.0°C

$10^2[S_2O_8^{2-}]_o$ (mole/l)	10^5 Initial rate (mole/l/min)
3.000	1.00
4.000	1.23
5.000	1.58
6.000	2.09
7.000	2.55
8.000	2.63

In this graph and all the following graphs the numbers on the lines refer to the tables from which the data are plotted.

Fig. 2

$[S_2O_8^{2-}]$ v. time

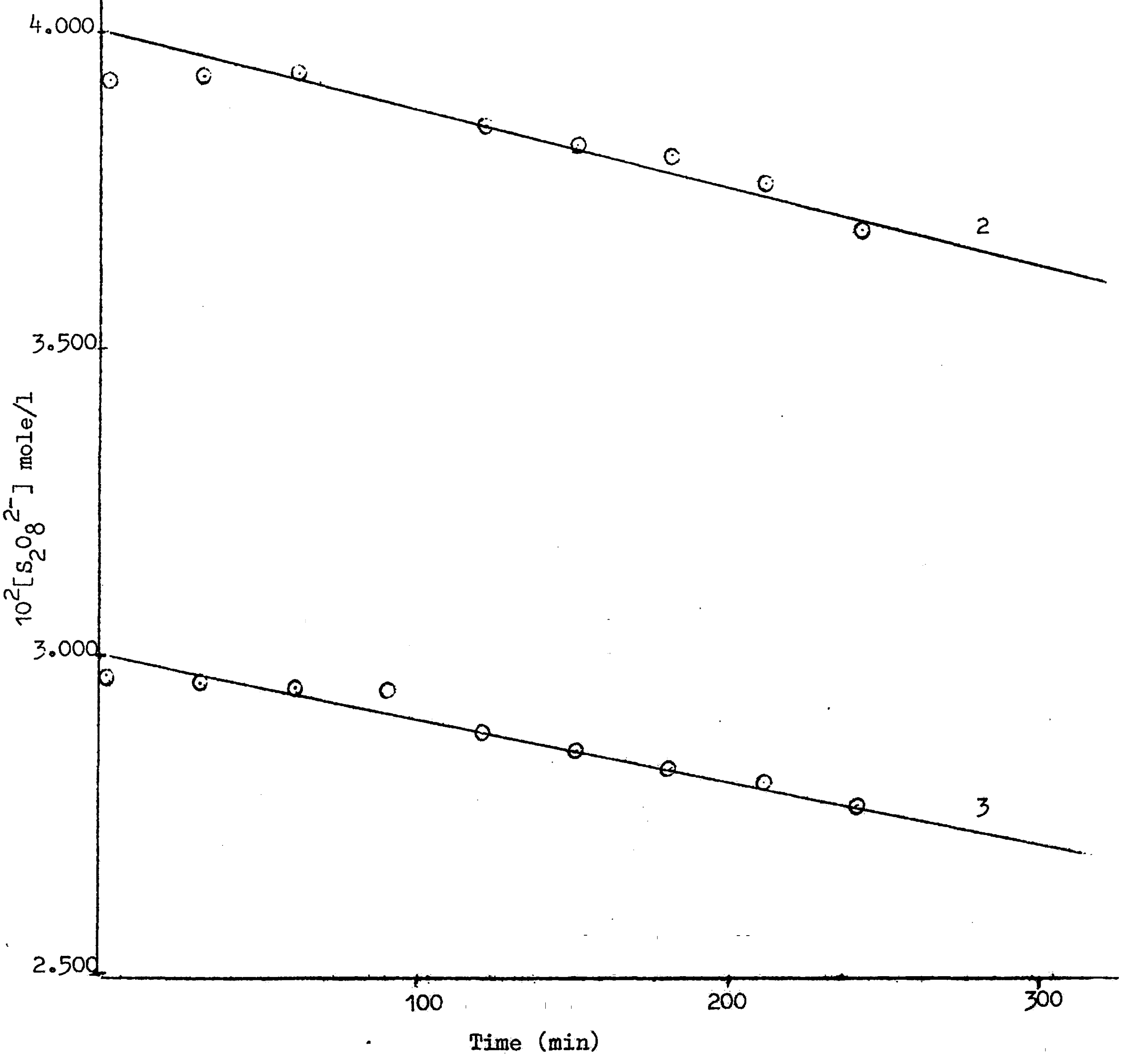
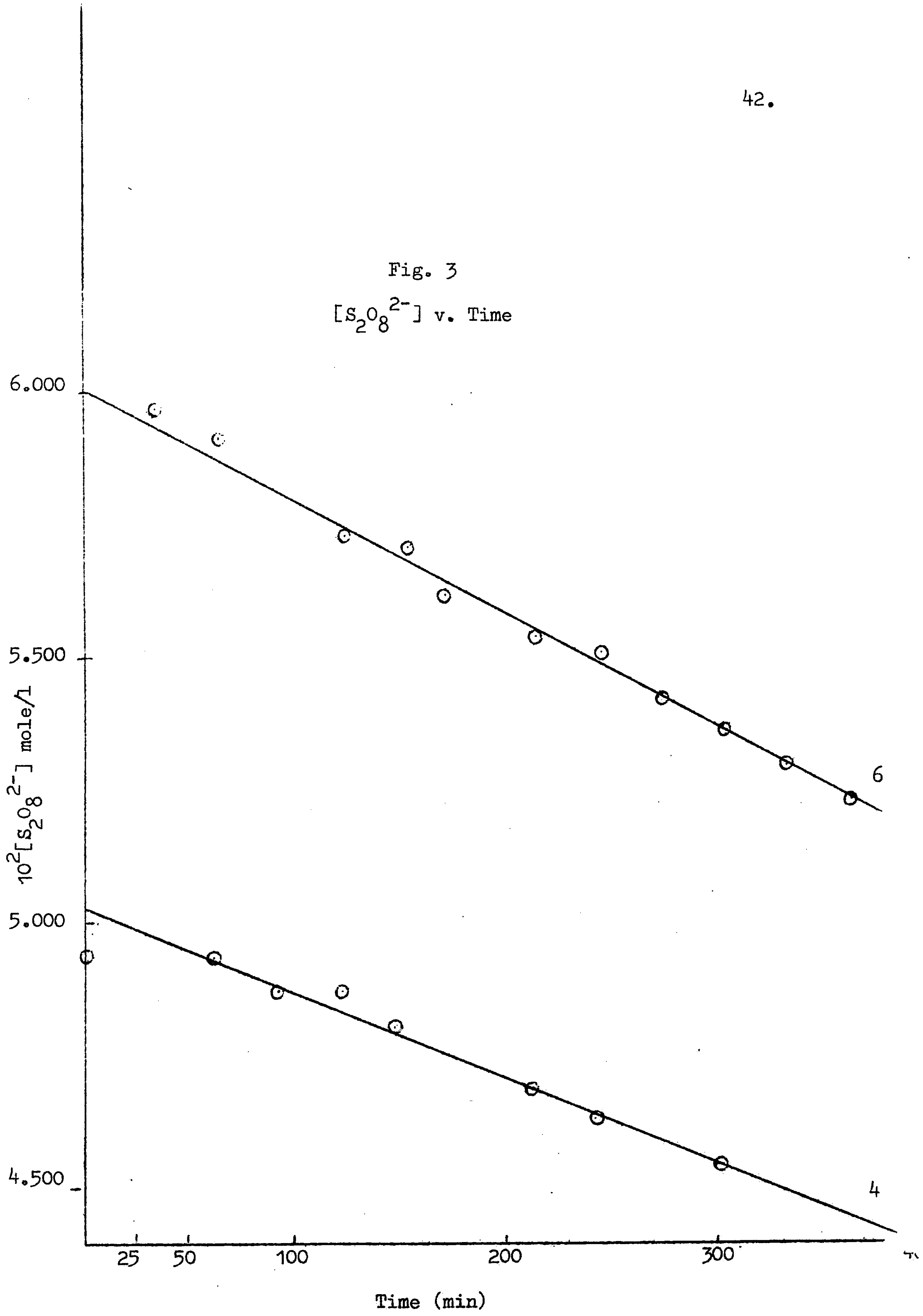


Fig. 3

$[S_2O_8^{2-}]$ v. Time



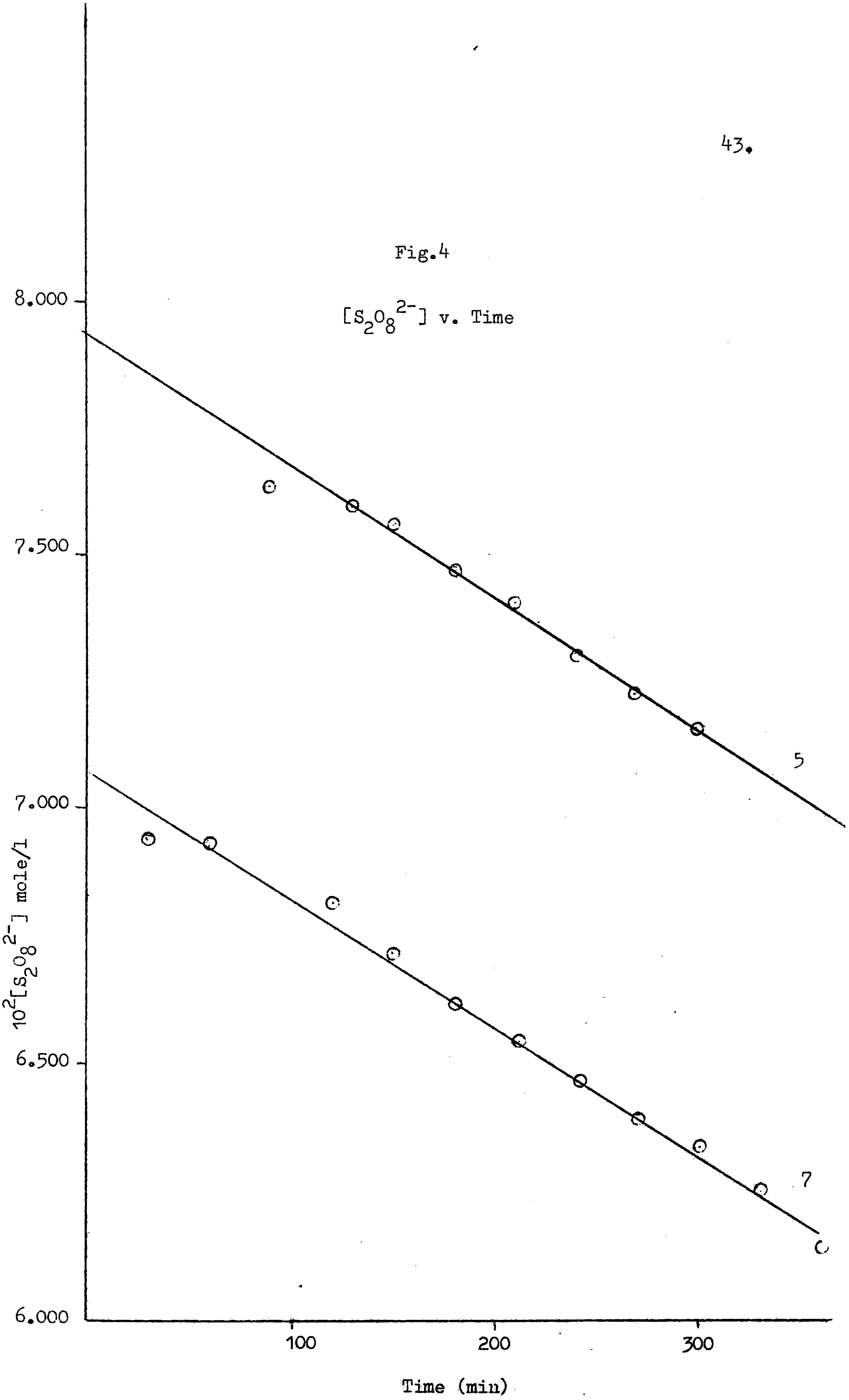


Fig.4

$[S_2O_8^{2-}]$ v. Time

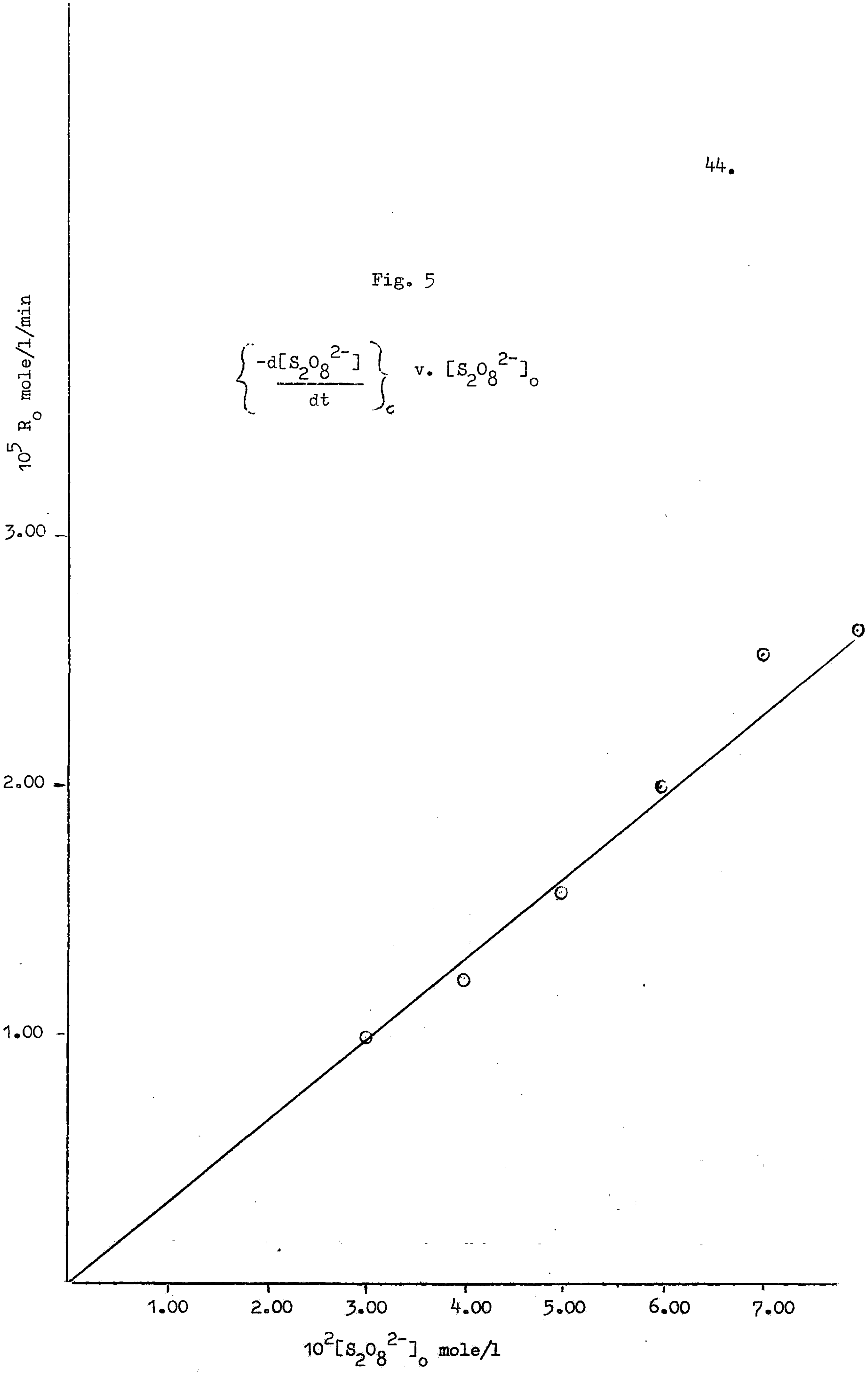


Fig. 5

$$\left\{ \frac{-d[S_2O_8{}^{2-}]}{dt} \right\}_c \text{ v. } [S_2O_8{}^{2-}]_o$$

The thermal decomposition of peroxodisulphate

Table 9 and Figure 6 show a representative sample of kinetic runs for the thermal decomposition of peroxodisulphate in the absence of manganese(II) under conditions which are similar to those of the redox reaction. The concentration of peroxodisulphate was again determined iodometrically. 5 ml Samples were withdrawn and added to 5 ml of chilled water. This was followed by the addition of 5 ml of 4% $NaHCO_3$ solution and 1 ml of 0.5 mole/l H_2SO_4. The mixture was shaken and the iodide added; the liberated iodine was then titrated against standard thiosulphate.

Table 9

All concentrations are in units of mole/l

$[S_2O_8^{2-}]$ = 0.07880 mole/l $(NH_4)_2 S_2O_8$

$[K_2SO_4]$ = 0.250

Temperature = 60.0°C

$[S_2O_3^{2-}]$ = 0.02239

Time (min)	Titre (ml)	$10^2[S_2O_8^{2-}]$	$2 + \log [S_2O_8^{2-}]$
60	34.00	7.613	0.8815
120	33.44	7.487	0.8743
160	33.17	7.427	0.8708
240	32.35	7.243	0.8599
360	31.40	7.030	0.8470
420	30.98	6.936	0.8411
450	30.74	6.883	0.8378
480	30.65	6.863	0.8365

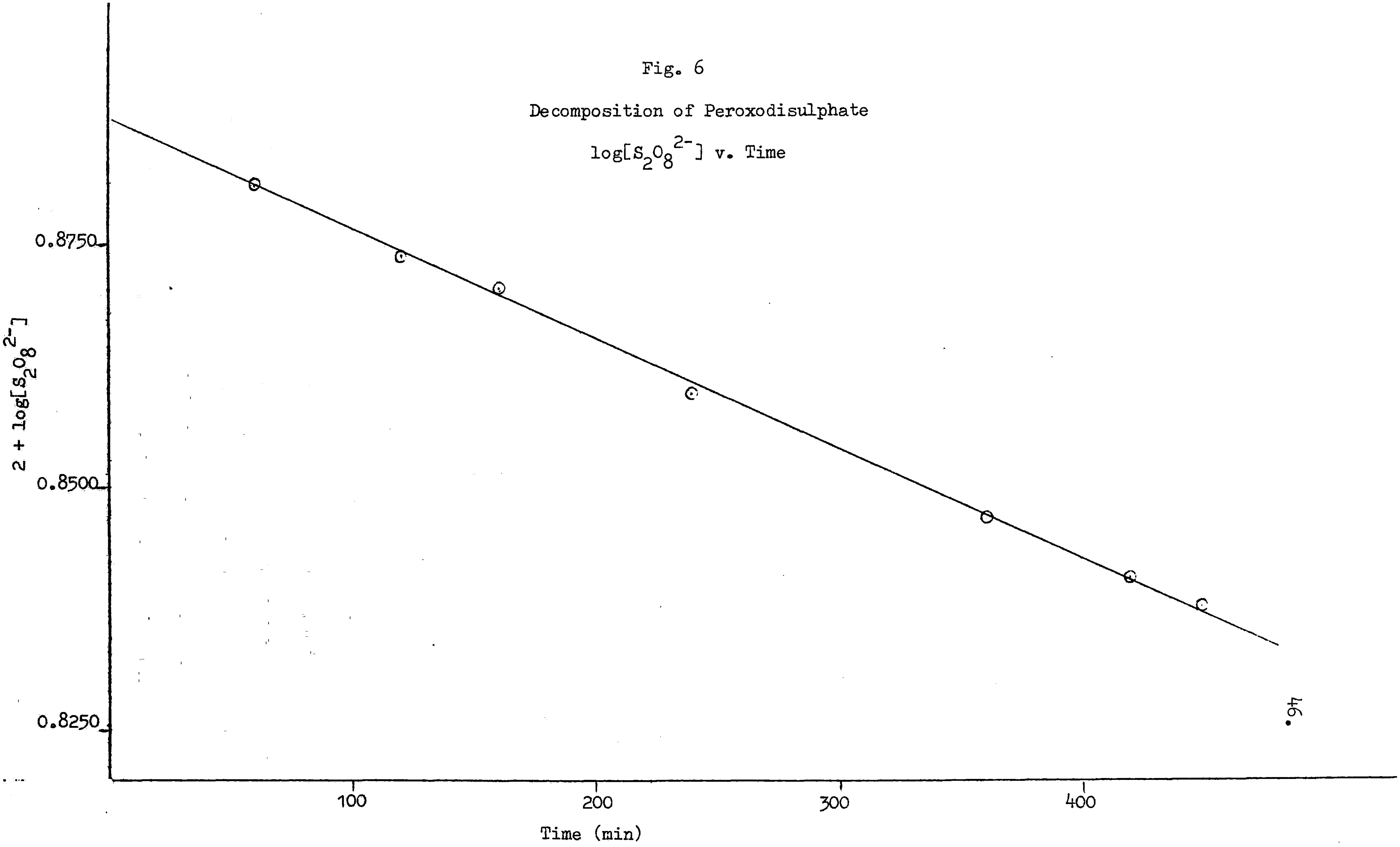


Fig. 6

Decomposition of Peroxodisulphate

$\log[S_2O_8^{2-}]$ v. Time

Determination of concentration of Mn(II)

When manganese(II) is present in a sample in relatively small concentration (ca. 2 mg/100 ml solution) it can be converted to permanganate and the latter determined spectrophotometrically. Manganese(II) reacts with periodate in presence of an excess of a mixture of concentrated nitric acid and concentrated sulphuric acid (c.f.(56)), according to the stoicheiometric equation [68].

$$2Mn^{2+} + 5IO_4^- + 3H_2O = 2MnO_4^- + 5IO_3^- + 6H^+ \quad ...... \quad [68]$$

Permanganate was found to have a maximum absorbance at 525 nm under the experimental conditions (Fig.7).

In the following work the reaction was followed by estimating the unreacted manganese(II). At appropriate intervals 5 ml samples were added to a filtration system, to which chilled water had been added in order to quench the reaction, and the manganese dioxide was filtered off. The filter paper was carefully flushed with chilled water at least four times and this was found to be enough to wash through all the manganese(II) ion. The filtrate was treated with a mixture of A.R. concentrated nitric acid and sulphuric acid and then an excess of A.R. potassium periodate was added. The mixture was then boiled for at least three minutes to convert manganese(II) to permanganate. In the cases where the initial concentration of manganese(II) was relatively high (above 0.0250 mole/l) the filtrate was diluted quantitatively and a sample of the diluted solution was used for the determination of manganese(II). This was necessary because it was found that at such concentrations the conversion to permanganate was quite difficult and precipitates tended to form when the mixture was boiled. The solution was allowed to cool and was transferred quantitatively to a measuring flask. The absorbance of this solution was then measured in

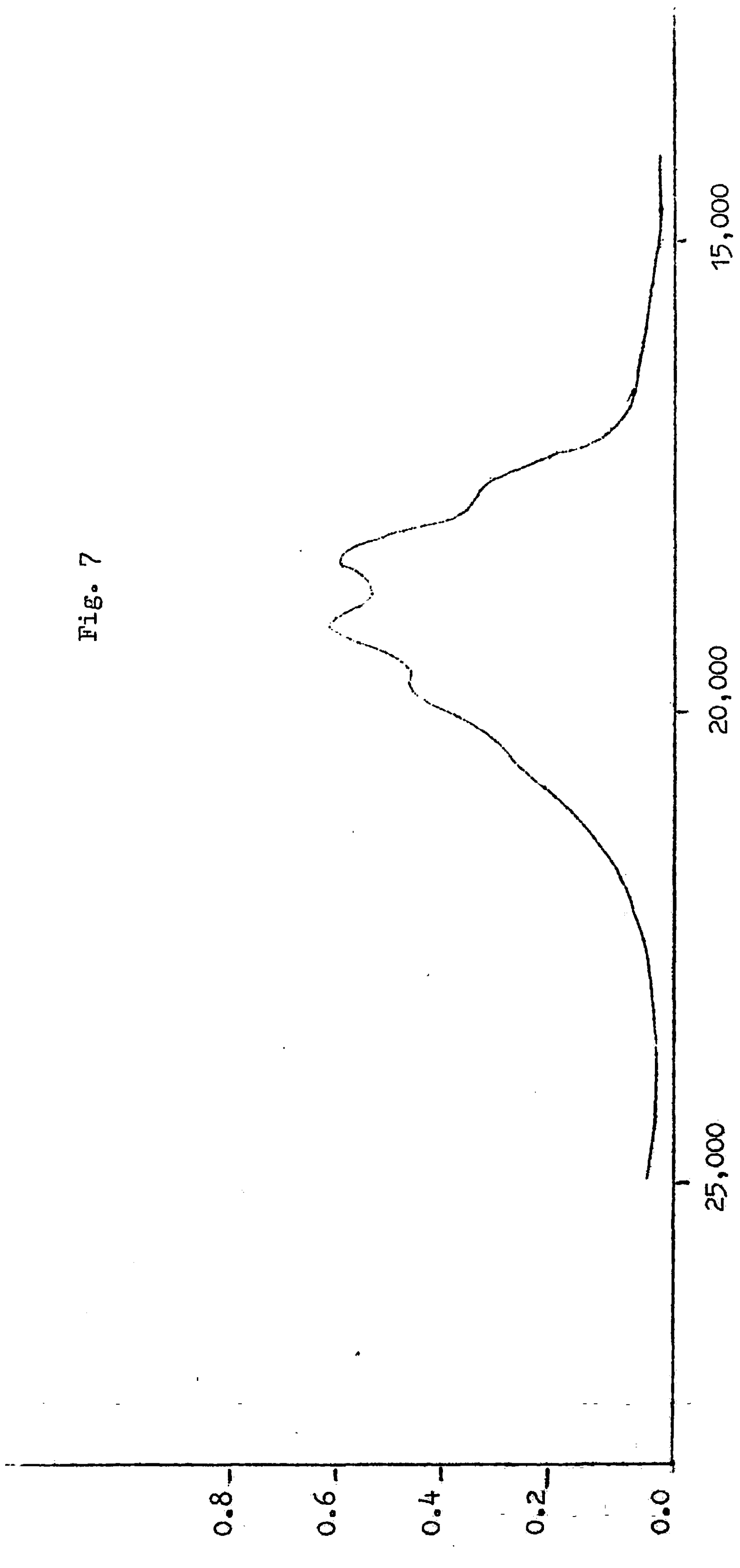


Fig. 7

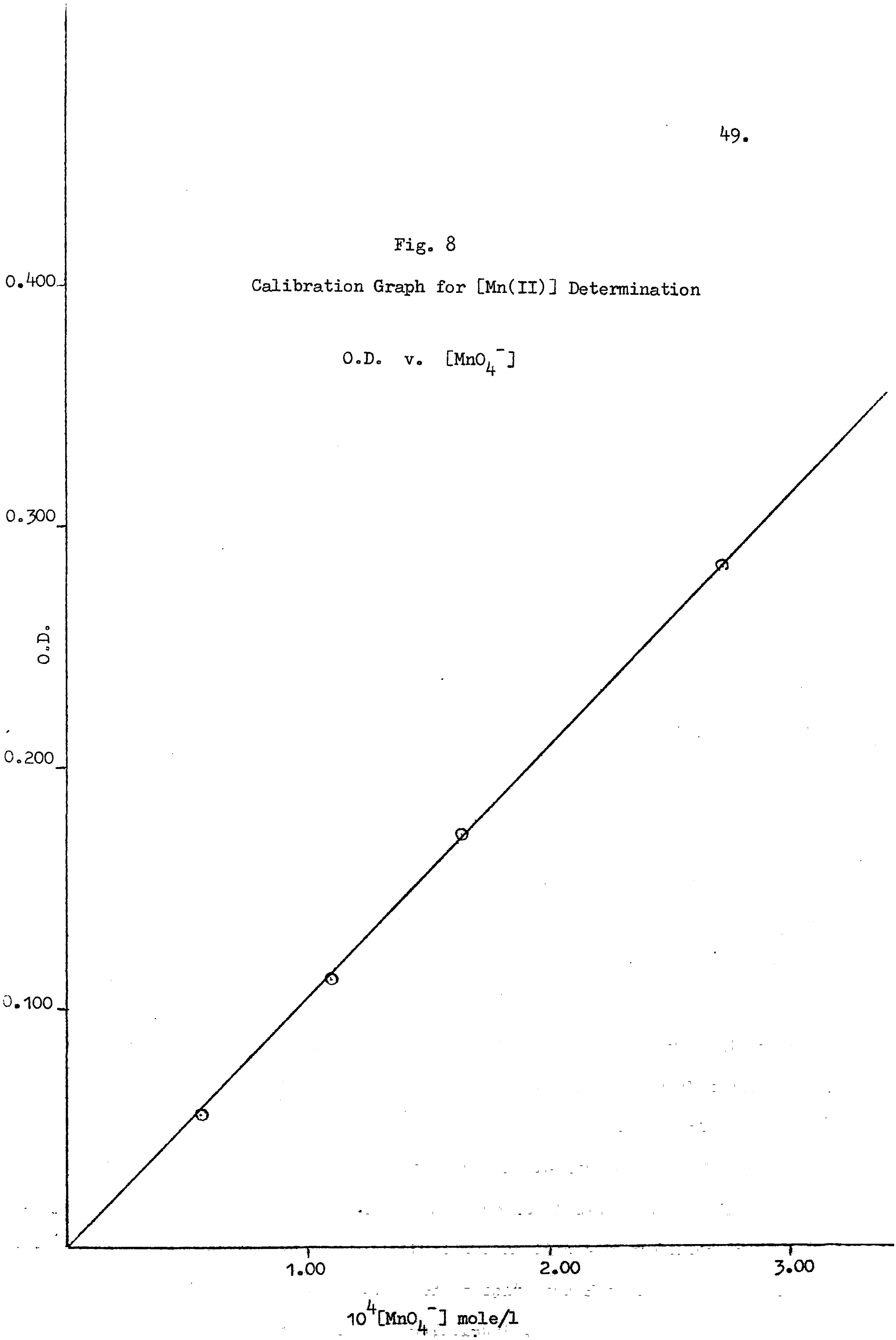


Fig. 8

Calibration Graph for [Mn(II)] Determination

O.D. v. $[MnO_4^-]$

a Unicam SP.500 spectrophotometer at 525 nm using 5 mm cells. At this wave length of maximum absorbance by the permanganate the solution obeys Beer's law (Fig. 8.). The extinction coefficient is calculated from this graph as 2.083×10^3. A few runs were carried out using a Perkin-Elmer double beam spectrophotometer 124(2) fitted with a digital scale and using 10 mm cells. The concentration of permanganate (and therefore of manganese(II)) was read from the appropriate calibration curve (Fig.8') or calculated using the value of the extinction coefficient cited above when the P.E.124(2) instrument was used.

Calculation of the rate

For each run the concentration of manganese(II) was plotted against time and a straight line was observed for large fractional extents of reaction in each case indicating zero order kinetics with respect to manganese(II). The slope of this line was taken as the initial rate of the reaction.

An attempt to use near equivalent concentrations of peroxodisulphate and manganese(II) at low concentrations of about 0.01 mole/l failed to give satisfactory results because the reaction was inconveniently slow. On the other hand when the initial concentration of manganese(II) was above 0.03 mole/l at the initial peroxodisulphate concentration of 0.08 mole/l the estimation of the former was quite difficult as mentioned above and therefore 0.03 mole/l of manganese(II) was taken as the upper limit in order to avoid any error that might have been introduced if the samples were to be diluted. In looking at the $[Mn^{2+}]$/time plots that follow, one, therefore has to bear in mind that peroxodisulphate is always in excess and that its decomposition in any run is always less than 10% and this explains why no curvature of the straight line occurs during the part of the reaction which is followed, despite the fact that the reaction is found to be first order in peroxodisulphate.

Order with respect to peroxodisulphate

The effect of varying the initial concentration of peroxodisulphate on the rate of the reaction was re-examined by estimating the unreacted manganese(II) concentration and calculating the initial rate of disappearance of manganese(II). The initial concentration of manganese(II) was held constant at 0.008010 mole/l and that of peroxodisulphate was varied between 0.04982 mole/l and 0.1200 mole/l. The ionic strength of the reaction mixture was maintained at approximately 1.00 mole/l by making it 0.250 mole/l in potassium sulphate.

In each run 5 ml samples were withdrawn at appropriate intervals and after filtering off the manganese dioxide, the filtrate was treated with concentrated nitric acid and sulphuric acid, boiled with excess potassium periodate, cooled and then quantitatively transferred to a 100 ml volumetric flask and the optical density of the solution measured. The initial rate of the reaction was calculated from the $[Mn^{2+}]$/time plots (Fig. 9).

The initial rate of the disappearance of manganese(II) was plotted against the initial concentration of peroxodisulphate (Fig. 10). The result was, once more, a straight line passing through the origin, which confirmed that the reaction is first order with respect to peroxodisulphate (at least in its initial stages). Moreover, the slope of this line gives the observed first order rate constant (k_{obs}) as 3.27×10^{-4} min^{-1} and this value compares rather well with the value of 3.29×10^{-4} min^{-1} obtained from Fig. 5 in which the initial rate of disappearance of peroxodisulphate is plotted against its initial concentration. These results confirm:

(a) that peroxodisulphate and manganese(II) react in equimolar amounts and,

(b) that all of the peroxodisulphate that decomposes goes to oxidize manganese(II) while this is present.

The experimental data are given in Tables 10 - 16 and the $[Mn^{2+}]$/time plots are shown in Fig. 9 while in Fig. 10 the initial rate (R_o) is plotted against the first power of initial peroxodisulphate concentration. In all the runs:

$[Mn^{2+}]_o$ = 0.008010 mole/l

$[K_2SO_4]$ = 0.250 mole/l

Temperature = 60.0°C

$[S_2O_8^{2-}]_o$ varies as shown, all concentrations being expressed in units of mole/l.

Table 10

$[S_2O_8^{2-}]_o$ = 0.08000

Time (min)	Absorbance	$10^3[Mn^{2+}]$
60	0.327	6.46
105	0.275	5.26
150	0.206	3.96
180	0.166	3.20
304	0.028	0.540
330	0.002	0.040

Table 11

$[S_2O_8^{2-}]_o$ = 0.06896

Time (min)	Absorbance	$10^3[Mn^{2+}]$
45	0.363	6.78
90	0.305	5.86
150	0.235	4.51
195	0.185	3.56
240	0.140	2.68
285	0.084	1.62
330	0.038	0.66

Table 12

$[S_2O_8^{2-}]_o = 0.08987$

Time (min)	Absorbance	$10^3[Mn^{2+}]$
45	0.338	6.48
90	0.271	5.20
150	0.185	3.56
195	0.117	2.24
240	0.063	1.20
285	0.010	0.20
330	0.012	0.22

Table 13

$[S_2O_8^{2-}]_o = 0.04982$

Time (min)	Absorbance	$10^3[Mn^{2+}]$
45	0.376	7.20
90	0.334	6.40
135	0.307	5.88
180	0.252	4.88
225	0.228	4.38
285	0.180	3.46
315	0.155	2.98

Table 14

$[S_2O_8^{2-}]_o = 0.06016$

Time (min)	Absorbance	$10^3[Mn^{2+}]$
45	0.360	6.92
90	0.326	6.22
135	0.271	5.20
180	0.225	4.32
225	0.182	3.50
285	0.127	2.44
315	0.096	1.84

Table 15

$[S_2O_8^{2-}]_o = 0.1004$

Time (min)	Absorbance	$10^3[Mn^{2+}]$
30	0.366	7.04
60	0.303	5.80
90	0.250	4.80
120	0.219	4.06
150	0.151	2.90
180	0.105	2.02
210	0.052	1.00

Table 16

$[S_2O_8^{2-}]_o$ = 0.1200

Time (min)	Absorbance	$[10^3[Mn^{2+}]$
30	0.348	6.68
60	0.285	5.48
90	0.236	4.52
120	0.166	3.20
150	0.094	1.81
180	0.035	0.68
210	0.006	0.12

Table 17

Variation of Initial Rate (R_o) with Initial Peroxodisulphate concentration

$[Mn^{2+}]_o$ = 0.008010 mole/l

$[K_2SO_4]$ = 0.250 mole/l

Temperature = 60.0°C

$10^2[S_2O_8^{2-}]_o$ mole/l	10^5 R_o mole/l/min
4.982	1.57
6.016	1.88
6.896	2.23
8.000	2.70
8.987	2,82
10.04	3.20
12.00	3.99

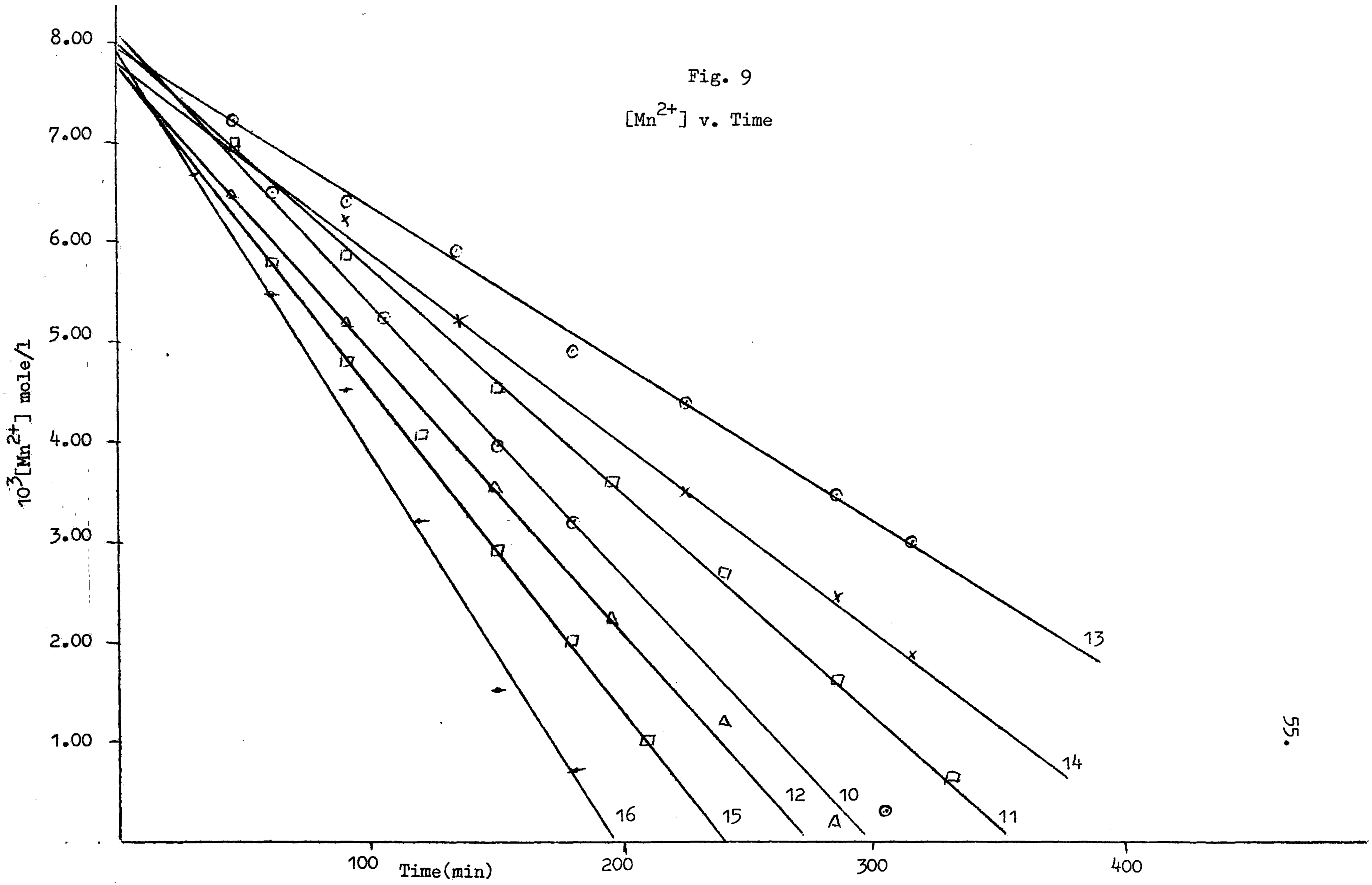


Fig. 9

$[Mn^{2+}]$ v. Time

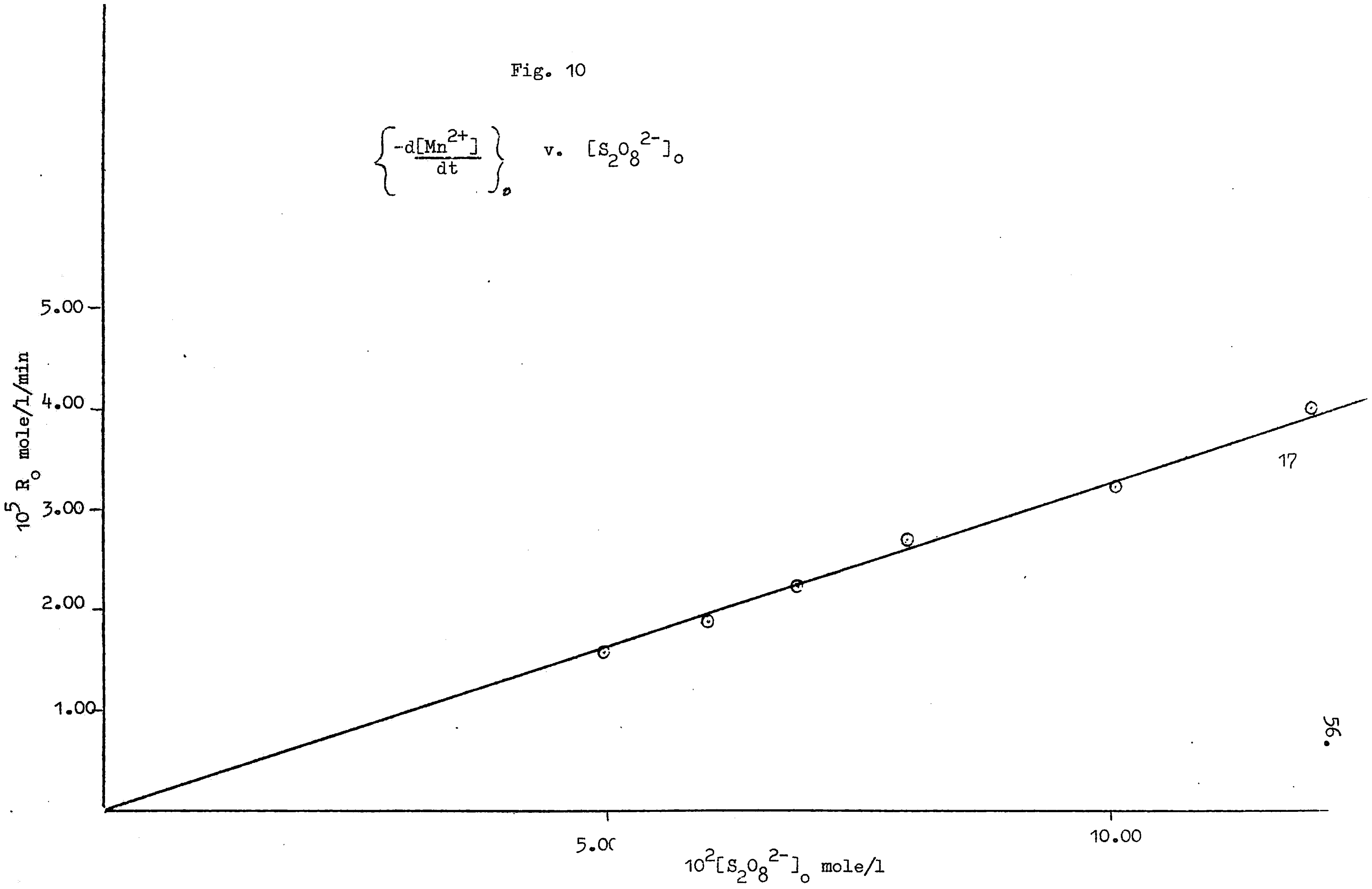


Fig. 10

$\left\{ \frac{-d[Mn^{2+}]}{dt} \right\}_o$ v. $[S_2O_8^{2-}]_o$

Order with respect to manganese(II)

The effect of varying the initial concentration of manganese(II) on the initial rate of the reaction was investigated. The initial concentration of peroxodisulphate was held constant at 0.08000 mole/l while that of manganese(II) was varied from 0.005180 mole/l to 0.03180 mole/l. The reaction mixture was made 0.250 mole/l in potassium sulphate to maintain a fairly constant ionic strength of about 1.00 mole/l.

The plot of manganese(II) concentration versus time gave a straight line in each case, as mentioned earlier, thus indicating zero order kinetics with respect to this reactant. Moreover, a plot of initial rate versus initial manganese(II) concentration (Fig. 13) gave a straight line parallel to the concentration axis, confirming the zero order with respect to manganese(II).

The experimental data are given in Tables 18-24 while the [Mn(II)]/time plots are shown in Figs. 11-12. The detailed procedure for the determination of [Mn(II)] is stated for each run.

For all the runs the following initial conditions are applicable:

$[S_2O_8{}^{2-}]_o = 0.08000$ mole/l

$[K_2SO_4] = 0.250$ mole/l

Temperature = 60.0°C

All concentrations are in units of mole/l.

Table 18

$[Mn^{2+}]_o$ = 0.005180

5 ml sample treated as described in p. 47 , resulting solution diluted to 100 ml and O.D. measured.

Time (min)	Absorbance	$10^3[Mn^{2+}]$
45	0.211	4.04
90	0.139	2.68
120	0.106	2.04
180	0.021	0.400
240	0.002	0.040

Table 19

$[Mn^{2+}]_o$ = 0.01060

5 ml sample treated as in all previous runs and resulting solution diluted to 250 ml.

Time (min)	Absorbance	$10^3[Mn^{2+}]$
150	0.144	6.90
210	0.107	5.15
270	0.080	3.80
330	0.043	2.05
390**	0.036	0.680
450**	0.017	0.320

** MnO_4^- solution diluted to 100 ml.

Table 20

$[Mn^{2+}]_o$ = 0.008450

Procedure for analysis as in Table 18 above

Time (min)	Absorbance	$10^3[Mn^{2+}]$
50	0.339	6.48
90	0.289	5.54
120	0.245	4.70
150	0.209	4.01
180	0.163	3.14
210	0.121	2.32
240	0.081	1.56

Table 21

$[Mn^{2+}]_o$ = 0.02120

Analysis as in Table 19 above.

Time (min)	Absorbance	$10^2[Mn^{2+}]$
150	0.365	1.76
210	0.332	1.59
270	0.300	1.44
330	0.272	1.30
390	0.241	1.155
450	0.209	1.00
480	0.189	0.905

Table 22

$[Mn^{2+}]_o$ = 0.02575

Analysis : 5 ml sample treated as usual but diluted to 500 ml before O.D. was measured.

Time (min)	Absorbance	$10^2[Mn^{2+}]$
60	0.255	2.44
180	0.228	2.19
210	0.212	2.03
240	0.202	1.94
295	0.193	1.85
360	0.180	1.72
420	0.161	1.54
450	0.151	1.44

Table 23

$[Mn^{2+}]_o$ = 0.03175

5 ml sample diluted to 50 ml and then 5 ml of this diluted sample treated as usual, diluting MnO_4^- solution to 100 ml and O.D. measured.

Time (min)	Absorbance	$10^2[Mn^{2+}]$
60	0.160	3.08
120	0.150	2.88
180	0.138	2.66
240	0.132	2.54
300	0.124	2.38
360	0.115	2.20
420	0.105	2.02

Table 24

Variation of R_o with $[Mn^{2+}]_o$

$[S_2O_8^{2-}]_o$ = 0.08000 mole/l

$[K_2SO_4]$ = 0.250 mole/l

Temperature = 60°C

$10^2[Mn^{2+}]_o$ mole/l	10^5 R_o mole/l/min
0.5180	2.70
0.8010	2.69
0.8450	2.67
1.060	2.67
2.120	2.60
2.580	2.70
3.180	2.82

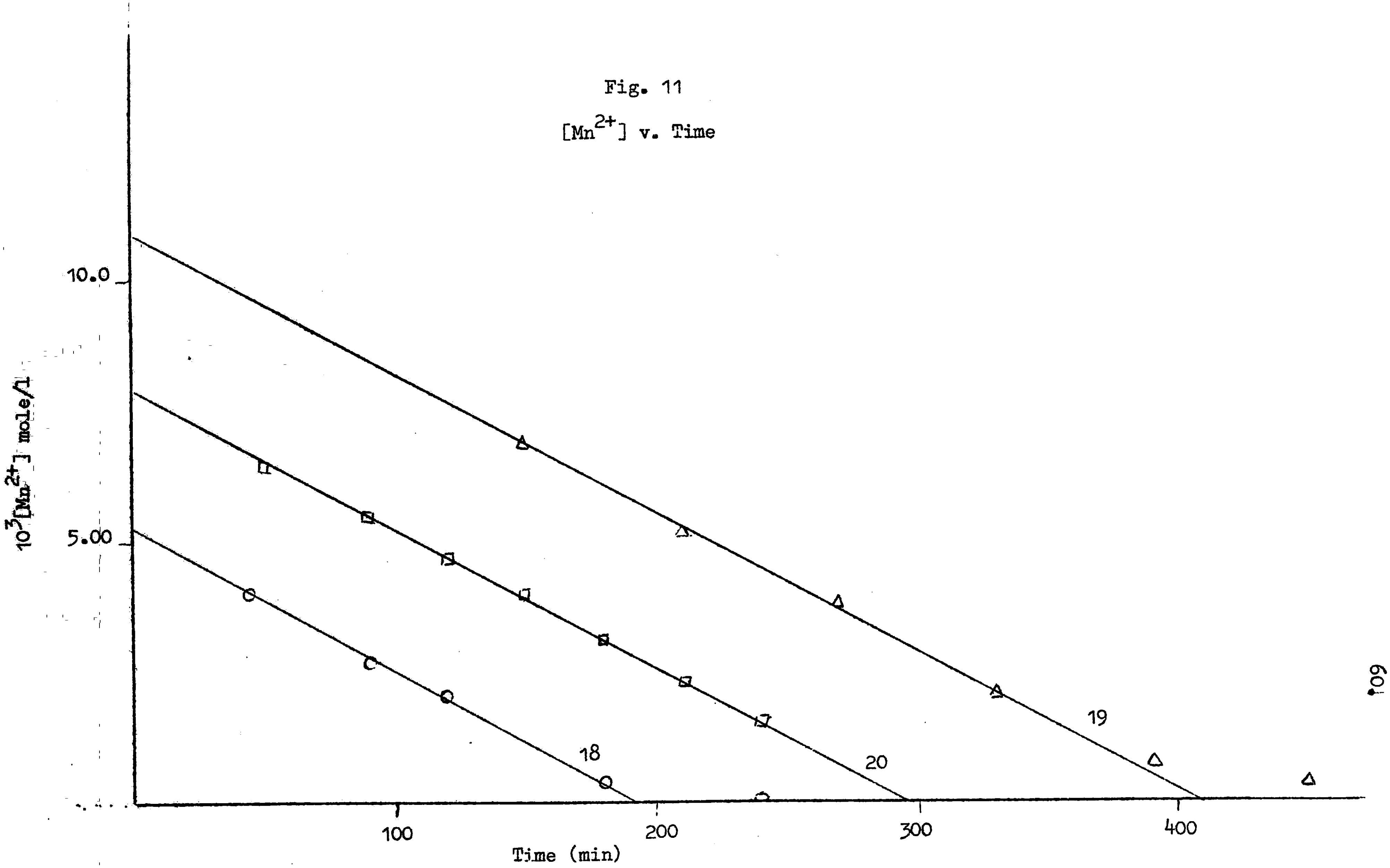


Fig. 11

$[Mn^{2+}]$ v. Time

Fig. 12

[Mn^{2+}] v. Time

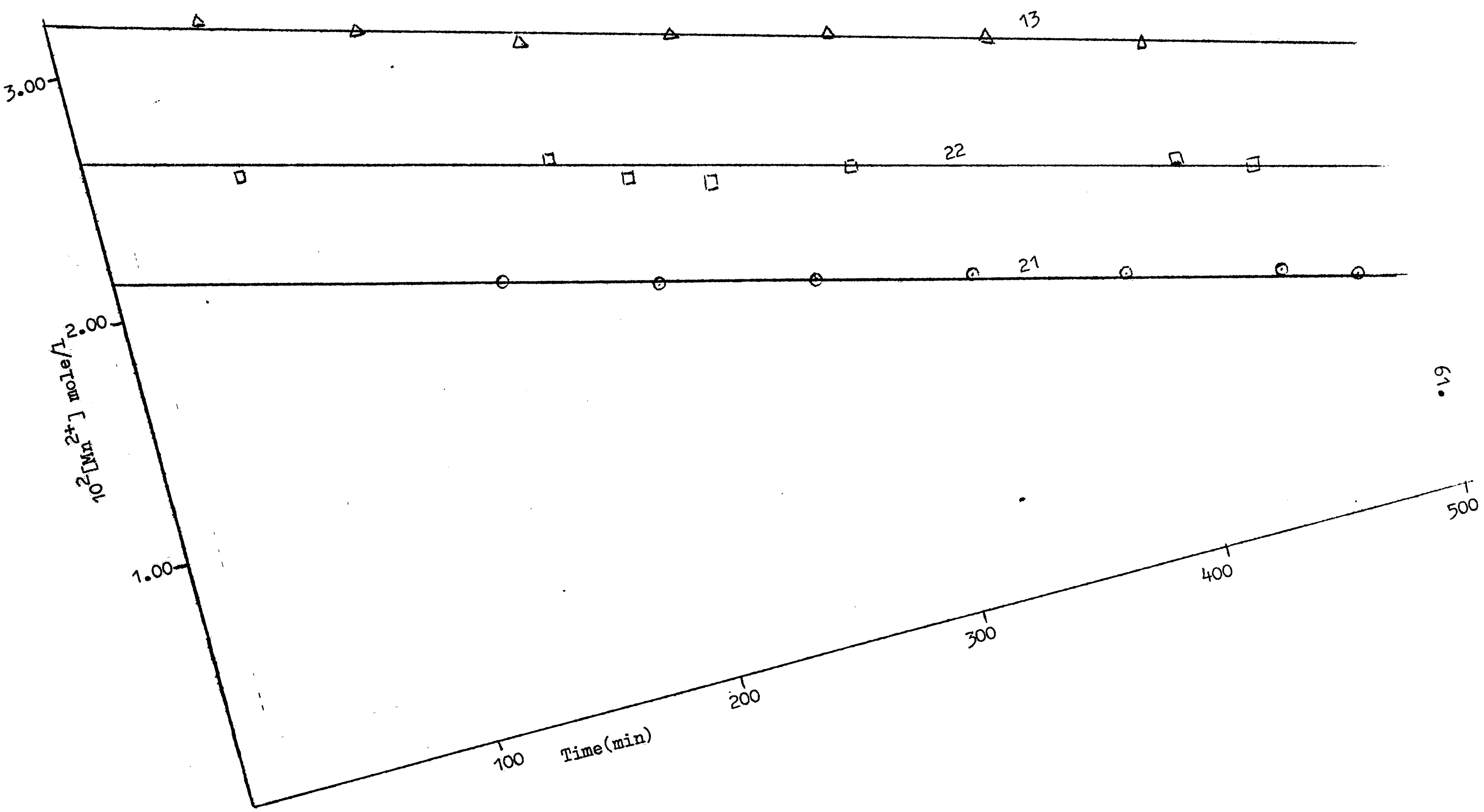
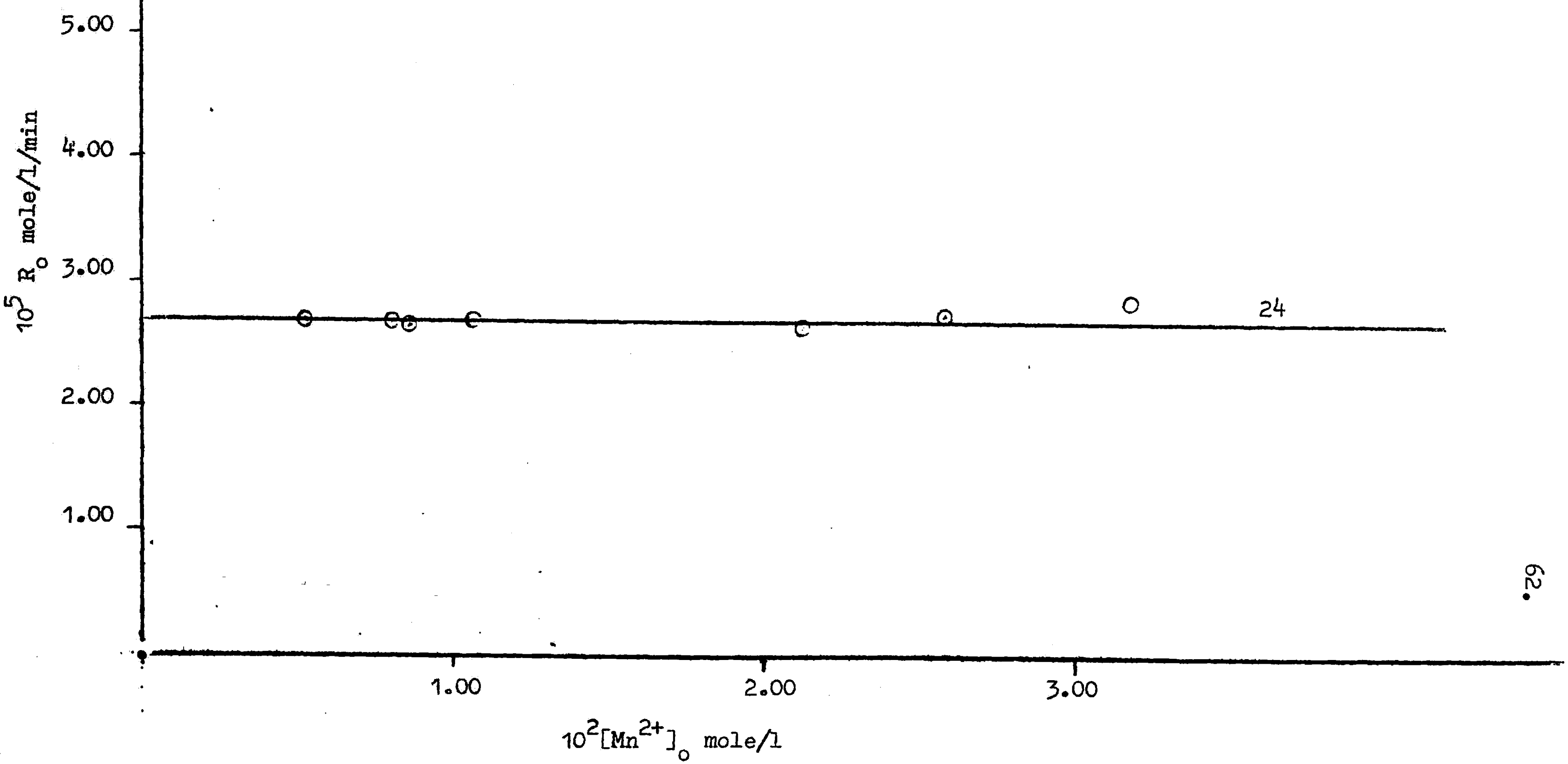


Fig. 13

Order with Respect to Manganese(II)

$\left\{\frac{-d[Mn^{2+}]}{dt}\right\}_0$ v. $[Mn^{2+}]_0$



Salt effect

The effect which added salts may have on the rate of a chemical reaction may be seen by considering a reaction which has as its rate determining step the bimolecular reaction of two ions A and B (with charges Z_A and Z_B) to form the activated complex AB* which eventually turns into the reaction products (equation [69]).

$$A + B = AB^* = \text{Products} \qquad \ldots\ldots [69]$$

The rate of this reaction is given by

$$\text{rate} = k[A][B] \qquad \ldots\ldots [70]$$

where k is the experimental rate constant. However the rate of the reaction is also proportional to the concentration of the activated complex.

$$\text{rate} = k'[AB^*] \qquad \ldots\ldots [71]$$

The equilibrium constant K for the formation of the complex is given by equation [72].

$$K = \frac{a_{AB^*}}{a_A \cdot a_B} = \frac{[AB^*]}{[A][B]} \cdot \frac{f_{AB^*}}{f_A \cdot f_B} \qquad \ldots\ldots [72]$$

where a stands for the activity and f for the activity coefficient of the respective species.

From equation [72]

$$[AB^*] = K[A][B] \cdot F \qquad \ldots\ldots [73]$$

where

$$F = \frac{f_A\, f_B}{f_{AB^*}} \qquad \ldots\ldots [74]$$

Introducing [73] into [71] gives

$$\text{rate} = k'K[A][B] \cdot F \qquad \ldots\ldots [75]$$

Equating [75] and [70] gives

$$k = k'K \cdot F = k_o \cdot F \qquad \ldots\ldots [76]$$

and taking logarithms

$$\log k = \log k_o + \log F \qquad \ldots\ldots [77]$$

According to the simplest form of the Debye-Huckel theory, applicable to very dilute solutions, the activity coefficient is related to the charge Z and ionic strength I by the equation

$$\log f = - QZ^2 I^{\frac{1}{2}} \qquad \ldots\ldots [78]$$

where Q is a constant.

Taking logarithms of [74]

$$\log F = \log f_A + \log f_B - \log f_{AB*} \qquad \ldots\ldots [79]$$

Introducing [78] into [79] and bearing in mind that the charge on the activated complex is the algebraic sum of Z_A and Z_B

$$\log F = - QI^{\frac{1}{2}} \left\{ Z_A^2 + Z_B^2 - (Z_A + Z_B)^2 \right\} = 2QZ_AZ_BI^{\frac{1}{2}} \qquad \ldots\ldots [80]$$

Substituting for log F in [77] gives

$$\log k = \log k_o + 2QZ_AZ_BI^{\frac{1}{2}} \qquad \ldots\ldots [81]$$

The value of Q is approximately 0.51 in aqueous solution at 25° and 0.55 at 60°C.

Equation [81] thus implies that any added salt irrespective of its nature will have a profound effect on reactions involving ions. The rate will decrease if A and B are oppositely charged, and increase if the charges are similar while if either A or B is neutral the ionic strength effect should be zero.

Although equation [81] is valid in very dilute solutions, deviations from linearity are observed when log k is plotted against the square root of I beyond 0.001 mole/l which is also the limit of equation [78] from which equation [81] was derived.

Equation [82] proposed by Davies(57) is an improvement of equation [78] and the other improved forms of it proposed by Debye and Huckel. Davies' equation

$$\log f = - QZ_AZ_B\left(\frac{I^{\frac{1}{2}}}{1 + I^{\frac{1}{2}}} - 0.30\ I\right) \qquad \ldots\ldots \quad [82]$$

leads to

$$\log k = \log k_o + 2QZ_A \cdot Z_B\ F' \qquad \ldots\ldots \quad [83]$$

in which

$$F' = \left(\frac{I^{\frac{1}{2}}}{1 + I^{\frac{1}{2}}} - 0.30\ I\right) \qquad \ldots\ldots \quad [84]$$

Again a plot of log k as a function of F' should result in a straight line the slope of which gives $Z_A \cdot Z_B$. Equation [83] holds to ionic strengths of up to 0.2 mole/l. Even this improved range is lower than the lowest possible ionic strength in this work because at low concentration of peroxodisulphate the reaction becomes too slow to be followed.

In addition to the ionic strength effect discussed above added salts may form ion-pairs especially at higher concentration where the Debye-Huckel and Davies equations no longer apply. Ion-pairing may change the concentration of the reacting species as well as the ionic strength, and most important ion-pairing may involve one or more reactants thus introducing considerable changes in the electrostatic interactions between the reacting ions.

Even though exact agreement between theory and observation at I = 1 is not expected; if allowance is made for ion-pairing, the Davies' equation should give an approximate account of activity coefficients and therefore rates, sufficiently true to indicate at least the correct sign of variation of log k with a suitable function of I.

Finally it has to be remembered that the treatment depends upon A and B being identifiable and/or of calculable concentration. They may be the reactants as added to the mixture but they may also be derived from the "made up" reactants via a series of pre-equilibria.

The effect of added salts on the rate of the reaction was investigated at constant initial peroxodisulphate and manganese(II) concentrations. The added salts were potassium sulphate, sodium sulphate and sodium perchlorate. The individual runs are shown in Tables 25-40 and Figs. 14-29.

It can be seen from Table 41 and Fig. 30 which summarise the effect of the added salts that the variation of potassium ion concentration has little noticeable effect except at relatively high concentrations ($[K^+] > 0.4$ mole/l), when the rate is diminished.

Sodium ion has a specific negative effect even at concentrations as low as 0.1 mole/l and the effect is the same whether it is added as sulphate or perchlorate (whereas addition of sulphate seems to produce a different effect when added as K_2SO_4 rather than Na_2SO_4), and this is an indication that the effect is due solely to the cation rather than anion or ionic strength, the effect of which passes through a shallow minimum over the range investigated. Thus the effect of sodium ion and of potassium ion at high concentration may be due to ion-pair formation which decreases the concentration of peroxodisulphate, therefore causing the small decrease observed in the rate of the reaction.

The following experimental conditions apply to Tables 25-40. All concentrations in units of mole/l.

$[S_2O_8^{2-}]_o = 0.08000$

$[Mn(II)]_o = 0.008450$

Temperature = 60.0°C

Table 25

$[K_2SO_4]$ = Nil

I = 0.274

Time (min)	Absorbance	$10^3[Mn^{2+}]$
30	0.364	7.00
60	0.342	6.56
135	0.224	4.30
180	0.153	2.94
211	0.110	2.12
270	0.025	0.48

Table 26

$[K_2SO_4]$ = 0.0500

I = 0.424

Time (min)	Absorbance	$10^3[Mn^{2+}]$
30	0.362	6.96
60	0.331	6.36
135	0.217	4.16
180	0.149	2.86
210	0.107	2.06
270	0.024	0.46

Table 27

$[K_2SO_4]$ = 0.100

I = 0.574

Time (min)	Absorbance	$10^3[Mn^{2+}]$
30	0.392	7.52
60	0.332	6.38
90	0.285	5.46
120	0.243	4.66
150	0.202	3.88
180	0.147	2.82
220	0.090	1.72

Table 28

$[K_2SO_4]$ = 0.150

I = 0.724

Time (min)	Absorbance	$10^3[Mn^{2+}]$
30	0.369	7.08
60	0.340	6.52
90	0.286	5.48
120	0.252	4.84
150	0.202	3.88
280	0.147	2.82
220	0.099	1.90

Table 29

$[K_2SO_4]$ = 0.200

I = 0.874

Time (min)	Absorbance	$10^3[Mn^{2+}]$
50	0.334	6.42
90	0.269	5.16
120	0.240	4:60
150	0.189	3.62
180	0.161	3.10
210	0.119	2.28
240	0.072	1.38

Table 30

$[K_2SO_4]$ = 0.250

I = 1.02

Time (min)	Absorbance	$10^3[Mn^{2+}]$
50	0.339	6.48
90	0.289	5.54
120	0.245	4.70
150	0.209	4.01
180	0.163	3.14
210	0.121	2.32
240	0.081	1.56

Table 31

$[NaClO_4] = 0.200$

$I = 0.474$

Time (min)	Absorbance	$10^3[Mn^{2+}]$
45	0.354	6.78
90	0.297	5.70
135	0.232	4.46
180	0.179	3.44
225	0.118	2.26
270	0.062	1.20
300	0.028	0.54

Table 32

$[NaClO_4] = 0.400$

$I = 0.674$

Time (min)	Absorbance	$10^3[Mn^{2+}]$
41	0.360	6.92
60	0.332	6.38
105	0.277	5.32
155	0.209	4.00
195	0.154	2.96
240	0.099	1.90
270	0.047	0.90

Table 33

$[NaClO_4] = 0.600$

$I = 0.874$

Time (min)	Absorbance	$10^3[Mn^{2+}]$
40	0.356	6.84
60	0.341	6.54
105	0.273	5.24
150	0.215	4.12
195	0.164	3.16
240	0.092	1.78
270	0.071	1.36

Table 34

$[NaClO_4] = 0.8000$

$I = 1.07$

Time (min)	Absorbance	$10^3[Mn^{2+}]$
45	0.372	7.16
90	0.305	5.86
135	0.258	4.94
-	-	-
225	0.143	2.74
270	0.089	1.70
300	0.056	1.08

Table 35

$[NaClO_4] = 1.000$

$I = 1.27$

Time (min)	Absorbance	$10^3[Mn^{2+}]$
30	0.371	7.14
60	0.343	6.58
90	0.295	5.66
120	0.275	5.28
150	0.228	4.38
210	0.156	3.00

Table 36

$[Na_2SO_4]$ = 0.0500
I = 0.424

Time (min)	Absorbance	$10^3[Mn^{2+}]$
45	0.356	6.84
90	0.292	5.60
135	0.232	4.46
180	0.176	3.38
225	0.108	2.08
270	0.047	0.90
300	0.018	0.34

Table 37

$[Na_2SO_4]$ = 0.100
I = 0.574

Time (min)	Absorbance	$10^3[Mn^{2+}]$
45	0.331	6.36
90	0.282	5.42
135	0.220	4.22
180	0.151	2.90
225	0.094	1.80
270	0.031	0.60
300	0.005	0.10

Table 38

$[Na_2SO_4]$ = 0.200
I = 0.874

Time (min)	Absorbance	$10^3[Mn^{2+}]$
45	0.337	6.46
90	0.286	5.48
135	0.238	4.56
225	0.114	2.20
270	0.052	1.00
300	0.025	0.48

Table 39

$[Na_2SO_4]$ = 0.250
I = 1.02

Time (min)	Absorbance	$10^3[Mn^{2+}]$
60	0.328	6.30
90	0.300	5.76
150	0.222	4.26
180	0.189	3.62
225	0.129	2.48
270	0.079	1.52
300	0.043	0.82

Table 40

$[Na_2SO_4]$ = 0.300
I = 1.17

Time (min)	Absorbance	$10^3[Mn^{2+}]$
45	0.364	6.98
90	0.308	5.92
135	0.143	4.66
180	0.193	3.70
225	0.147	2.82
270	0.094	1.82
300	0.051	0.98

Table 41

The Effect of Added Salts

All concentrations in units of mole/l

$[S_2O_8^{2-}]_o$ = 0.0800 mole/l of $(NH4)_2S_2O_8$

$[Mn^{2+}]_o$ = 0.008450

Temperature = 60.0°C.

Salt added	Concentration	$[M^+]$	I	$10^5 R_o$ mole/l/min
Nil	-	-	0.274	2.80
K_2SO_4	0.050	0.100	0.424	2.80
"	0.100	0.200	0.574	2.90
"	0.150	0.300	0.724	2.84
"	0.200	0.400	0.874	2.65
"	0.250	0.500	1.02	2.66
$NaClO_4$	0.200	0.200	0.474	2.49
"	0.400	0.400	0.674	2.53
"	0.600	0.600	0.874	2.41
"	0.800	0.800	1.07	2.31
"	1.00	1.00	1.27	2.32
Na_2SO_4	0.050	0.100	0.424	2.65
"	0.100	0.200	0.574	2.68
"	0.200	0.400	0.874	2.45
"	0.250	0.500	1.02	2.35
"	0.300	0.600	1.17	2.34

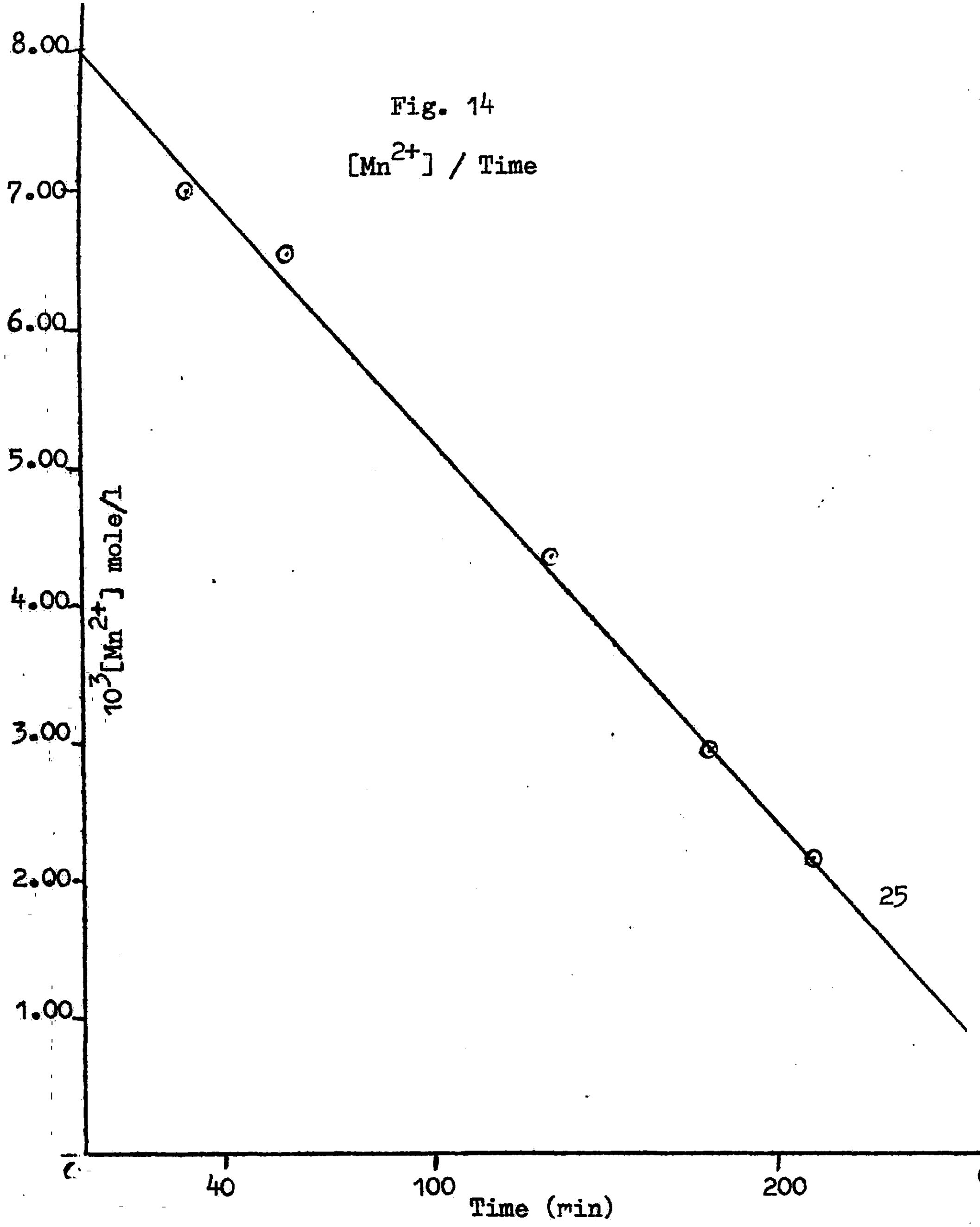


Fig. 14

$[Mn^{2+}]$ / Time

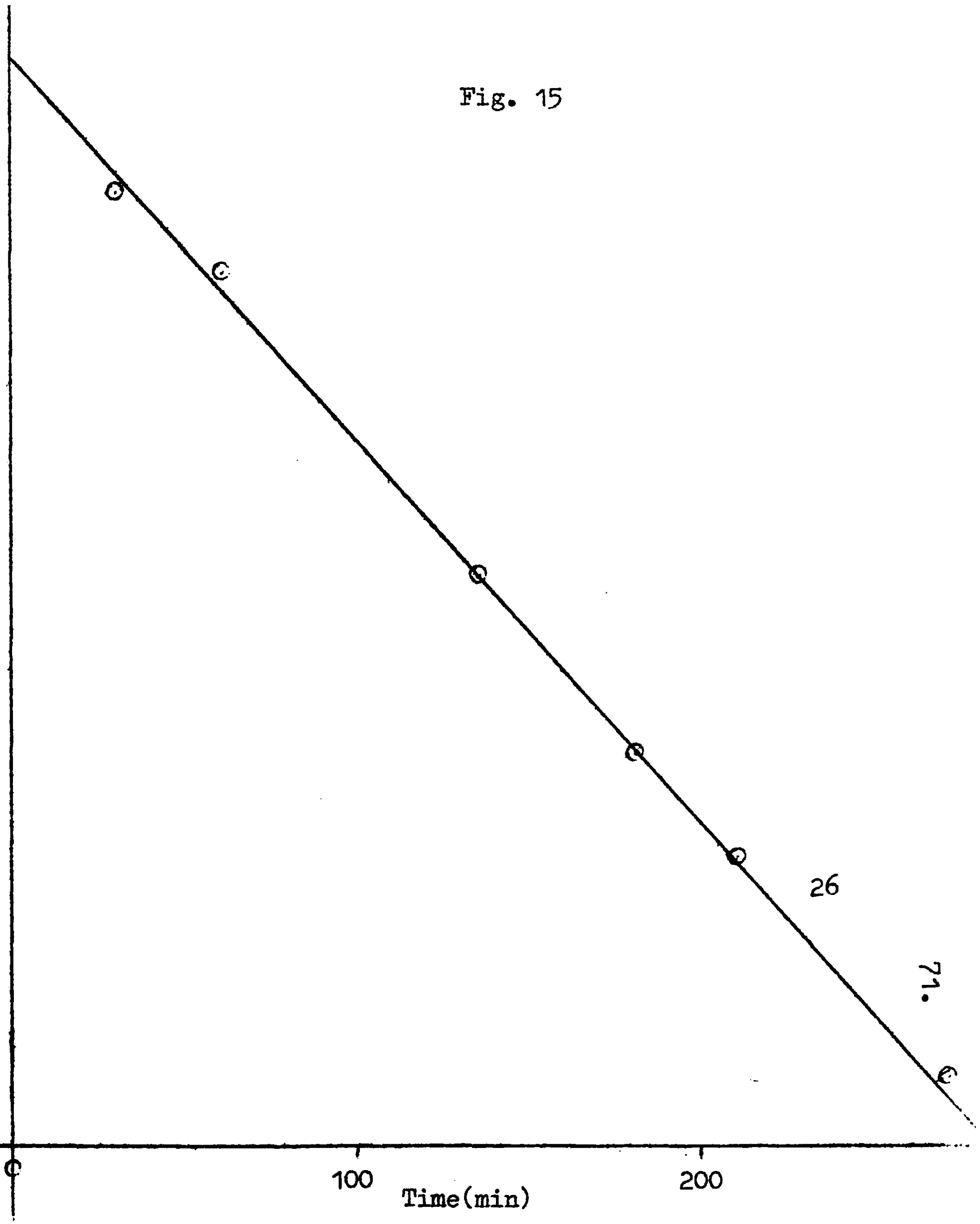


Fig. 15

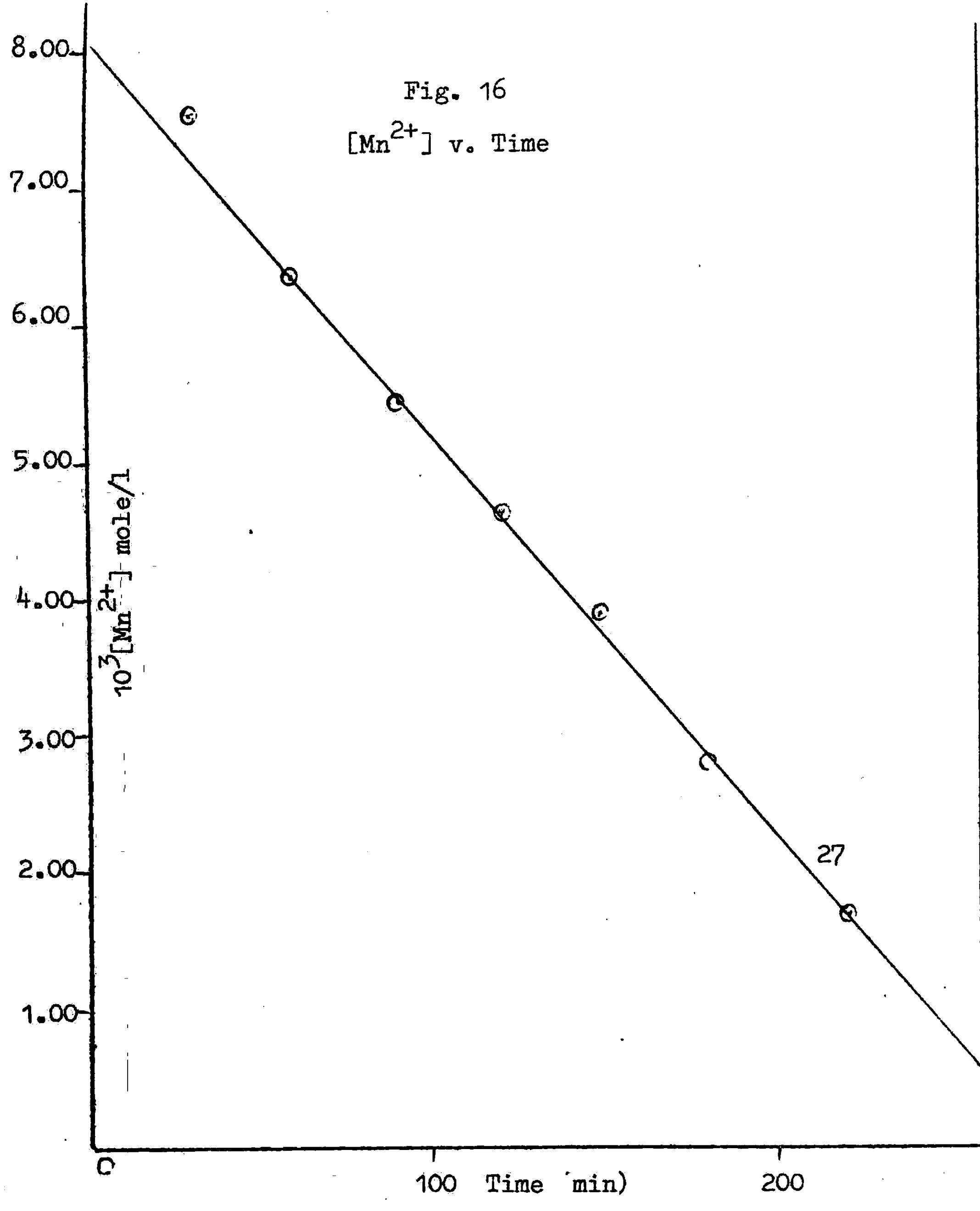


Fig. 16

$[Mn^{2+}]$ v. Time

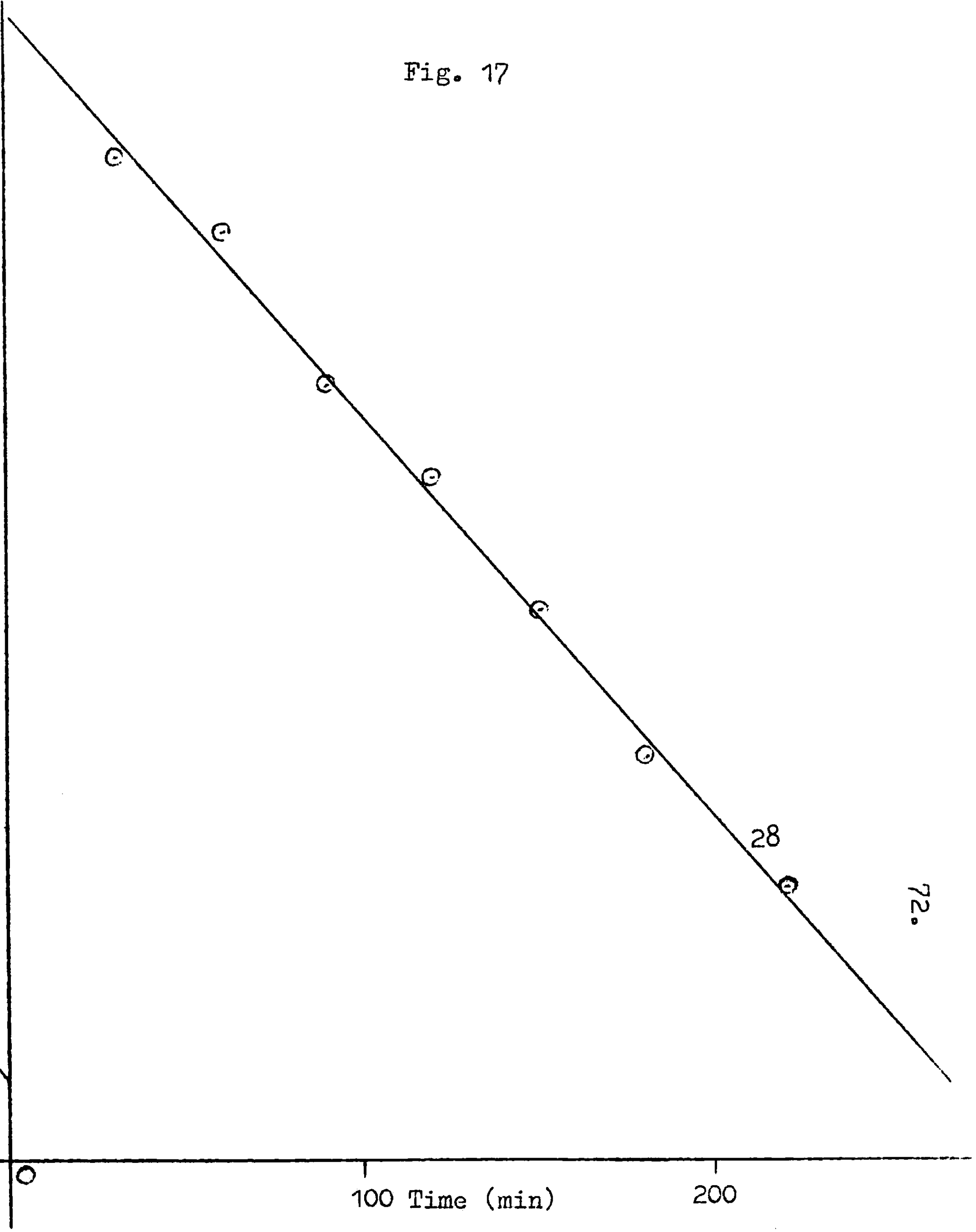


Fig. 17

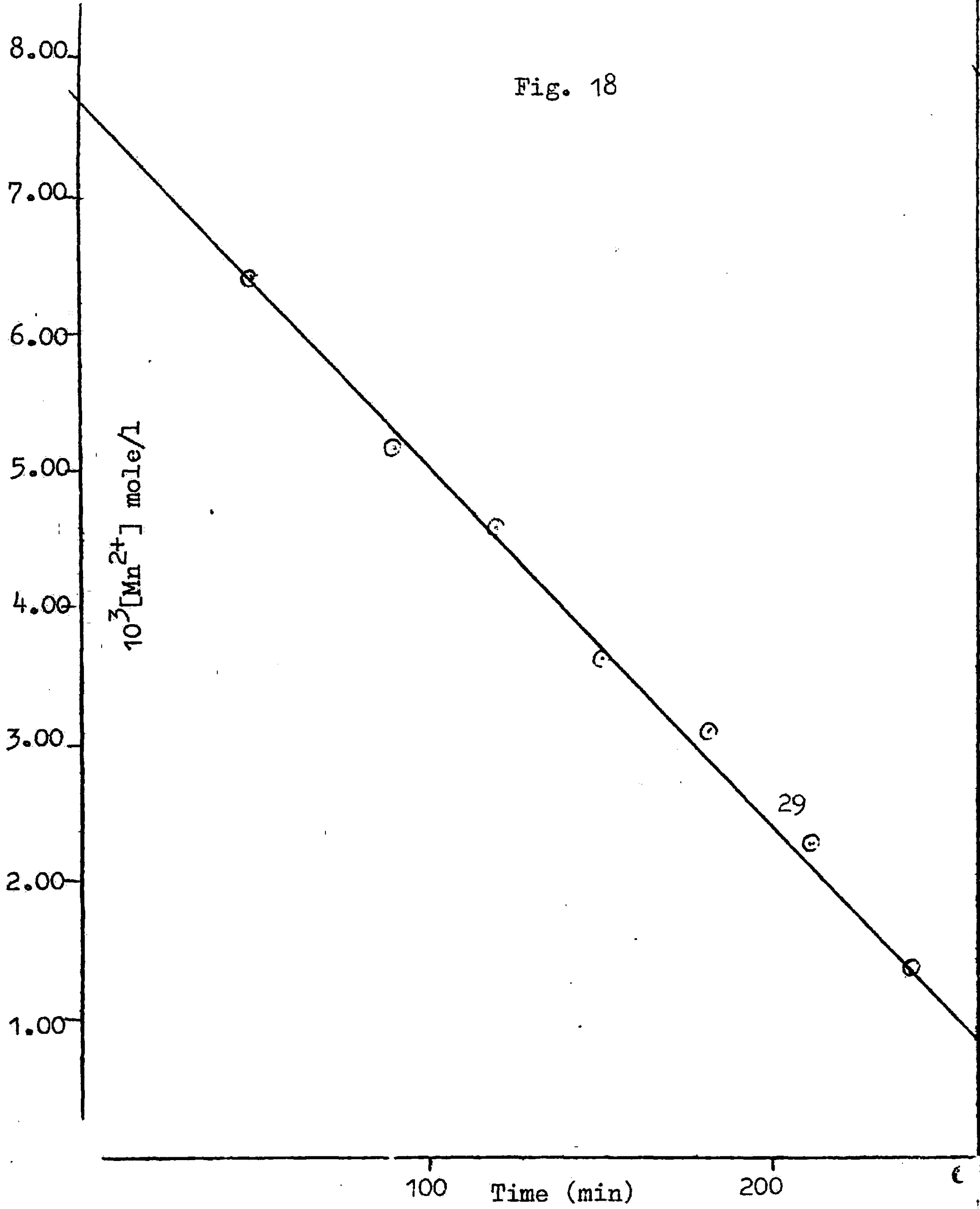

8.00
7.00
6.00
5.00
4.00
3.00
2.00
1.00
$10^3[Mn^{2+}]$ mole/l
29
100
200
Time (min)

Fig. 18

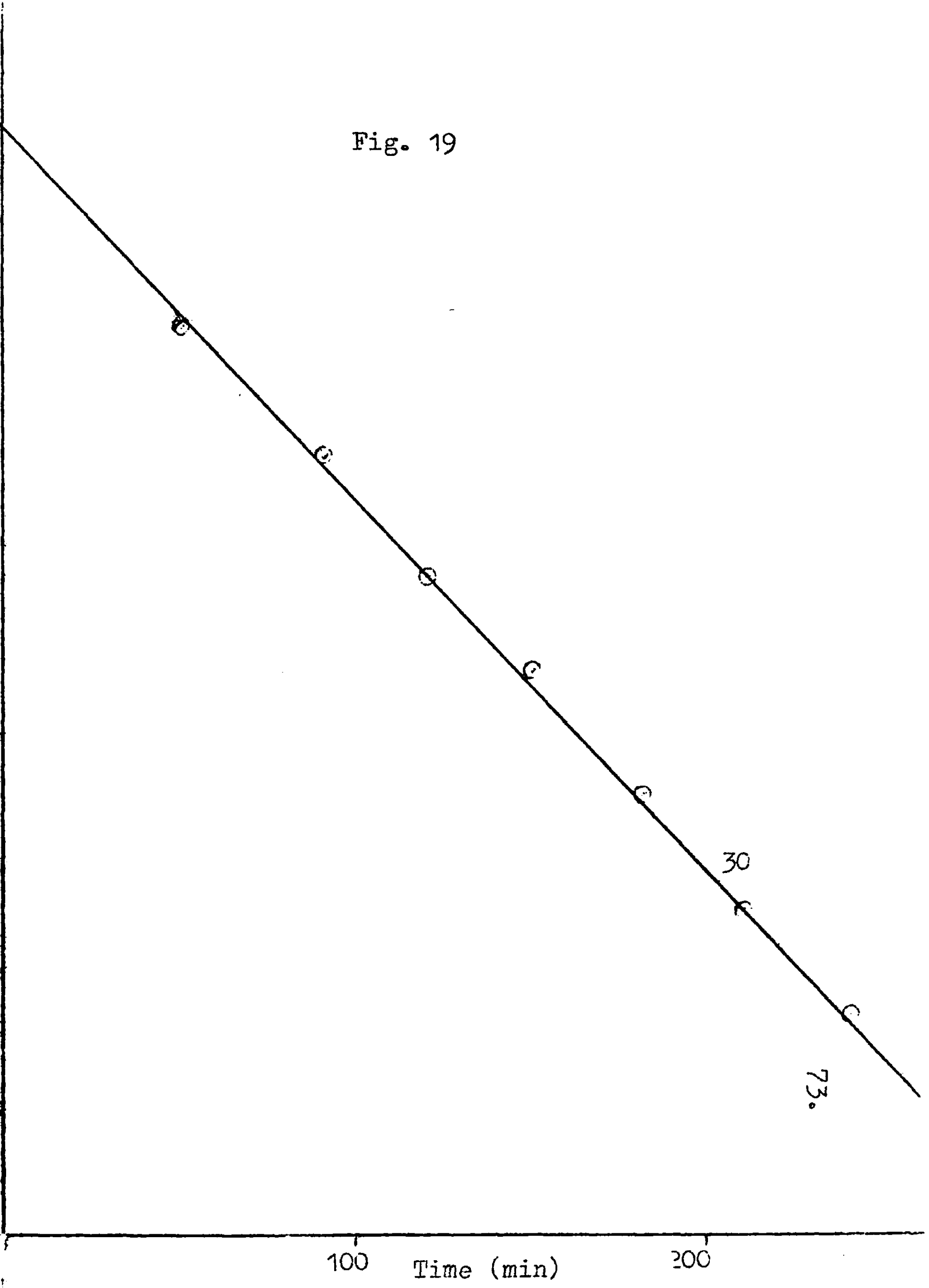

30
100
200
Time (min)

Fig. 19

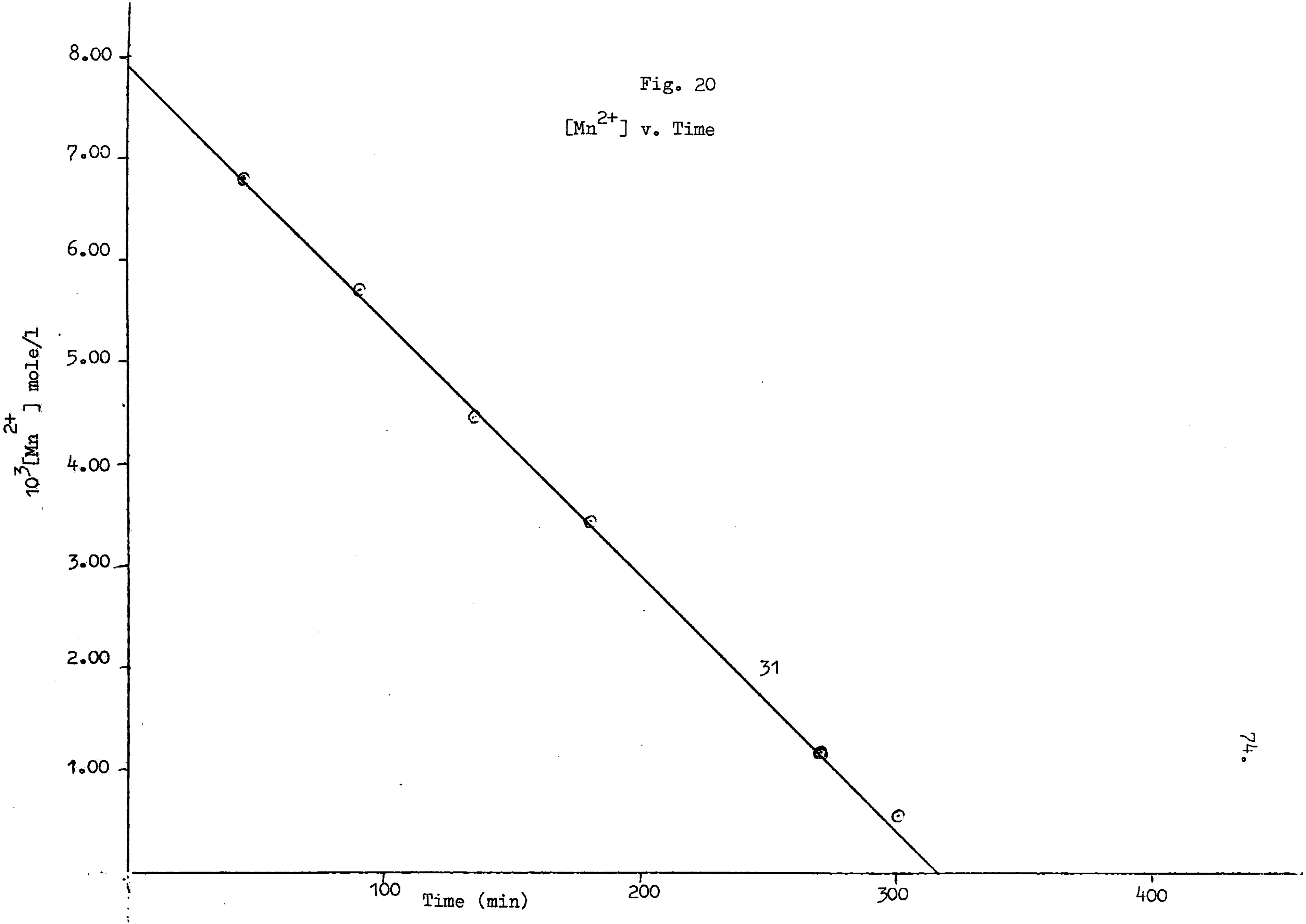


Fig. 20

$[Mn^{2+}]$ v. Time

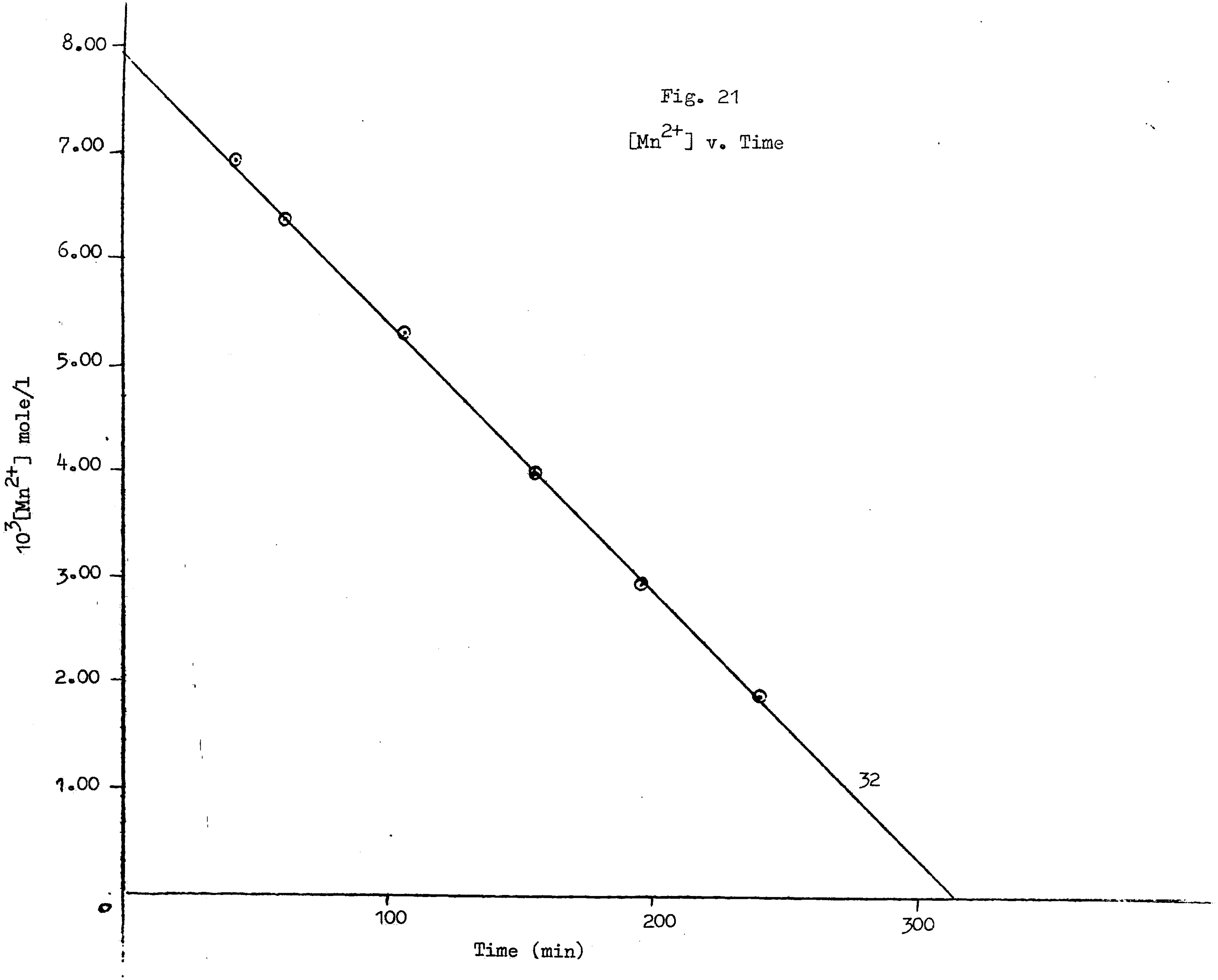


Fig. 21

$[Mn^{2+}]$ v. Time

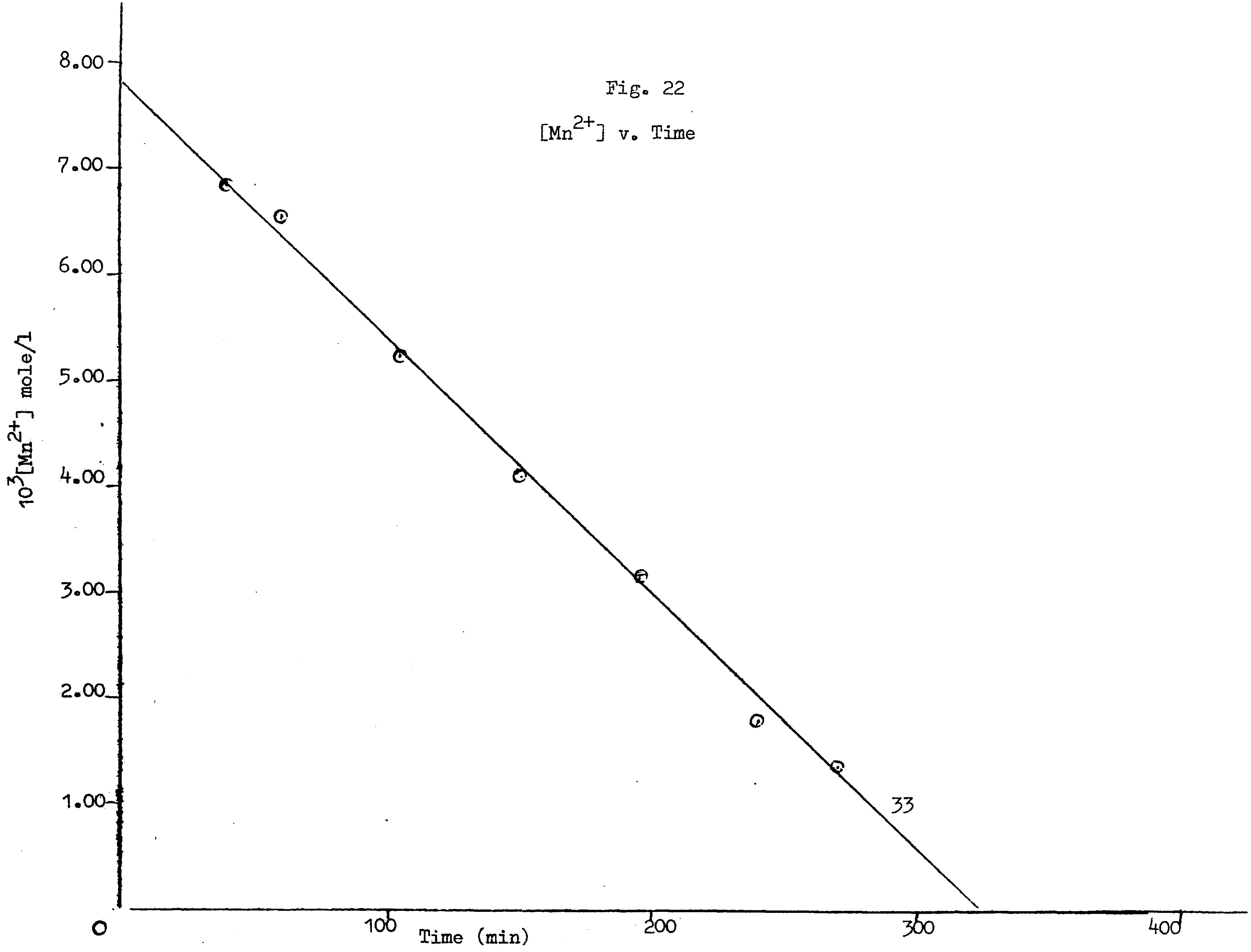


Fig. 22

[Mn^{2+}] v. Time

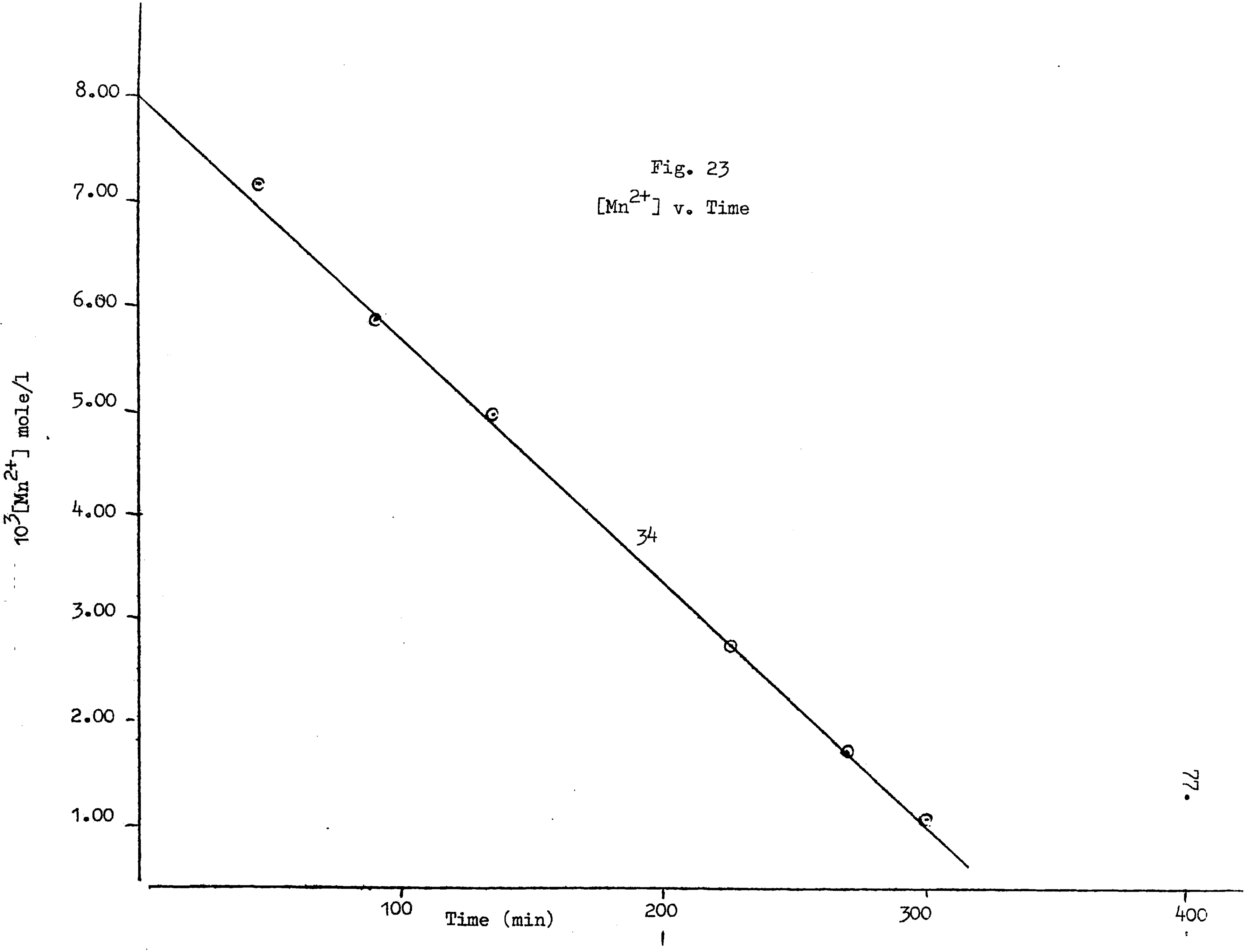


Fig. 23

$[Mn^{2+}]$ v. Time

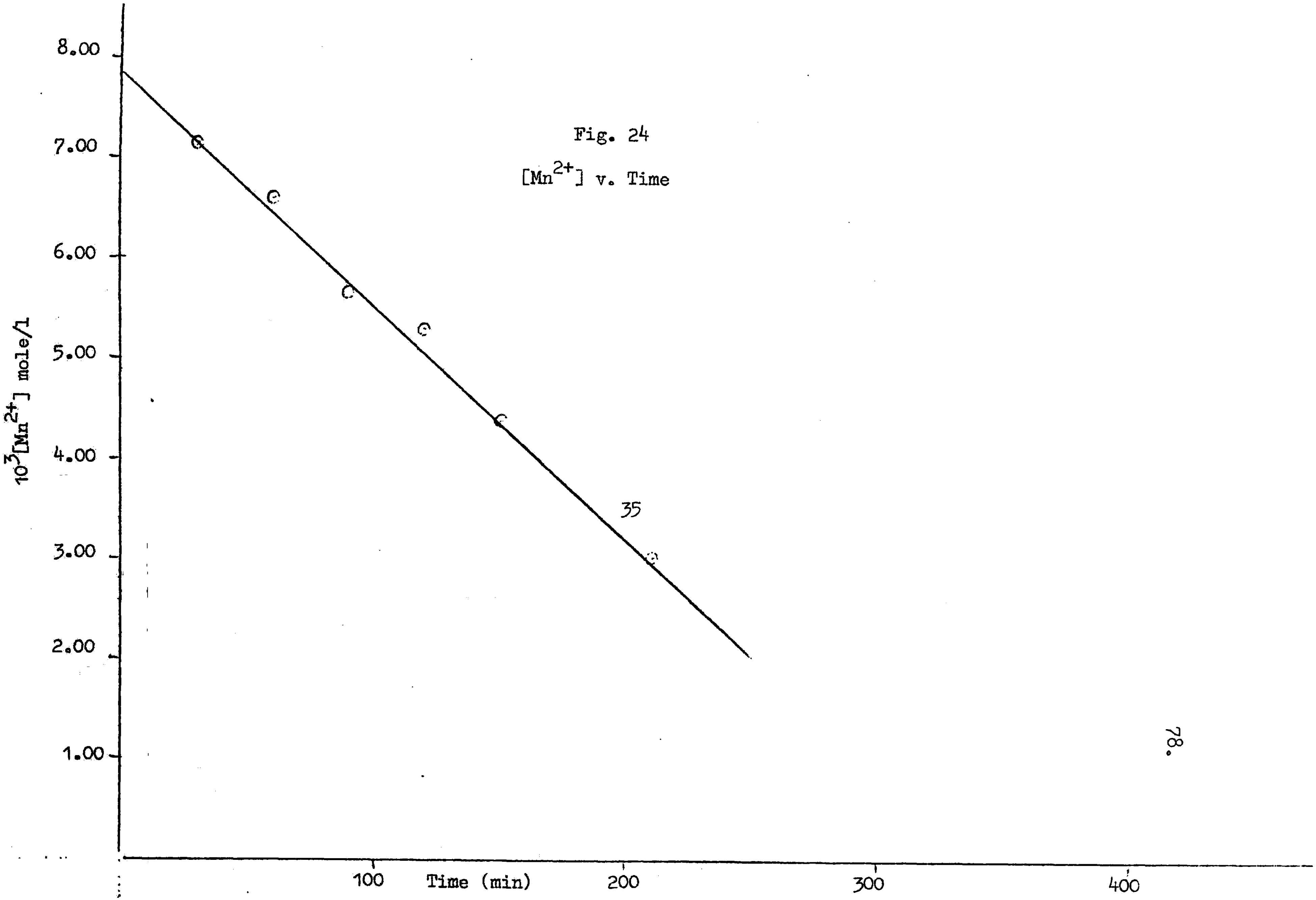


Fig. 24

[Mn^{2+}] v. Time

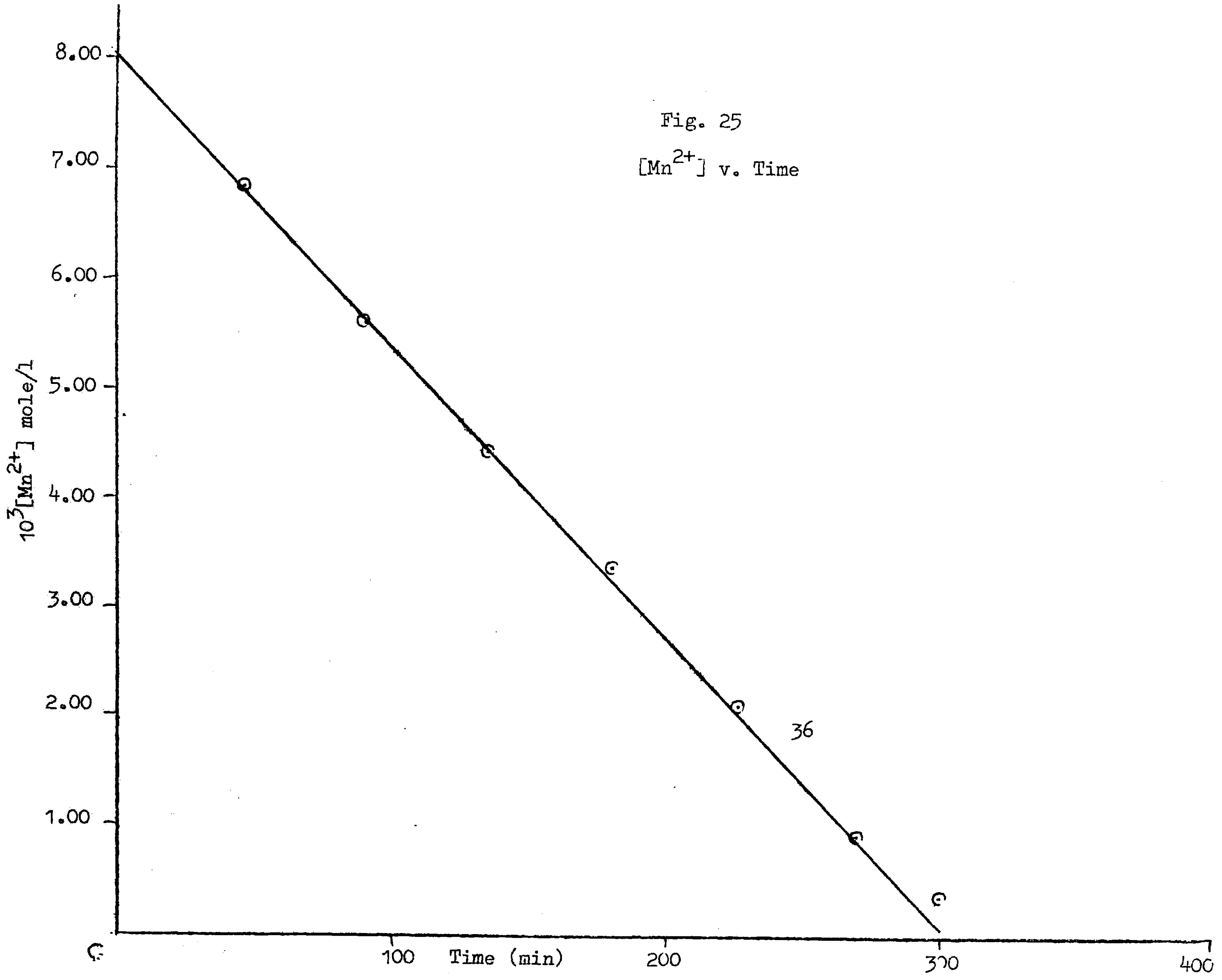


Fig. 25

$[Mn^{2+}]$ v. Time

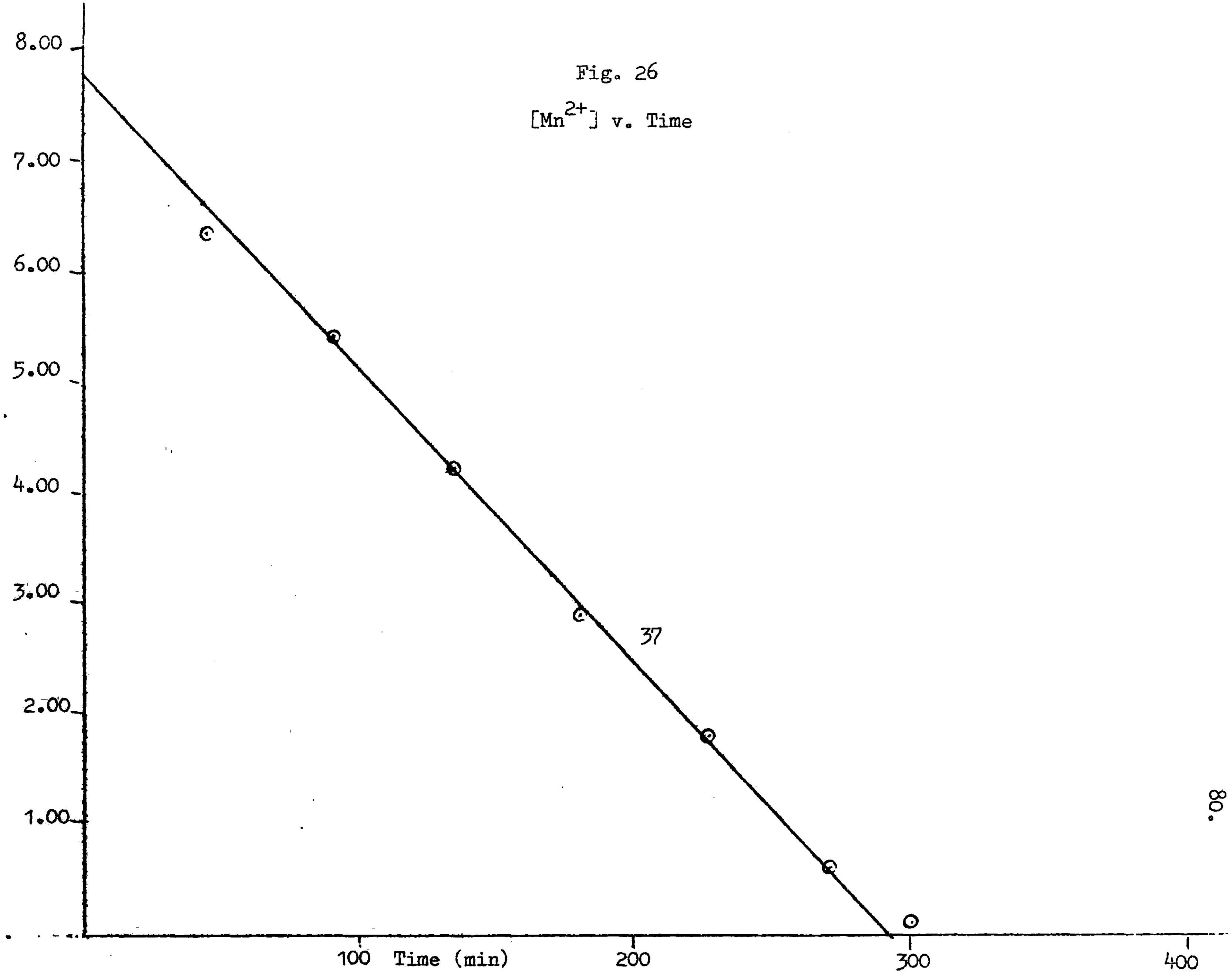


Fig. 26

$[Mn^{2+}]$ v. Time

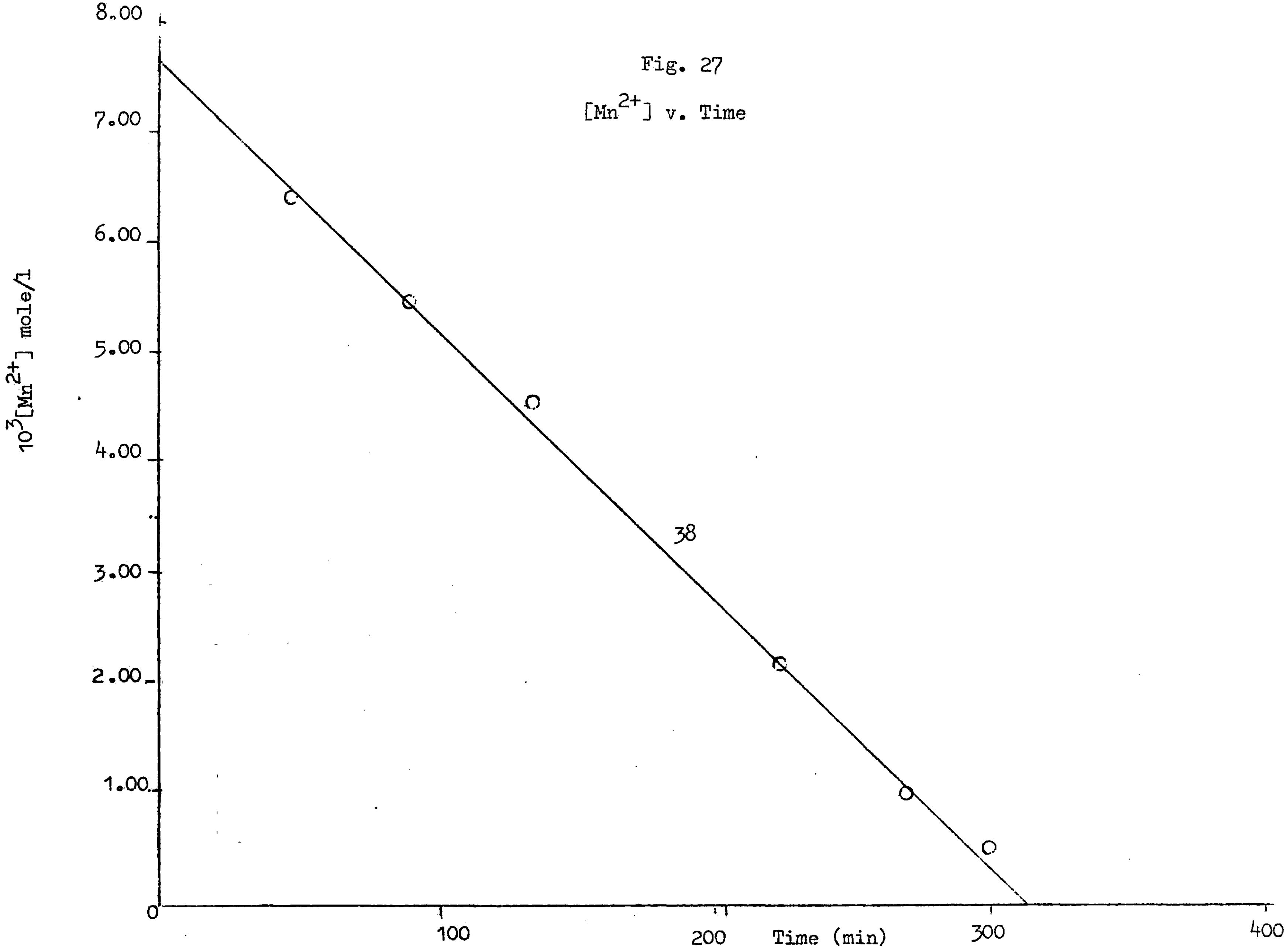


Fig. 27

$[Mn^{2+}]$ v. Time

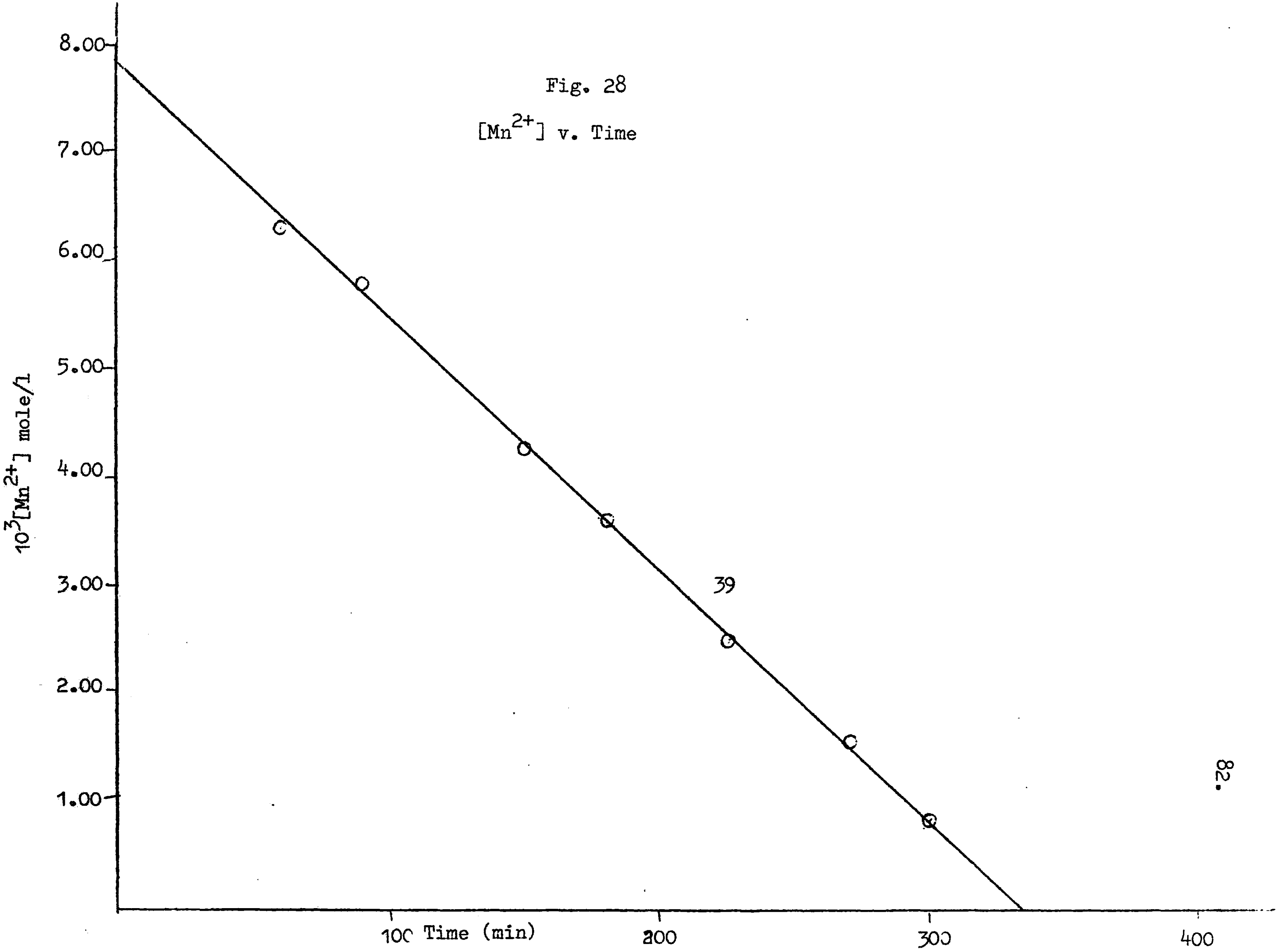


Fig. 28

$[Mn^{2+}]$ v. Time

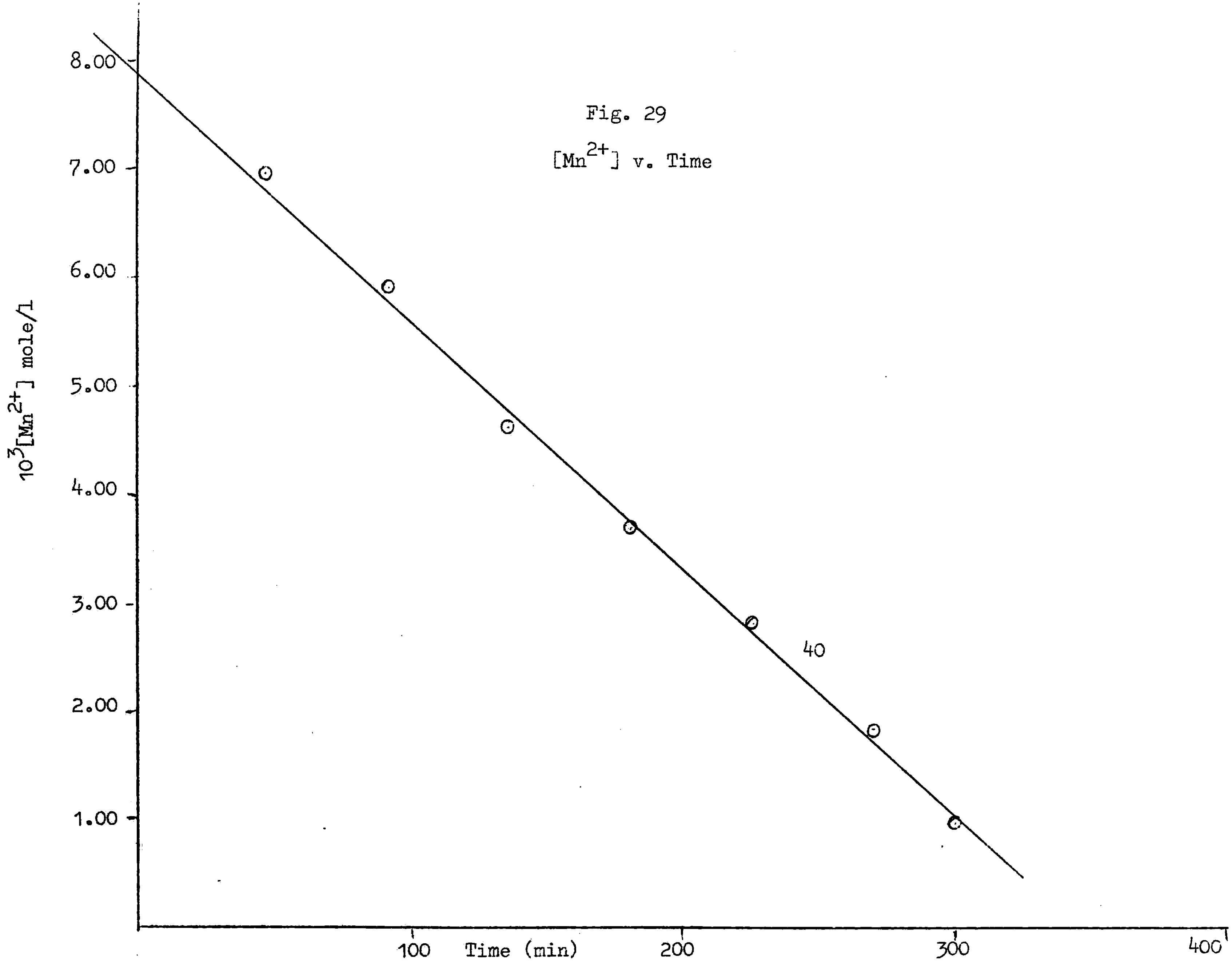


Fig. 29

$[Mn^{2+}]$ v. Time

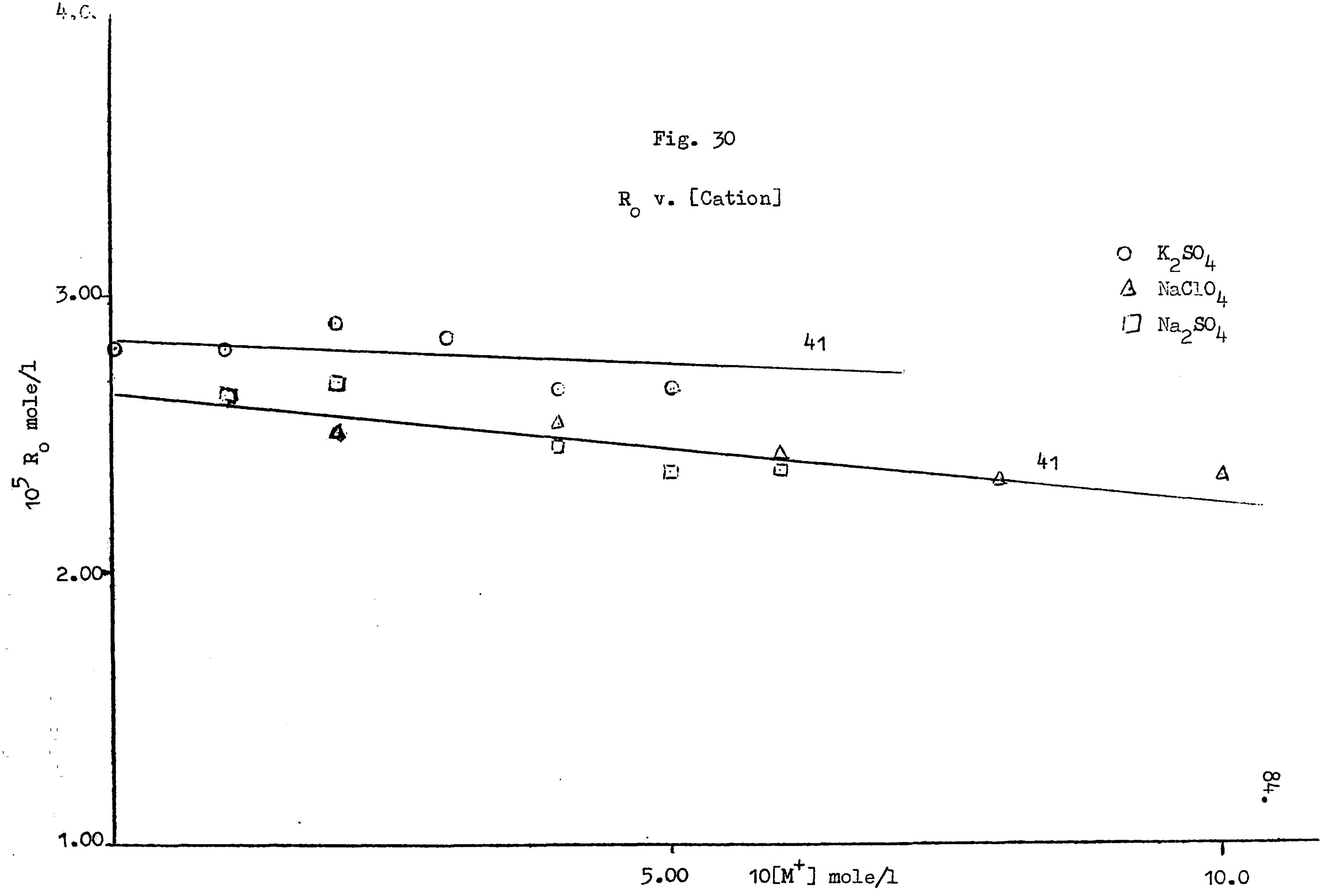


Fig. 30

R_o v. [Cation]

The temperature effect

In this set of runs (Tables 42-48 and Figs. 31-32) the effect of changing the temperature on the rate of the reaction was investigated. The initial concentrations of both peroxodisulphate and manganese(II) were kept constant at 0.08000 mole/l and 0.009350 mole/l respectively and the reaction mixture was 0.250 mole/l in potassium sulphate. The temperature was varied from 50.0°C to 80.0°C. The reaction was inconveniently slow at 50°C and too fast above 80°C. The first order rate constant was calculated by dividing the initial rate by the initial peroxodisulphate concentration. Log k was plotted against the reciprocal of temperature (Kelvin scale) and a straight line was obtained (Fig . ,33) and from the slope of this line the energy of activation was calculated according to the Arrhenius equation

$$\ln k = A - \frac{\Delta E}{R} \cdot \frac{1}{T} \qquad \ldots\ldots \quad [85]$$

The activation energy is found to be 31.5 kcal/mole which is 2.0 kcal/mole less than the activation energy for the uncatalyzed decomposition of peroxodisulphate (33.5 kcal/mole) reported by Kolhoff and Miller(26) and also found in this work under slightly different experimental conditions, This suggests that the presence of manganese(II) lowers the activation energy of the decomposition of peroxodisulphate although the reaction is independent of its concentration. The presence of manganese(II) also increases the rate of decomposition of peroxodisulphate. The first order rate constant for the thermal decomposition of peroxodisulphate at 60.0°C was found in increase from about 2.60×10^{-4} min^{-1} (see also Chapter III) in the absence of manganese(II) to 3.30×10^{-4} min^{-1} in its presence.

The value of A was determined by calculating the intercept of the straight line in Fig.33 on the Y-axis (i.e. $\frac{1}{T} = 0$). It was found to be 2.95×10^{15} sec^{-1}.

Table 42

Temperature = 50.0°C

Time (min)	Absorbance	$10^3[Mn^{2+}]$
45	0.461	8.84
90	0.456	8.76
135	0.452	8.68
180	0.436	8.36
225	0.401	7.68
270	0.398	7.64
315	0.391	7.32

Table 43

Temperature = 55.0°C

Time (min)	Absorbance	$10^3[Mn^{2+}]$
45	0.492	9.44
90	0.468	9.00
135	0.442	8.46
180	0.406	7.80
225	0.375	7.20
274	0.334	6.40
315	0.302	5.80

Table 44

Temperature = 65.0°C

Time (min)	Absorbance	$10^3[Mn^{2+}]$
31	0.825	7.92
60	0.651	6.25
90	0.459	4.41
120	0.282	2.70
150	0.105	1.01
180	0.017	0.16

Table 45

Temperature 70.0°C

Time (min)	Absorbance	$10^3[Mn^{2+}]$
15	0.817	7.84
30	0.606	5.82
45	0.428	4.11
60	0.253	2.43
75	0.078	0.748
90	0.013	0.124
105	0.013	0.124

Table 46

Temperature = 75.0°C

Time (min)	Absorbance	$10^3[Mn^{2+}]$
5	0.901	8.65
12	0.739	7.10
15	0.662	6.36
20	0.534	5.13
25	0.422	4.03
30	0.308	2.96
35	0.190	1.82
40	0.077	0.74

Table 47

Temperature = 80.0°C

Time (min)	Absorbance	$10^3[Mn^{2+}]$
5	0.823	7.90
10	0.598	5.74
15	0.388	3.72
20	0.183	1.76
25	0.012	0.12
30	0.017	0.16
35	0.003	0.02

Table 48

Temperature Effect

$[S_2O_8^{2-}]_o$ = 0.08000 mole/l

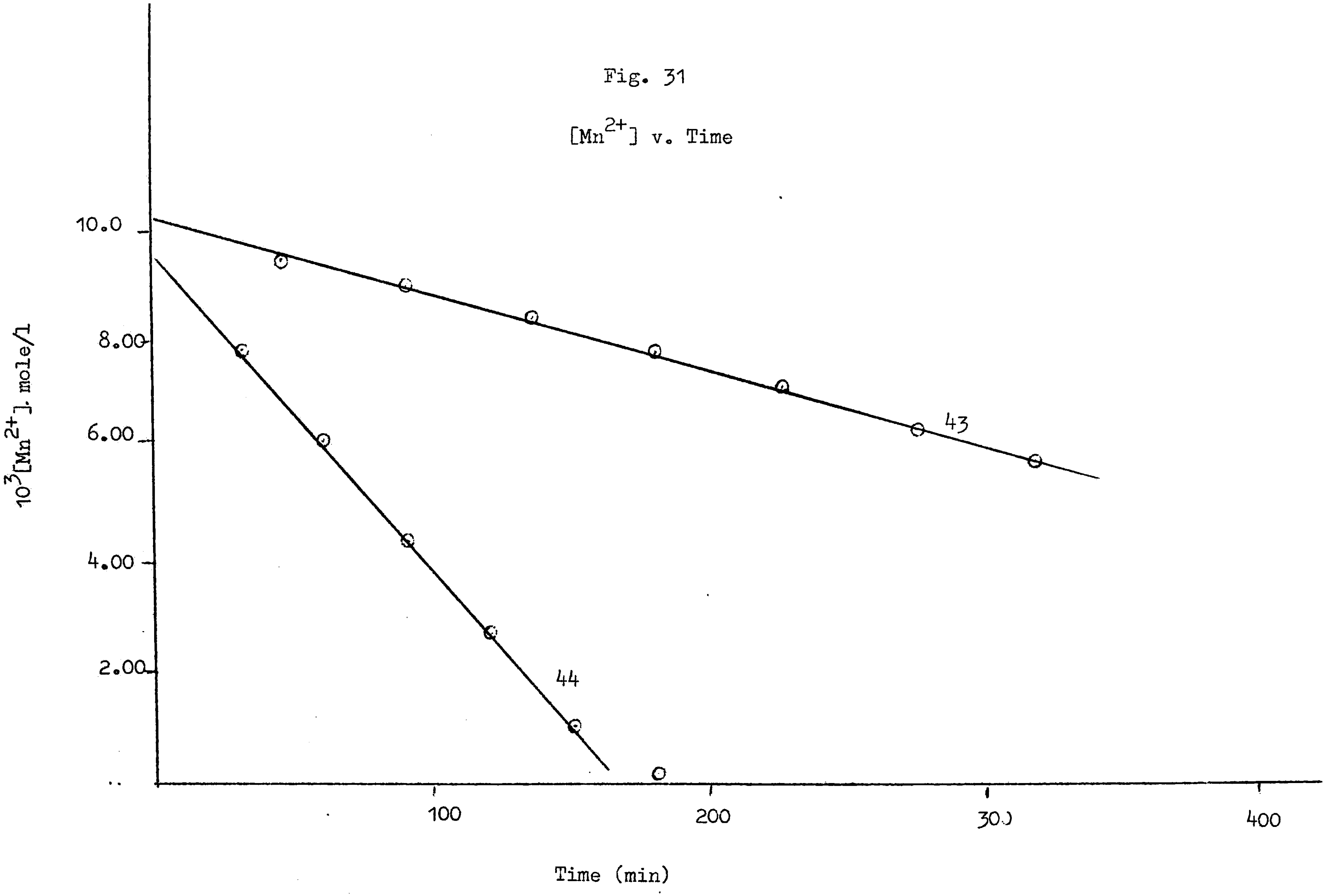
$[Mn^{2+}]_o$ = 0.009350 mole/l

$[K_2SO_4]$ = 0.250 mole/l

Temp. °C	$\frac{10^3}{T}$ °K^{-1}	10^5 R_o mole/l/min	10^4 k min^{-1}	4 + log k
50.0	3.0945	Reaction	slow	
55.0	3.0474	1.40	1.75	0.2430
60.0	3.0017	2.69	3.36	0.5263
65.0	2.9573	5.79	7.24	0.8597
70.0	2.9142	11.9	14.9	1.1732
75.0	2.8723	22.7	28.4	1.4533
80.0	2.8317	40.6	50.8	1.7059

Fig. 31

$[Mn^{2+}]$ v. Time



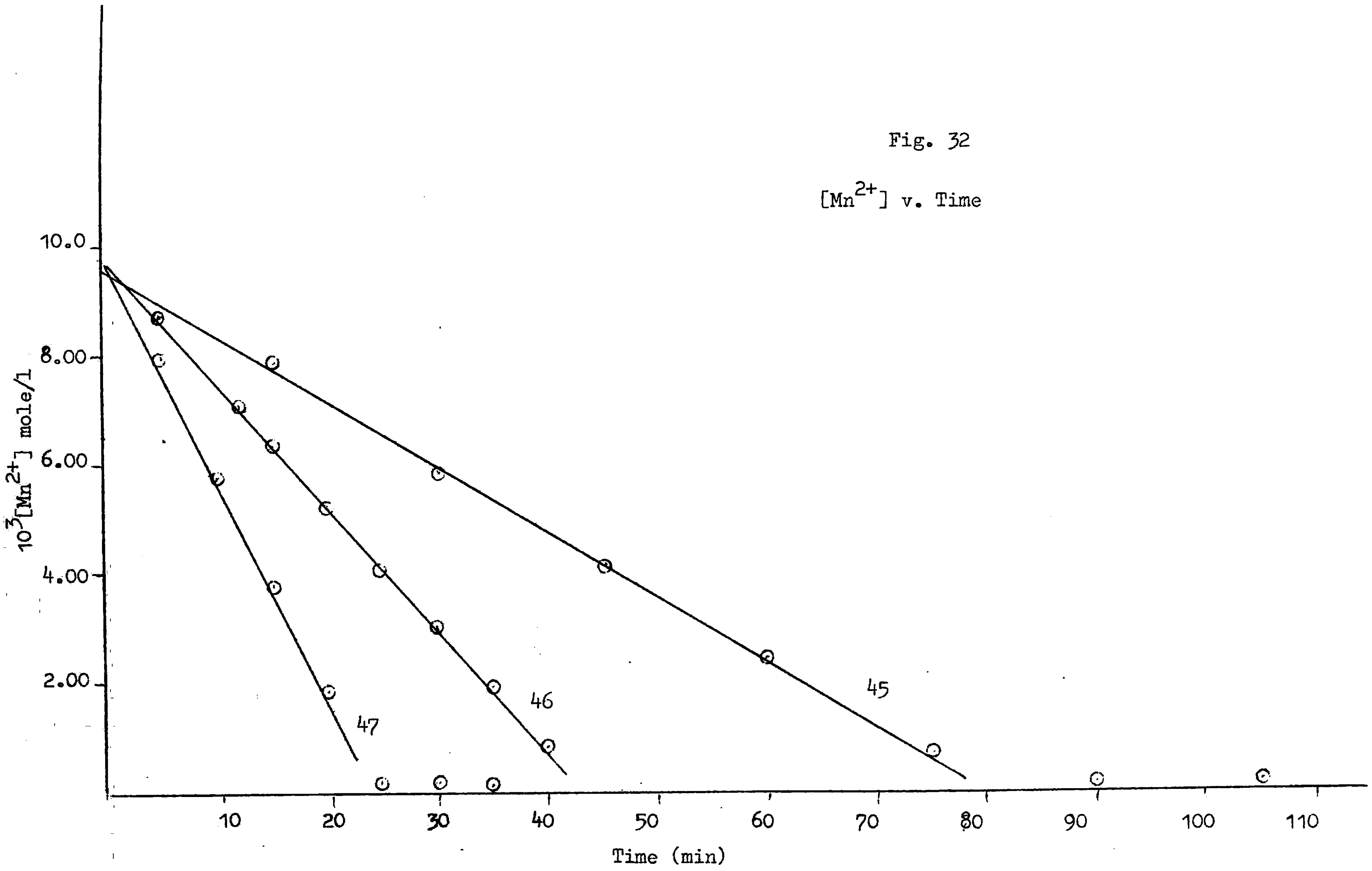


Fig. 32

$[Mn^{2+}]$ v. Time

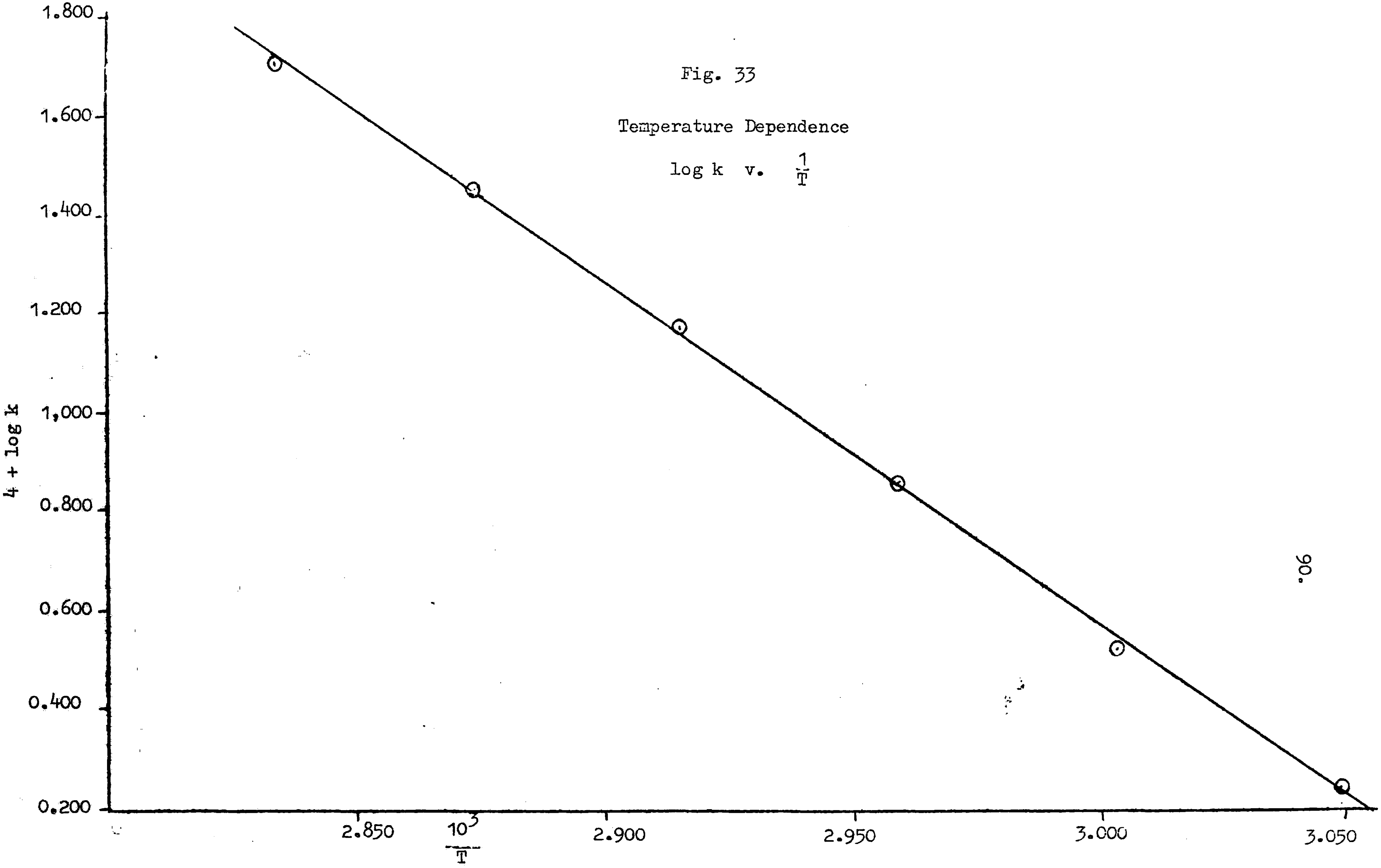


Fig. 33

Temperature Dependence

log k v. $\frac{1}{T}$

Change of pH

Table 49 shows the pH of the reactants in isolation. In this table A and B represent typical stock solutions of the two reactants which were thermostatted separately and 25 ml of each then pipetted and mixed together in the reaction vessel for the kinetic investigation. Table 50 - 53 and Fig.34 show how the pH of the reaction mixture changes with time. In the thermal decomposition of a solution of peroxodisulphate the pH decreases because of the stoicheiometric equation

$$S_2O_8^{2-} + H_2O = 2H^+ + 2SO_4^{2-} + \tfrac{1}{2}O_2 \qquad \ldots\ldots \quad [2]$$

as was pointed out in the main introduction. In the presence of manganese(II) the rate of production of hydrogen ions is increased markedly.

The third column of Tables 50 - 53 gives the hydrogen ion concentration and in Fig. 34 this concentration is plotted against time. In these tables it is assumed that the pH is a measure of hydrogen ion concentration (rather than activity) for simplification. Fig.34 shows a plot of hydrogen ion concentration versus time for a reaction mixture which is initially 0.1214 mole/l in peroxodisulphate and 0.008450 mole/l in manganese(II) ions - curve 52 - while curve 53 is the $[H^+]$/time plot for a solution which is 0.1600 mole/l in peroxodisulphate and containing no manganese(II) at all. The initial rates of production of hydrogen ion are 0.970×10^{-5} mole/l/ min and 0.667×10^{-5} mole/l/min respectively despite the higher initial peroxodisulphate concentration in the second case. This clearly shows that the presence of manganese(II) increases the rate of production of hydrogen ion which is an indication that this ion is a product of the redox reaction between peroxodisulphate and manganese(II).

However, as can be seen from Table 51 in which the pH does not fall far beyond 3 even after more than four hours, the hydrogen ion concentration does not reach such a value that might catalyze the reaction -- at least during that part of the reaction which was studied. Moreover our prime concern is with the initial kinetics, and the initial pH which is higher than 3 is too high to render the reaction catalyzed by hydrogen ion.

For establishment of the stoicheiometry it would be desirable if the observed pH change could be used to compare the rates of production of hydrogen ion with the rate of loss of manganese(II). A direct comparison for example of the results in Table 30 with those for a similar experiment described in Table 50 shows that $-d[Mn(II)]/dt = 2.66 \times 10^{-5}$ mole/l/min whilst $d[H^+]/dt = 0.56 \times 10^{-5}$ mole/l/min from 10 - 90 minutes. However, this comparison takes no note of the buffering effect produced by sulphate ion. Since the second dissociation constant of H_2SO_4 is 2×10^{-2} mole/l at $I = 0$, and the concentration of sulphate ion in 0.25 mole/l, much of the hydrogen ion will go to the production of HSO_4^-.

Thus noting that the pH variation from 10 - 90 minutes in Table 50 is 3.85 - 3.23 and using 2×10^{-2} mole/l for K_2 for sulphuric acid, the HSO_4^- concentration is calculated to rise from 0.0018 to 0.0074 mole/l over this time, i.e. there has been a (concealed) further production of hydrogen ion at the rate of 7.0×10^{-5} mole/l/min.

Thus a very approximate figure to compare with 2.66×10^{-5} mole/l/min of Mn(II) is 7.6×10^{-5} mole/l/min ($7.0 \times 10^{-5} + 0.56 \times 10^{-5}$); i.e. for every mole of manganese(II) oxidised about 3 moles of hydrogen ion are produced.

The fact that hydrogen ion is produced is undoubted, the above quantitative estimate must be regarded as approximate.

Table 49

pH of the Separate Reactants

Solution	Concentration	pH
$(NH_4)_2S_2O_8$ (A)	0.1600 mole/l	3.05
$(NH_4)_2S_2O_8$*	0.08000 " "	3.40
$MnSO_4$* (B)	0.01438 " "	6.38
$MnSO_4$**	0.007190	6.28

* 0.500 mole/l in K_2SO_4

** 0.2500 mole/l in K_2SO_4

Table 50

$[S_2O_8^{2-}]$ = 0.08000 mole/l

$[Mn^{2+}]_o$ = 0.007190 mole/l

$[K_2SO_4]$ = 0.250 mole/l

I = 1.02

Reaction started by mixing 25 ml of A and 25 ml of B of Table 49 above.

Time (min)	pH	$10^4[H^+]$ mole/l
0	3.95	1.12
10	3.85	1.41
35	3.53	2.95
45	3.47	3.39
67	3.32	4.79
90	3.23	5.89
120	3.14	7.27
140	3.08	8.32
165	3.01	9.77
180	2.97	10.72

Table 51

$[S_2O_8^{2-}]_o$ = 0.08000 mole/l

$[Mn^{2+}]_o$ = 0.003595 mole/l

$[K_2SO_4]$ = 0.250 mole/l

I = 1.01

Time	pH	$10^4[H^+]$ mole/l	Time	pH	$10^4[H^+]$ mole/l
5	4.15	0.708	140	3.097	7.998
10	4.040	0.912	150	3.068	8.551
20	3.830	1.479	165	3.032	9.290
30	3.660	2.188	180	2.988	10.28
45	3.510	3.090	190	2.978	10.52
50	3.480	3.340	200	2.952	11.17
60	3.410	3.890	210	2.927	11.83
70	3.360	4.365	225	2.912	12.25
80	3.308	4.920	235	2.902	12.53
90	3.262	5.470	240	2.888	12.94
105	3.206	6.223	245	2.892	12.82
120	3.153	7.031	250	2.882	13.12
130	3.122	7.551			

Table 52

$[S_2O_8^{2-}]_o$ = 0.1214 mole/l
$[Mn^{2+}]_o$ = 0.008450 mole/l
$[K_2SO_4]$ = 0.250 mole/l
I = 1.14

Time (min)	pH	$10^4[H^+]$ mole/l
7	3.772	1.690
9	3.732	1.854
11	3.688	2.057
13	3.650	2.239
15	3.618	2.410
17	3.592	2.559
19	3.560	2.754
21	3.535	2.917
23	3.507	3.112
25	3.487	3.258
27	3.472	3.373
30	3.438	3.648
33	3.417	3.828
35	3.398	3.999
38	3.378	4.188
40	3.366	4.305
43	3.345	4.519
45	3.326	4.721

Table 53

$[S_2O_8^{2-}]$ = 0.1600 mole/l
$[Mn^{2+}]$ = Nil
$[K_2SO_4]$ = 0.250 mole/l

Time (min)	pH	$10^4[H^+]$ mole/l
0	4.270	0.603
5	4.055	0.902
7	3.955	1.11
10	3.875	1.33
13	3.815	1.53
15	3.780	1.66
17	3.750	1.78
20	3.700	2.00
22	3.678	2.10
25	3.645	2.27
28	3.615	2.43
30	3.595	2.54

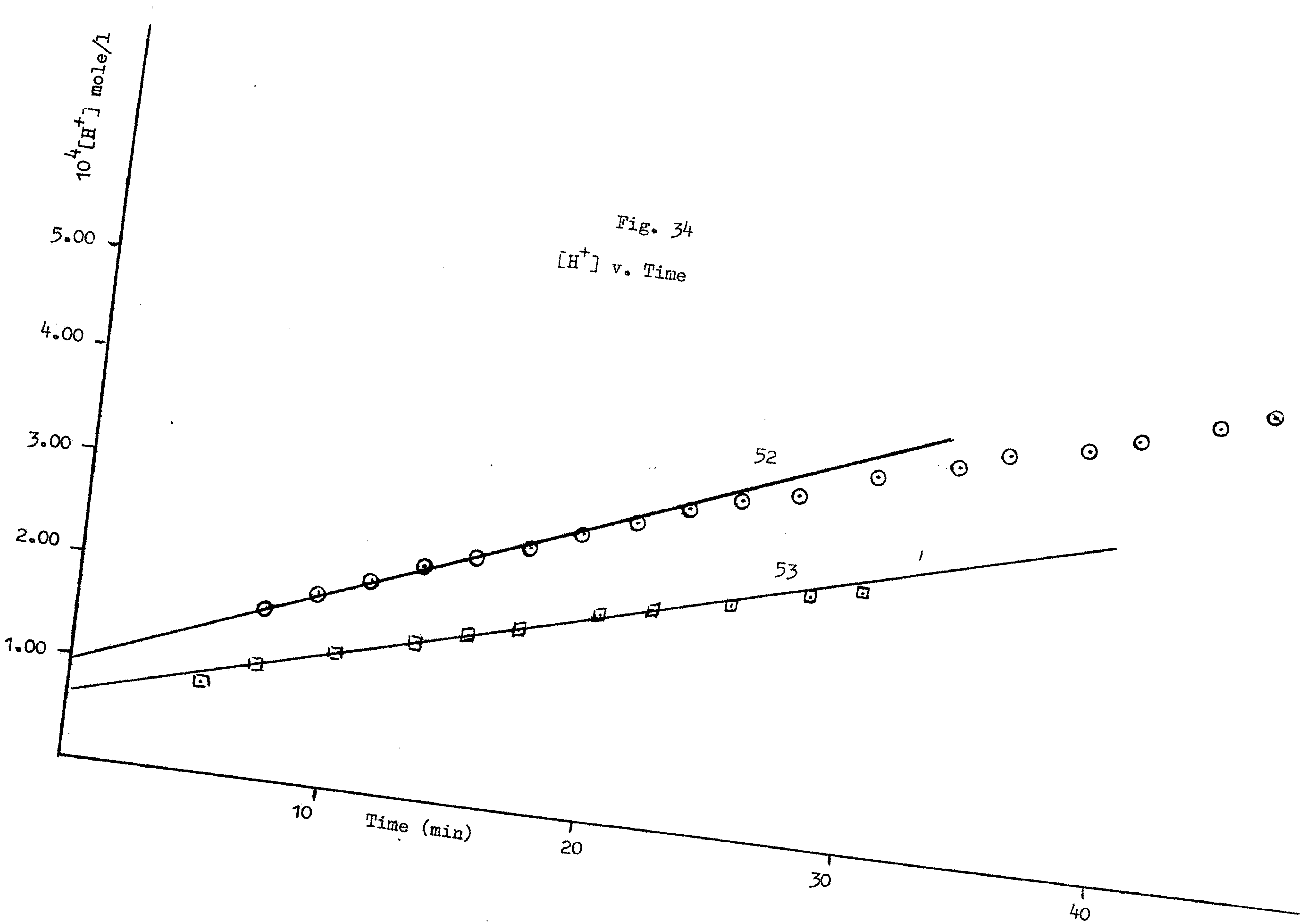


Fig. 34

$[H^+]$ v. Time

Effect of Agitation

As it was mentioned earlier, when the two reactants are mixed the solution becomes turbid and eventually a precipitate which was found to be manganese dioxide, is formed. The suspended solid product was observed to settle within an hour and the only disturbance to which the precipitated manganese dioxide was normally subjected was the disturbance caused by the removal of the sample for kinetic analysis, and this was done in such a way as to cause the minimum possible disturbance. To see if this disturbance - and the suspension of manganese dioxide - has any noticeable effect on the rate of the reaction two runs were performed simultaneously in which one of the two reaction vessels was subjected to continuous agitation which kept the manganese dioxide suspended in solution all the time. The other vessel was not disturbed except by the cautious removal of the sample. One of the two identical reaction vessels containing identical mixtures was mechanically shaken using an electrically operated glass shaker. The other flask was supported by a stand which rested on the floor without ever touching the bench on which the shaker was operating. The result of the two runs is shown in Table 54 and from Figs. 35-36 the rates for the agitated and, undisturbed are 2.76×10^{-5} mole/l/min, and 2.72×10^{-5} mole/l/min respectively. When one bears in mind the limits of the experimental error and the fact that in a normal run the solid product settles down and is not disturbed except by the removal of the samples one is led to the conclusion that disturbing the precipitate does not have any significant effect on the rate of the reaction.

Teble 54

$[S_2O_8^{2-}]_o$ = 0.08243 mole/l

$[Mn^{2+}]$ = 0.009889 mole/l

$[K_2SO_4]$ = 0.250 mole/l

Temperature = 60.0°C

Time (min)	Mechanically agitated		Undisturbed	
	Absorbance	$10^3[Mn^{2+}]$mole/l	Absorbance	$10^3[Mn^{2+}]$mole/l
45	0.855	8.21	0.861	8.27
75	0.780	7.49	0.785	7.54
105	0.701	6.73	0.699	6.71
135	0.608	5.84	0.614	5.90
180	0.476	4.57	0.492	4.72
225	0.349	3.35	0.357	3.43
270	0.219	2.10	0.233	2.23

The effect of added surface

It was pointed out in the main introduction that the thermal decomposition of peroxodisulphate and some reactions involving it exhibit chain characteristics and because chain reactions are sensitive to added surface it seemed appropriate to find out if the peroxodisulphate-manganese(II) reaction shows such an effect. Table 54 shows the results of three runs which are identical in all aspects except for the amount of glass wool which was used as the added surface. The initial rates (R_o) - shown in the bottom row of the table - are calculated from Fig. 37. The results show that the rate decreases with increasing amount of glass wool. Therefore added surface seems to retard the reaction. However, when these results

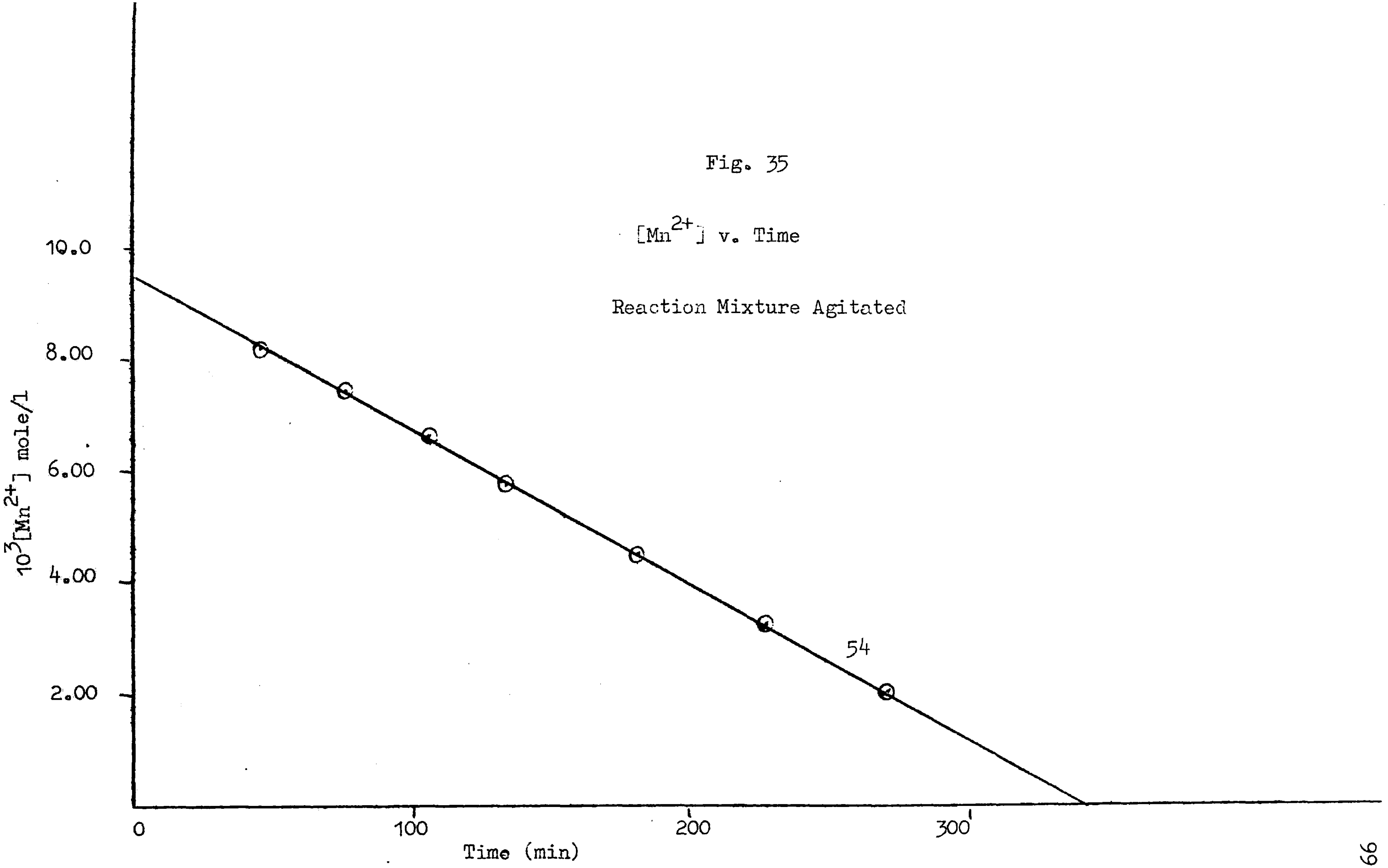


Fig. 35

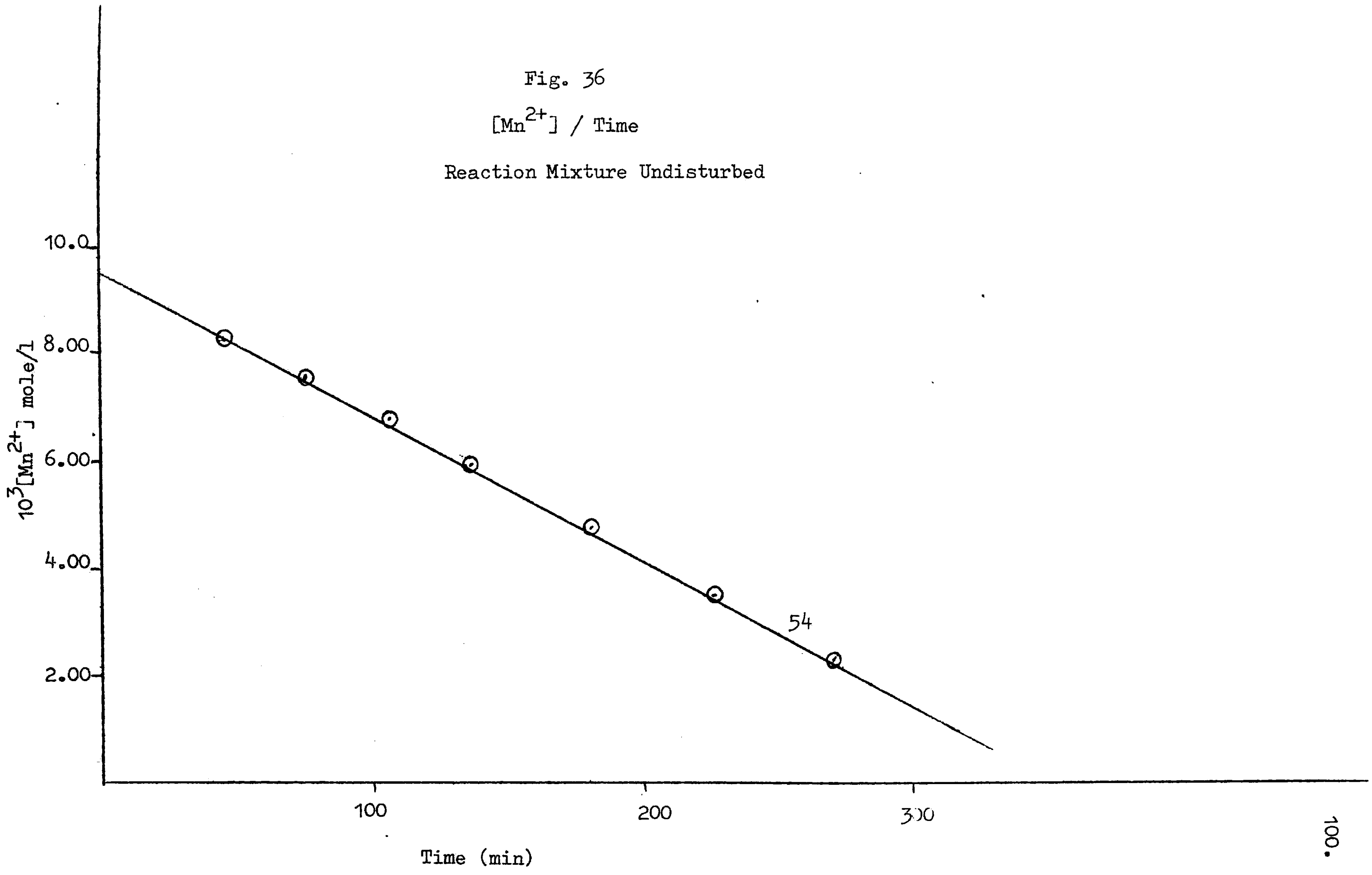
$[Mn^{2+}]$ v. Time

Reaction Mixture Agitated

Fig. 36

$[Mn^{2+}]$ / Time

Reaction Mixture Undisturbed



are compared with those on reproducibility - one could deduce that the glass wool, although washed several times with distilled and double distilled water and dried in the oven, might well have introduced impurities which affected the rate.

All runs used for discussion purposes involve no added surface and indeed refer to a constant area of surface available.

Table 55

$[S_2O_8^{2-}]_o$ = 0.08243 mole/l $[Mn^{2+}]$ = 0.009889 mole/l

$[K_2SO_4]$ = 0.250 mole/l Temperature = 60.0°C

Glass wool	Nil (a)		2.00 gm (b)		3.00 gm (c)	
Time (min)	Absorbance*	$10^3[Mn^{2+}]$	Absorbance*	$10^3[Mn^{2+}]$	Absorbance**	$10^3[Mn^{2+}]$
45	0.871	8.36	0.868	8.33	0.359	8.62
90	0.727	6.98	0.761	7.30	0.325	7.80
135	0.592	5.68	0.632	6.07	0.280	6.72
180	0.455	4.38	0.510	4.90	0.238	5.71
225	0.317	3.04	0.371	3.56	0.191	4.70
270	0.186	1.79	0.280	2.69	0.154	3.70
300	0.100	0.96	0.217	2.08	0.112	2.69
10^5 R_o mole/l	2.88		2.53		2.25	

* 5 ml sample diluted to 100 ml

** 5 ml sample diluted to 250 ml

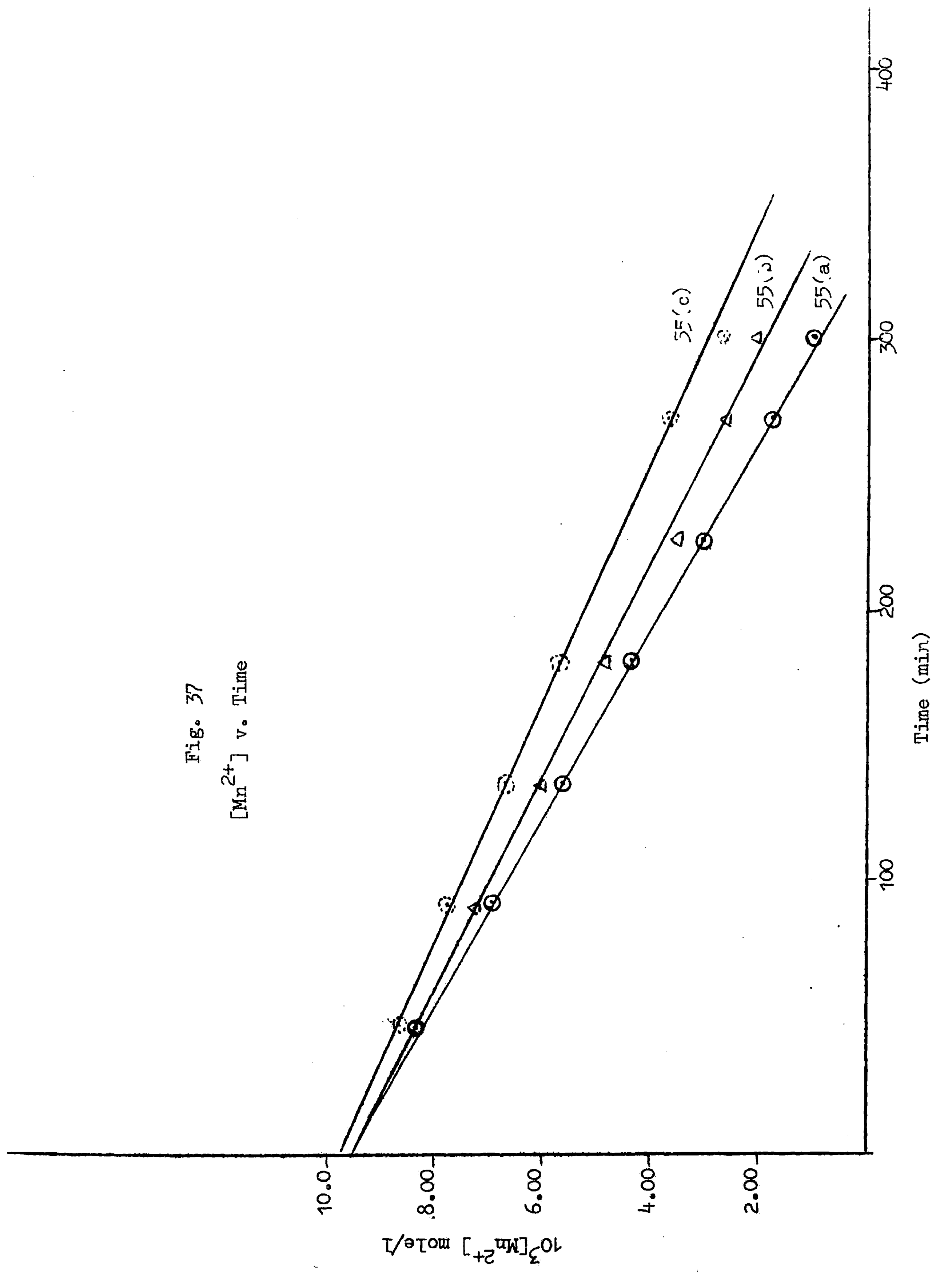


Fig. 37

$[Mn^{2+}]$ v. Time

The effect of free-radical capturing agents

When searching for a suitable buffer potassium hydrogen phthalate (Analar grade) was tried. A reaction mixture which was 0.0800 mole/l in peroxodisulphate, 0.0100 mole/l in manganese(II), 0.250 mole/l in potassium sulphate and 0.1 (or 0.05) mole/l in phthalate was observed to stay clear when kept at 60° for as long as 8 hours indicating that no oxidation of manganese(II) takes place in the presence of phthalate. However it was not possible to follow the concentration of manganese(II) as phthalate was found to interfere with its spectrophotometric determination, but the absence of any precipitate or even a suspension of manganese dioxide was a clear indication that no oxidation of manganese was taking place.

To pursue the effect further, reaction mixtures similar to those above (except for the absence of phthalate) were made 0.1 and 0.05 mole/l in allyl alcohol, an effective free radical trap. This was found to bring the redox reaction to a virtual stop.

The effect of the two compounds (i.e. phthalate and allyl alcohol) shows that the redox reaction between manganese(II) and peroxodisulphate involves free radicals and probably a chain mechanism.

Reproducibility

The manganese(II) - peroxodisulphate reaction was found to be very sensitive to the quality of the water used. Like some other reactions of peroxodisulphate with inorganic substrates(38,39) the results were reproducible only when water re-distilled from alkaline potassium permanganate was used and only when the re-distillation was carried out with the utmost care. Runs made using the same lot of double distilled water were quite reproducible within themselves but this consistency was not always the case when runs of one lot of water were compared with those made using a different lot. However, a number of carefully collected lots of water gave the rate of 2.69 x 10^{-5} mole/l/min at 60°C with the initial peroxodisulphate concentration of 0.08000 mole/l - concentration of manganese(II) being of little importance as rate is independent of it. This value was used as a standard for checking the quality of water.

Tables 56 A, B and Figs. 38-41 show the results of four runs using two different lots of water (A and B) and in which the consistency of each pair is quite reasonable but the comparison with the other pair is quite poor. Both lots of water were rejected.

Table 56

Lot A

$[S_2O_8^{2-}]_o$ = 0.08000 mole/l $[Mn^{2+}]_o$ = 0.007190 mole/l

$[K_2SO_4]$ = 0.250 mole/l   Temperature = 60.0°C

Time (min)	Run 1		Run 2	
	Absorbance	$10^3[Mn^{2+}]$	Absorbance	$10^3[Mn^{2+}]$
30	0.331	6.36	0.334	6.40
90	0.291	5.58	0.280	5.36
150	0.226	4.34	0.222	4.26
210	0.169	3.24	0.172	3.30
270	0.112	2.16	0.113	2.18
10^5 R_o mole/l/min	1.83		1.78	

Table 56

Lot B

$[S_2O_8^{2-}]_o$ = 0.08000 mole/l $[Mn^{2+}]_o$ = 0.007725 mole/l

$[K_2SO_4]$ = 0.250 mole/l Temperature = 60.0°C

Time (min)	Run 1		Run 2	
	Absorbance	$10^3[Mn^{2+}]$	Absorbance	$10^3[Mn^{2+}]$
30	0.354	6.80	0.358	6.88
60	0.318	6.10	0.337	6.46
120	0.276	4.90	0.271	5.20
150	0.235	4.50	0.235	4.50
180	0.198	3.80	0.191	3.66
240	0.143	2.74	0.154	2.96
300	0.087	1.66	0.087	1.66
10^5 R_o mole/l/min	1.90		1.93	

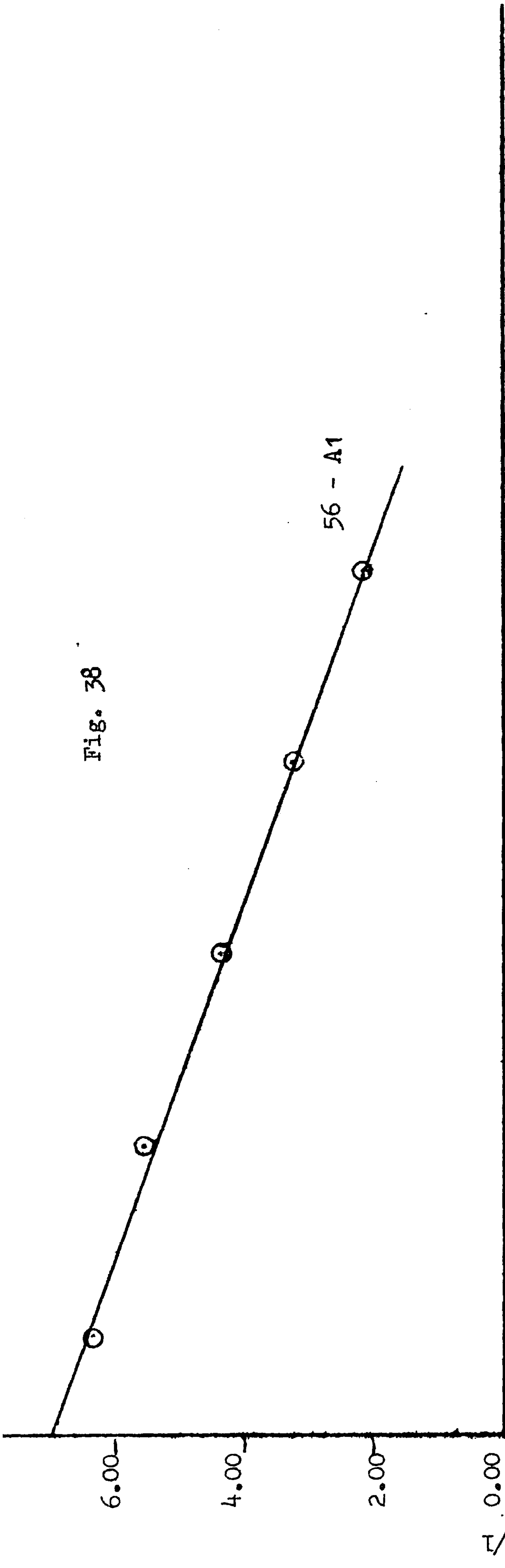

56 - A1
6.00
4.00
2.00
0.00
$10^3[Mn^{2+}]$ mole/l

Fig. 38

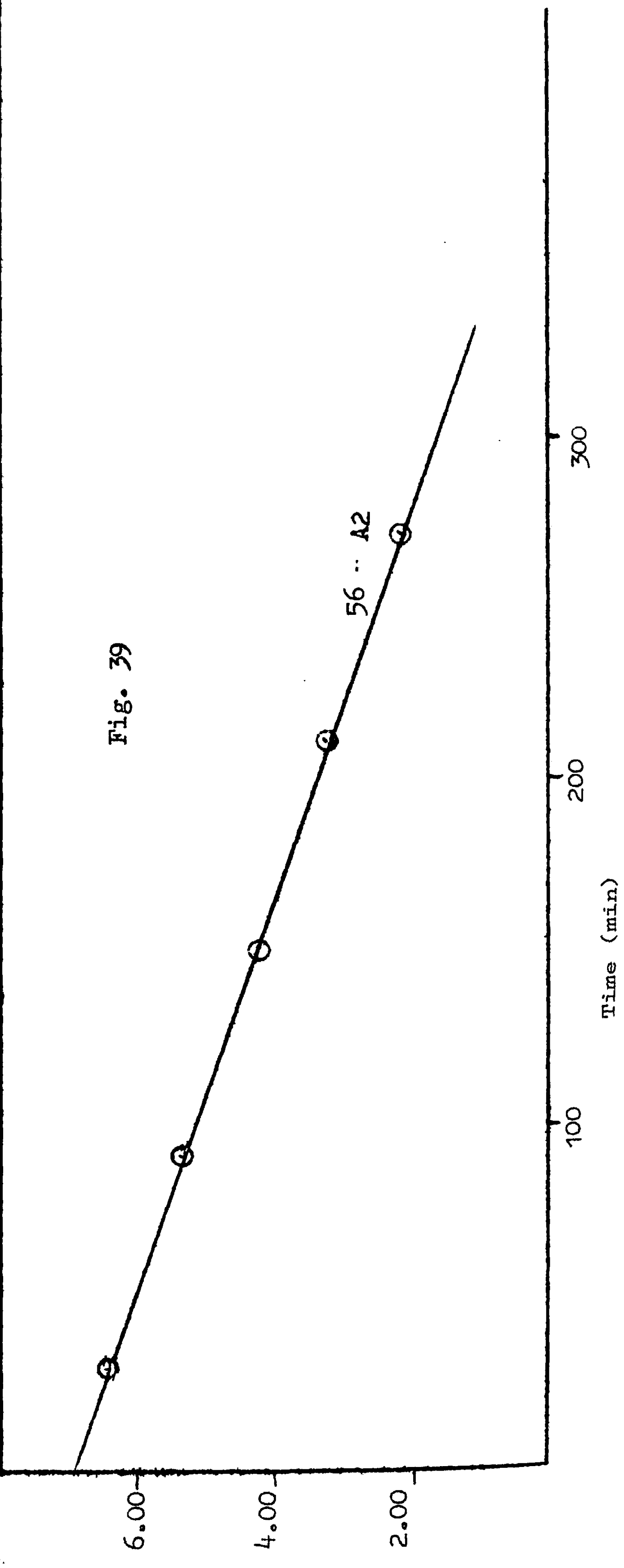

56 - A2
6.00
4.00
2.00
100
200
300
Time (min)

Fig. 39

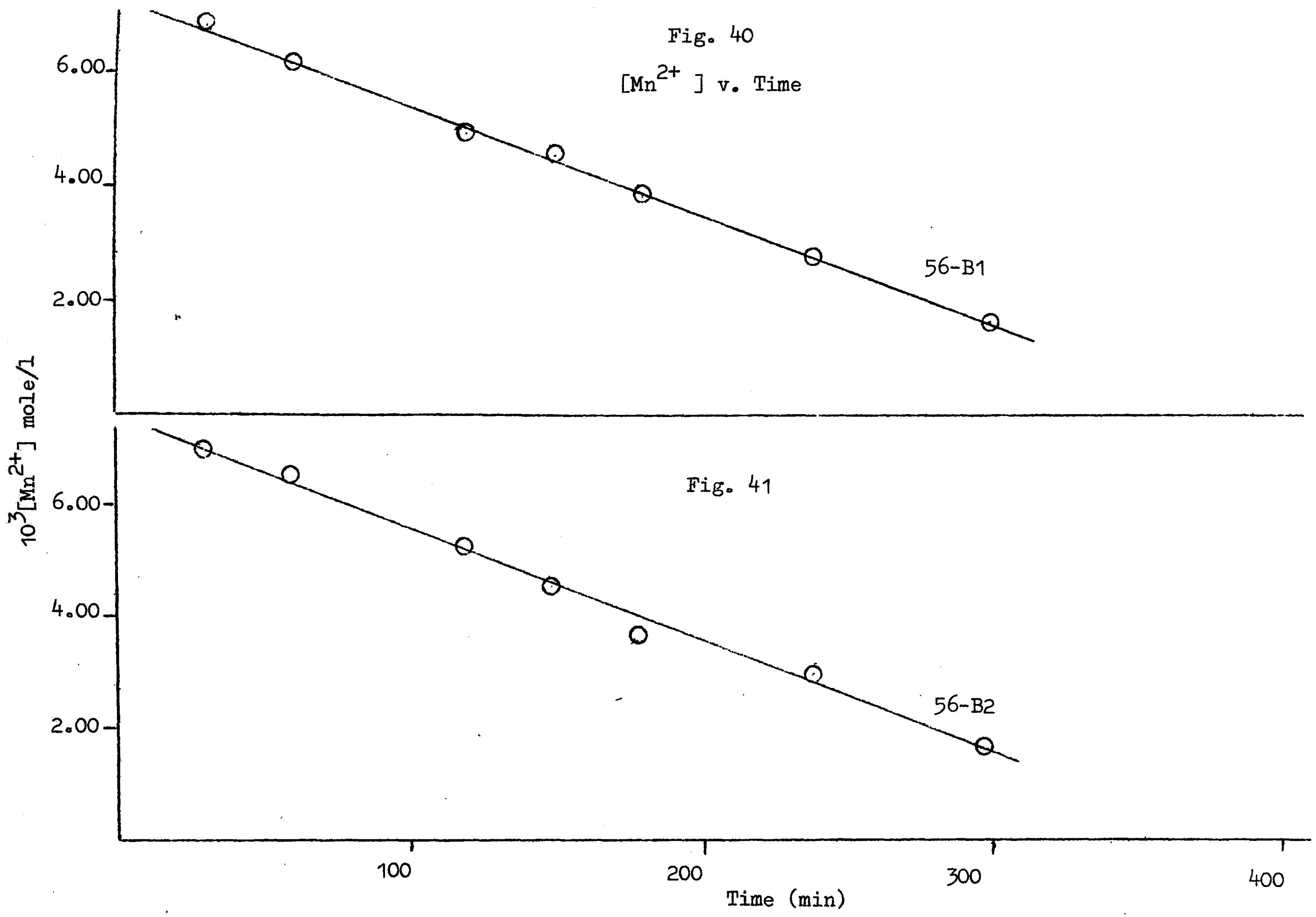


Fig. 40

[Mn^{2+}] v. Time

Fig. 41

D I S C U S S I O N

The experimental results presented in the preceding sections can be summarised as follows:

1. The rate of the reaction is independent of manganese(II) concentration and is first order in peroxodisulphate concentration, and despite this
2. The observed first order rate constant for the redox reaction is approximately 27% higher than the first order rate constant for the thermal decomposition of peroxodisulphate.
3. The activation energy for this redox reaction is relatively high (31.5 kcal/mole) and is only 2 kcal/mole lower than the activation energy for the thermal decomposition of peroxodisulphate (33.5 kcal/mole).
4. The rate of the reaction is almost independent of ionic strength - apart from the effect of ion-pairing on the concentration of peroxodisulphate.
5. Added surface (glass wool) may retard the reaction.
6. The redox reaction is inhibited by phthalate and allyl alcohol.
7. The rate of the reaction is sensitive to the quality of the water used.
8. The initial rate of disappearance of peroxodisulphate is equal to that of manganese(II) which suggests that the two reactants are consumed in equimolar quantities. Moreover hydrogen ion and manganese dioxide are produced. Therefore the stoicheiometry of the reaction may be expressed as

$$Mn(II) + S_2O_8^{2-} + 2H_2O = MnO_2 + 2SO_4^{2-} + 4H^+ \qquad \text{......} \quad [86]$$

9. The rate law is

$$\frac{-d[S_2O_8^{2-}]}{dt} = \frac{-d[Mn(II)]}{dt} = k_{obs.}[S_2O_8^{2-}] \qquad \text{......} \quad [87]$$

where $k_{obs.} \cong 3.30 \times 10^{-4}\ min^{-1}$ at 60°C and in a solution which is 0.250 mole/l in potassium sulphate.

The rate law may also be expressed as

$k_{obs.} = 2.95 \times 10^{15} \exp\left(\frac{-31,500}{RT}\right) \sec^{-1}$ ...... [88]

in the temperature range 55° - 80°C and in 0.250 mole/l K_2SO_4 solution.

A proposed mechanism

The fact that the reaction is first order with respect to peroxodisulphate and zero order with respect to manganese(II) and the high energy of activation suggest that the reaction has its rate determining step in the thermal decomposition of peroxodisulphate, but any proposed mechanism must also explain why the presence of manganese(II) increases the rate of decomposition of peroxodisulphate although the rate of the reaction is independent of its (Mn(II)) concentration. The sensitivity of the reaction to impurities in the solvent (water), the possible sensitivity to surface and the effect of free radical capturing agents suggest that the reaction may have a chain mechanism.

A possible chain mechanism which can explain the observed kinetics is the following:

$S_2O_8^{2-} \xrightarrow{k_5} 2SO_4^-$ slow ...... [5]

$SO_4^- + H_2O \xrightarrow{k_6} HSO_4^- + OH$ ...... [6]

$Mn(II) + OH \xrightarrow{k_{89}} Mn(III) + OH^-$ ...... [89]

$Mn(III) + S_2O_8^{2-} \xrightarrow{k_{90}} Mn(IV) + SO_4^{2-} + SO_4^-$ ...... [90]

$Mn(III) + SO_4^- \xrightarrow{k_{91}} Mn(IV) + SO_4^{2-}$ ...... [91]

OH^- will, in an acid medium, mainly disappear to produce water. An overall rapid set of steps summarised as

$Mn(IV) + 2H_2O = MnO_2 + 4H^+$ ...... [92]

will then lead to the observed hydrated manganese dioxide.

This mechanism together with [92] is consistent with the stoicheiometry expressed in equation [86] in that $S_2O_8^{2-}$ and Mn(II) are consumed mole for mole, $4H^+$ are produced in precipitating MnO_2 and one OH^- and one H^+ (in HSO_4^{4-}) are produced for every OH radical so that the $4H^+$ product is undisturbed.

In this mechanism step [5] is the rate determining step and it can be taken as established (see Chapter I).

SO_4^- once formed will be very reactive and the most likely species for it to meet in early encounters is the solvent. Hence the well documented equation [6].

OH will also be a reactive species. It does not seem likely that it will react with water or any dissolved oxygen. The simplest reaction it can undergo to produce a stable species is to accept an electron. Thus some potential reducing agent must be its likely partner in reaction. The only species present in any quantity is Mn(II). Hence equation [89].

Mn(III) is not the observed product, so some reaction leading to another one electron oxidation is required. Mn(III) is an intermediate so present in small concentrations. Hence its likely oxidant, if the reaction is to bea main reaction path, must be in large amount. Hence equation [90].

Suppose equation [90] is nonexistent, in which case the rate of disappearance of peroxodisulphate will be given by [93]

$$\frac{-d[S_2O_8^{2-}]}{dt} = k_5[S_2O_8^{2-}] + 0 \qquad \ldots\ldots \quad [93]$$

This, however, contradicts the observed fact that in the presence of Mn(II) k_{obs} is 27% larger than k_5. Therefore [90] is necessary

Suppose [91] is nonexistent and let

$$[SO_4^-] = x$$

$$[OH] = y$$

$$[Mn(III)] = z$$

Hence

$$\frac{-d[S_2O_8^{2-}]}{dt} = k_5[S_2O_8^{2-}] + k_{90}\, z\, [S_2O_8^{2-}] \qquad \text{......} \quad [94]$$

$$\frac{-d[Mn(II)]}{dt} = k_{89}\, y\, [Mn(II)] \qquad \text{......} \quad [95]$$

and $$\frac{d[Mn(IV)]}{dt} = k_{90}\, z\, [S_2O_8^{2-}] \qquad \text{......} \quad [96]$$

It was experimentally observed that [94] and [95] are equal. But since the rate of disappearance of Mn(II) should be the same as the rate of appearance of Mn(IV) [95] and [96] must be equal, which will lead to the equality of [96] and [94] which of course is impossible. Therefore [91] is also necessary.

Therefore the mechanism needs both equation [90] and [91] - the former being followed by the latter and not vice versa. Hence

$$\frac{-d[S_2O_8^{2-}]}{dt} = \frac{-d[Mn(II)]}{dt} = \frac{d[Mn(IV)]}{dt} \qquad \text{......} \quad [97]$$

or

$$k_5[S_2O_8^{2-}] + k_{90}\, z\, [S_2O_8^{2-}] = k_{89}\, y\, [Mn(II)] = k_{90}\, z\, [S_2O_8^{2-}] + k_{91}\, z\, x \qquad \text{......} \quad [98]$$

From the steady state approximation

$$\frac{dy}{dt} = k_6\, x - k_{89}\, y\, [Mn(II)] = 0 \qquad \text{......} \quad [99]$$

Therefore

$$k_6\, x = k_{89}\, y\, [Mn(II)] \qquad \text{......} \quad [100]$$

Substituting $k_6\, x$ for $k_{89}\, y\, [Mn(II)]$ in [98] and dividing by k_6 gives

$$\frac{k_5}{k_6}[S_2O_8^{2-}] + \frac{k_{90}}{k_6}\, z\, [S_2O_8^{2-}] = x$$

and substituting for x in

$$k_5[S_2O_8^{2-}] + k_{90}\, z\, [S_2O_8^{2-}] = k_{90}\, z\, [S_2O_8^{2-}] + k_{91}\, z\, x \qquad \text{....} \quad [98]$$

gives

$$k_5 = k_{91}\, z \left(\frac{k_5}{k_6} + \frac{k_{90}}{k_6}\, z \right) \qquad \ldots\ldots \quad [101]$$

or

$$k_{90}\, k_{91}\, z^2 + k_5\, k_{91}\, z - k_5\, k_6 = 0 \qquad \ldots\ldots \quad [102]$$

and this is a quadratic equation of the form

$$a\, z^2 + b\, z + c = 0 \qquad \ldots\ldots \quad [103]$$

Therefore

$$z = \frac{-k_5\, k_{91} + \sqrt{k_5^{\,2}\, k_{91}^{\,2} + 4\, k_5\, k_6\, k_{90}\, k_{91}}}{2\, k_{90}\, k_{91}} \qquad \ldots\ldots \quad [104]$$

k_5 is likely to be the smallest term and clearly it is much smaller than k_6 whence

$$k_5^{\,2}\, k_{91}^{\,2} \ll 4\, k_5\, k_6\, k_{90}\, k_{91}$$

Using the Binomial theorem, where b is very small;

$$(a + b)^{\frac{1}{2}} \approx a^{\frac{1}{2}} + \tfrac{1}{2}\, a^{-\frac{1}{2}}\, b \qquad \ldots\ldots \quad [105]$$

Applying the approximation [105] for the numerator in equation [104] gives

$$\text{numerator} \approx \sqrt{4\, k_5\, k_6\, k_{90}\, k_{91}} + \frac{k_5^{\,2}\, k_{91}^{\,2}}{4\sqrt{k_5\, k_6\, k_{90}\, k_{91}}} - k_5\, k_{91}$$

$$\approx \sqrt{4\, k_5\, k_6\, k_{90}\, k_{91}} + k_5\, k_{91} \left\{ \frac{k_5\, k_{91}}{4\sqrt{k_5\, k_6\, k_{90}\, k_{91}}} - 1 \right\}$$

$$\approx \sqrt{4\, k_5\, k_6\, k_{90}\, k_{91}} \qquad \ldots\ldots \quad [106]$$

Therefore

$$z = \sqrt{\frac{k_5\, k_6}{k_{90}\, k_{91}}} \qquad \ldots\ldots \quad [107]$$

$$\frac{-d[S_2O_8{}^{2-}]}{dt} = k_5[S_2O_8{}^{2-}] + k_{90}\, z\, [S_2O_8{}^{2-}] \qquad \ldots\ldots \; [94]$$

Substituting for z in [94] gives

$$\frac{-d[S_2O_8{}^{2-}]}{dt} = k_5[S_2O_8{}^{2-}] + \sqrt{\frac{k_5\, k_6\, k_{90}}{k_{91}}}\, [S_2O_8{}^{2-}]$$

$$= \left(k_5 + \sqrt{\frac{k_5\, k_6\, k_{90}}{k_{91}}}\right) [S_2O_8{}^{2-}] \qquad \ldots\ldots \; [108]$$

Equation [108] is similar to the empirical rate equation [87].

Hence

$$k_{obs} = k_5 + \sqrt{\frac{k_5\, k_6\, k_{90}}{k_{91}}} \qquad \ldots\ldots \; [109]$$

Equation [109] explains why the presence of manganese(II) increases the rate of deomposition of peroxodisulphate although the reaction rate is independent of its concentration. The presence of manganese(II) therefore increases the rate of decomposition of peroxodisulphate by the term under the square root sign.

Using the values 3.30×10^{-4} min^{-1} and 2.60×10^{-4} min^{-1} reported earlier for k_{obs} and k_5 gives the ratio

$$\frac{k_6\, k_{90}}{k_{91}} \simeq 1.9 \times 10^{-5}$$

The mechanism is also in accordance with the results of ionic effect experiments, as none is expected for the decomposition of peroxodisulphate which is the rate determining step. It is also in general agreement with the few first order reactions of peroxodisulphate reported with inorganic substrates as discussed in Chapter I.

CHAPTER III

THE OXIDATION OF NITRITE

CHAPTER III

EXPERIMENTAL

Preliminary

At the commencement of this investigation a literature survey indicated that no previous study had been made of the reaction between nitrite and peroxodisulphate. After the completion of the study an abstract(66) was discovered of a Ph.D. thesis concerned with the reaction.

The two reagents were found to react but the reaction at around pH 7 was found to be inconveniently slow to study below 60°C. Because nitrite was found to be quite stable around this pH (see below) the reaction was carried out at 60°C and at pH values of approximately 6.4.

The reaction was followed by the iodometric estimation of peroxodisulphate as no convenient way of monitoring nitrite concentration was found because peroxodisulphate was observed to interfere with the spectrophotometric determination of nitrite which is described below.

The reaction was studied at a constant and high ionic strength of about 1 and at constant cation concentration because cations were found to affect the rate of the reaction. The cation concentration was kept constant by adding the appropriate amounts of potassium and sodium nitrates as these were the two cations (other than a minute amount of hydrogen ion) present.

Chemicals

All the chemicals used in this reaction were Analar Grade - unless otherwise stated. The two reactants were potassium peroxodisulphate and sodium nitrite. The former was chosen instead of ammonium peroxodisulphate - which was used in the other two reactions reported in this work and which is much more soluble than the potassium salt - in order to minimise the number of cations present and because potassium ions are present in the phosphate buffer system (see later). Unfortunately it was not possible to have the reactants completely in the form of either the potassium or the sodium salts because neither A.R. sodium peroxodisulphate nor A.R. potassium nitrite is available, and since the purity of materials was found to be important the use of general purpose reagents was abandoned.

Preparation of Solutions

For each kinetic run two solutions A and B were prepared using water which had been re-distilled from alkaline permanganate solution. A was the peroxodisulphate solution while B was a mixture of nitrite, buffer (KH_2PO_4 and and Na_2HPO_4) and the added salts (KNO_3 and $NaNO_3$). The solutions were prepared in such a way that the concentration of each constituent was double the value required in the final reaction mixture.

Peroxodisulphate solutions were always prepared fresh and never used after more than 48 hours from the time of preparation. These solutions were made by accurately weighing out the required amount of salt and were then standardised at 60°C iodometrically.

The nitrite solutions were standardised by the method of Simpson and Laird(58) in which a sample of the nitrite solution is added dropwise, with continuous (magnetic) stirring to an excess of acidified standard permanganate solutions and titrating the excess against standard oxalate solution. The concentration of nitrite was also checked spectrophotometrically by the method of Shin(59) in which the nitrite is quantitatively used up in a diazotization reaction and the resulting diazonium salt coupled to form a coloured azo compound. This method, however, is suitable only for low concentrations of nitrite - less than 2×10^{-5} mole/l - and therefore it was necessary to dilute a sample of the solution under test to an appropriate concentration. 10 ml of the diluted sample was then added to a 100 ml volumetric flask which was filled to about two thirds with water. 5 ml of 0.5% sulphanilamide (in 50% HCl) was added and the flask shaken well.

After about three minutes 2 ml of 0.1% solution of the coupling agent, N-(1-naphthyl)ethylenediaminedihydrochloride, was added. The solution was topped up, mixed well and left in the dark for about 20 minutes. The absorbance of the resulting solution was then measured in a Perkin-Elmer PE.124 spectrophotometer fitted with a digital scale, at 536 nm at which it is a maximum (Fig.42) and at which the solution obeys Beer's law (Fig.43). The concentrations were read from the calibration curve and calculated accordingly. However, this method was not useful for following the reaction because peroxodisulphate was found to interfere, but it was useful in the standardisation of nitrite solutions.

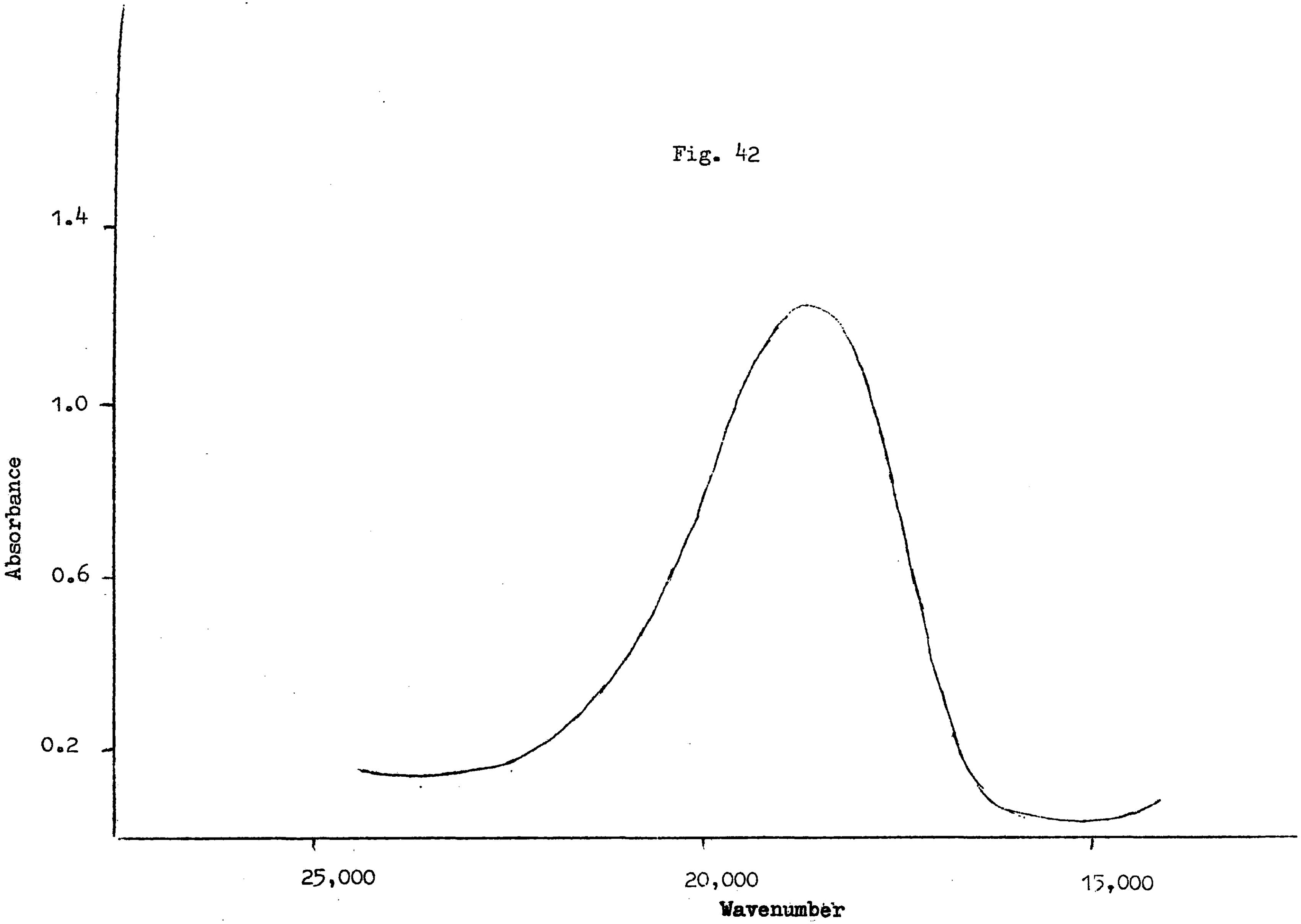
Stability of nitrite at 60°C

The stability of nitrite under the experimental conditions was checked by thermostatting two solutions (C_1 and C_2) each of which was 0.5 mole/l in each of monohydrogen orthophosphate and dihydrogen orthophosphate. In C_1 the concentration of nitrite was 0.0540 mole/l, whilst in C_2 the concentration was 0.1065 mole/l. At appropriate time intervals 1 ml samples were withdrawn, diluted to 1000 ml, and 10 ml of this treated for spectrophotometric determination of nitrite as described above. The pH of the two solutions were 6.52 and 6.53 respectively. The results which are shown in Table 58 below indicate that nitrite is quite stable at 60° and pH 6.5.

Table 58

Time (hours)	Absorbance (C_1)	Absorbance (C_2)
1.0	.268	0.513
2.0	.268	0.523
2.5	.268	0.528
3.0	.267	0.525
4.5	.272	0.526
5.5	.269	0.527
23	.268	0.524

Fig. 42



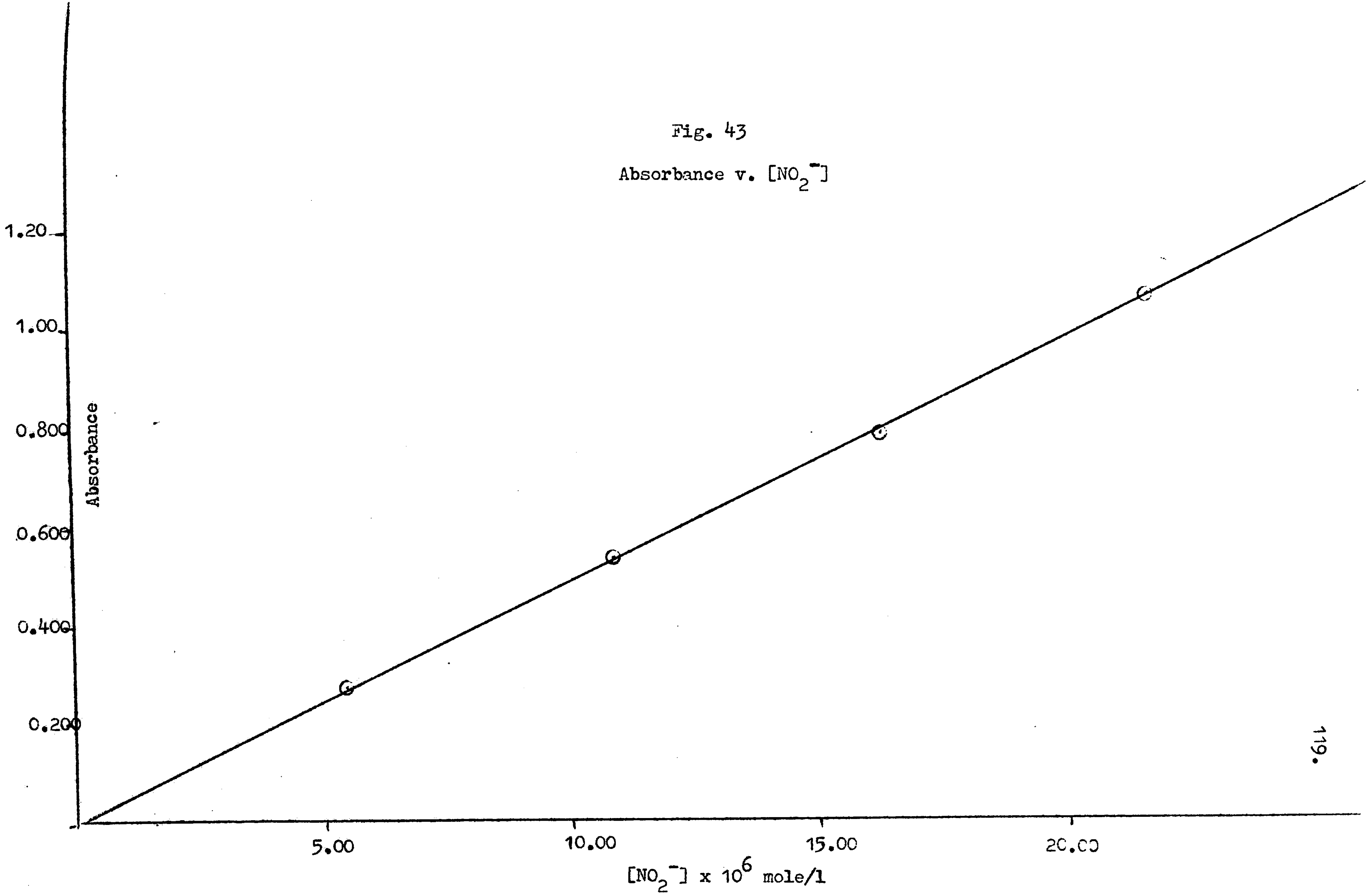


Fig. 43

Absorbance v. $[NO_2^-]$

Iodometric determination of peroxodisulphate concentration

To examine if the presence of nitrite affects the iodometric estimation of peroxodisulphate the concentration of a solution which was 0.160 mole/l in peroxodisulphate was checked in the presence and absence of nitrite. 5 ml Samples of the peroxodisulphate solution were added to flasks each containing 5 ml of 40% potassium iodide both in the presence and in the absence of different volumes of approximately 0.1 mole/l nitrite solution which was also 0.2 mole/l in each of Na_2HPO_4 and KH_2PO_4. The flasks were stoppered and kept in the dark for 30 minutes and the resulting iodine was titrated against 0.1570 mole/l thiosulphate solution. The results which are given in Table 59 prove that nitrite does not interfere with the iodometric estimation of peroxodisulphate.

Table 59

Effect of Nitrite on Peroxodisulphate Estimation

Volume of 0.16 mole/l $S_2O_8^{2-}$ = 5 ml

Volume of nitrite solution added (ml)	Titre (ml)
Nil	10.20
Nil	10.20
Nil	10.20
Nil	10.20
5	10.20
5	10.20
5	10.15
10	10.20

Experimental Procedure

Solutions A and B (see above) were thermostatted separately for 30 minutes. 25 ml Of B were transferred to the reaction vessel (100 ml R.B. Quick-fit flask), followed by 25 ml of A, the mixture was then shaken vigorously and the flask stoppered. Zero time was taken as the time when the pipette delivering A was half empty. All pipettes whether used for transferring the reactants or removing the samples were preheated at 60°C. At appropriate time intervals 5 ml samples were withdrawn and added to a similar volume of chilled distilled water in 250 ml iodine flasks. Purified nitrogen gas was then bubbled for 10 minutes through the quenched sample to remove any dissolved oxygen (see later), 5 g of solid potassium iodide were added and the flask stoppered and kept in the dark for 30 minutes before titrating the resulting iodine against standard thiosulphate solution.

The initial rate was calculated from a plot of peroxodisulphate concentration against time.

Order with respect to peroxodisulphate

The order of the reaction with respect to peroxodisulphate was investigated at constant nitrite concentration, pH, ionic strength and cation concentration. Nitrite concentration was kept constant at 0.07768 mole/l while the concentration of peroxodisulphate was varied from approximately 0.01 mole/l to about 0.12 mole/l. The data of the kinetic runs are given in Tables 70-77 and the $[S_2O_8^{2-}]$/time plots from which initial rates were calculated are shown in Figs. 44-51. When the initial rate is plotted against initial concentration (Fig.52) a straight line, passing through most of the points below $[S_2O_8^{2-}]_o < 0.05$ mole/l and through the origin, is obtained. This indicates that the reaction is first order with respect to peroxodisulphate.

The slope of this line which is the observed pseudo-first order initial rate constant is 2.264 x 10^{-3} min^{-1}. An attempt was also made to get more accurate values for initial rates from $\log[S_2O_8^{2-}]$/time plots (since reaction is first order in $S_2O_8^{2-}$) - Figs. 35-60 and Table 79. These initial rates were again plotted against initial peroxodisulphate concentration (Fig. 61) and the result was a straight line passing through the origin and having a slope of 2.307 x 10^{-3} min^{-1}.

Therefore at constant nitrite concentration, pH, ionic strength and cation concentration the initial rate of the reaction (R_o) may be represented by equation [110],

$$R_o = \left\{\frac{-d[S_2O_8^{2-}]}{dt}\right\} = k_{obs}[S_2O_8^{2-}]_o \qquad \text{......} \quad [110]$$

where k_{obs} - the initial pseudo-first order rate constant - has the value of (2.286 ± 0.030) x 10^{-3} min^{-1} under the present experimental conditions taking the average of the two values cited above.

The following conditions apply to Tables 60-68. All the initial concentrations are nominal and do not take account of any ion-pairing that may occur, and the unit of concentration is mole/l throughout.

$[NO_2^-]_o$ = 0.07768

$[HPO_4^{2-}]$ = 0.200

$[H_2PO_4^-]$ = 0.200

$[K^+]$ = 0.500

$[Na^+]$ = 0.500

$I \simeq 1.23$

Temperature = 60.0°C

$pH_o \simeq 6.45$

Table 60

$[S_2O_8^{2-}]_o$ = 0.009795

$[Na_2S_2O_3]$ = 0.005952

Time (min)	Titre (ml)	$10^2[S_2O_8^{2-}]$	$3 + \log[S_2O_8^{2-}]$
5	16.20	0.9642	0.9842
10	16.11	0.9589	0.9818
15	15.92	0.9476	0.9766
20	15.75	0.9374	0.9719
25	15.55	0.9255	0.9663
30	15.39	0.9160	0.9619
35	15.20	0.9049	0.9565

Table 61

$[S_2O_8^{2-}]_o$ = 0.01928

$[Na_2S_2O_3]$ = 0.005952

Time (min)	Titre (ml)	$10^2[S_2O_8^{2-}]$	$3 + \log[S_2O_8^{2-}]$
5	32.02	1.906	1.2801
10	31.70	1.887	1.2758
15	31.34	1.865	1.2707
20	30.90	1.839	1.2646
25	30.60	1.821	1.2603
30	30.23	1.799	1.2551
35	29.91	1.780	1.2504

Table 62

$[S_2O_8{}^{2-}]_o$ = 0.03950

$[Na_2S_2O_3]$ = 0.01122

Time (min)	Titre (ml)	$10^2[S_2O_8{}^{2-}]$	$3 + \log[S_2O_8{}^{2-}]$
5	34.04	3.819	1.5819
10	33.58	3.768	1.5761
15	33.24	3.730	1.5717
20	32.84	3.685	1.5663
25	32.41	3.634	1.5604
30	32.06	3.597	1.5560
35	31.81	3.569	1.5524

Table 63

$[S_2O_8{}^{2-}]_o$ = 0.05754

$[Na_2S_2O_3]$ = 0.01122

Time (min)	Titre (ml)	$10^2[S_2O_8{}^{2-}]$	$3 + \log[S_2O_8{}^{2-}]$
5	50.71	5.690	1.7551
10	49.92	5.601	1.7483
15	49.75	5.582	1.7468
20	49.22	5.522	1.7421
25	48.76	5.471	1.7381
30	48.24	5.413	1.7334
35	47.46	5.325	1.7263

Table 64

$[S_2O_8^{2-}]_o$ = 0.09780

$[Na_2S_2O_3]$ = 0.02747

Time (min)	Titre (ml)	$10^2[S_2O_8^{2-}]$	$3 + \log[S_2O_8^{2-}]$
5	35.15	9.656	1.9848
10	34.89	9.584	1.9816
15	34.51	9.480	1.9768
20	34.12	9.373	1.9718
25	33.80	9.285	1.9677
30	33.43	9.183	1.9629
35	33.03	9.073	1.9577

Table 65

$[S_2O_8^{2-}]_o$ = 0.1179

$[Na_2S_2O_3]$ = 0.02747

Time (min)	Titre (ml)	$10^2[S_2O_8^{2-}]$	$3 + \log[S_2O_8^{2-}]$
5	42.50	11.67	2.0671
10	42.03	11.55	2.0626
15	41.54	11.41	2.0573
20	41.12	11.30	2.0531
25	40.77	11.20	2.0492
30	40.33	11.08	2.0444
35	39.81	10.94	2.0391

Table 66

$[S_2O_8^{2-}]_o$ = 0.03805

$[Na_2S_2O_3]$ = 0.01076

Time (min)	Titre (ml)	$10^2[S_2O_8^{2-}]$	$3 + \log[S_2O_8^{2-}]$
5	34.95	3.761	1.5753
10	34.50	3.712	1.5696
15	34.17	3.677	1.5655
20	33.86	3.643	1.5615
25	33.50	3.605	1.5569
30	33.11	3.563	1.5518
35	32.54	3.501	1.5442
40	32.24	3.469	1.5402

Table 67

$[S_2O_8^{2-}]_o$ = 0.02793

$[Na_2S_2O_3]$ = 0.02793

Time (min)	Titre (ml)	$10^2[S_2O_8^{2-}]$	$3 + \log[S_2O_8^{2-}]$
5	25.67	2.762	1.4412
10	25.50	2.744	1.4384
15	25.12	2.703	1.4319
25	24.53	2.639	1.4215
30	24.38	2.623	1.4188
35	24.07	2.590	1.4133

Table 68

Order with Respect to Peroxodisulphate

$10^2[S_2O_8^{2-}]_o$	10^5 R_o mole/l/min
0.9795	2.18
1.928	4.40
2.793	6.00
3.805	8.35
3.950	9.00
5.754	11.05
9.780	20.10
11.79	24.60

Table 69

The initial rates cited in this Table are calculated from the equation

$$R_o = k_{obs}[S_2O_8^{2-}]_o \qquad \text{......} \quad [107]$$

in which k_{obs} is the initial pseudo-first order rate constant calculated from $\log[S_2O_8^{2-}]$/time plots for each run:

$10^2[S_2O_8^{2-}]_o$ mole/l	10^3k_{obs} min^{-1}	10^5 R_o mole/l/min
0.9795	2.33	2.29
1.928	2.33	4.51
2.793	2.30	6.43
3.805	2.34	8.91
3.950	2.28	9.02
5.754	2.02	11.62
9.780	2.12	20.70
11.79	2.15	25.30

Fig. 44

$[S_2O_8^{2-}]$ v. Time

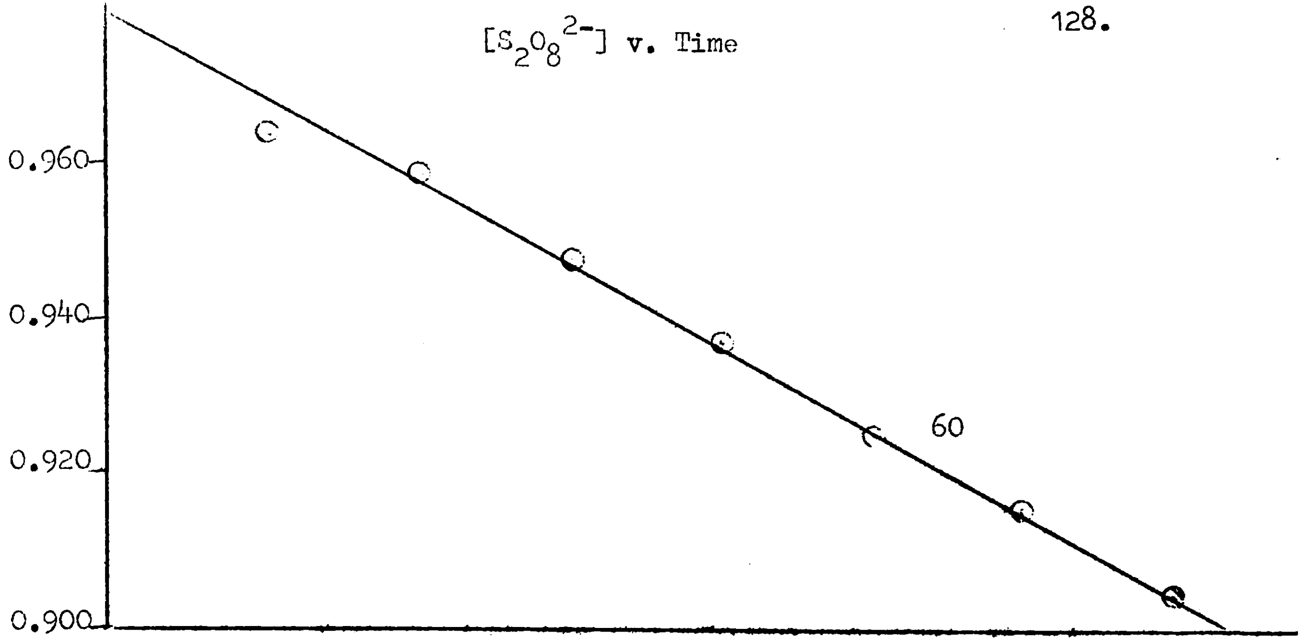


Fig. 45

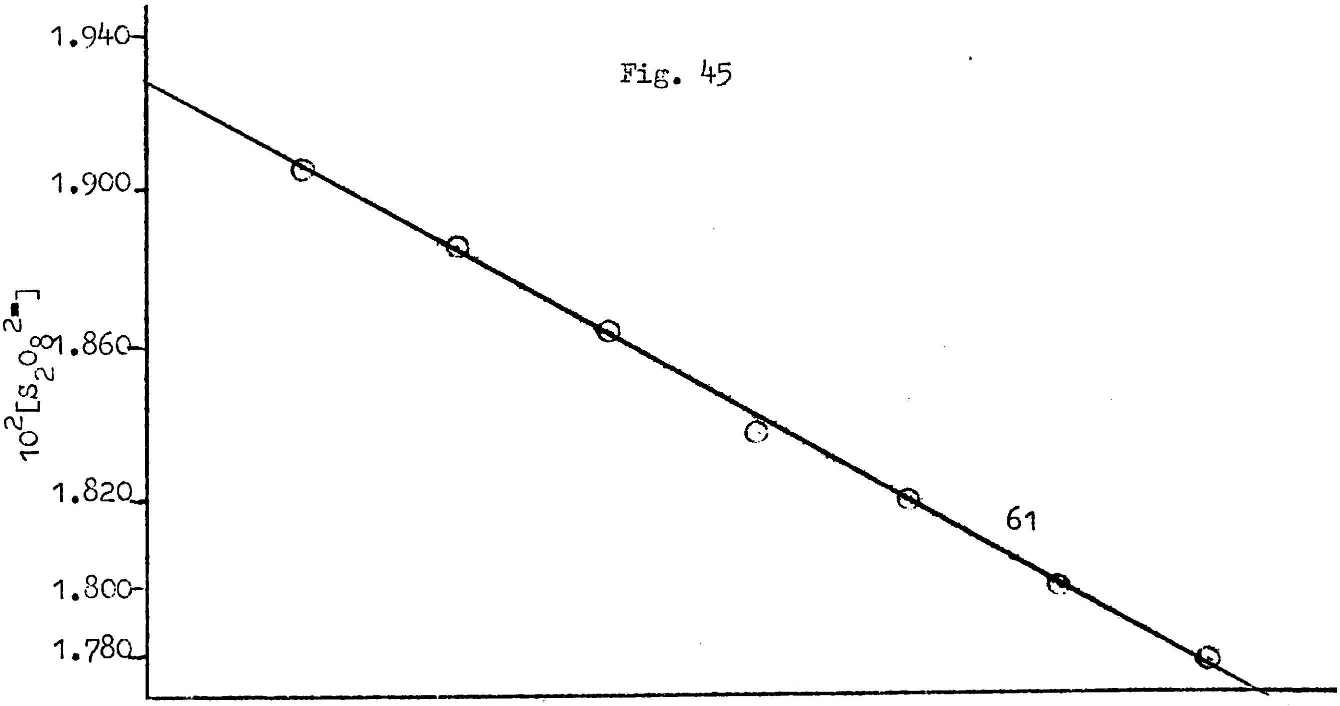
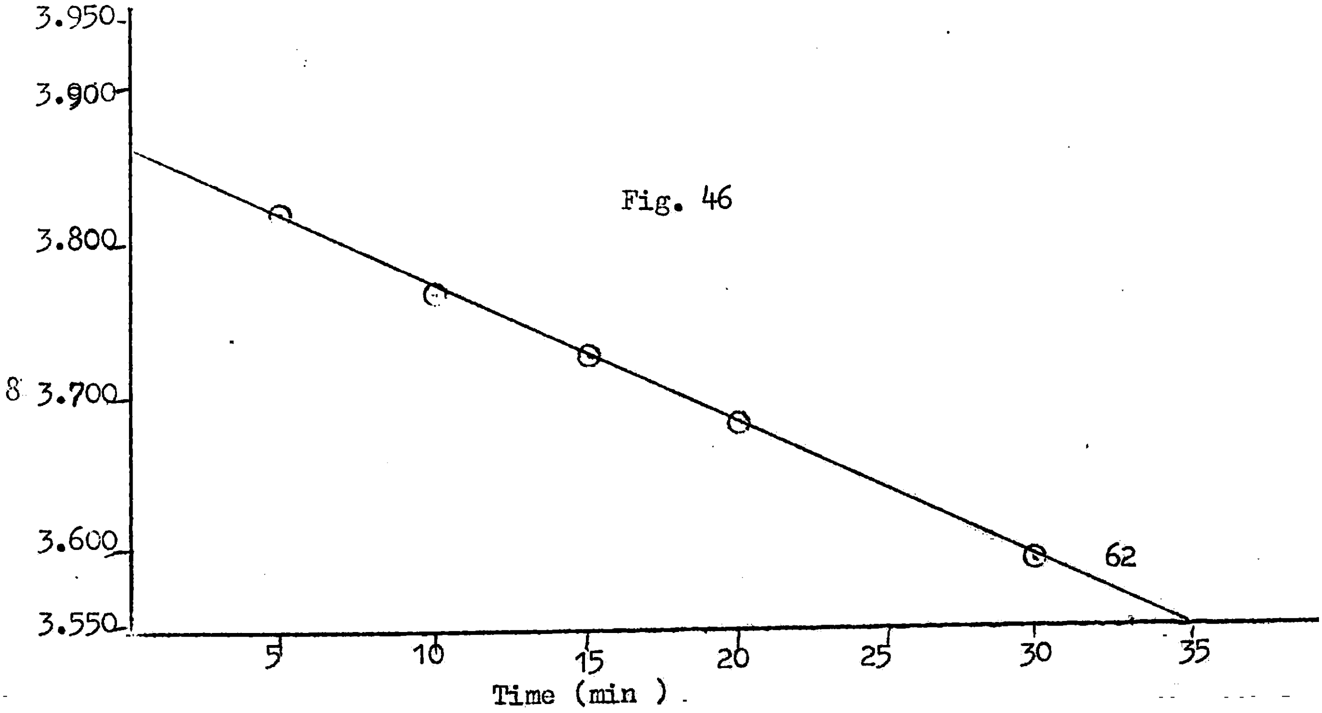


Fig. 46



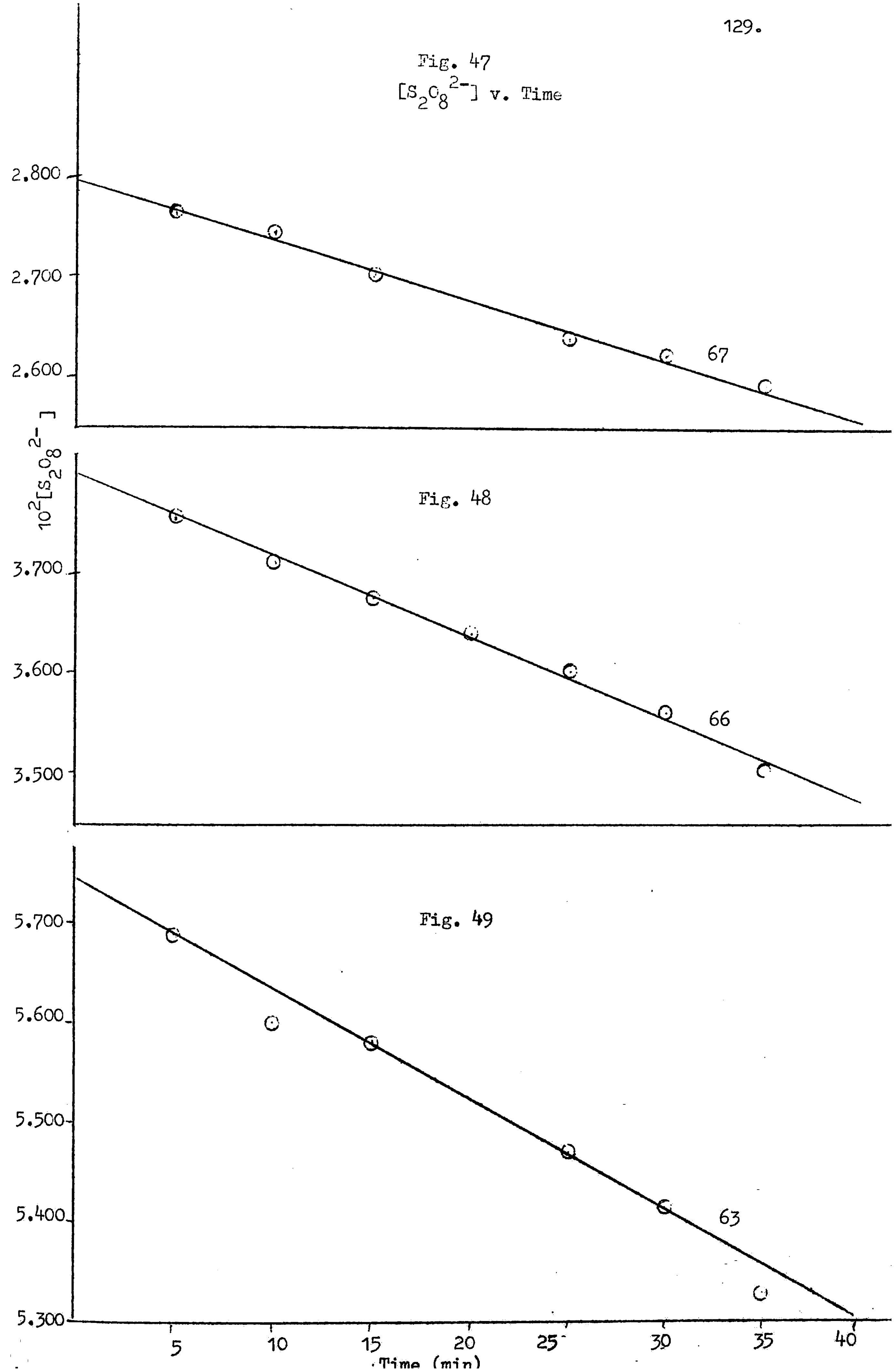


Fig. 47

$[S_2O_8^{2-}]$ v. Time

Fig. 48

Fig. 49

Fig. 50

$[S_2O_8^{2-}]$ v. Time

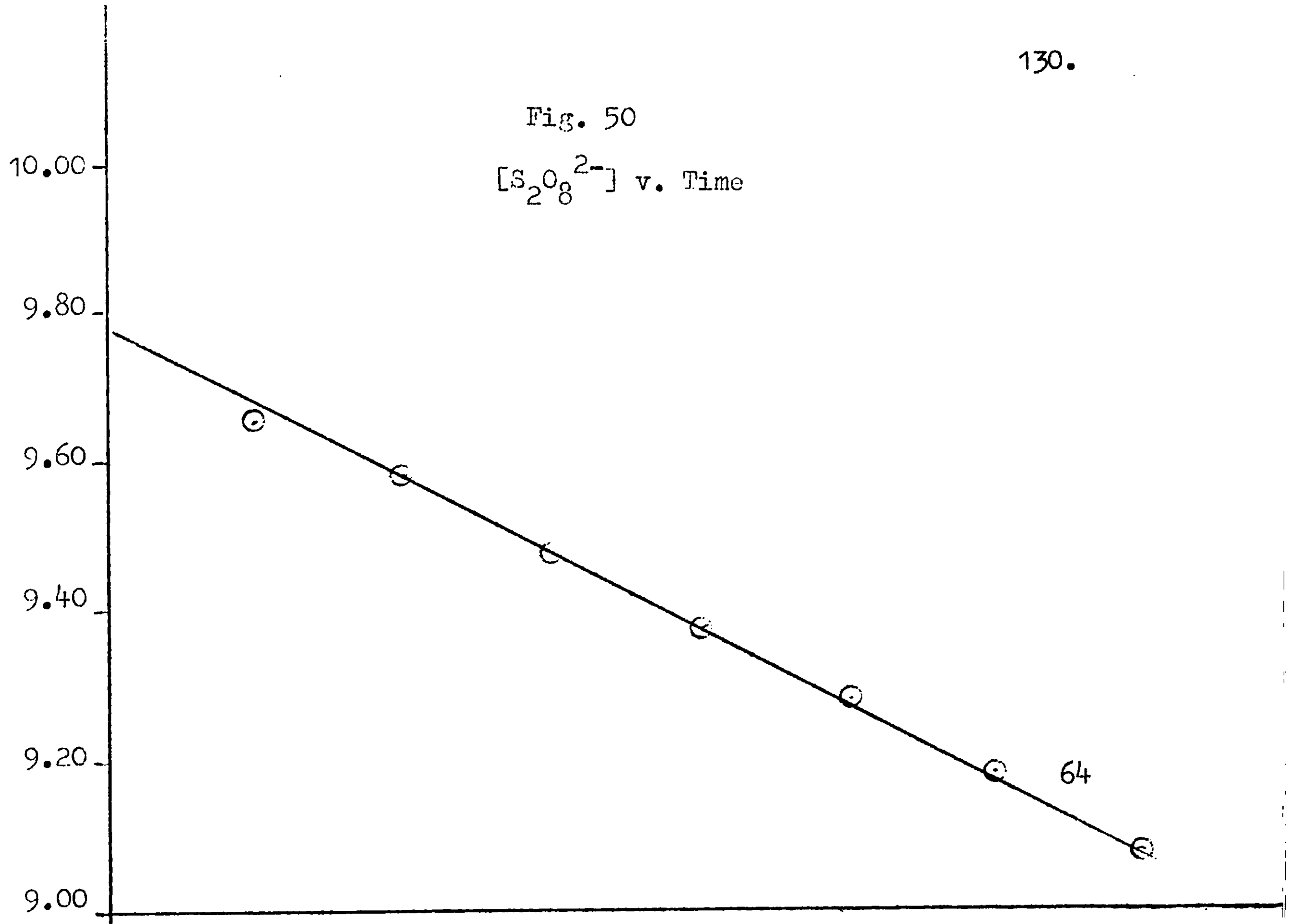
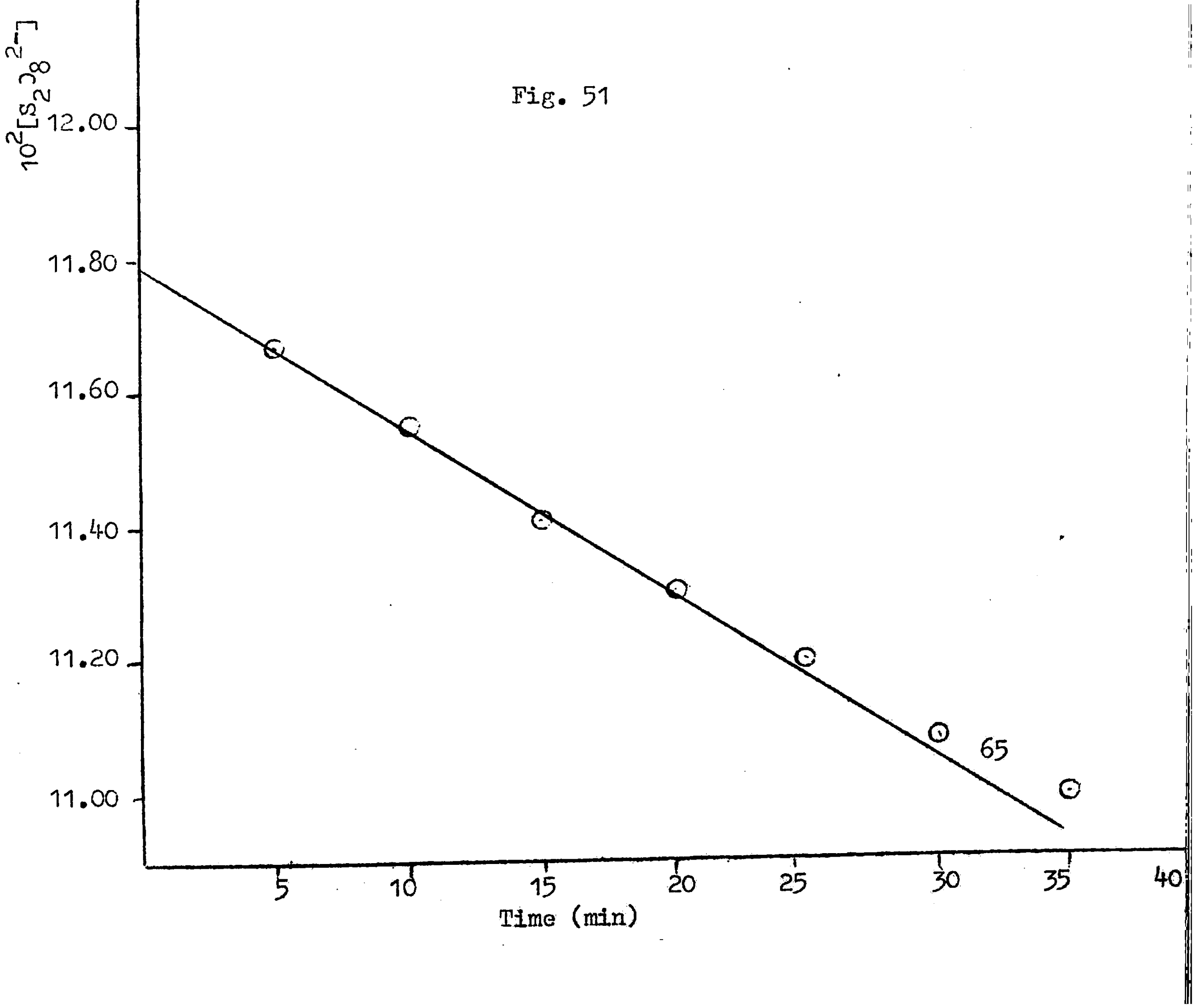


Fig. 51



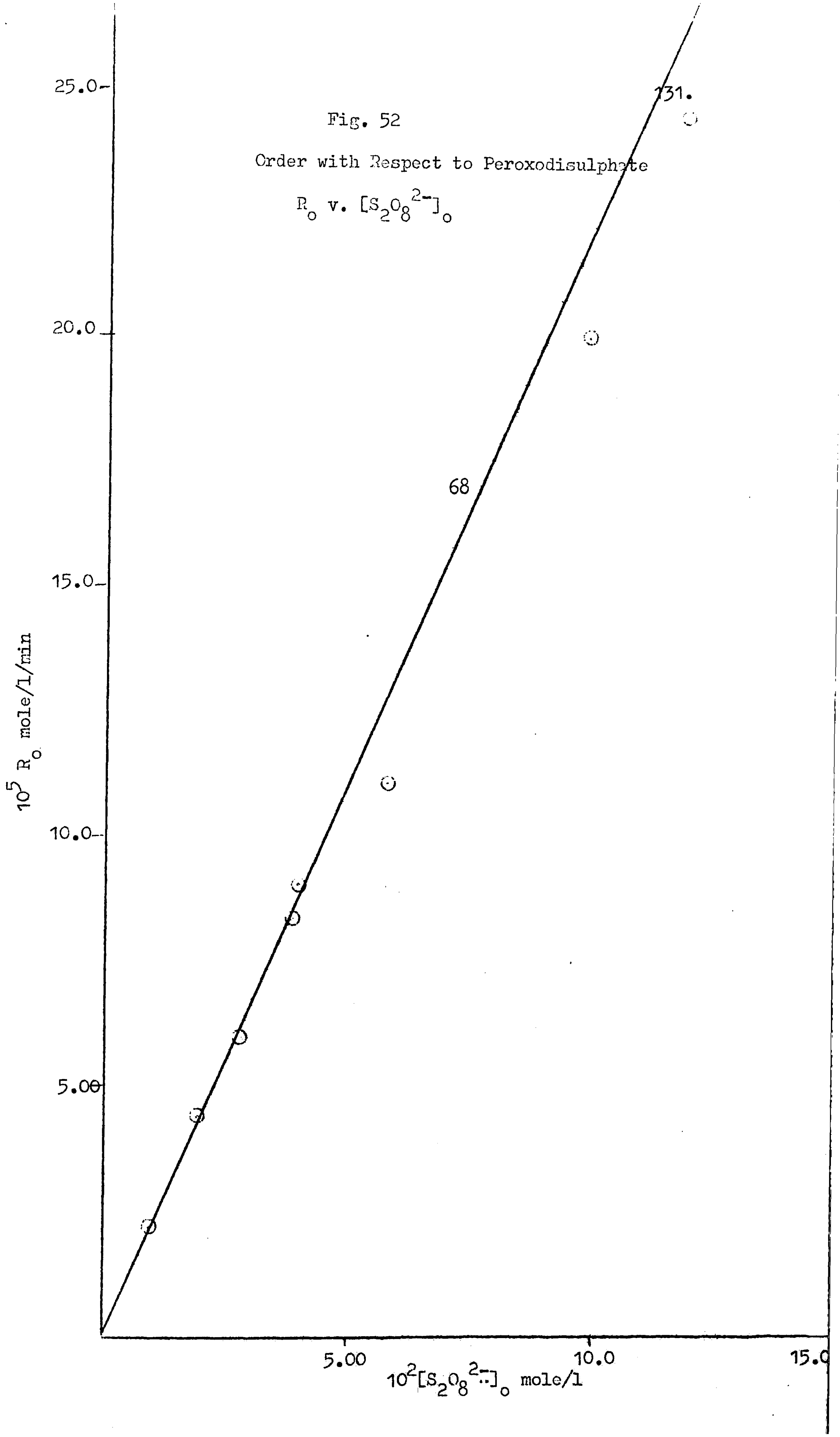


Fig. 52

Order with Respect to Peroxodisulphate

R_o v. $[S_2O_8^{2-}]_o$

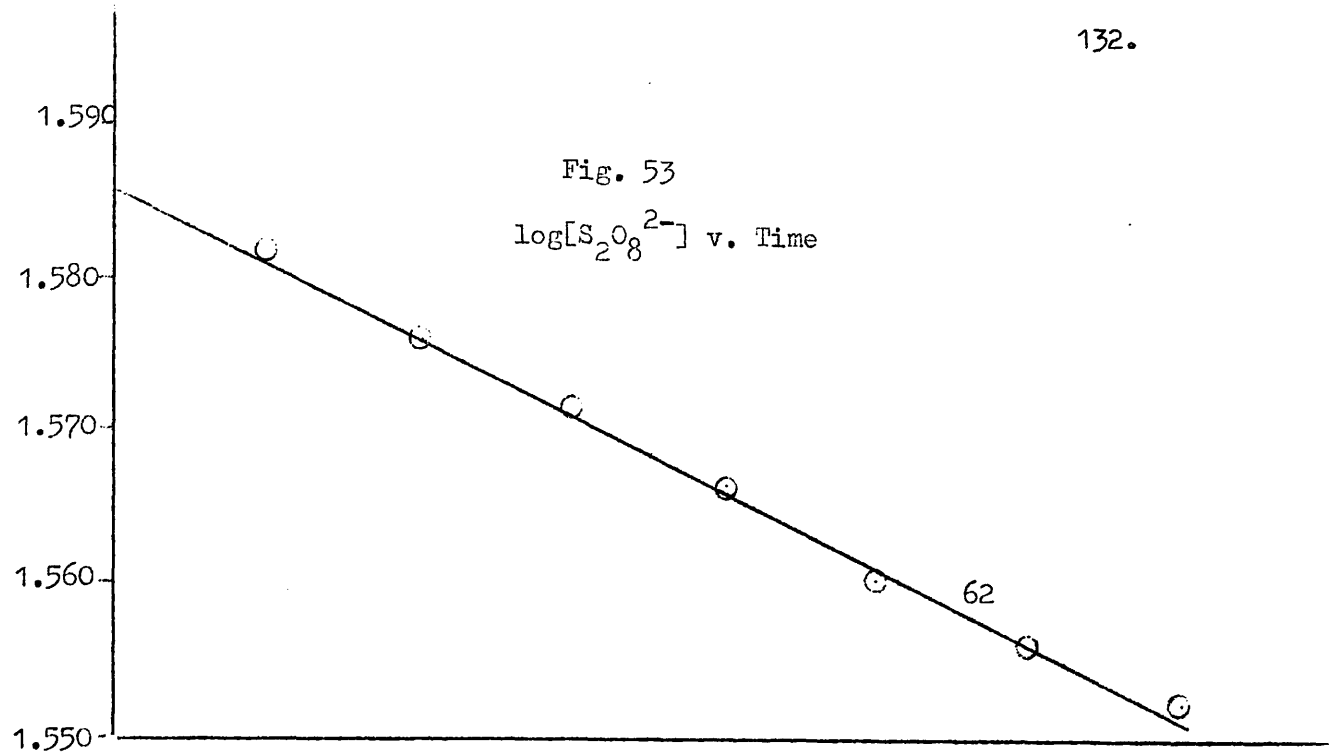


Fig. 53

$\log[S_2O_8^{2-}]$ v. Time

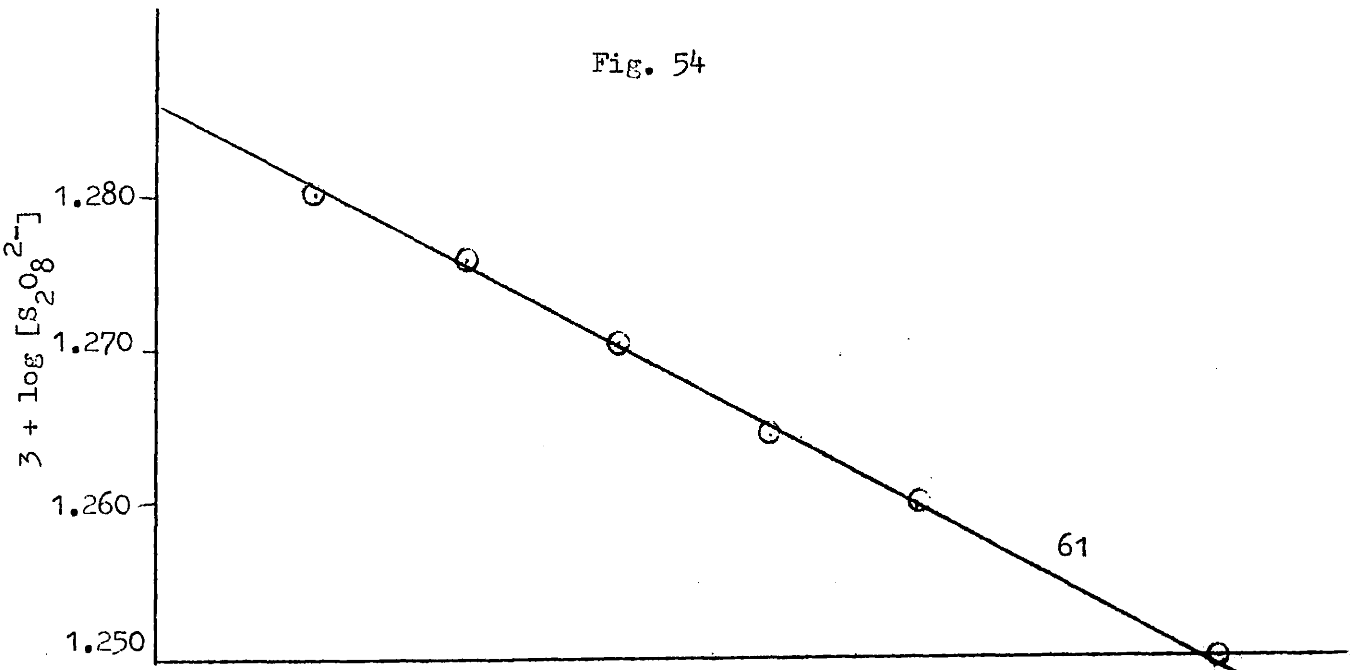


Fig. 54

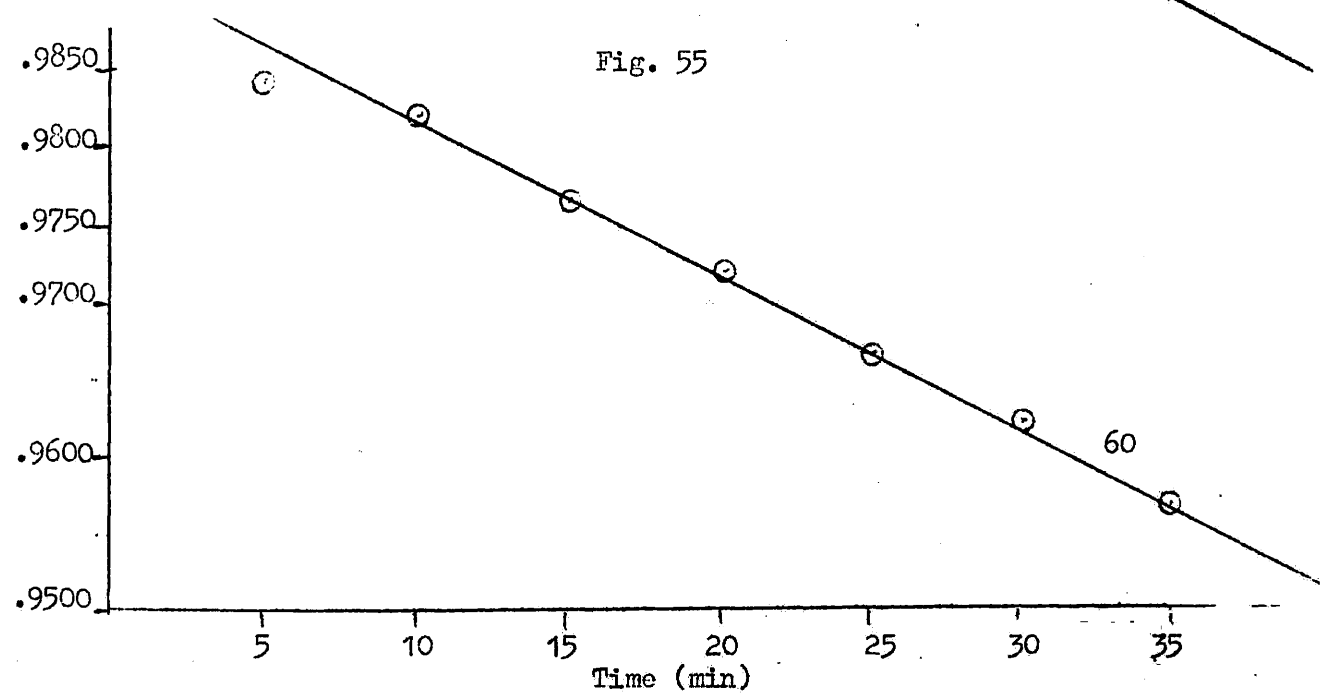


Fig. 55

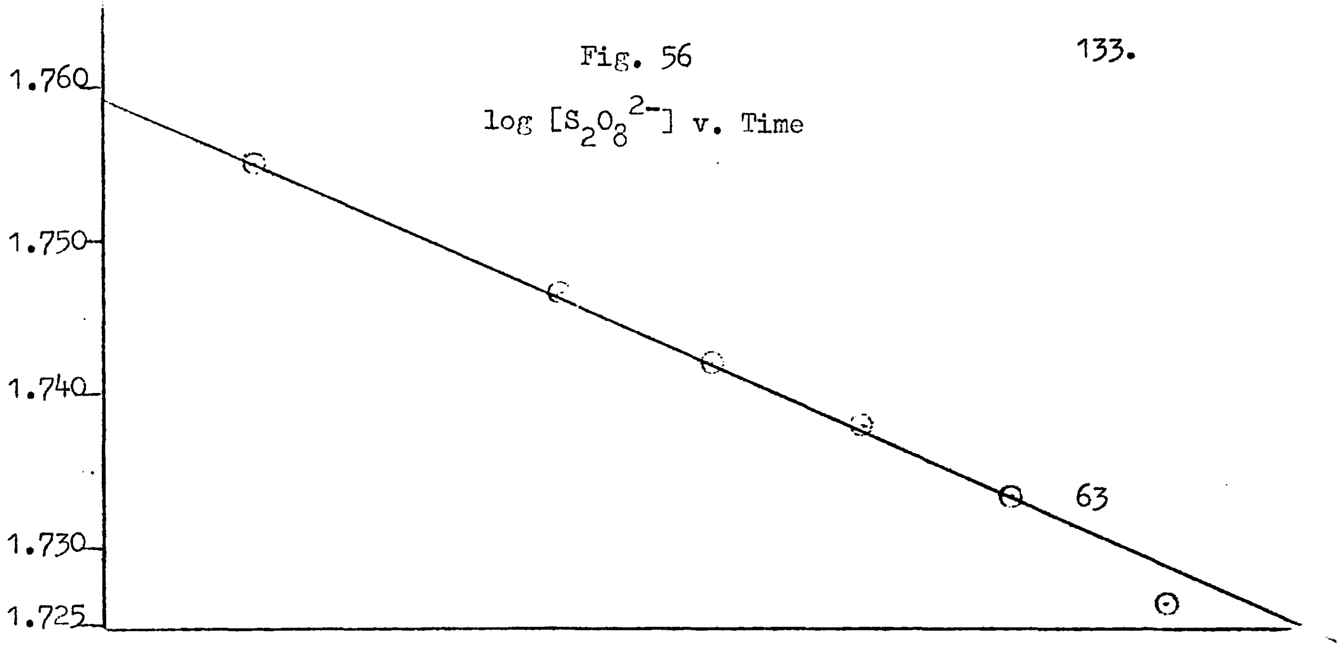


Fig. 56

log $[S_2O_8^{2-}]$ v. Time

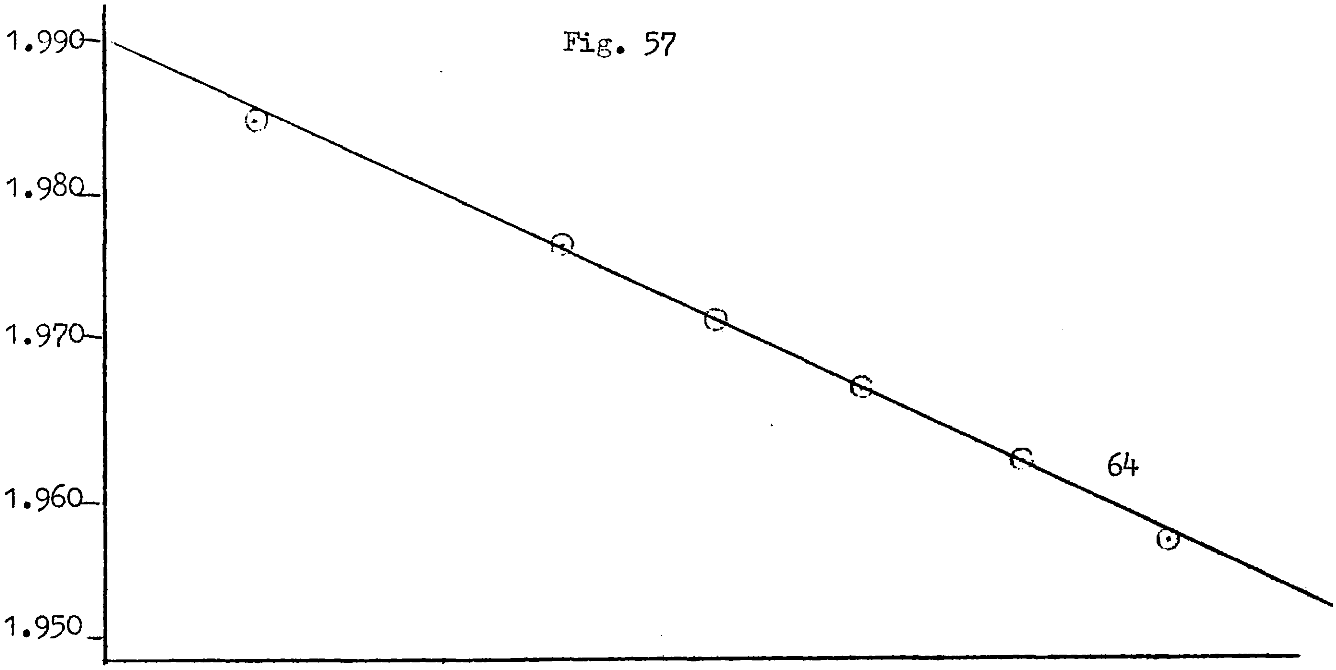


Fig. 57

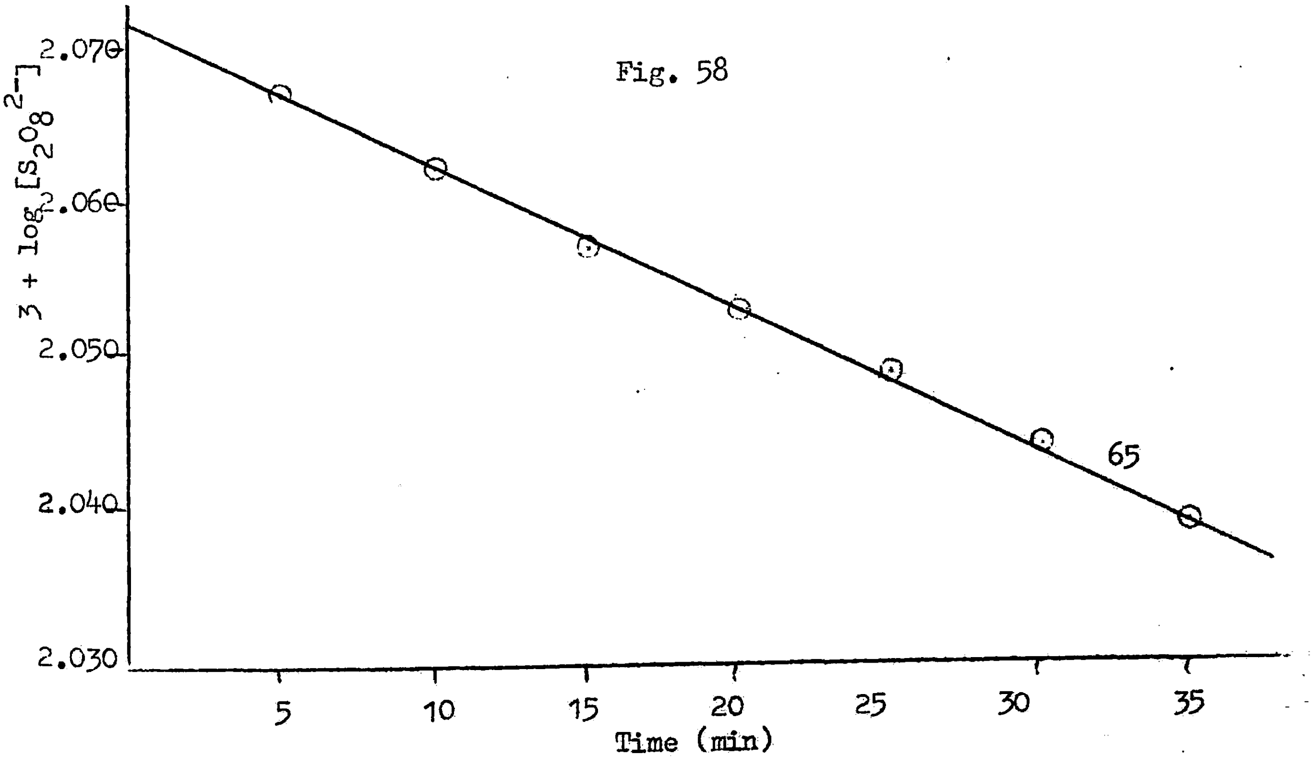


Fig. 58

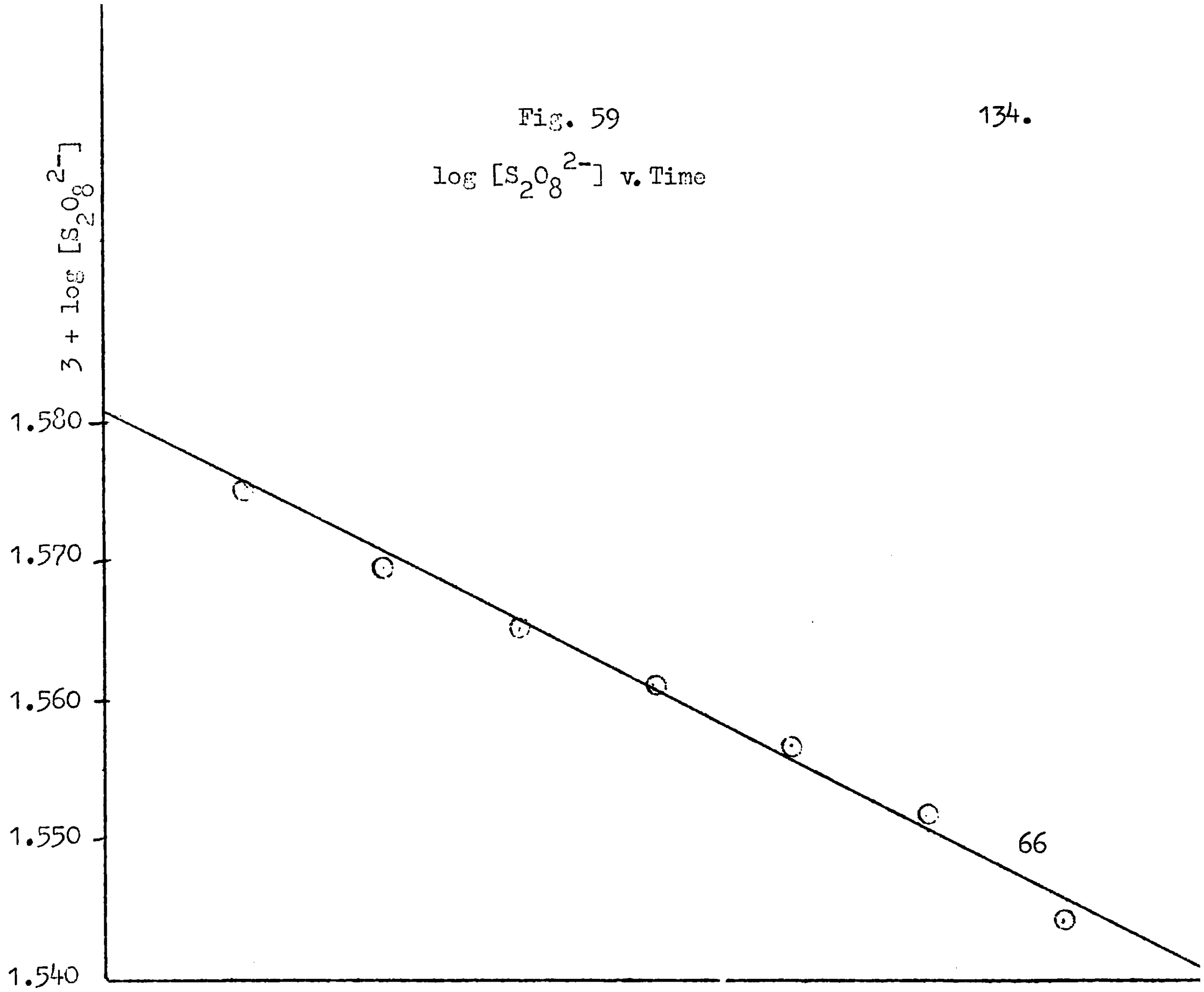


Fig. 59

log $[S_2O_8^{2-}]$ v. Time

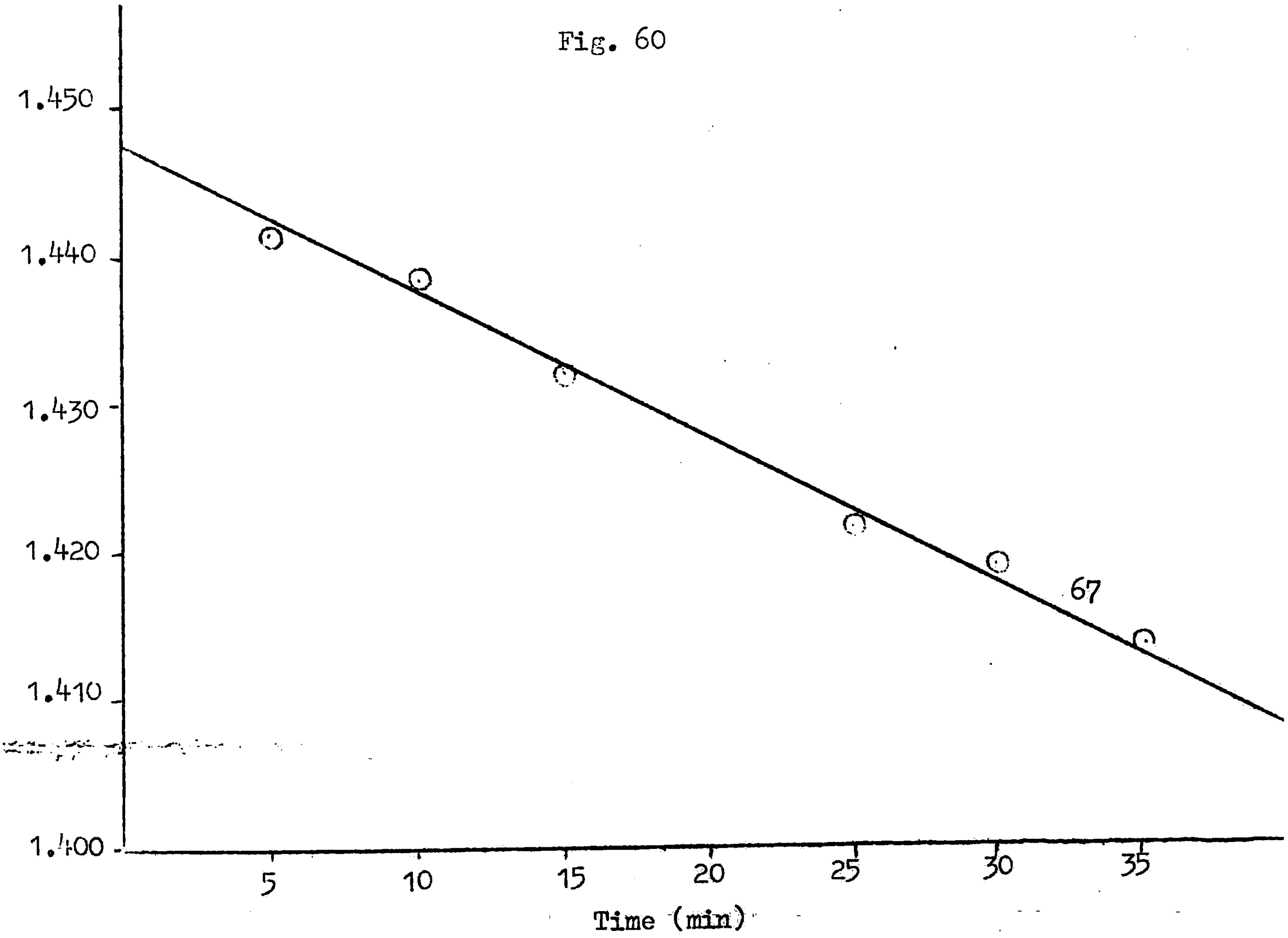


Fig. 60

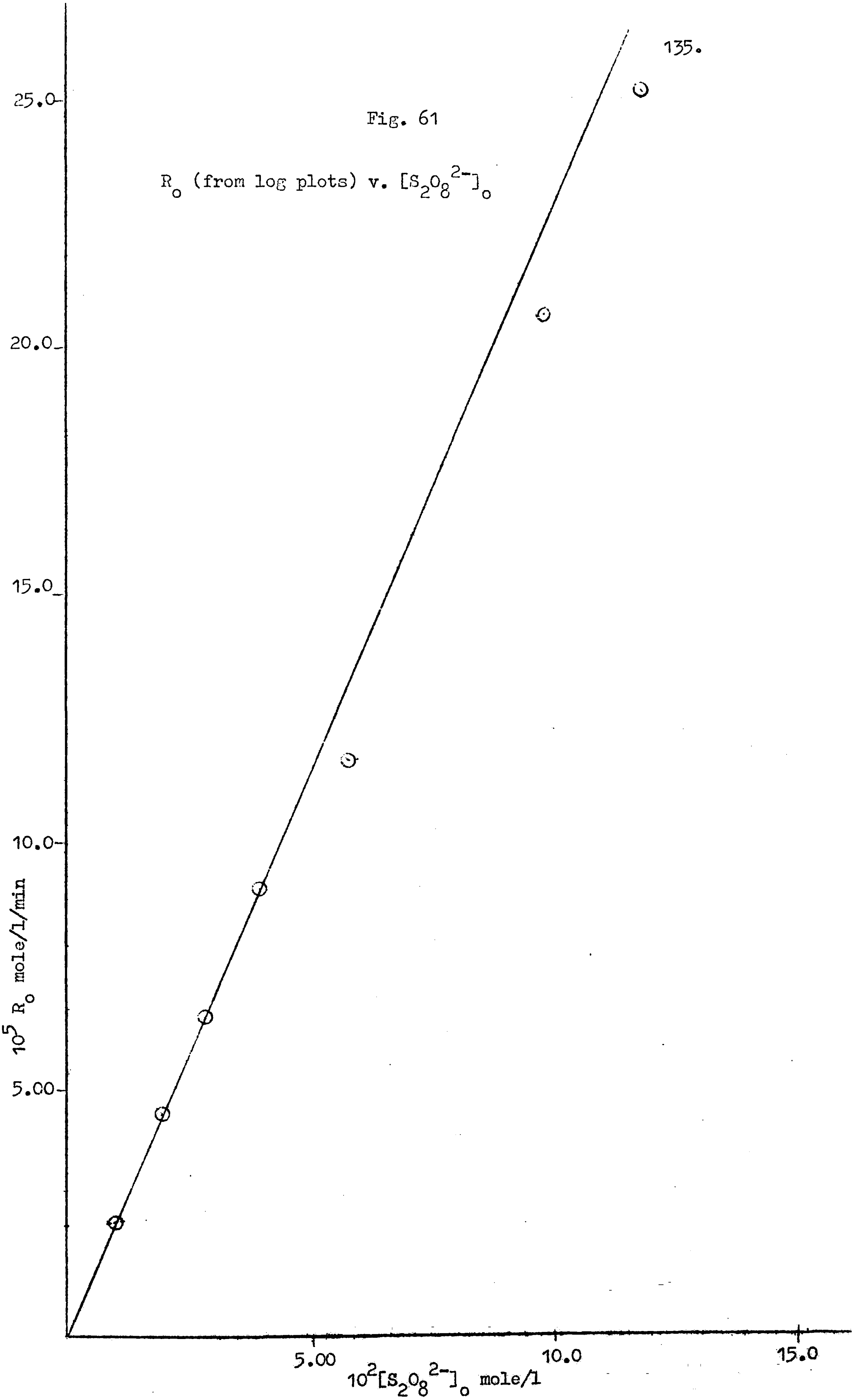


Fig. 61

R_o (from log plots) v. $[S_2O_8^{2-}]_o$

Order with respect to nitrite

The order of the reaction with respect to nitrite was investigated using constant experimental conditions of temperature, pH, peroxodisulphate concentration, ionic strength and cation concentration. The initial concentration of nitrite was varied between 0.005 mole/l and 0.1 mole/l (Tables 70-71 and Fig.62).

When the initial rate (of disappearance of peroxodisulphate) was plotted against the initial concentration of nitrite (Fig.63) a straight line intercepting the y-axis at $R_1 = 2.00 \times 10^{-5}$ mole/l/min, was obtained. The slope of this line is 2.010×10^{-3} min^{-1}. Therefore it looks as if peroxodisulphate disappears via two paths; one which is independent of nitrite and another which is first order in nitrite. The initial rate (R_o) of disappearance of peroxodisulphate at constant peroxodisulphate concentration and under the experimental conditions which apply to Fig.63 can, therefore be represented by equation [111].

$$R_o = R_1 + C[NO_2^-]_o \qquad \ldots\ldots \quad [111]$$

where R_1 is the intercept of Fig.63 and C is the slope of the straight line in the same figure. When the intercept [R_1) is divided by peroxodisulphate concentration the value 2.61×10^{-4} min^{-1} is obtained and this as will be seen later (p.146) is the initial first order rate constant for the decomposition of peroxodisulphate under the present experimental conditions and in the absence of nitrite. Moreover it was established in the previous section that the reaction is first order with respect to peroxodisulphate and therefore equation [111] may be rewritten as

$$R_o = k_1[S_2O_8^{2-}]_o + k_2[S_2O_8^{2-}]_o[NO_2^-]_o \qquad \ldots\ldots \quad [112]$$

The first term on the right hand side of equation [112] represents the intercept in Fig.63 and the slope C is given by

$$C = k_2[S_2O_8^{2-}]_o \qquad \ldots\ldots \quad [113]$$

in which k_2 is the observed initial second order rate constant for the redox reaction between nitrite and peroxodisulphate. Substituting the relevant values for C and $[S_2O_8^{2-}]_o$ gives the value of k_2 as 2.61×10^{-2}ℓ/mole/min under the experimental conditions cited below. However, when the concentration of nitrite is kept constant equation [112] reduces to

$$R_o = (k_1 + C') [S_2O_8^{2-}]_o \qquad \ldots\ldots \; [114]$$

where C' is a constant which is given by

$$C' = k_2[NO_2^-]_o \qquad \ldots\ldots \; [115]$$

Equation [114] is similar to equation [110]

$$R_o = k_{obs}[S_2O_8^{2-}]_o \qquad \ldots\ldots \; [110]$$

Therefore k_{obs} (the slope of Fig.52) is given by equation [116]

$$k_{obs} = k_1 + C' = k_1 + k_2[NO_2^-]_o \qquad \ldots\ldots \; [116]$$

or

$$k_2 = \frac{k_{obs} - k_1}{[NO_2^-]_o} \qquad \ldots\ldots \; [117]$$

and substituting the appropriate values in equation [117] gives the value of k_2 as 2.61×10^{-2}ℓ/mole/min. This value is the same as the value of k_2 as calculated from the nitrite dependence (Fig.60) in this section. Introducing this value of k_2 and the value of k_1 in equation [112] gives the rate law at this stage as

$$R_o = (2.61 \times 10^{-4} + 2.61 \times 10^{-2} [NO_2^-]_o)[S_2O_8^{2-}]_o \text{mole/l/min} \qquad \ldots\ldots \; [118]$$

at 60.0°C.

Experimental conditions

The following experimental conditions hold for Tables 70-71 and Figs. 62-63. All concentration units are mole/l.

$[S_2O_8^{2-}]_0$ = 0.07702

$[H_2PO_4^-]$ = 0.200

$[HPO_4^{2-}]$ = 0.200

$[K^+]$ = 0.500

$[Na^+]$ = 0.500

I $\simeq$ 1.2

pH $\simeq$ 6.45

Temperature = 60.0°C

Table 70

$[Na_2S_2O_3]$ = 0.03083 in (a) and (b) and 0.03058 in (c)

$10^2[NO_2^-]_0$	(a) 0.500		(b) 1.000		(c) 2.500	
Time (min)	Titre (ml)	$10^2[S_2O_8^{2-}]$	Titre (ml)	$10^2[S_2O_8^{2-}]$	Titre (ml)	$10^2[S_2O_8^{2-}]$
5	25.11	7.741	25.09	7.735	25.01	7.648
10	25.01	7.710	25.01	7.711	24.87	7.605
15	24.98	7.701	24.95	7.692	24.78	7.578
20	24.90	7.677	24.89	7.674	24.69	7.550
25	24.91	7.680	24.85	7.661	24.53	7.501
30	24.85	7.661	24.76	7.634	24.42	7.468
35	24.83	7.655	24.71	7.618	24.31	7.434

Table 71

$[Na_2S_2O_3]$ = 0.03058

$10^2[NO_2^-]_o$	(a) 3.750		(b) 6.000		(c) 10.00	
Time (min)	Titre (ml)	$10^2[S_2O_8^{2-}]$	Titre (ml)	$10^2[S_2O_8^{2-}]_o$	Titre (ml)	$10^2[S_2O_8^{2-}]$
5	24.90	7.614	24.87	7.605	24.80	7.584
10	24.73	7.562	24.57	7.514	24.41	7.465
15	24.50	7.492	24.39	7.458	24.01	7.342
20			24.15	7.385	23.62	7.223
25	24.32	7.437	23.89	7.306	23.30	7.125
30	24.16	7.388	23.63	7.226	22.95	7.018
35	23.98	7.333	23.43	7.165	22.63	6.920

Table 72

Order with Respect to Nitrite

$10^2[NO_2^-]$	10^5 R_o mole/l/min
0.5000	3.00
1.000	3.70
2.500	7.20
3.750	9.20
6.000	14.7
10.00	24.4

Fig. 62

$[S_2O_8^{2-}]$ v. Time

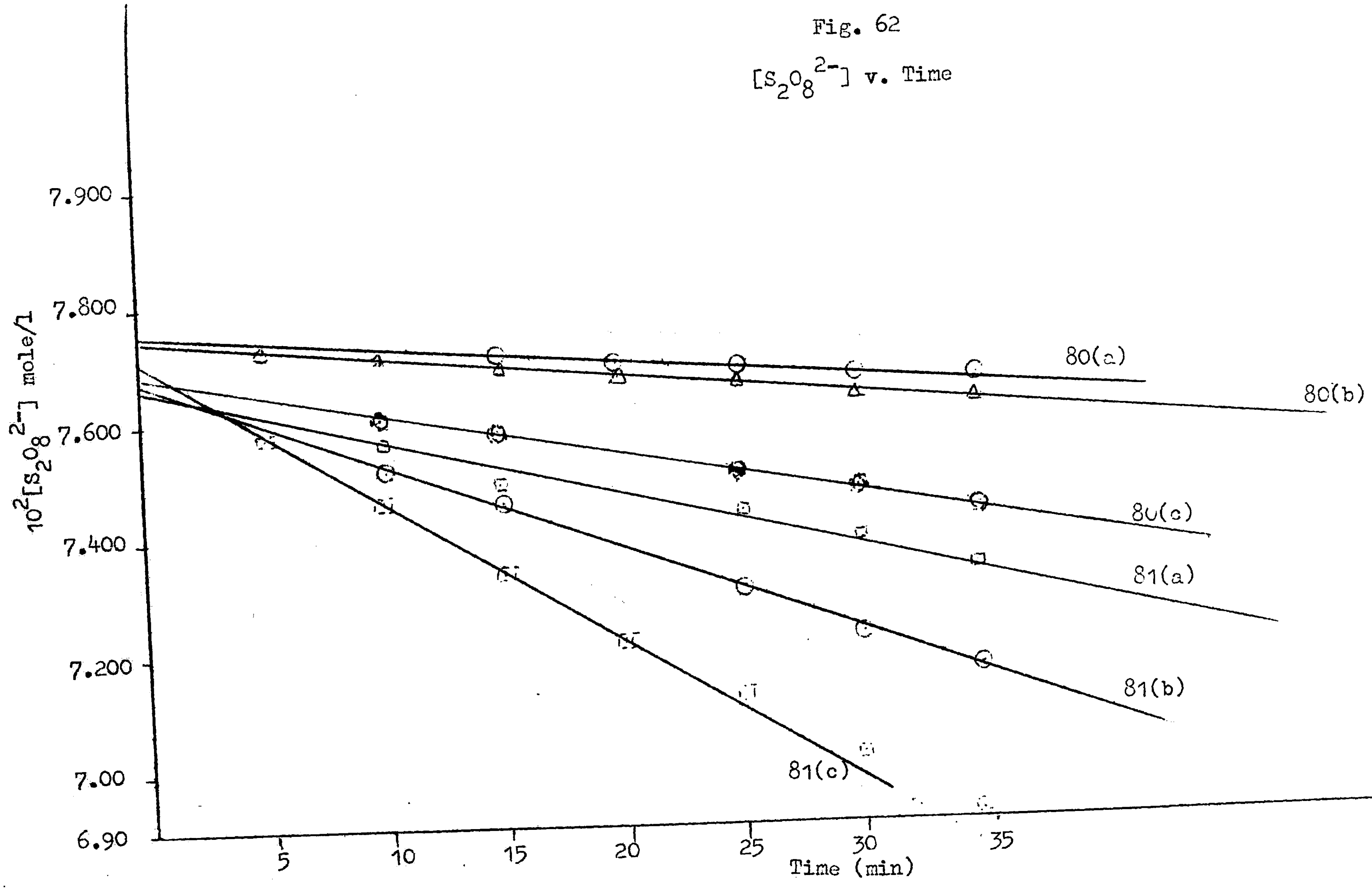
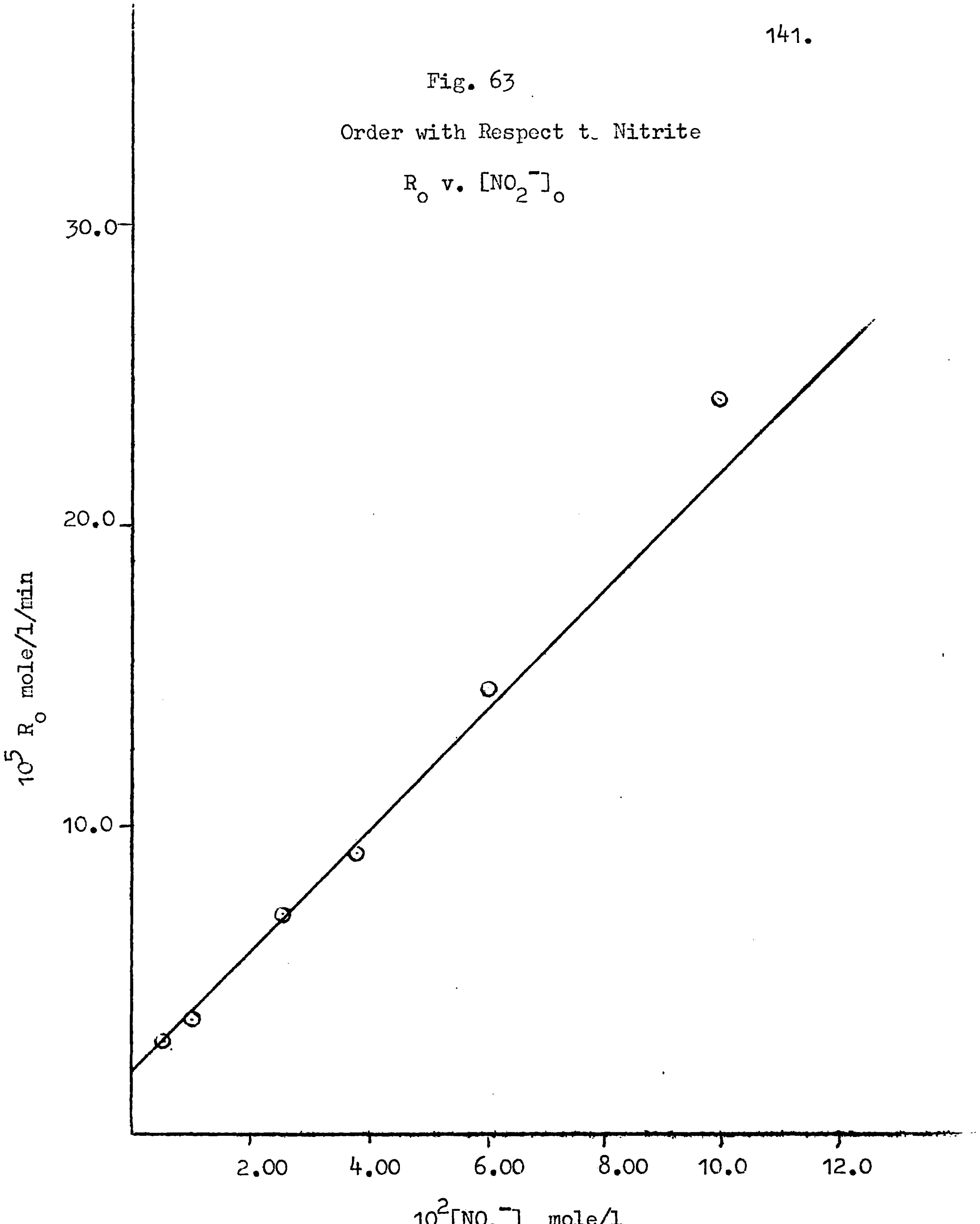


Fig. 63

Order with Respect t. Nitrite

R_o v. $[NO_2^-]_o$



Note that R_o is measured by monitoring $[S_2O_8^{2-}]$

Kinetics of the whole reaction

Having seen that equation [112] was a reasonable assessment of the initial rate of the reaction, the whole course of the reaction was investigated to see if the same rate law applies throughout. Equation [112] can be written as

$$\frac{dx}{dt} = k_1(a - x) + k_2(a - x)(b - x) \qquad \ldots\ldots \quad [119]$$

where a and b are the initial concentrations of peroxodisulphate and nitrite respectively and x is the decrease in the concentration of each reactant, the assumption being that the two reactants are consumed in equal amounts which is only approximately true.

The integration of equation [119] leads to

$$\frac{k_1 t}{2.3} = \frac{1}{1 + k_3(b - a)} \log \frac{a}{1 + k_3 b} + \frac{1}{1 + k_3(b - a)} \log \frac{1 + k_3(b - x)}{(a - x)} \qquad \ldots\ldots \quad [120]$$

in which k_3 is defined by

$$k_3 = {}^{k_2}\!/_{k_1} \qquad \ldots\ldots \quad [121]$$

Since the first term in the right hand side of equation [120] is constant throughout one run, this equation can be written as

$$\frac{k_1 t}{2.3} = C + F \qquad \ldots\ldots \quad [122]$$

in which C is a constant and F stands for the second term on the right hand side of equation [120]. Therefore if the initial rate law holds for the whole course of the reaction, a plot of F against time should give a straight line the slope of which is a measure of k_1. Introducing the values of k_1 and k_2, of the previous section, into equation [121] gives the value of k_3 as 100 and this value is used in calculating F in Tables 73-76 which show the data for four runs which proceeded for more than 24 hours resulting in about 70% to 90% reaction.

When F is plotted against time a good straight line is obtained in each case. The values of k_1 obtained from these plots are given in Table 77. These values are between 1.1% and 10.0% higher than the value of 2.61×10^{-4} min^{-1} which was independently determined from the $\log[S_2O_8^{2-}]$/timeplots for the decomposition of peroxodisulphate under similar experimental conditions and in the absence of nitrite (Fig.64). Despite this variation in the value of k_1 it is fair to conclude that equation [112] applies for the whole course of the reaction.

Experimental conditions

The following experimental conditions with concentrations in mole/l apply to runs represented in Table 73-78 and the corresponding plots (Figs.64-67).

$[H_2PO_4^-]$ = 0.200

$[HPO_4^{2-}]$ = 0.200

$[K^+]$ = 0.500

$[Na^+]$ = 0.500

I $\simeq$ 1.2

pH_o $\simeq$ 6.40

Temperature = 60.0°C.

Nitrite and peroxodisulphate concentrations are shown above the individual tables.

Table 73

$[S_2O_8^{2-}]_o$ = 0.07667

$[NO_2^-]_o$ = 0.07450

$[Na_2S_2O_3]$ = 0.02084

Time (hours)	Titre (ml)	a - x	b - x	F
1.00	31.97	0.06663	0.06446	2.615
2.00	28.35	0.05908	0.05691	2.623
3.00	25.37	0.05287	0.05070	2.631
5.00	21.38	0.04446	0.04229	2.644
7.00	17.79	0.03707	0.03490	2.659
9.00	15.38	0.03205	0.02988	2.676
11.00	13.51	0.02815	0.02598	2.690
13.00	12.11	0.02524	0.02307	2.704
25.50	6.94	0.01446	0.01229	2.796

Table 74

$[S_2O_8^{2-}]_o$ = 0.03839

$[NO_2^-]_o$ = 0.03725

$[Na_2S_2O_3]$ = 0.02084

Time (hours)	Titre (ml)	a - x	b - x	F
1.00	17.05	0.03553	0.03439	2.369
2.00	15.80	0.03293	0.03179	2.375
3.00	14.82	0.03088	0.02974	2.380
5.00	13.11	0.02732	0.02618	2.396
7.00	11.70	0.02438	0.02324	2.410
9.00	10.59	0.02207	0.02093	2.423
11.00	9.62	0.02005	0.01891	2.439
13.00	8.80	0.01834	0.01720	2.452
25.5	5.56	0.01159	0.01045	2.536

Table 75

$[S_2O_8^{2-}]_o$ = 0.04925

$[NO_2^-]_o$ = 0.05960

$[Na_2S_2O_3]$ = 0.01012

Time (hours)	Titre (ml)	a - x	b - x	F
1.50	40.57	0.04106	0.05141	1.069
3.00	34.31	0.03471	0.04506	1.081
4.50	30.12	0.03048	0.04083	1.092
6.50	25.32	0.02562	0.03597	1.108
9.00	22.73	0.02300	0.03335	1.118
10.50	18.75	0.01898	0.02933	1.139
12.00	17.02	0.01722	0.02757	1.148
24.00	8.84	0.00895	0.01930	1.238
26.00	7.55	0.00764	0.01799	1.255

Table 76

$[S_2O_8^{2-}]_o$ = 0.02463

$[NO_2^-]_o$ = 0.02890

$[Na_2S_2O_3]$ = 0.01012

Time (hours)	Titre (ml)	a - x	b - x	F
1.50	21.82	0.02208	0.02725	1.468
3.00	19.88	0.02011	0.02528	1.479
4.50	18.26	0.01848	0.02365	1.490
6.50	16.43	0.01663	0.02180	1.504
9.00	14.63	0.01481	0.01998	1.520
11.00	13.31	0.01346	0.01863	1.534
24.00	7.72	0.00781	0.01298	1.627
26.00	7.21	0.00730	0.01247	1.640
28.00	6.80	0.00688	0.01205	1.652

Table 77

Ref.	$10^2[S_2O_8^{2-}]_o$	$10^2[NO_2^-]_o$	$10^4\ k_1\ min^{-1}$
Fig. 67	2.464	2.890	2.70
Fig. 65	3.839	3.725	2.64
Fig. 66	4.925	5.960	2.87
Fig. 65	7.667	7.450	2.84

Table 78

Decomposition of Peroxodisulphate

$[S_2O_8^{2-}]_o$ = 0.07667
$[NO_2^-]_o$ = Nil
$[Na_2S_2O_3]$ = 0.02084

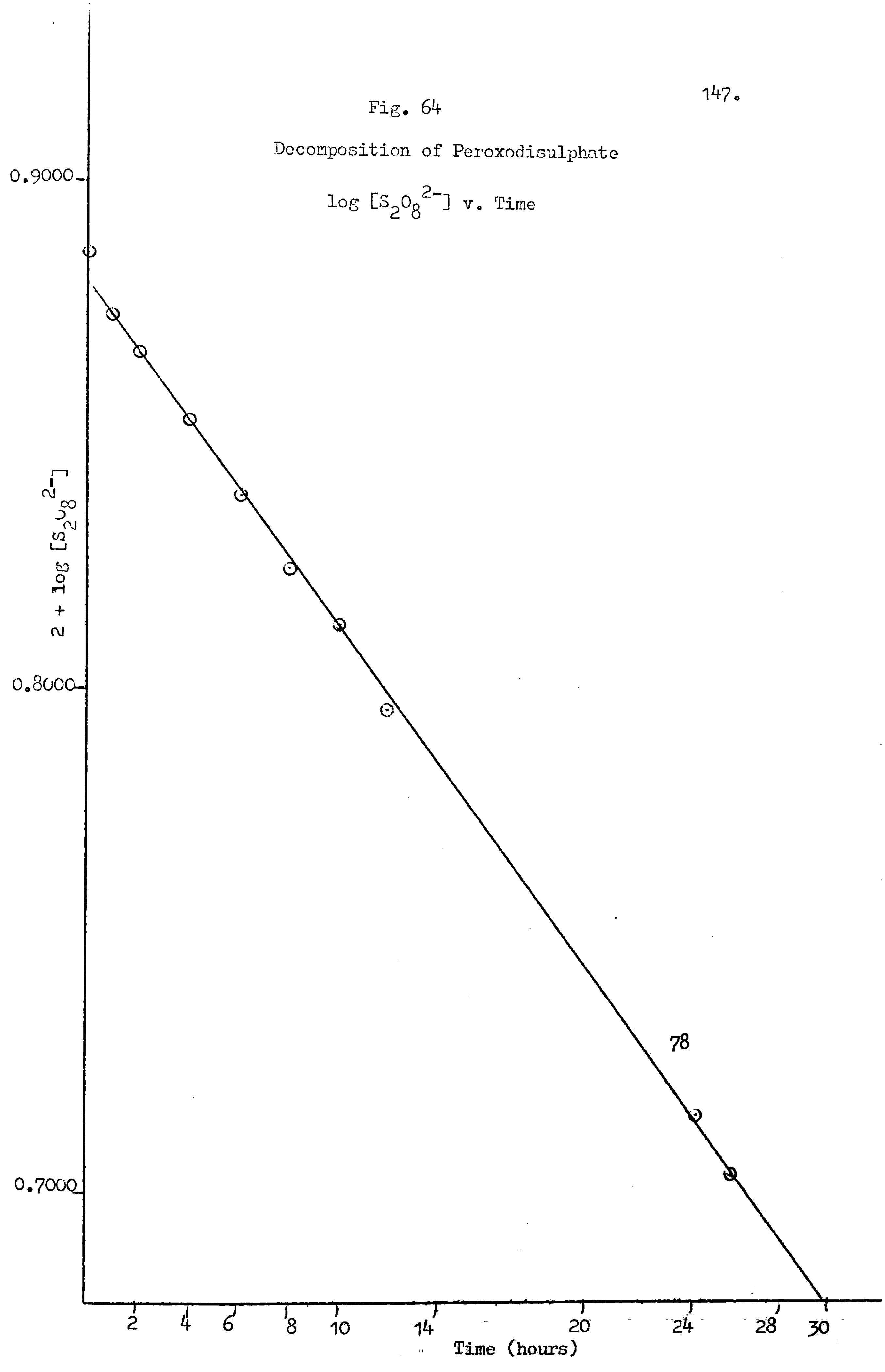
Time (hours)	Titre	$10^2[S_2O_8^{2-}]$	$2 + \log[S_2O_8^{2-}]$
0.00	36.67	7.642	0.8832
1.00	36.03	7.509	0.8756
2.00	35.47	7.392	0.8687
4.00	34.39	7.167	0.8553
6.00	33.24	6.927	0.8405
8.00	32.70	6.710	0.8267
10.00	31.31	6.525	0.8145
12.00	30.14	6.281	0.7981
24.50	25.03	5.216	0.7173
26.00	24.37	5.079	0.7058

$k_1 = 2.61 \times 10^{-4}\ min^{-1}$ (Fig.64)

Fig. 64

Decomposition of Peroxodisulphate

log $[S_2O_8^{2-}]$ v. Time



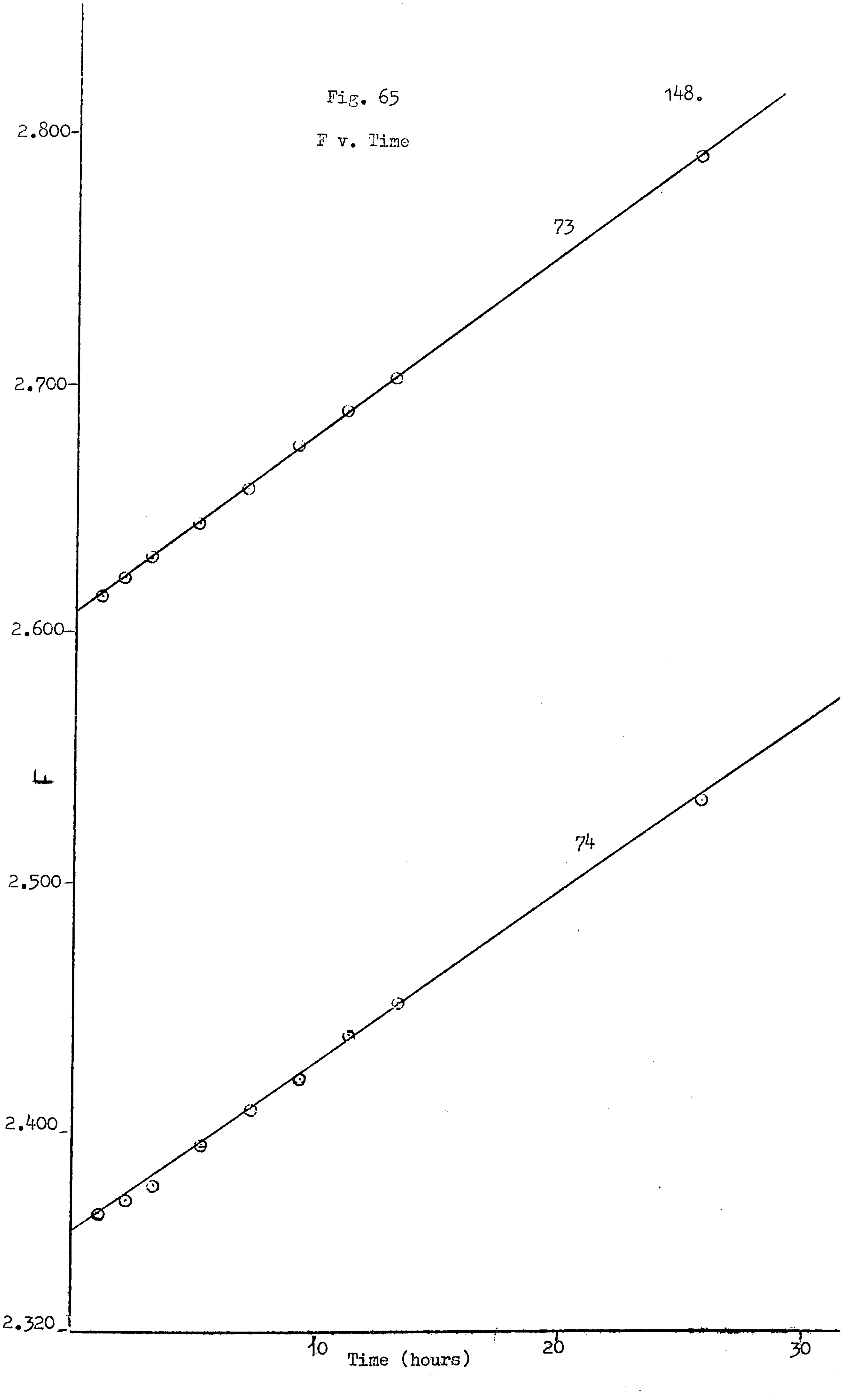


Fig. 65

F v. Time

Fig. 66

F v. Time

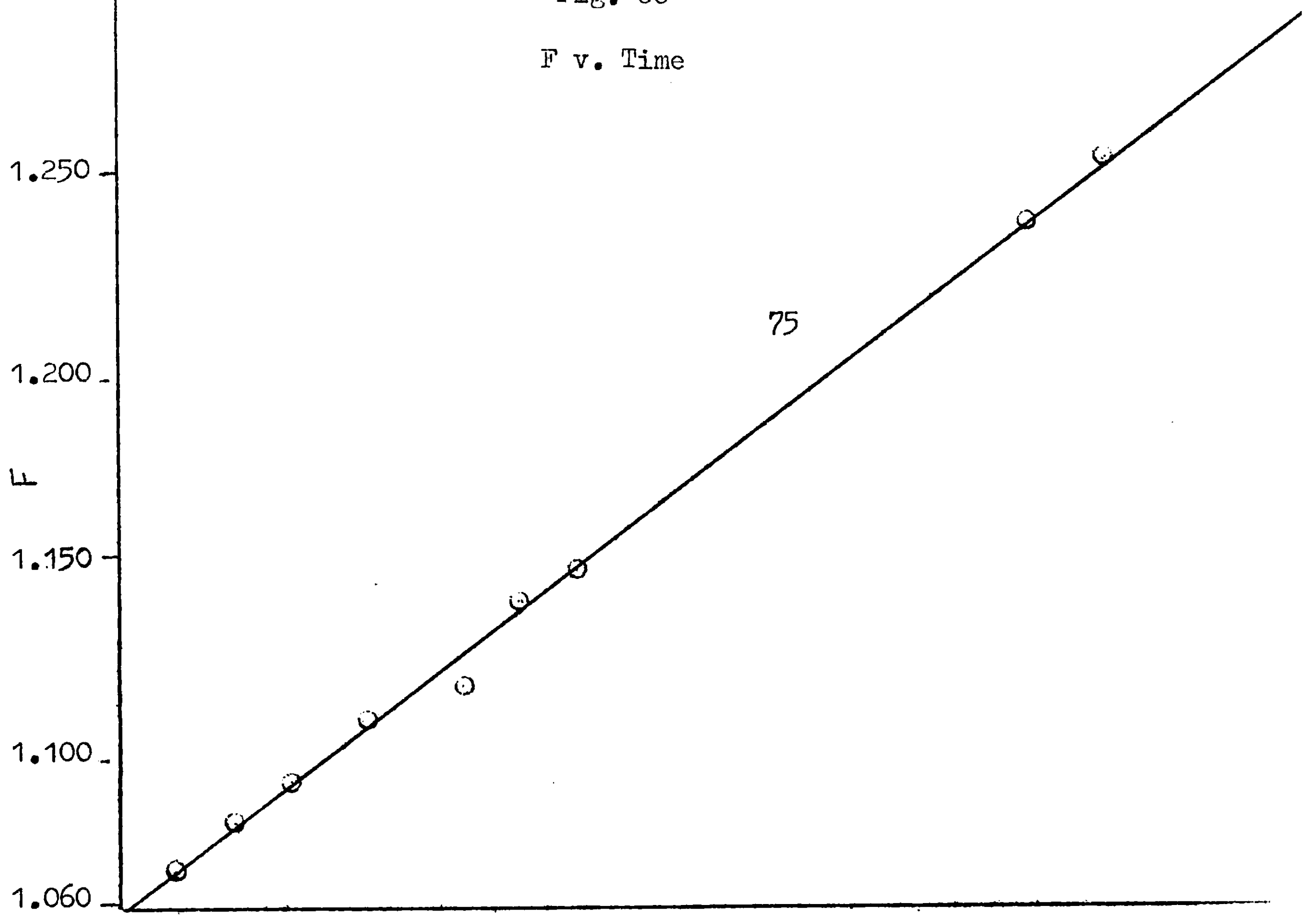
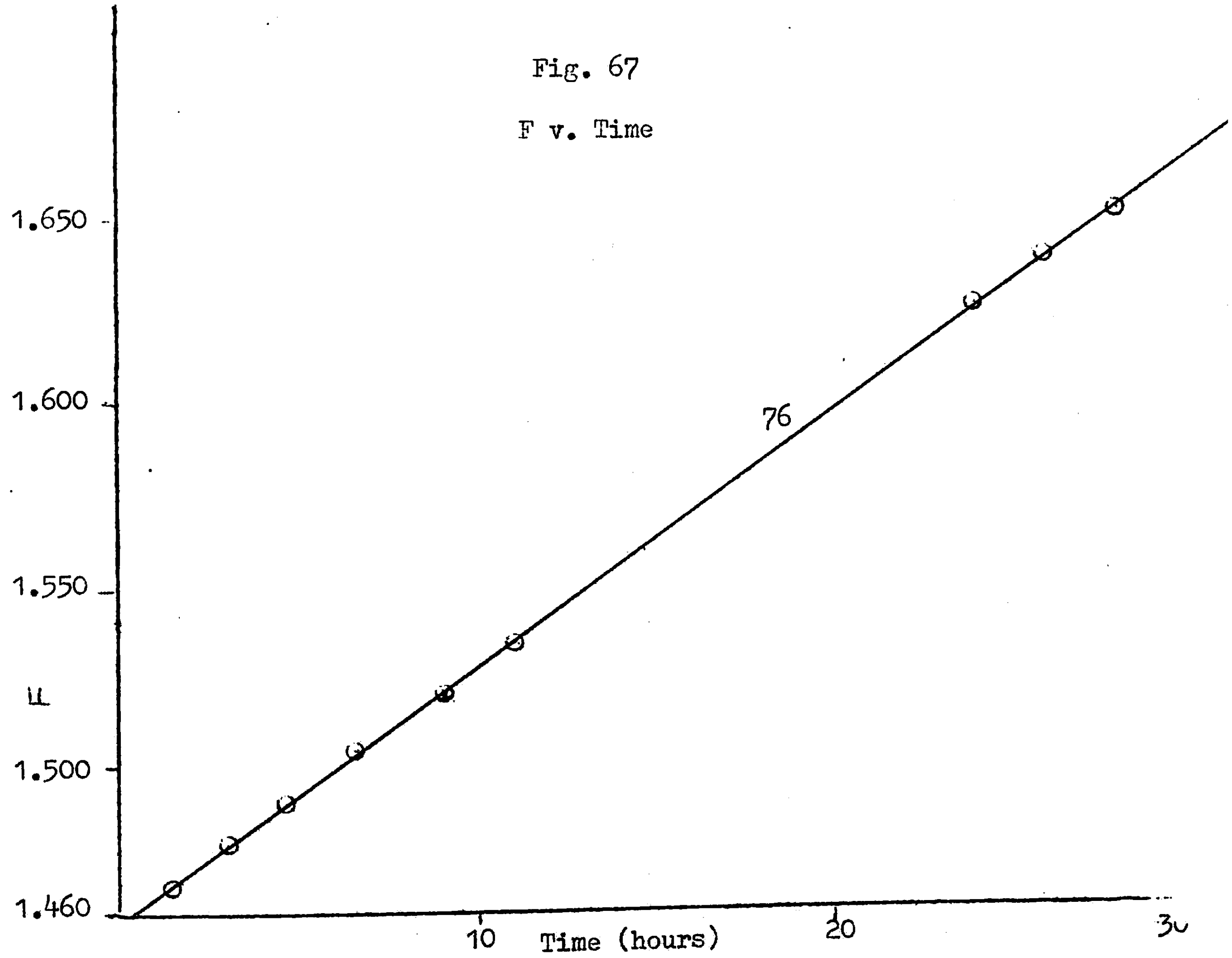


Fig. 67

F v. Time



The effect of added salts

In order to study the effect of added salts and ionic strength on the rate of reaction, it was thought reasonable to work at low ionic strengths and to keep the number of cations to a minimum and if possible to one. However, keeping the ionic strength low implies working at low concentrations of reactants, but the reaction becomes reasonably fast only above about 0.05 mole/l of each reactant, and this by itself - without the buffer - results in an ionic strength over 0.2 which is rather too high as a starting ionic strength for any (definite) conclusions to be drawn.

In an effort to make potassium ion the only cation present in the reaction mixture G.P.R. potassium nitrite was tried instead of A.R. sodium nitrite but the results were unreliable and therefore the latter was again resorted to, thus working with both potassium and sodium ions in the system. The method of preparation of the buffer was modified in this part of the work. Instead of using a mixture of disodium hydrogen orthophosphate and potassium dihydrogen orthophosphate the buffer was prepared by titrating a known volume of standard potassium dihydrogen orthophosphate with standard potassium hydroxide to pH 6.47 which was the pH of a solution 0.40 mole/l in each of Na_2HPO_4 and KH_2PO_4. In order to keep the ionic strength to a minimum it was necessary to keep the concentration of the buffer to a minimum, but it was found that 0.06 mole/l total phosphate was needed to be an effective buffer in the initial stages of the reaction.

The effects of added potassium nitrate, potassium sulphate, sodium nitrate and caesium nitrate were studied. In each case the initial concentrations of the reactants, buffer and temperature were kept constant while varying the concentration of the added salt which in turn resulted in a change in ionic strength and in a small change in pH as a secondary effect.

The experimental data for individual kinetic runs are given in Tables 80-88 and Figs. 68-70, 72-74, and 76 and Table 89 summarises the results for all the salts used. When the initial rate is plotted against the cation concentration (Fig. 71, 75, 77) a straight line is obtained in each case showing a first order dependence on cation concentration. The intercepts of these plots (i.e. R_o at $[M^+] = 0$) are different because of differing residual cation concentration(s) as is explained in the calculations below. The linear dependence in each case is clearly not an ionic strength effect especially as the effect of K^+ is the same whether added as KNO_3 or K_2SO_4 while NO_3^- produces a different effect when added as $NaNO_3$ rather than KNO_3. Moreover all experiments are made in the region of ionic strength where fairly small changes in activities accompany alterations in ionic strength, and if ionic strength were the dominant effect here a variation of rate with I would involve $I^{\frac{1}{2}}$ or a function such as $\left\{ I^{\frac{1}{2}} \big/ (1 + I^{\frac{1}{2}}) - B\,I \right\}$ as discussed in Chapter II. The linear relationship corresponds much more with specific cation effect. The fact that the linearity decreases in the order Cs^+ (probably) > K^+ > Na^+ is consistent with this, and that linearity is maintained up to about 1 mole/l (Cs^+, however, has been studied only up to about 0.5 mole/l because of the large effect it produces), is consistent with weak ion-pairing leading to the catalysis.

Calculations

A look at Figs. 71, 75 and 77 suggests that the cation dependence - other factors kept constant - may be represented by the equation

$$R_o = A + C'' [M^+] \qquad \ldots\ldots \quad [123]$$

in which R_o is the initial rate, A and C'' are constants and $[M^+]$ is the concentration of the cation. Moreover A (the intercept) and C'' (the slope of the line) are expressed by equations [124] and [125] respectively.

$$C'' = k_M [NO_2^-][S_2O_8^{2-}] \quad \ldots\ldots \quad [124]$$

$$A = k_1[S_2O_8^{2-}] + k_2^o[NO_2^-][S_2O_8^{2-}] + k_M'[M_1^+][NO_2^-][S_2O_8^{2-}] \quad \ldots\ldots \quad [125]$$

In these equations it is assumed that the effect of cations are additive and it is also assumed that only two cations are present for simplification (but see caesium ion effect below). In equations [124] and [125] k_M is the catalytic rate constant for the cation under study, M^+, k_M' is the catalytic constant for the residual cation, M_1^+, k_1 is the first order rate constant for the decomposition of peroxodisulphate, k_2^o is the second order rate constant for the redox reaction at zero cation concentration, $[M^+]$ and $[M_1^+]$ are the respective concentrations of the two cations. All concentrations in equations [123] and [124] and others derived from them (see below) are initial concentrations and the subscript o is dropped for convenience.

The values of k_M and k_2^o were calculated by substituting the appropriate values of C'' and A (Figs. 71, 75, 77) and those of other quantities in equations [123] and [124] as is shown below.

(a) k_M values:

(i) for potassium ion

slope = $C'' = 1.585 \times 10^{-4}\ \text{min}^{-1}$ (from Fig. 71)

$[S_2O_8^{2-}] = 0.07772$ mole/l

$[NO_2^-] = 0.07412$ mole/l

Substituting these values in equation [124]

$$k_{K^+} = \frac{1.585 \times 10^{-4}}{7.772 \times 7.412 \times 10^{-4}} = 2.75 \times 10^{-2}\ \text{l}^2/\text{mole}^2/\text{min}$$

(ii) for sodium ion (Fig.75)

$C'' = 0.894 \times 10^{-4}\ \text{min}^{-1}$

$[S_2O_8^{2-}] = 0.07445$ mole/l

$[NO_2^-] = 0.07449$ mole/l

Therefore

$$k_{Na^+} = \frac{0.0894 \times 10^{-4}}{7.445 \times 7.449 \times 10^{-4}} = 1.62 \times 10^{-2}\ l^2/mole^2/min$$

(iii) similarly for caesium ion (Fig.77)

$$k_{Cs^+} = \frac{1.830 \times 10^{-4}}{7.740 \times 7.449 \times 10^{-4}} = 3.17 \times 10^{-2}\ l^2/mole^2/min$$

(b) k_2^o values:

(i) from K^+ effect (Fig.71): in this case the intercept A is given by rewriting equation [125] specifically as

$$A = k_1[S_2O_8^{2-}] + k_2^o[NO_2^-][S_2O_8^{2-}] + k_{Na^+}[Na^+][NO_2^-][S_2O_8^{2-}] \qquad \text{...... [126]}$$

because sodium ion is the residual cation.

$A = 4.00 \times 10^{-5}$ mole/l/min

$k_1 = 2.61 \times 10^{-4}\ min^{-1}$ (see p.146)

$k_{Na^+} = 1.62 \times 10^{-2}\ l^2/mole^2/min$

$[S_2O_8^{2-}] = 0.07772$ mole/l

$[NO_2^-] = 0.07412$ mole/l

$[Na^+] = 0.07412$ mole/l

Subatituting these values in equation [126] gives

$$4.00 \times 10^{-5} = 2.61 \times 10^{-4}\ (0.07772) + k_2^o\ (0.07412)(0.07772) + 1.617 \times 10^{-2}\ (0.07412)^2\ (0.07772)$$

and solving for k_2^o gives

$$k_2^o \simeq \frac{1.281 \times 10^{-5}}{7.412 \times 7.772 \times 10^{-4}} = 2.22 \times 10^{-3}\ l/mole/min$$

(ii) from Na^+ effect (Fig.75): in this case the residual cation is the potassium ion and therefore equation [125] may be written as

$$A = k_1[S_2O_8^{2-}] + k_2^o[NO_2^-][S_2O_8^{2-}] + k_{K^+}[K^+][NO_2^-][S_2O_8^{2-}] \qquad \text{...... [127]}$$

$A = 7.07 \times 10^{-5}$ mole/l/min

$k_1 = 2.61 \times 10^{-4}$ min^{-1}

$k_{K^+} = 2.751 \times 10^{-2}$ l^2/mole^2/min

$[K^+] = 0.2510$ mole/l

$[S_2O_8^{2-}] = 0.07445$ mole/l

$[NO_2^-] = 0.07449$ mole/l

Substituting these values into equation [127] and solving for k_2^o gives

$$k_2^o = \frac{1.298 \times 10^{-5}}{7.445 \times 7.449 \times 10^{-4}} = 2.34 \times 10^{-3} \text{ l/mole/l}$$

(iii) from Cs^+ effect: in this case both potassium and sodium ions are originally present in the system and therefore the intercept of Fig.77 incorporates terms involving both these ions and therefore equation [125] is expanded accordingly and rewritten as

$$A = k_1[S_2O_8^{2-}] + k_2^o[NO_2^-][S_2O_8^{2-}] + \left\{ k_{K^+}[K^+] + k_{Na^+}[Na^+] \right\} [NO_2^-][S_2O_8^{2-}] \quad \ldots\ldots [128]$$

$A = 8.03 \times 10^{-5}$ mole/l/min

$k_1 = 2.61 \times 10^{-4}$ min^{-1}

$k_{K^+} = 2.751 \times 10^{-2}$ l^2/mole^2/min

$k_{Na^+} = 1.617 \times 10^{-2}$ l^2/mole^2/min

$[K^+] = 0.2524$ mole/l

$[Na^+] = 0.07449$ mole/l

$[S_2O_8^{2-}] = 0.07740$ mole/l

$[NO_2^-] = 0.07449$ mole/l

Introducing these values into equation [128] and solving for k_2^o gives

$$k_2^o = 2.28 \times 10^{-3} \text{ l/mole/min}$$

Table 79 gives a summary of the results of these calculations and a look at this table shows that cations catalyze the reaction in the ascending order $Na^+ < K^+ < Cs^+$. Moreover the values of k_2^o calculated from different plots are so close that the assumption of additivity in equation [125] is to be taken as valid.

Table 79

Cation Effect

Cation	10^2 k_M l^2/mole^2/min	10^3 k_2^o l/mole/min
Na^+	1.62	2.34
K^+	2.75	2.22
Cs^+	3.17	2.28

Potassium ion effect

The effect of potassium ion on the rate of the reaction was studied at the constant experimental conditions shown below. The effects of both potassium nitrate (Tables 80-81 and Fig.68) and potassium sulphate (Tables 82-84 and Fig.69-70) were investigated. In runs 84a and 84b the required amount of potassium sulphate was weighed directly into the reaction vessel because of solubility problems, while in all the other runs solution B (see p. 116) - as usual - contained the added salt.

Experimental conditions with concentrations in mole/l.

$[S_2O_8^{2-}]_o$ = 0.07772

$[NO_2^-]_o$ = 0.07412

$[Na^+]$ = 0.07412

[Phosphate]total = 0.06835

Temperature = 60.0°C

Table 80

The Effect of Added KNO_3

$[Na_2S_2O_3]$ = 0.02083

$[KNO_3]$ added	(a)	Nil	(b)	1.000	(c)	0.100
$[K^+]$ total		0.2510		1.2510		0.3510
pHo		6.373		6.157		6.345
Time (min)	Titre (ml)	$10^2[S_2O_8^{2-}]$	Titre (ml)	$10^2[S_2O_8^{2-}]$	Titre (ml)	$10^2[S_2O_8^{2-}]$
5	-	-	38.08	7.593	36.62	7.628
10	38.39	7.655	37.67	7.511	36.42	7.536
15	38.20	7.617	37.01	7.380	36.14	7.523
20	38.01	7.579	36.31	7.240	35.97	7.493
25	37.75	7.527	36.05	7.188	35.82	7.461
30	37.60*	7.497*	35.33	7.045	35.54	7.403
40	37.33**	7.444**	34.75	6.929	35.10	7.311
60	36.82	7.343	33.79	6.738	34.48	7.182

* time 31 minutes

** time 42 minutes

Table 81

The Effect of Added KNO_3

$[Na_2S_2O_3]$ = 0.02083

$[KNO_3]$added	(a)	0.800	(b)	0.3000	(c)	0.6000
$[K^+]$ total		1.0510		0.5510		0.8510
pHo		6.177		6.247		6.163
Time (min)	Titre (ml)	$10^2[S_2O_8^{2-}]$	Titre (ml)	$10^2[S_2O_8^{2-}]$	Titre (ml)	$10^2[S_2O_8^{2-}]$
5	36.22	7.545	36.72	7.649	36.30	7.561
10	35.76	7.449	36.41	7.584	35.84	7.466
15	35.32	7.357	36.05	7.509	35.48	7.390
20	34.77	7.243	35.81	7.459	35.07	7.305
25	34.38	7.161	-	-	-	-
30	33.93	7.068	35.24	7.340	34.31	7.147
40	33.30	6.936	34.57	7.201	33.61	7.001
50	-	-	34.08	7.099	32.82	6.836
60	32.02	6.670	33.61	7.001	32.62	6.795

Table 82

The Effect of Added K_2SO_4

$[Na_2S_2O_3]$ = 0.02126 in a and b and 0.02108 in c

$[K_2SO_4]$added	(a)	0.1014	(b)	0.0512	(c)	0.2513
$[K^+]$total		0.4510		0.3510		0.7536
pHo		6.265		6.307		6.204
Time (min)	Titre (ml)	$10^2[S_2O_8^{2-}]$	Titre (ml)	$10^2[S_2O_8^{2-}]$	Titre (ml)	$10^2[S_2O_8^{2-}]$
5	36.31	7.720	36.50	7.760	36.68	7.732
10	35.98	7.649	36.22	7.700	36.26	7.648
15	35.67	7.583	36.02	7.658	35.92	7.572
20	35.44	7.535	35.74	7.598	35.62	7.509
30	34.90	7.420	35.34	7.513	34.99	7.376
40	34.37	7.307	34.81	7.401	34.76	7.327
50	33.86	7.199	34.45	7.324	35.08	7.184
60	33.60	7.143	33.94	7.216	33.75	7.115

Table 83

The Effect of Added K_2SO_4

$[Na_2S_2O_3]$ = 0.02108

$[K_2SO_4]$added	(a)	0.3108	(b)	0.1488	(c)	0.2003
$[K^+]$total		0.8726		0.5486		0.6516
pHo		6.222		6.260		6.215
Time (min)	Titre (ml)	$10^2[S_2O_8^{2-}]$	Titre (ml)	$10^2[S_2O_8^{2-}]$	Titre (ml)	$10^2[S_2O_8^{2-}]$
5	36.52	7.698	36.91	7.781	36.62	7.719
10	36.17	7.625	36.61	7.717	36.30	7.652
15	35.66	7.517	36.30	7.652	35.94	7.576
20	35.21	7.422	35.95	7.578	35.58	7.500
30	34.71	7.313	35.33	7.448	34.92	7.361
40	33.96	7.159	34.86	7.348	33.99*	7.152*
50	33.37	7.034	34.28	7.226	33.79	7.123
60	33.00	6.956	33.88	7.142	33.40	7.041

* time 47 minutes

Table 84

The Effect of Added K_2SO_4

$[Na_2S_2O_3]$ = 0.02108

$[K_2SO_4]$added $[K^+]$total pHo	(a) 0.3805 1.012 6.183		(b) 0.4960 1.243 6.153	
Time (min)	Titre (ml)	$10^2[S_2O_8^{2-}]$	Titre (ml)	$10^2[S_2O_8^{2-}]$
5	-	-	35.73	7.532
10	35.62	7.509	35.17	7.414
15	35.17	7.414	34.72	7.319
20	34.80	7.336	34.15	7.199
25	34.22	7.214	33.73	7.110
35	33.62	7.087	32.97	6.950
45	33.10	6.977	32.31	6.811
60	32.30	6.808	31.45	6.630

Sodium ion effect

The effect of added sodium ion, in the form of sodium nitrate, on the rate of the reaction was investigated at the following constant experimental conditions. Concentrations as usual in units of mole/l.

$[S_2O_8^{2-}]_o$ = 0.07445

$[NO_2^-]_o$ = 0.07449

[Phosphate]total = 0.06835

$[K^+]$ residual = 0.2510

The concentration of sodium ion was varied between 0.0700 to 1.20 mole/l. The experimental data are given in Tables 85 - 86 and Figs. 72 - 74.

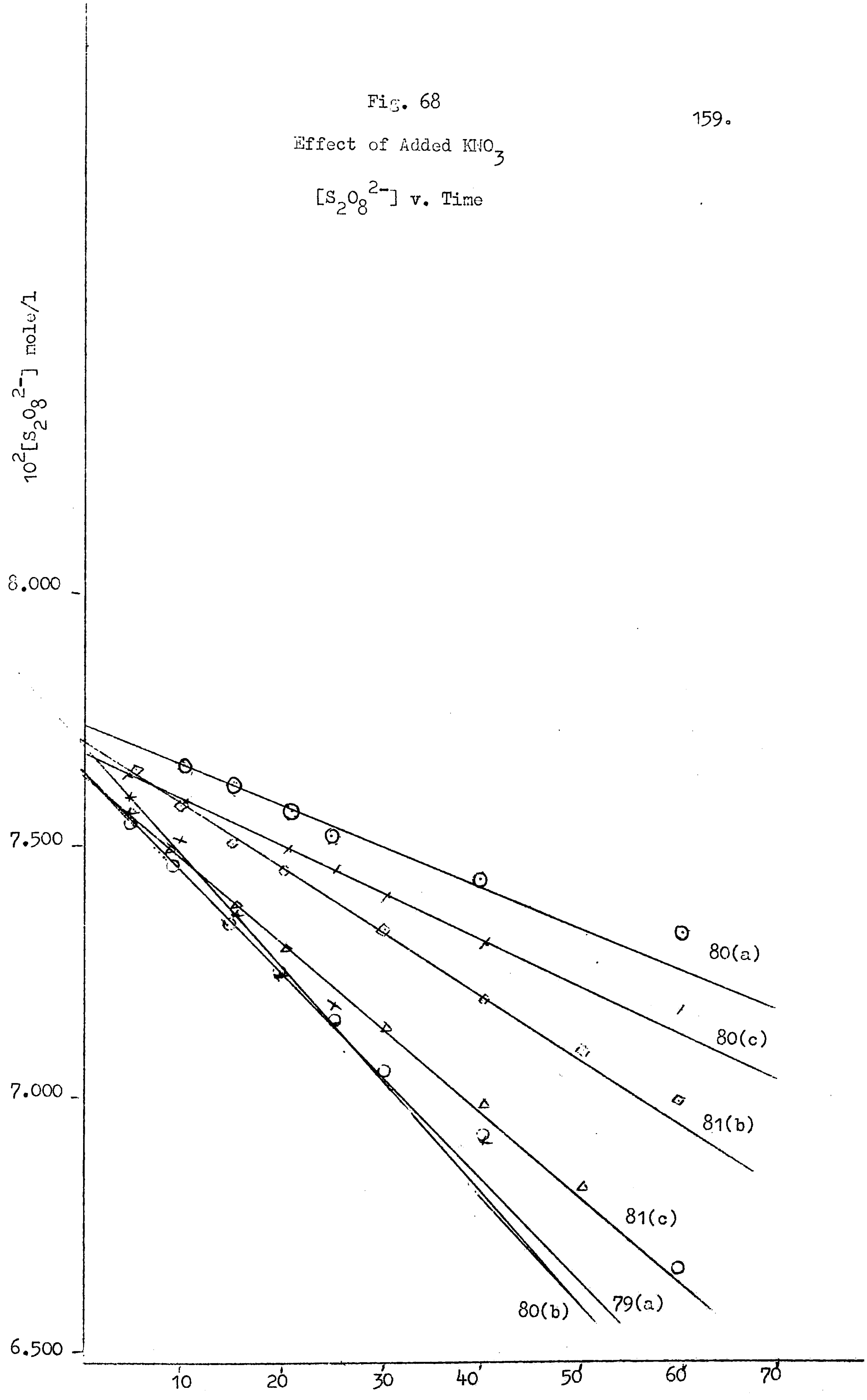


Fig. 68

Effect of Added KNO_3

$[S_2O_8^{2-}]$ v. Time

Fig. 69

Effect of Added K_2SO_4

$[S_2O_8^{2-}]$ v. Time

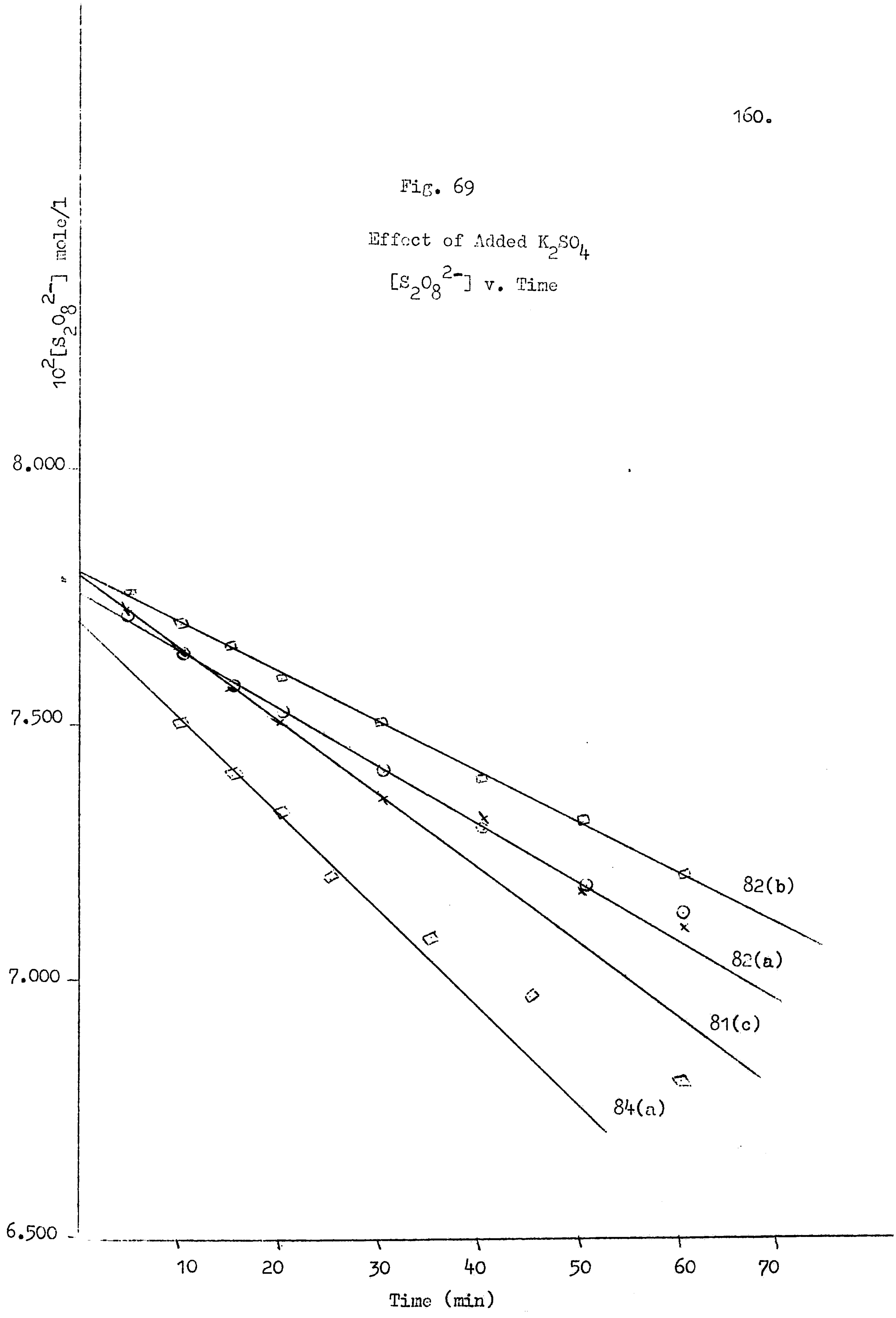
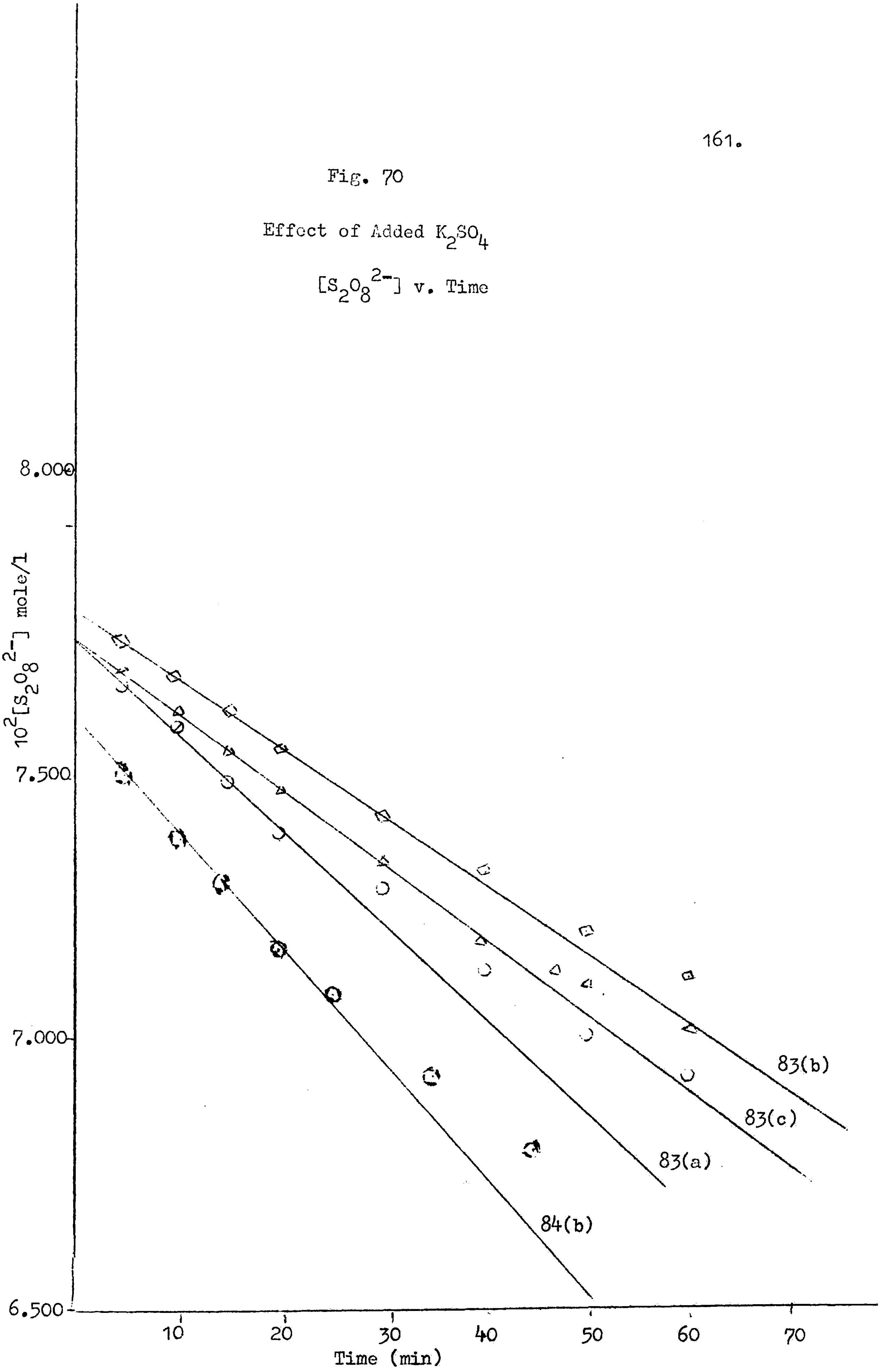


Fig. 70

Effect of Added K_2SO_4

$[S_2O_8^{2-}]$ v. Time



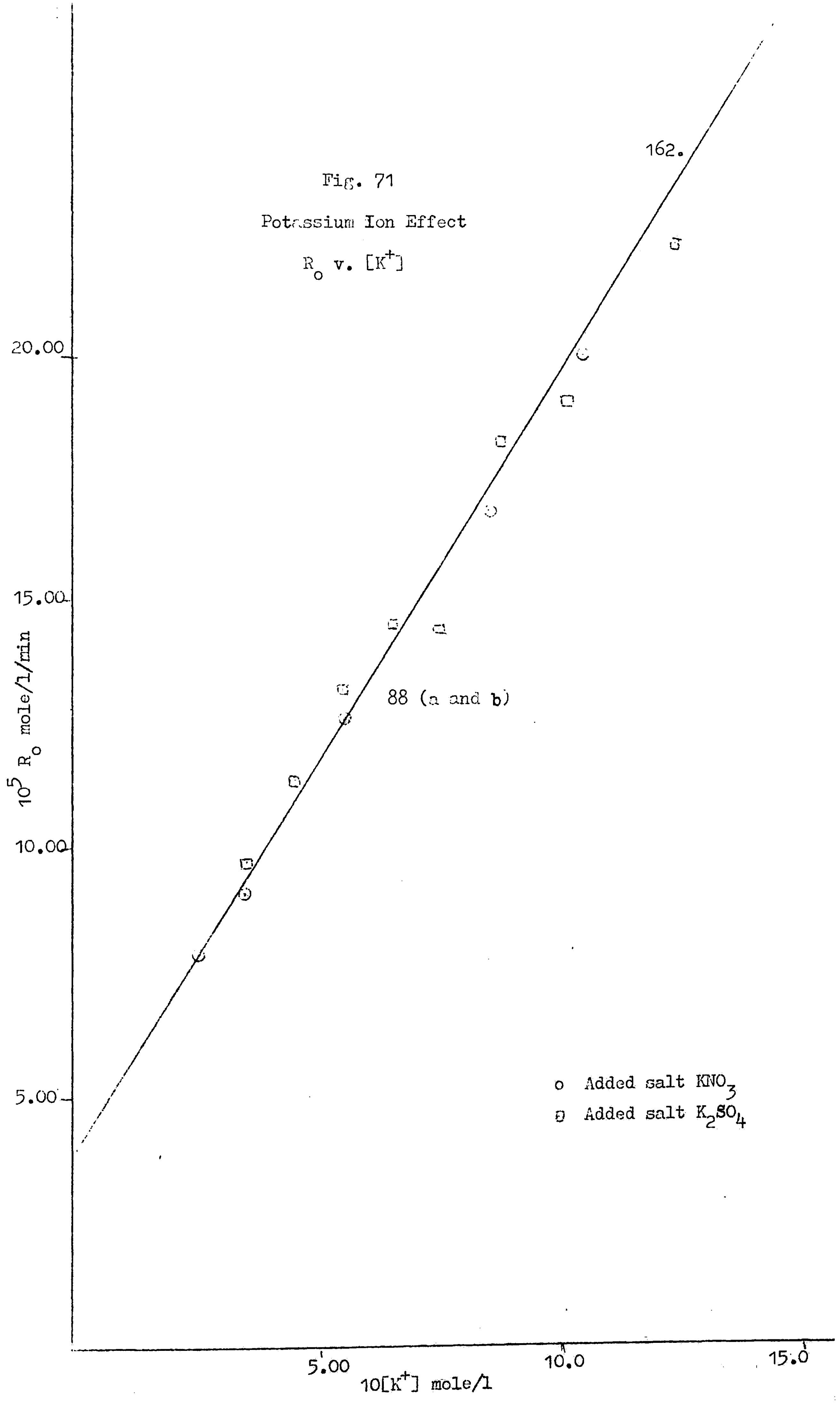


Fig. 71

Potassium Ion Effect

R_o v. $[K^+]$

Table 85

Effect of Added $NaNO_3$

$[Na_2S_2O_3]$ = 0.02062

$[NaNO_3]$	(a) 0.5000		(b) Nil		(c) 1.000		(d) 0.1000	
$[Na^+]$	0.5745		0.07445		1.07445		0.17445	
pHo	6.117		6.367		5.967		6.265	
Time (ml)	Titre (ml)	$10^2[S_2O_8^{2-}]$	Titre (ml)	$10^2[S_2O_8^{2-}]$	Titre (ml)	$10^2[S_2O_8^{2-}]$	Titre (ml)	$10^2[S_2O_8^{2-}]$
5	37.42	7.716	37.40	7.712	37.32	7.695	37.27	7.685
10	37.16	7.662	37.22	7.675	36.99	7.627	37.00	7.629
15	36.82	7.592	37.02	7.634	36.58	7.543	36.80	7.588
20	36.53	7.532	36.74	7.576	36.23	7.471	36.52*	7.530*
30	35.90	7.403	36.42	7.510	35.66	7.332	36.27	7.479
40	35.36	7.291	36.06	7.436	34.72	7.159	35.90	7.403
50	34.96	7.209	35.68	7.357	34.31	7.075	35.41	7.302
60	34.56	7.126	-	-	33.70	6.949	34.92	7.201

* time 21 minutes

Table 86

Effect of Added $NaNO_3$

$[Na_2S_2O_3]$ = 0.02126

	(a)		(b)		(c)		(d)	
$[NaNO_3]$	0.3000		1.2000		0.6466		0.7973	
$[Na^+]$	0.37445		1.27445		0.7211		0.8718	
pHo	6.173		5.888		6.027		6.000	
Time (min)	Titre (ml)	$10^2[S_2O_8^{2-}]$	Titre (ml)	$10^2[S_2O_8^{2-}]$	Titre (ml)	$10^2[S_2O_8^{2-}]$	Titre (ml)	$10^2[S_2O_8^{2-}]$
5	36.50	7.760	36.21*	7.698*	36.31	7.720	36.30	7.717
10	36.32	7.722	35.87	7.626	35.93	7.639	35.96	7.645
15	36.11	7.677	35.43	7.532	35.59	7.566	35.62	7.573
20	35.80	7.611	34.97	7.435	35.29	7.503	35.31	7.507
25	-	-	34.63	7.362	-	-	-	-
30	35.30	7.505	-	-	34.61	7.358	34.62	7.360
35	-	-	33.90	7.207	-	-	-	-
40	34.81	7.401	-	-	34.08	7.245	34.08	7.245
50	34.23	7.277	33.22**	7.063**	33.60	7.143	33.50	7.122
60	33.80	7.186	32.51	6.912	33.12	7.041	33.05	7.026

* time 6 minutes
** time 45 minutes

Fig. 72

Sodium Ion Effect

$[S_2O_8^{2-}]$ v. Time

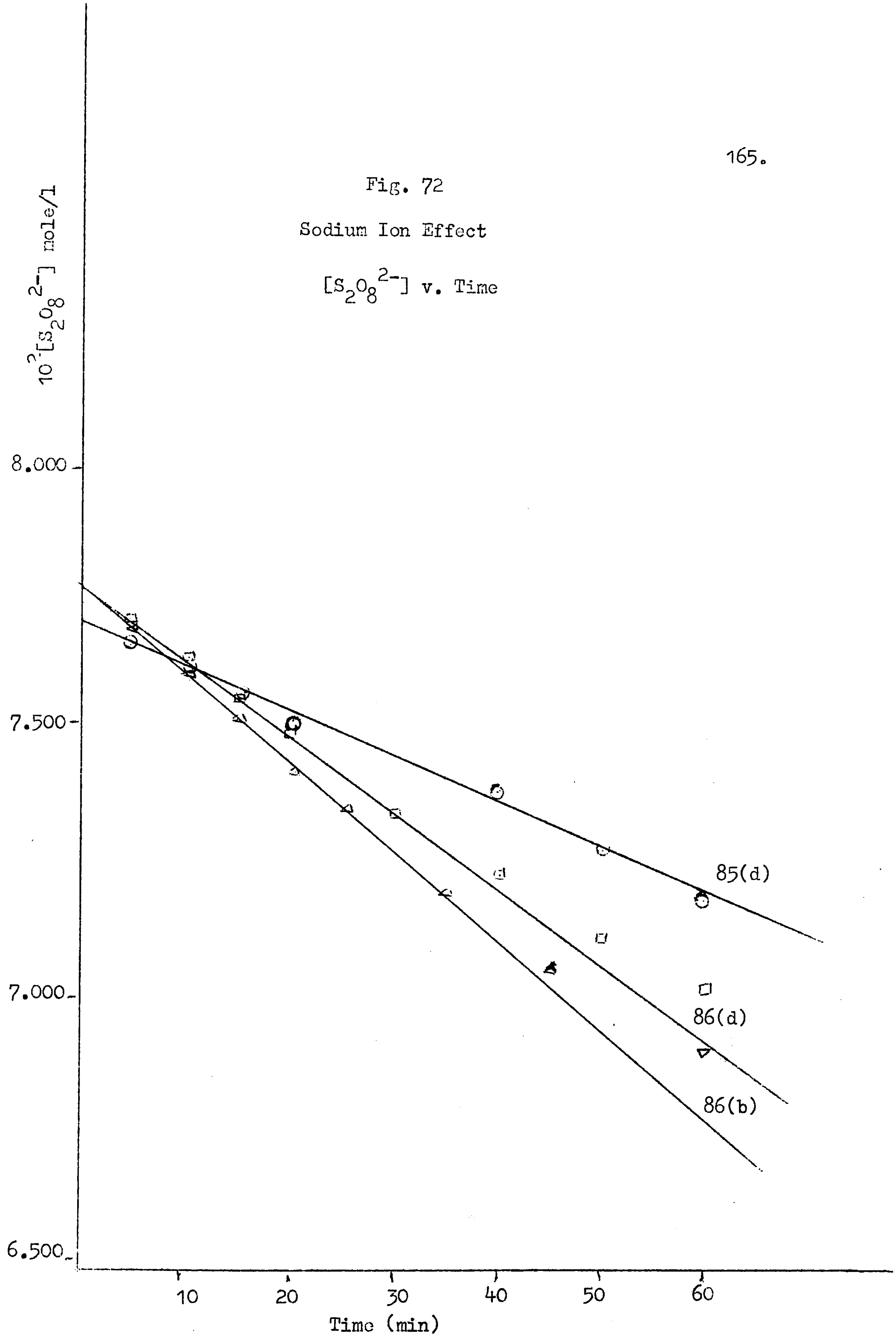


Fig. 73

Sodium Ion Effect

$[S_2O_8^{2-}]$ v. Time

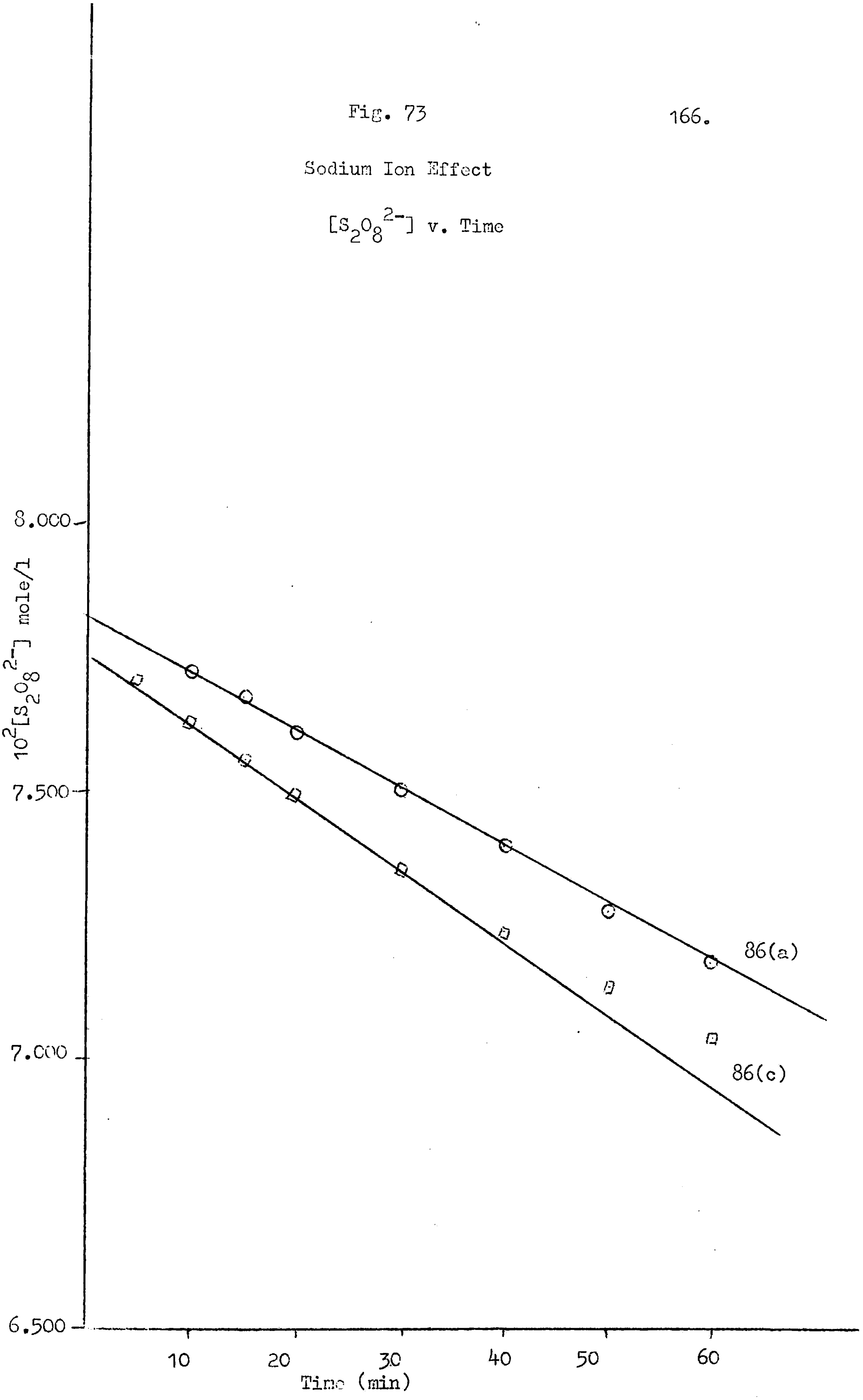
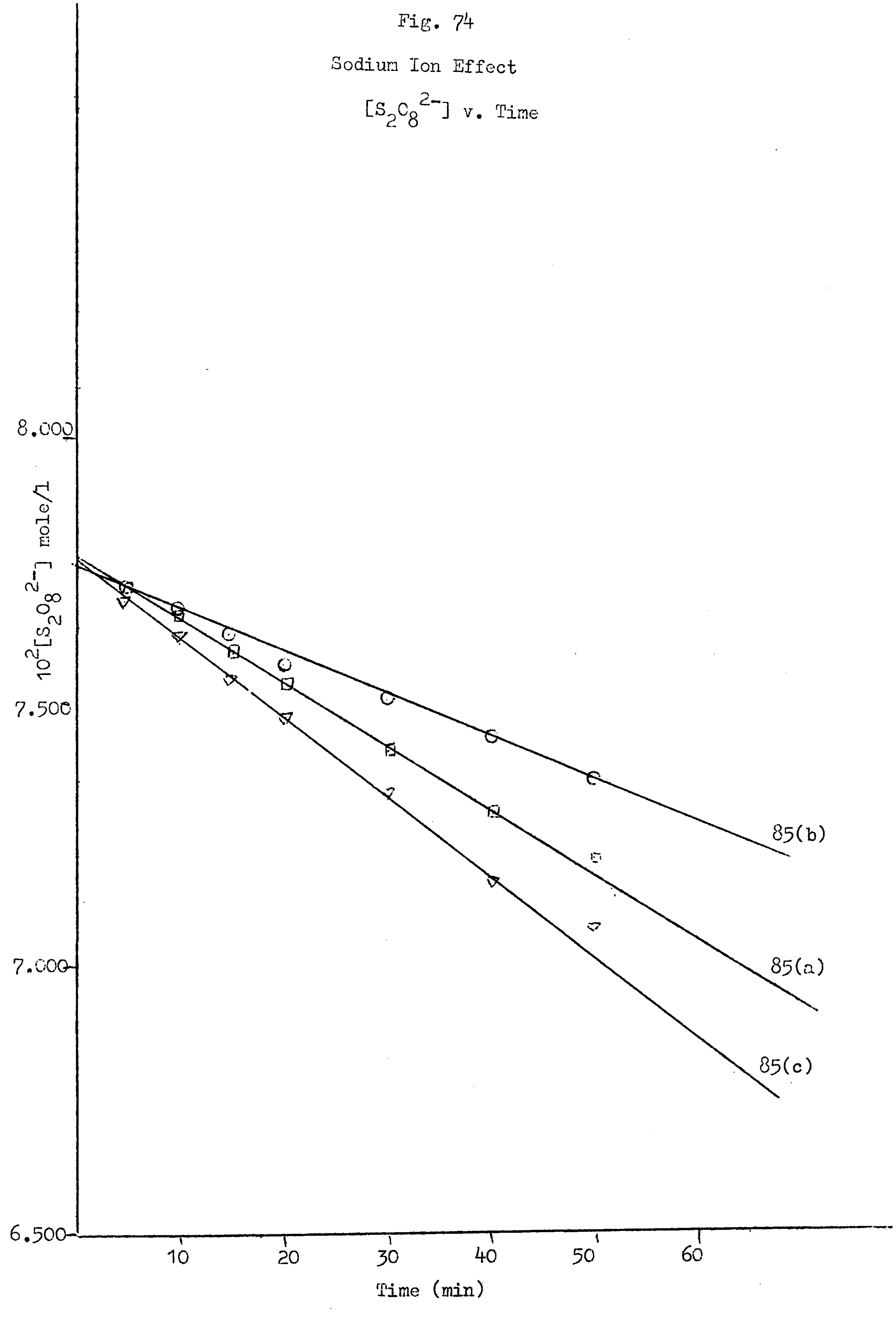


Fig. 74

Sodium Ion Effect

$[S_2O_8^{2-}]$ v. Time



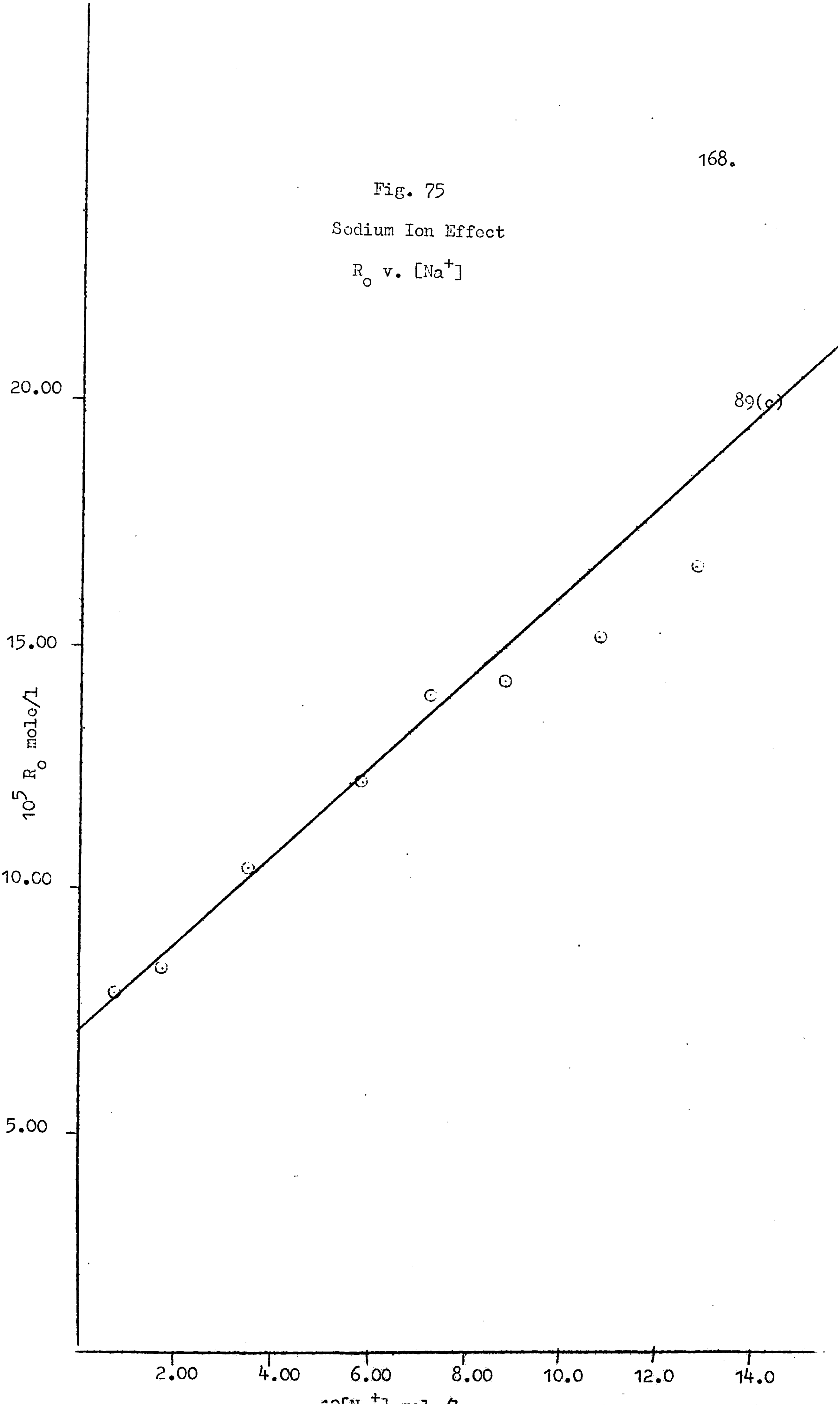


Fig. 75

Sodium Ion Effect

R_o v. $[Na^+]$

Caesium ion effect

The effect of caesium ion on the rate of the reaction was studied at the experimental conditions shown below. The salt used was reagent grade caesium nitrate as the Analar was not available. Caesium ion concentration was varied from about 0.05 mole/l to about 0.5 mole/l.

Conditions : concentration in units of mole/l.

$[S_2O_8^{2-}]_o$ = 0.07740

$[NO_2^-]_o$ = 0.07449

[Phosphate]total = 0.06835

$[Na^+]$ = 0.07450

$[K^+]$ = 0.2524

Temperature = 60.0°C

Table 87

Caesium Ion Effect

$[Na_2S_2O_8]$ = 0.02077

$[Cs^+]$ pHo	(a) 0.05147 6.412		(b) 0.1013 6.412		(c) 0.2009 6.387	
Time (min)	Titre (ml)	$10^2[S_2O_8^{2-}]$	Titre (ml)	$10^2[S_2O_8^{2-}]$	Titre (ml)	$10^2[S_2O_8^{2-}]$
5	37.07	7.691	37.05	7.695	37.02	7.689
10	36.73	7.629	36.74	7.631	36.75	7.633
15	36.53	7.587	36.54	7.587	36.38	7.556
20	36.36	7.552	36.29	7.537	36.14	7.506
25	36.20	7.519	36.08	7.494	35.89	7.454
30	-	-	-	-	35.70	7.415
35	35.75	7.425	35.60	7.394	-	-
45	35.30	7.332	35.18	7.307	35.12*	7.294*
60	34.80	7.228	34.51	7.168	34.18	7.099

* time 41 minutes

Table 88

Caesium Ion Effect

$[Na_2S_2O_3]$ = 0.02077

$[Cs^+]$ pHo	(a) 0.3075 6.372		(b) 0.4032 6.345		(c) 0.5075 6.300	
Time (min)	Titre (ml)	$10^2[S_2O_8^{2-}]$	Titre (ml)	$10^2[S_2O_8^{2-}]$	Titre (ml)	$10^2[S_2O_8^{2-}]$
5	36.85	7.654	36.91	7.666	36.74	7.631
10	36.43	7.567	36.53	7.587	36.28	7.535
15	36.20	7.519	36.11	7.500	35.85	7.446
20	35.82	7.440	35.79	7.434	35.52	7.378
25	35.60	7.394	35.39	7.351	35.07	7.284
30	35.22	7.315	35.05	7.280	34.78	7.224
35	-	-	34.71	7.209	34.43	7.151
40	34.50*	7.166*	-	-	-	-
45	-	-	34.27	7.118	33.83	7.026
60	33.63	6.985	-	-	-	-

* time 42 minutes

Fig. 76

Caesium Ion Effect

$[S_2O_8^{2-}]$ v. Time

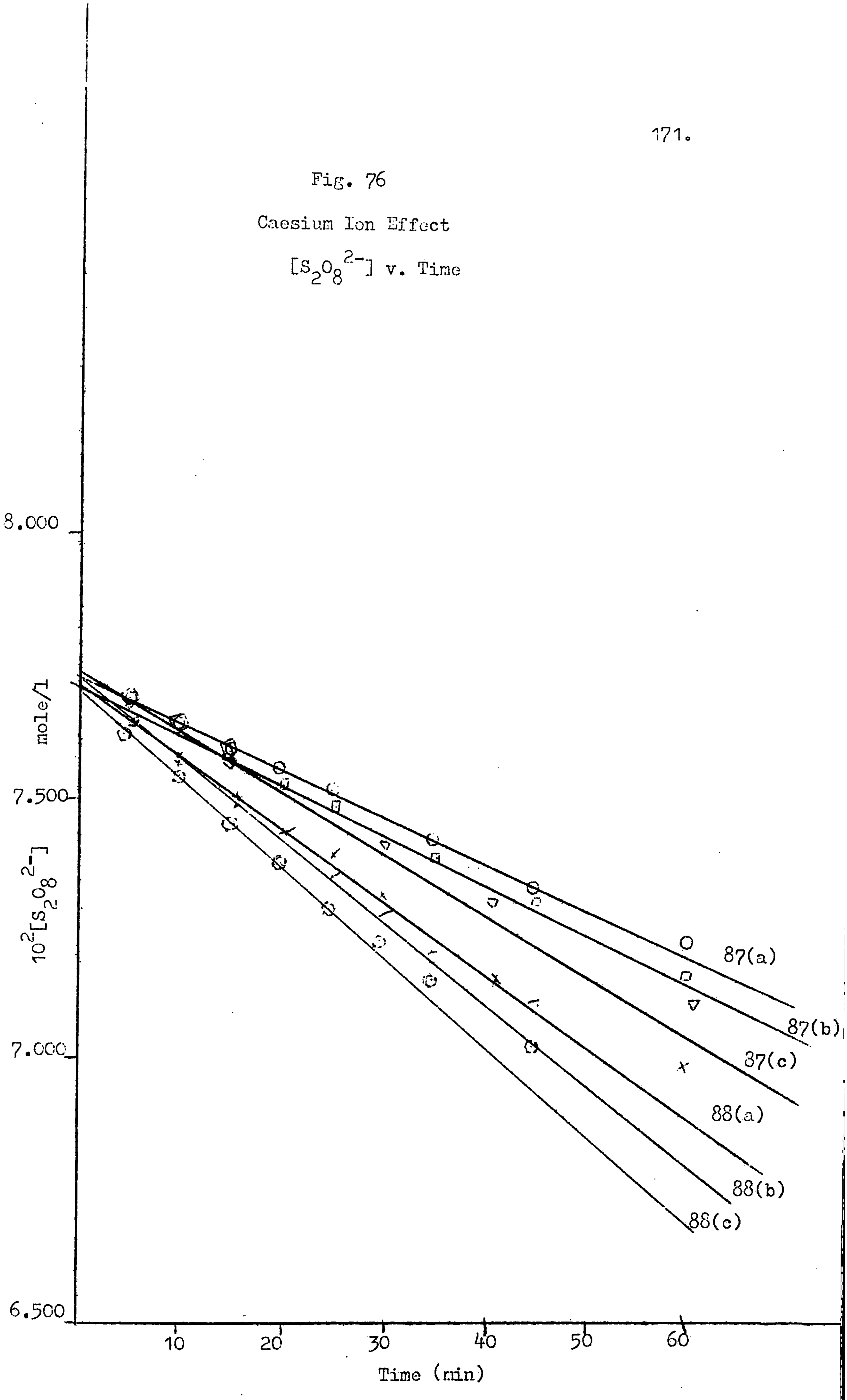


Fig. 77

Caesium Ion Effect

R_o v. $[Cs^+]$

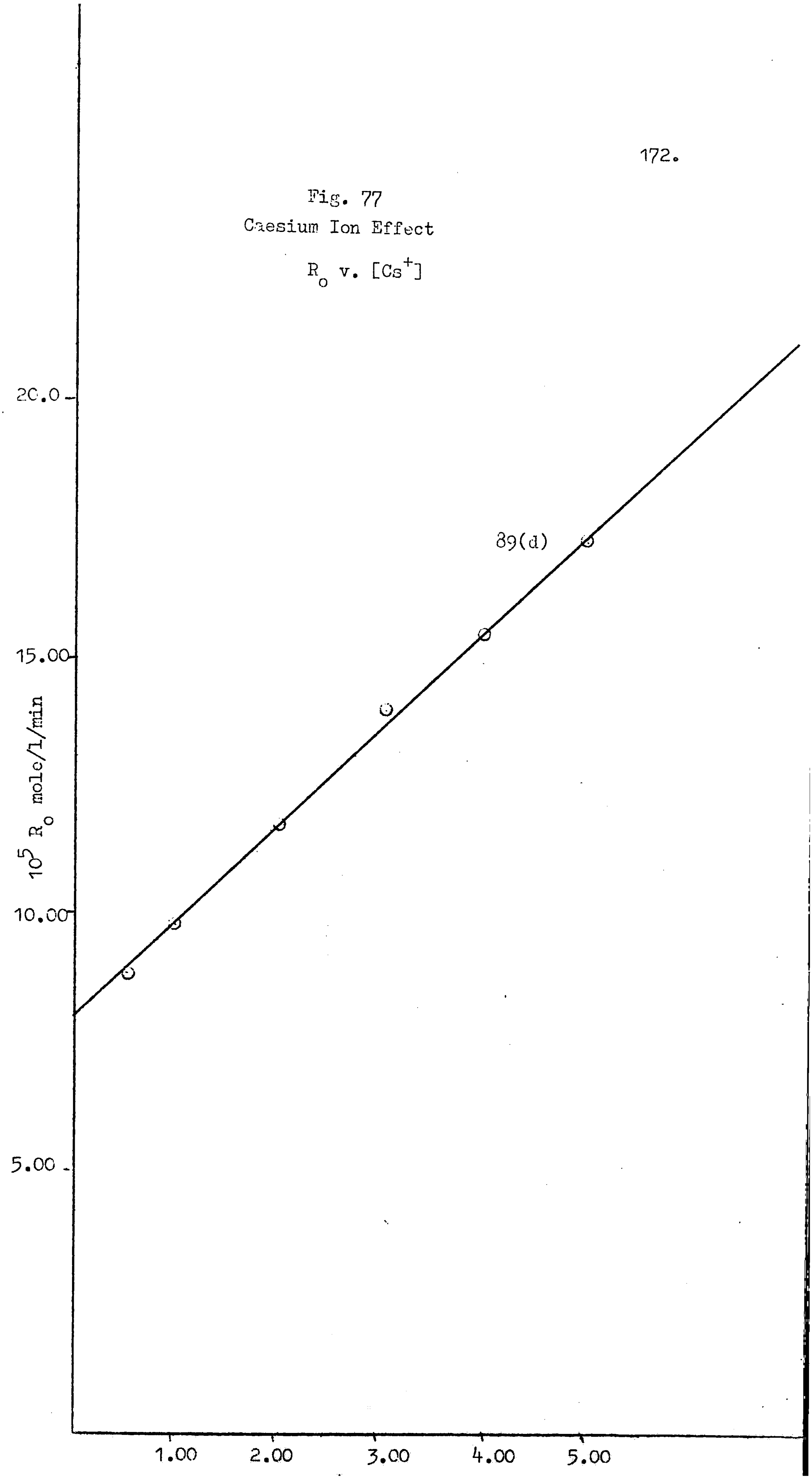


Table 89

Cation Effect

	Salt added	$10[M^+]$total (mole/l)	10^5 R (mole/l/min)
(a)	KNO_3	2.510	7.95
		3.510	9.20
		5.510	12.70
		8.510	16.90
		10.51	20.20
		12.51	22.20
(b)	K_2SO_4	3.510	9.70
		4.510	11.40
		5.486	13.30
		6.500	14.60
		7.536	14.50
		8.726	18.30
		10.12	19.10
		12.43	22.30
(c)	$NaNO_3$	0.7445	8.00
		1.7445	8.40
		3.7445	10.45
		5.7445	12.20
		7.211	14.00
		8.718	14.30
		10.7445	15.20
		12.7445	16.70
(d)	$CsNO_3$	0.5147	8.90
		1.013	9.80
		2.0009	11.75
		3.0750	14.00
		4.032	15.50
		5.075	17.30

Hydrogen ion effect

The effect of varying the pH of the reaction mixture on the rate was investigated at constant experimental conditions. The pH was varied by varying the ratio $[HPO_4^{2-}]/[H_2PO_4^-]$ keeping the concentration of both sodium and potassium ions constant by adding the required amount of the respective nitrate. In doing so it was assumed that anions do not have specific effects on the reaction as was concluded in the previous section. The main effect of varying this ratio will be to change the pH and may be to cause a change in ion-pairing as the dinegative ion will be expected to form ion-pairs with the cations more than the mono-negative ion, and hence producing a change in the concentration of free cation.

The pH was measured - as in other parts - with a Pye Dynakap pH meter using a combined glass electrode. From a plot of pH against time the initial pH was found by extrapolation.

The experimental data are given in Tables 90-91 and Figs. 78-84 while Table 92 summarises the results. It is seen from the latter table that a variation of pH in the range 8.338 - 5.790, corresponding to a change of hydrogen ion concentration of about 0.046 - 16.2 x 10^{-7} mole/l, produces very little effect on the rate of the reaction. The small increase in rate below pH 6.14 may be due to an ion-pairing effect because at the lower pH values the concentration of $H_2PO_4^-$ is higher than the concentration of HPO_4^{2-}. The former ion will not pair with Na^+ or K^+ so well as the latter. Hence there will be more free Na^+ and K^+ to assist the reaction as the pH is lowered causing the small increase observed.

It is also clear that small differences in pH in earlier experiments do not affect the conclusion reached there.

Experimental conditions

The following experimental conditions apply to Tables 90-91.

Concentrations in units of mole/l.

$[S_2O_8^{2-}]_o$ = 0.07778

$[NO_2^-]_o$ = 0.07731

$[K^+]$ = 0.500

$[Na^+]$ = 0.500

I $\simeq$ 1.2

Temperature = 60.0°C

Table 90

Hydrogen Ion Effect

$[S_2O_3^{2-}]$ = 0.02659

pHo	(a) 8.338		(b) 6.777		(c) 6.597	
Time (min)	Titre (ml)	$10^2[S_2O_8^{2-}]$	Titre (ml)	$10^2[S_2O_8^{2-}]$	Titre (ml)	$10^2[S_2O_8^{2-}]$
5	29.03	7.719	28.96	7.700	29.05	7.716
10	28.81	7.661	28.69	7.629	28.82	7.655
15	28.51	7.581	28.41	7.554	28.51	7.572
20	28.27	7.517	28.12	7.477	28.20	7.490
25	27.91	7.421	27.84	7.403	27.96	7.426
30	27.65	7.352	27.53	7.320	27.67	7.354
35	27.38	7.280	27.23	7.240	-	-
45	26.83	7.134	26.63	7.081	26.74*	7.102*
60	26.16	6.956	25.97	6.905	-	-

* time 47 minutes

Table 91

Hydrogen Ion Effect

$[S_2O_3^{2-}]$ = 0.02656 in a
= 0.02651 in b
= 0.02184 in c and d

pHo	(a) 6.355		(b) 6.143		(c) 6.011		(d) 5.790	
Time (min)	Titre (ml)	$10^2[S_2O_8^{2-}]$	Titre (ml)	$10^2[S_2O_8^{2-}]$	Titre (ml)	$10^2[S_2O_8^{2-}]$	Titre (ml)	$10^2[S_2O_8^{2-}]$
5	29.20	7.756	-	-	-	-	-	-
10	28.75*	7.636*	28.72	7.614	34.59	7.554	34.58	7.552
15	28.60	7.596	28.39	7.527	34.29	7.489	34.28	7.487
20	28.27	7.509	28.08	7.445	33.86	7.395	33.97	7.380
25	27.96	7.426	27.81	7.373	33.46	7.308	33.47	7.310
30	27.69	7.354	27.44	7.275	33.07	7.222	33.12	7.233
35	27.40	7.277	27.12	7.190	32.70	7.142	32.68	7.137
45	-	-	26.58	7.046	32.41**	7.078**	32.30**	7.054**
60	26.10	6.932			32.08***	7.006***	32.03***	6.995***

* time = 12 minutes

** time 40 minutes

*** time 45 minutes

Table 92

Hydrogen Ion Effect

pH	10^4 R_o mole/l/min
8.338	1.53
6.777	1.56
6.597	1.50
6.355	1.60
6.143	1.68
6.011	1.67
5.790	1.69

Temperature effect

It has been established in the previous sections that the rate law at constant pH, cation concentration etc., is given by

$$R = k_1[S_2O_8^{2-}] + k_2[S_2O_8^{2-}][NO_2^-] \qquad \ldots\ldots \quad [112]$$

or

$$R = R_1 + R_2 \qquad \ldots\ldots \quad [129]$$

where R is the overall initial rate for the nitrite-peroxodisulphate reaction and R_1 and R_2 are the respective initial rates for the k_1 and k_2 paths. The effect of temperature on both paths was investigated by following both the nitrite-peroxodisulphate reaction and the decomposition of peroxodisulphate at each temperature under similar experimental conditions as shown below. R and R_1 were calculated from the appropriate $[S_2O_8^{2-}]$/time graphs while k_1 was calculated from log $[S_2O_8^{2-}]$/time graphs as the decomposition of peroxodisulphate is a well established first order reaction (see main introduction). R_2 and k_2 were calculated from equations [130] and [131] respectively

$$R_2 = R - R_1 \qquad \ldots\ldots \quad [130]$$

$$k_2 = \frac{R_2}{[S_2O_8^{2-}]_o[NO_2^-]_o} \qquad \ldots\ldots \quad [131]$$

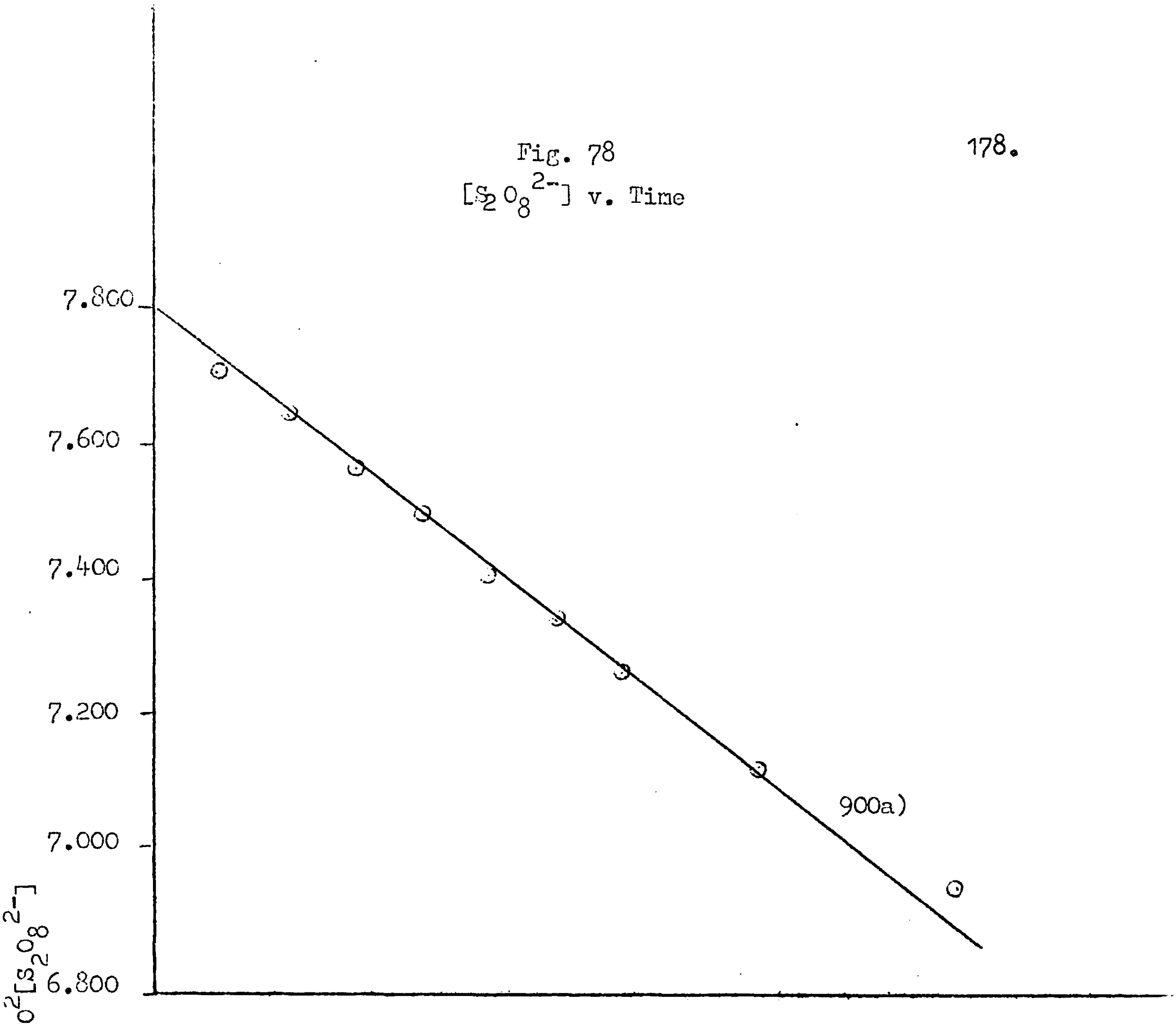


Fig. 78

$[S_2O_8^{2-}]$ v. Time

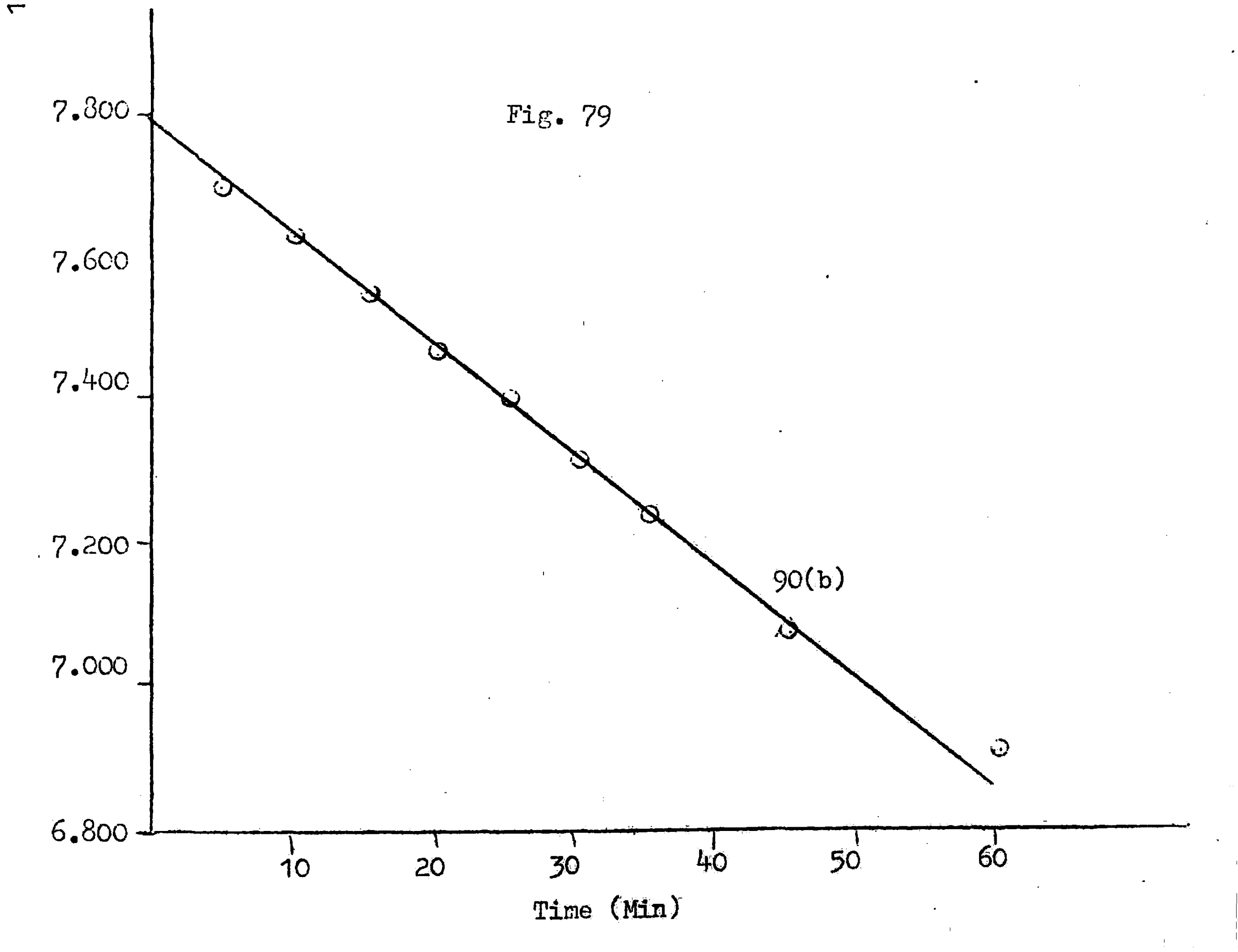


Fig. 79

Fig. 80

$[S_2O_8^{2-}]$ v. Time

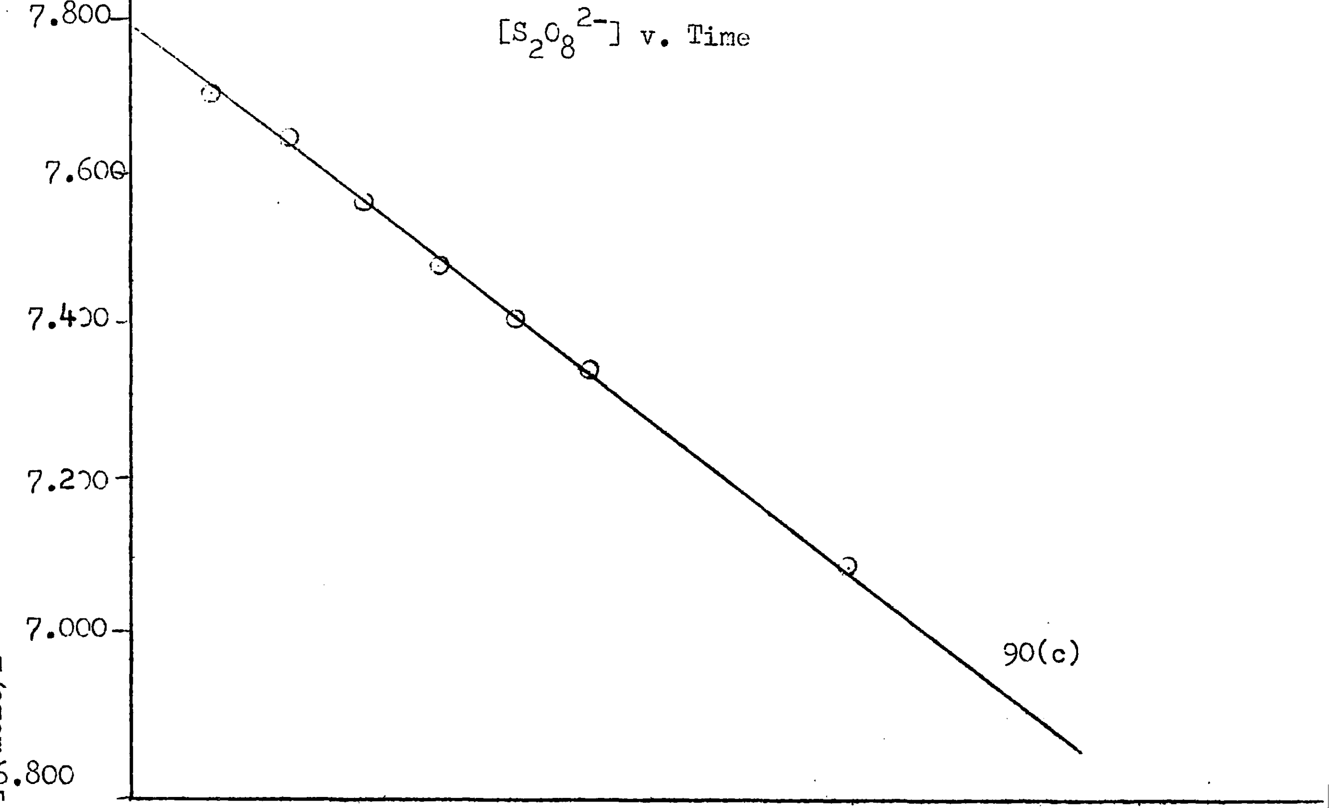


Fig. 81

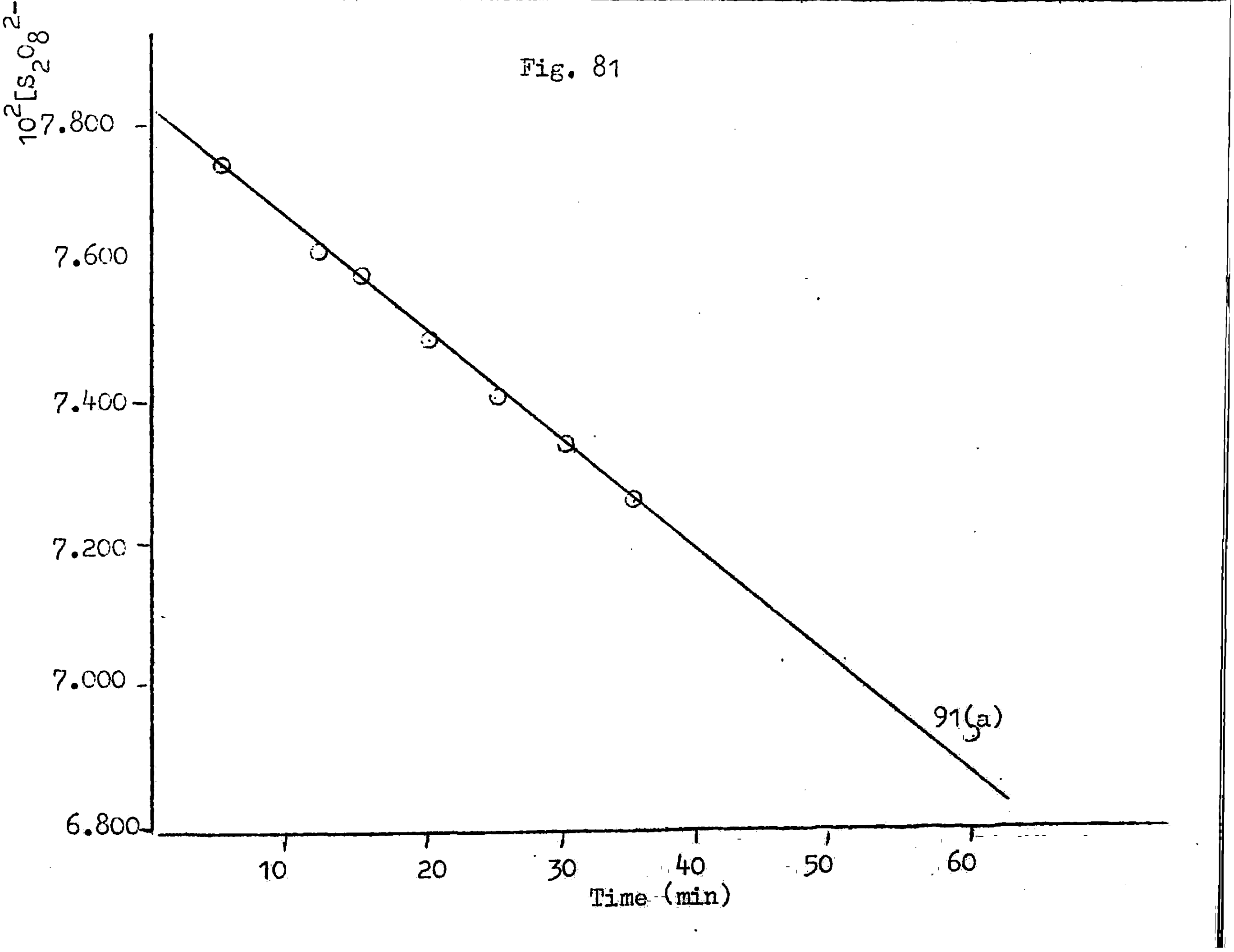


Fig. 82

$[S_2O_8^{2-}]$ v. Time

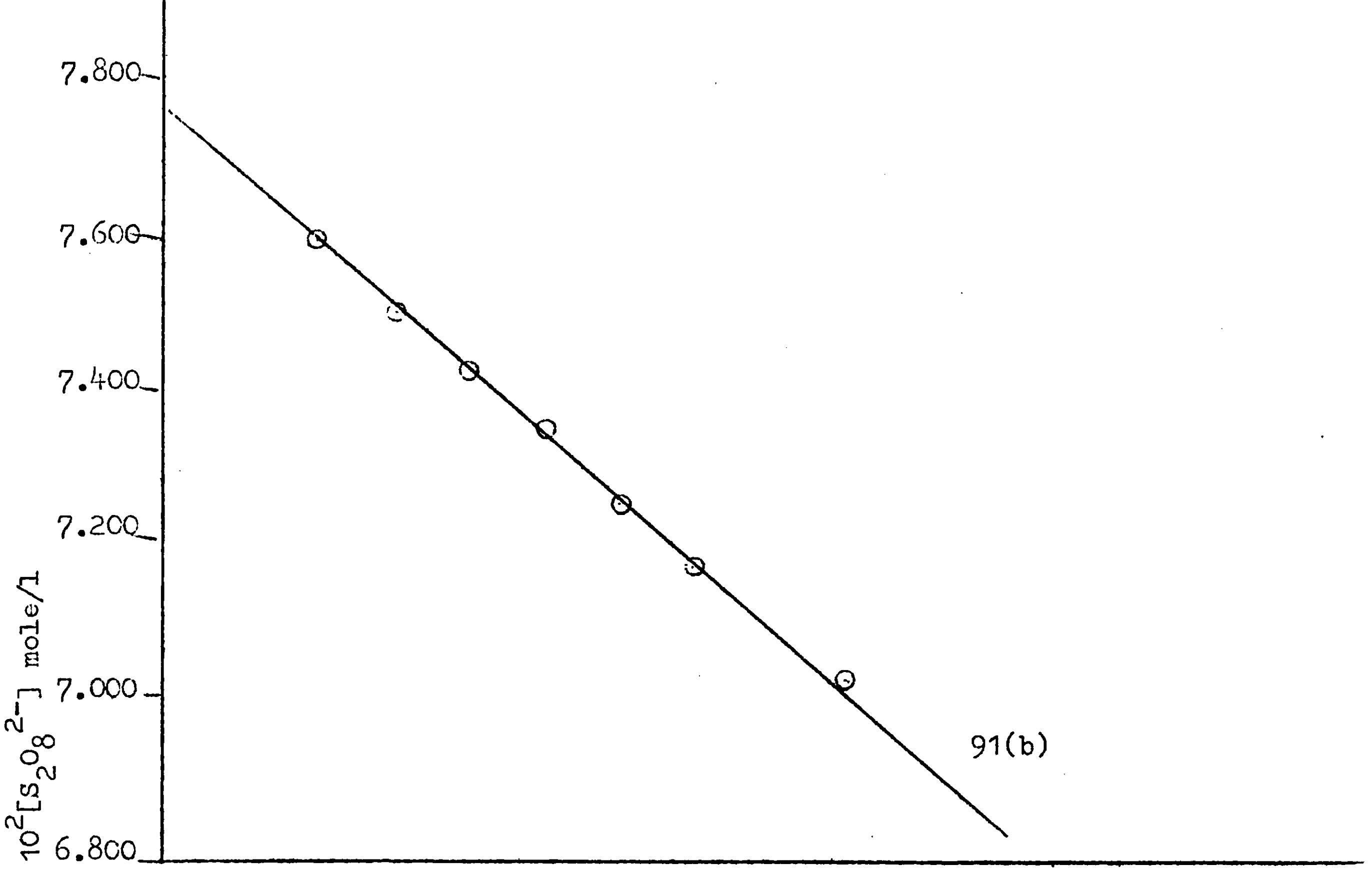


Fig. 83

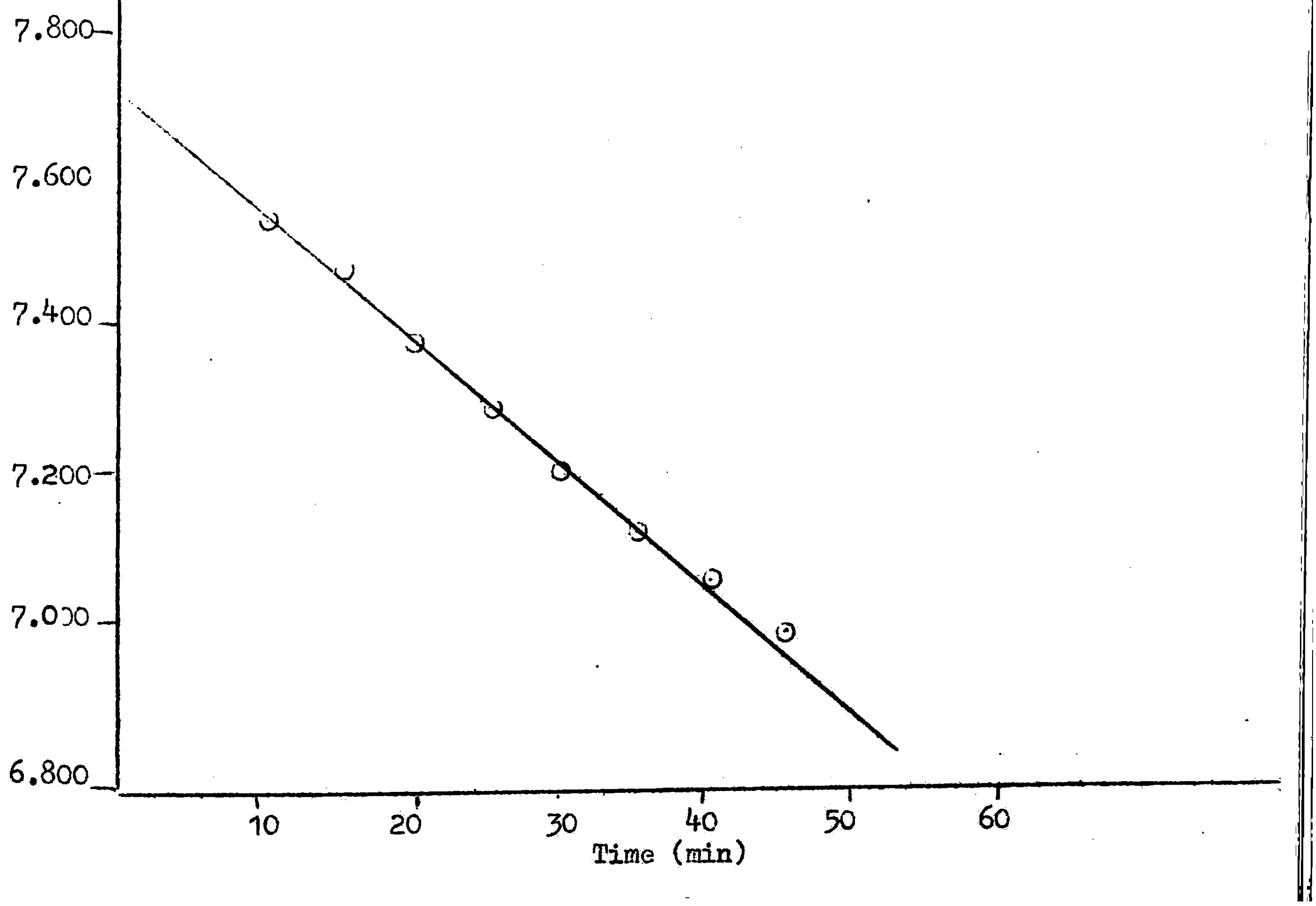
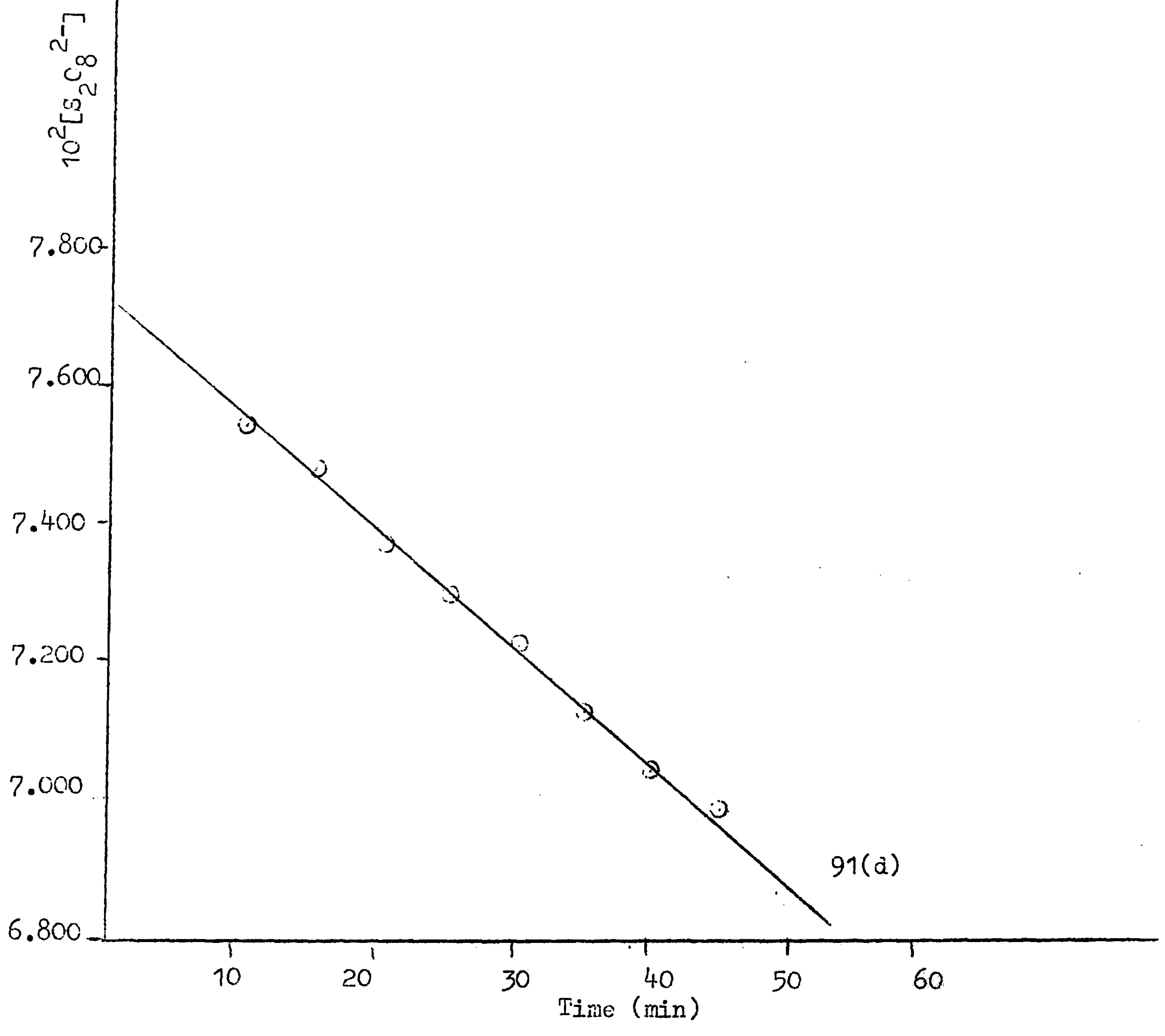


Fig. 84

$[S_2O_8^{2-}]$ v. Time



From a plot of log k versus $\frac{1}{T}$ the Arrhenius parameters for each path were calculated and they were:

(a) k_1 path:

(i) $E = 33.5 \pm 0.1$ kcal/mole which is in good agreement with the value of 33.5 kcal/mole reported by Kolthoff and Miller under slightly different conditions.

(ii) $A = 4.38 \times 10^{16}$ sec^{-1}

(b) k_2 path:

(i) $E = 14.0$ kcal/mole

(ii) $A = 9.18 \times 10^{5}$ M^{-1}sec^{-1}

The following experimental conditions apply for Tables 93-100 and Figs.85-89.

Concentrations in mole/l of species present.

$[S_2O_8{}^{2-}]_o$ = 0.03919

$[NO_2{}^-]_o$ = 0.07731

$[H_2PO_4{}^-]$ = 0.200 as put in

$[HPO_4{}^{2-}]$ = 0.200 as put in

$[K^+]$ = 0.500

$[Na^+]$ = 0.500

These same conditions apply for the runs involving the decomposition of peroxodisulphate except that there is no nitrite present in this case.

Table 93

Effect of Temperature on Overall Rate (R)

$[S_2O_3^{2-}]$ = 0.01060 mole/l in a

= 0.01091 " in b

= 0.01435 " in c

Temperature (°C)	(a) 55.0		(b) 60.0		(c) 65.0	
Time (min)	Titre	$10^2[S_2O_8^{2-}]$	Titre	$10^2[S_2O_8^{2-}]$	Titre	$10^2[S_2O_8^{2-}]$
5	36.62	3.882	35.35	3.857	26.36	3.781
10	36.40	3.858	34.91	3.809	25.87	3.712
15	-	-	34.57	3.772	25.37	3.641
20	35.80	3.795	34.14	3.725	24.87	3.569
25	-	-	-	-	24.46	3.510
30	35.20	3.731	33.27*	3.630*	24.04	3.450
35	34.92	3.702	33.02	3.602	23.66	3.395
40	34.67	3.675	32.70	3.568	23.22	3.332
45	-	-	-	-	-	-
50	34.20	3.625	-	-	22.53	3.233
60	33.70	3.572	31.33	3.418	-	-

* time 31 minutes

Table 94

Effect of Temperature on Overall Rate (R)

$[S_2O_3^{2-}]$ = 0.01435 mole/l

Temperature (°C)	70.0°		75.0°	
Time (min)	Titre (ml)	$10^2[S_2O_8^{2-}]$	Titre (ml)	$10^2[S_2O_8^{2-}]$
5	25.48*	3.656*	25.29	3.629
10	24.92	3.576	24.27	3.483
15	24.30	3.487	23.23	3.334
20	23.53**	3.377**	22.36	3.209
25	23.02	3.303	21.45	3.078
30	22.49	3.227	20.69	2.969
35	21.92	3.146	19.92	2.859
40	21.40	3.071	19.15	2.748
45	20.89	2.998	18.57	2.668
50	-	-	-	-
60	-	-	-	-

* time 5.5 minutes

** time 21 minutes

Table 95

Decomposition of Peroxodisulphate

Temperature = 55.0°C

$[S_2O_3^{2-}]$ = 0.01061

Time (min)	Titre (ml)	$10^2[S_2O_8^{2-}]$	$2 + \log[S_2O_8^{2-}]$
30	37.07	3.925	0.5938
60	36.91	3.912	0.5924
90	36.75	3.896	0.5906
120	36.67	3.887	0.5896
162	36.63	3.883	0.5891
180	36.56	3.875	0.5883
210	36.52	3.871	0.5878
240	36.52	3.871	0.5878
255	36.46	3.865	0.5871

Table 96

Decomposition of Peroxodisulphate

Temperature = 65.0°

$[S_2O_3^{2-}]$ = 0.01435 mole/l

Time (min)	Titre (ml)	$10^2[S_2O_8^{2-}]$	$2 + \log[S_2O_8^{2-}]$
30	26.69	3.830	0.5832
75	26.07	3.741	0.5730
105	25.57	3.669	0.5646
150	25.01	3.589	0.5550
180	24.58	3.527	0.5474
210	24.19	3.471	0.5404
225	24.03	3.448	0.5376
240	23.78	3.412	0.5331
255	23.64	3.392	0.5305

Table 97

Decomposition of Peroxodisulphate

Temperature = 70.0°C

$[S_2O_3^{2-}]$ = 0.01435 mole/l

Time (min)	Titre (ml)	$10^2[S_2O_8^{2-}]$	$2 + \log[S_2O_8^{2-}]$
15	25.99	3.730	0.5717
30	25.44	3.651	0.5624
60	24.64	3.536	0.5485
90	23.76	3.410	0.5328
180	21.63	3.104	0.4920
210	20.72	2.973	0.4732
225	20.42	2.930	0.4669
240	20.06	2.879	0.4593

Table 98

Decomposition of Peroxodisulphate

Temperature = 75.0°C

$[S_2O_3^{2-}]$ = 0.01435

Time (min)	Titre (ml)	$10^2[S_2O_8^{2-}]$	$2 + \log[S_2O_8^{2-}]$
15	25.92	3.720	0.5705
30	24.95	3.580	0.5539
45	24.03	3.448	0.5376
60	23.21	3.331	0.5225
75	22.36	3.209	0.5063
90	21.58	3.097	0.4909
105	20.83	2.989	0.4755
120	20.12	2.887	0.4605
135	19.48	2.795	0.4464

Table 99

Temperature Effect

(1) k_1 path (Decomposition of Peroxodisulphate)

Temperature(°C)	$\frac{10^3}{T}$ (°K^{-1})	$10^5\ k_1(\text{min}^{-1})$	$5 + \log k_1$
55.0	3.0474	10.67	1.0282
60.0	3.0017	26.10	1.4166
65.0	2.9573	54.71	1.7381
70.0	2.9142	114.2	2.0577
75.0	2.8723	238.4	2.3773

Table 100

Temperature Effect

(2) k_2 path from Overall Reaction

Temperature °C	$\frac{10^3}{T}$(°K^{-1})	10^5R	10^5R_1	10^5R_2	10^2k_2	$2+\log k_2$
55.0	3.0474	6.250	0.430	5.820	1.920	0.2833
60.0	3.0013	8.800	1.022*	7.780	2.570	0.4099
65.0	2.9573	13.50	2.140	11.36	3.730	0.5717
70.0	2.9142	19.05	4.200	14.85	4.900	0.6902
75.0	2.8723	29.05	9.030	20.02	6.590	0.8189

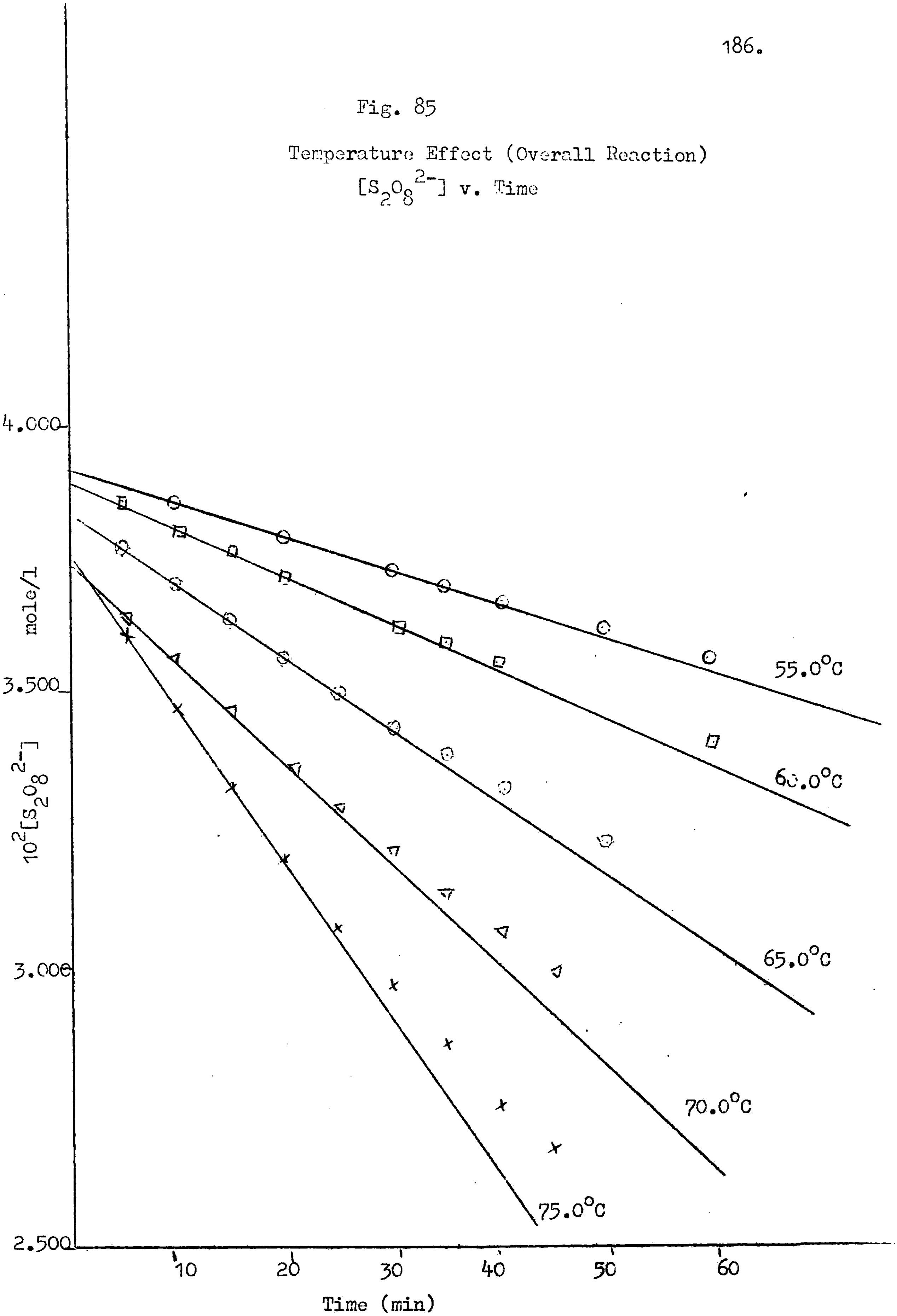
R in units of mole/l/min

k_2 in units of l/mole/min

* calculated from $R_1 = 2.61 \times 10^{-4}[S_2O_8^{2-}]$.

Fig. 85

Temperature Effect (Overall Reaction)
$[S_2O_8^{2-}]$ v. Time



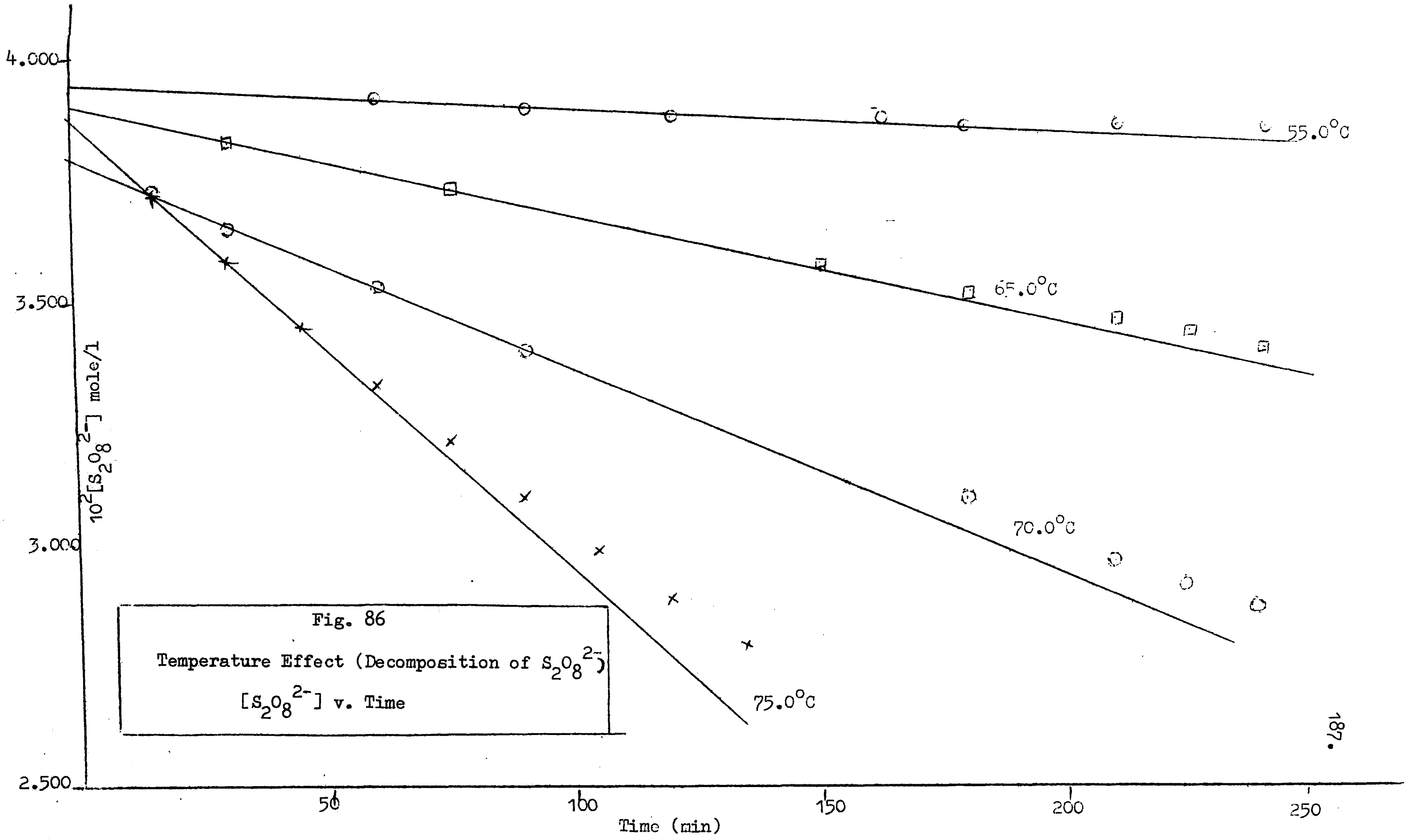


Fig. 86

Temperature Effect (Decomposition of $S_2O_8^{2-}$)

$[S_2O_8^{2-}]$ v. Time

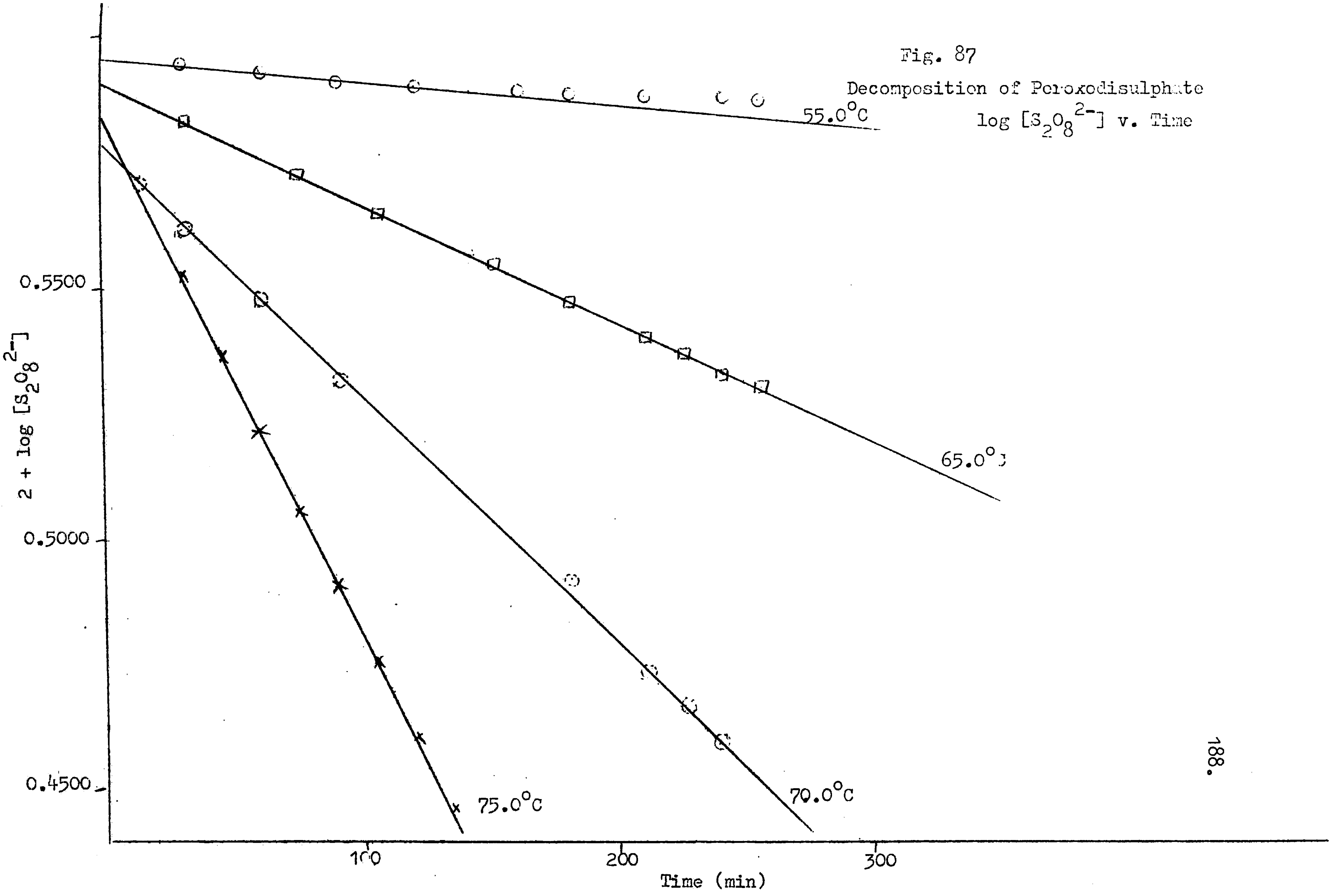


Fig. 87

Decomposition of Peroxodisulphate

log [$S_2O_8^{2-}$] v. Time

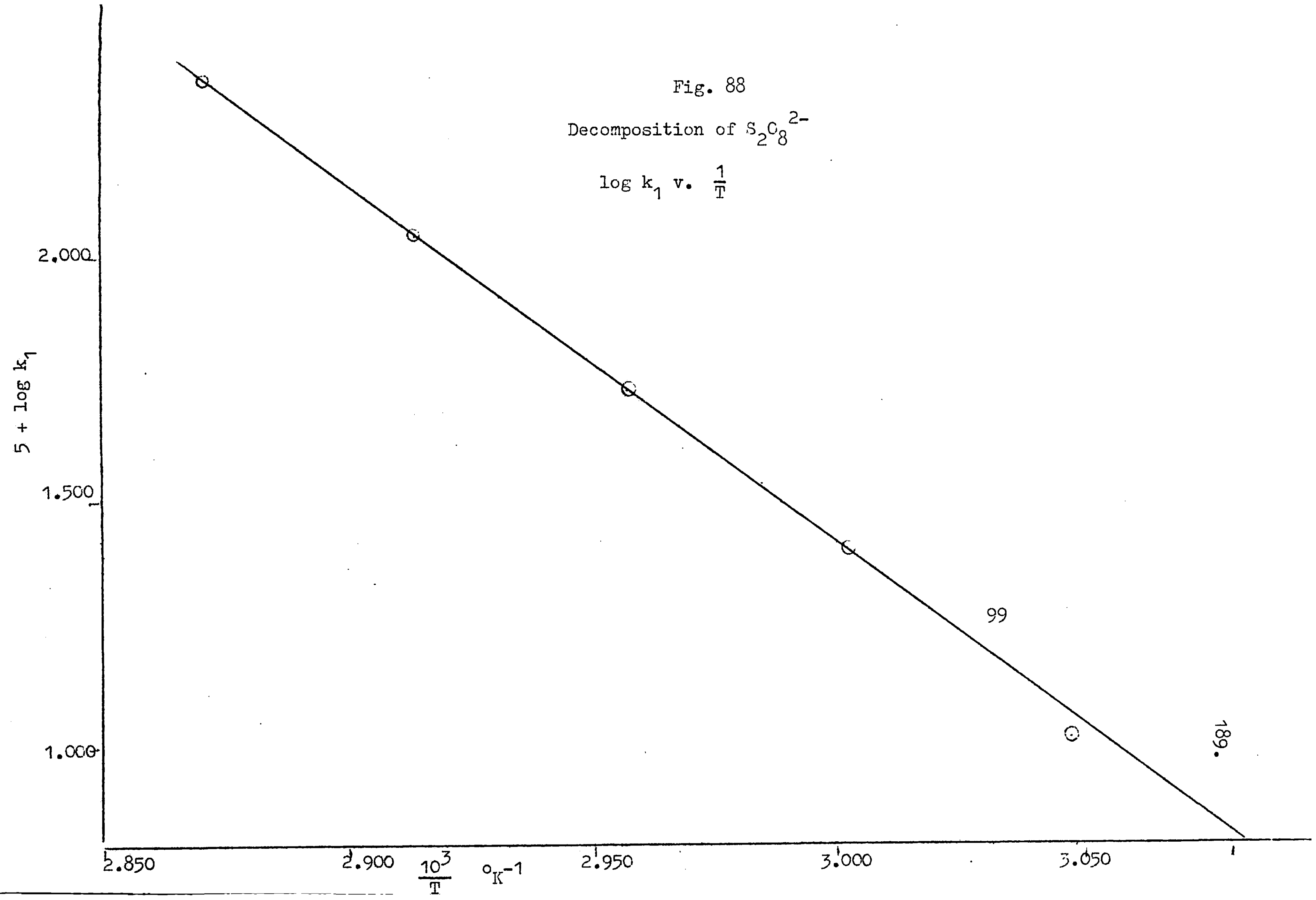


Fig. 88

Decomposition of $S_2O_8^{2-}$

log k_1 v. $\frac{1}{T}$

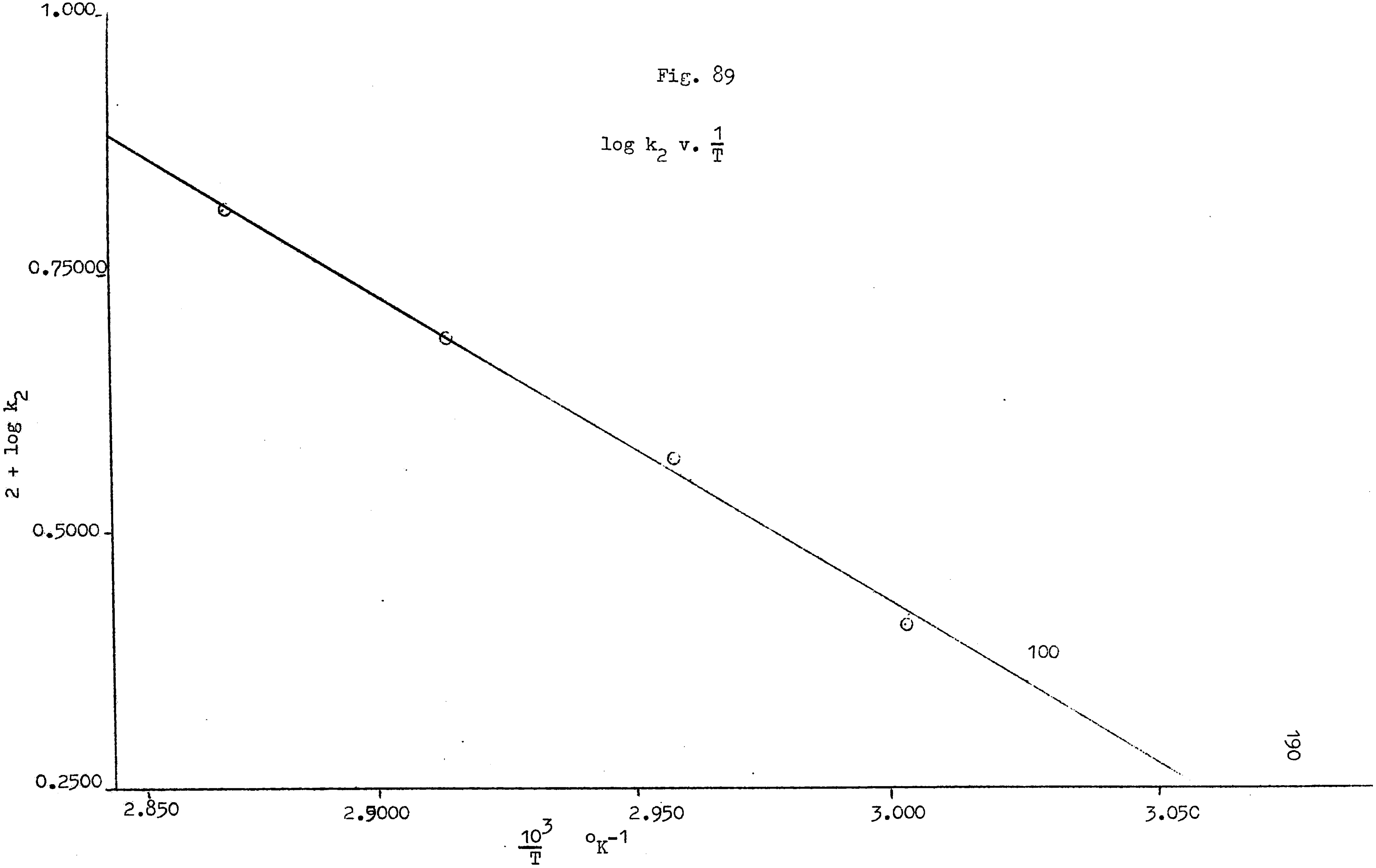


Fig. 89

$\log k_2$ v. $\frac{1}{T}$

Stoicheiometry

The rate law (at constant pH, cation concentration etc.,)

$$R = k_1[S_2O_8^{2-}] + k_2[S_2O_8^{2-}][NO_2^-] \qquad \ldots\ldots \quad [112]$$

shows that peroxodisulphate disappears via two reaction paths and it has been shown that the ratio k_2/k_1 - under certain experimental conditions - is approximately 100 if the concentration units in k_2 are expressed in mole/l. A high concentration of nitrite and a low concentration of peroxodisulphate will be expected to favour the k_2 path. Thus by increasing the ratio $[NO_2^-]/[S_2O_8^{2-}]$ the rate of the k_2 path can be made so high relative to that of the k_1 path, that the latter can be made negligible and therefore any stoicheiometric study under such conditions will be approximately that of the k_2 path.

Table 101 includes the results of two experiments (a and b) in which the ratio $[NO_2^-]/[S_2O_8^{2-}]$ is approximately 20/1 and 40/1 corresponding to relative rates - of the k_2 path to k_1 path - of 100/1 and 200/1 respectively. In these conditions the thermal decomposition of peroxodisulphate can be ignored as a contributor to the reaction. In these two experiments the remaining nitrite was determined by the method of Simpson and Laird (described earlier), after checking for the complete reaction of all the peroxodisulphate by adding a sample to an iodide solution and testing for iodine. The average stoicheiometry (calculated as $S_2O_8^{2-}/NO_2^-$) is 1.005 ± 0.074, which indicates that the two reactants are consumed in equimolar quantities in the k_2 path.

The other experiments reported in Table 101 are similar to many of the actual kinetic runs. In these experiments (c - f) the stoicheiometry of the reaction was studied by estimating both peroxodisulphate and nitrite in the same sample. The method consisted of determining peroxodisulphate in the usual way by reacting it with excess iodide and titrating the liberated iodine with standard thiosulphate solution and then transferring the solution resulting from the titration quantitatively into a volumetric flask and analyzing a sample of this solution for nitrite spectrophotometrically as was described earlier. The reference solution was identical to the sample in all aspects except for the absence of the coupling agent,

The results in Table 101 show that the stoicheiometry of the reaction is variable and that it probably depends on the relative and actual concentrations of the reactants, but it is generally greater than 1.100 under the experimental conditions of the actual kinetic runs. This again confirms that equation [112] is a reasonable rate law, and that peroxodisulphate partly oxidizes nitrite to nitrate (see below) and partly disappears through some other path which is independent of nitrite, and this, probably, is a reaction with water to produce oxygen

$$S_2O_8^{2-} + H_2O = 2SO_4^{2-} + 2H^+ + \tfrac{1}{2}O_2 \qquad \ldots\ldots [2]$$

a reaction which is well established in the absence of nitrite$^{(2)}$. However, two efforts to measure the volume of oxygen evolved accounted for only about 9.24% and 8.81% of peroxodisulphate but because of the small volume of gas involved the results are not very accurate.

Qualitative test for nitrate

Samples of the reaction mixture were acidified and reacted with sulphamic acid to destroy any remaining nitrite until a further addition of the acid gave no nitrogen gas.

$$HNO_2 + HOSO_2NH_2 = N_2 + H_2SO_4 + H_2O \qquad \ldots\ldots [132]$$

The solution was then tested for nitrate (brown ring test). Each time the result was positive.

The stoicheiometry of the k_2 path can therefore be represented by equation [133]

$$S_2O_8^{2-} + NO_2^- + H_2O = 2SO_4^{2-} + NO_3^- + 2H^+ \qquad \ldots\ldots [133]$$

Table 101

	Time (hours)	$[S_2O_8^{2-}]$	$[NO_2^-]$	$S_2O_8^{2-}/NO_2^-$
(a)	0	0.04938	1.0094	
	24	Nil	0.9628	1.060
(b)	0	0.02690	1.0436	
	24	Nil	1.0153	0.950
(c)	0	0.01930	0.1203	
	29	0.00130	0.1058	1.240
(d)	0	0.01930	0.2083	
	29	0.00109	0.1931	1.230
(e)	0	0.07858	0.07000	
	4	0.04926	0.04460	1.154
	6	0.03941	0.03507	1.121
(f)	0	0.07835	0.06901	
	5	0.04240	0.03669	1.114

In all experiments

$[H_2PO_4^-] = [HPO_4^{2-}] = 0.200$ mole/l as put in.

In experiments c - f

$[Na^+] = [K^+] = 0.500$ mole/l
Temperature = 60.0°C

The effect of allyl alcohol

The effect of free radical scavengers on the rate of the reaction was investigated by adding allyl alcohol to a typical reaction mixture. Contrary to what was reported in the abstract mentioned in the beginning of this chapter, the effect of allyl alcohol, in the conditions of the present work, was to increase the rate of loss of peroxodisulphate, possibly because of the effect of the alcohol on the k_1 path. The results of some runs are shown in Table 102 and Fig. 90.

Table 102

All concentration in units of mole/l

$[S_2O_8^{2-}]_o$ = 0.07880

$[NO_2^-]_o$ = 0.06913

$[H_2PO_4^-]$ = $[HPO_4^{2-}]$ as put in

$[Na^+]$ = $[K^+]$ = 0.500 as put in

Temperature = 60.0°C

$[S_2O_3^{2-}]$ = 0.02490

Allyl alcohol	(a) Nil		(b) 0.18		(c) 0.29	
Time (min)	Titre (ml)	$10^2[S_2O_8^{2-}]$	Titre (ml)	$10^2[S_2O_8^{2-}]$	Titre (ml)	$10^2[S_2O_8^{2-}]$
5	31.24	7.780	30.95	7.707	30.65	7.632
10	30.98	7.713	30.59	7.617	30.41	7.572
15	-	-	30.06	7.485	29.96	7.460
16	30.63	7.627	-	-	-	-
20	30.44	7.580	29.71	7.398	29.60	7.370
25	30.12	7.500	29.21	7.273	29.06	7.236
30	29.84	7.430	28.83	7.179	28.56	7.111
35	-	-	28.59	7.119		
10^4R_o (mole/l/mm)	1.41		2.13		2.27	

E.S.R. Measurements

An effort to detect any free radicals or intermediates with unpaired electrons by e.s.r. spectroscopy failed to give any positive results. Radicals like SO_4^- and OH are not likely to give signals because of their short half lives and their low concentration but radicals like NO_2, if present in detectable concentration, were expected to show.

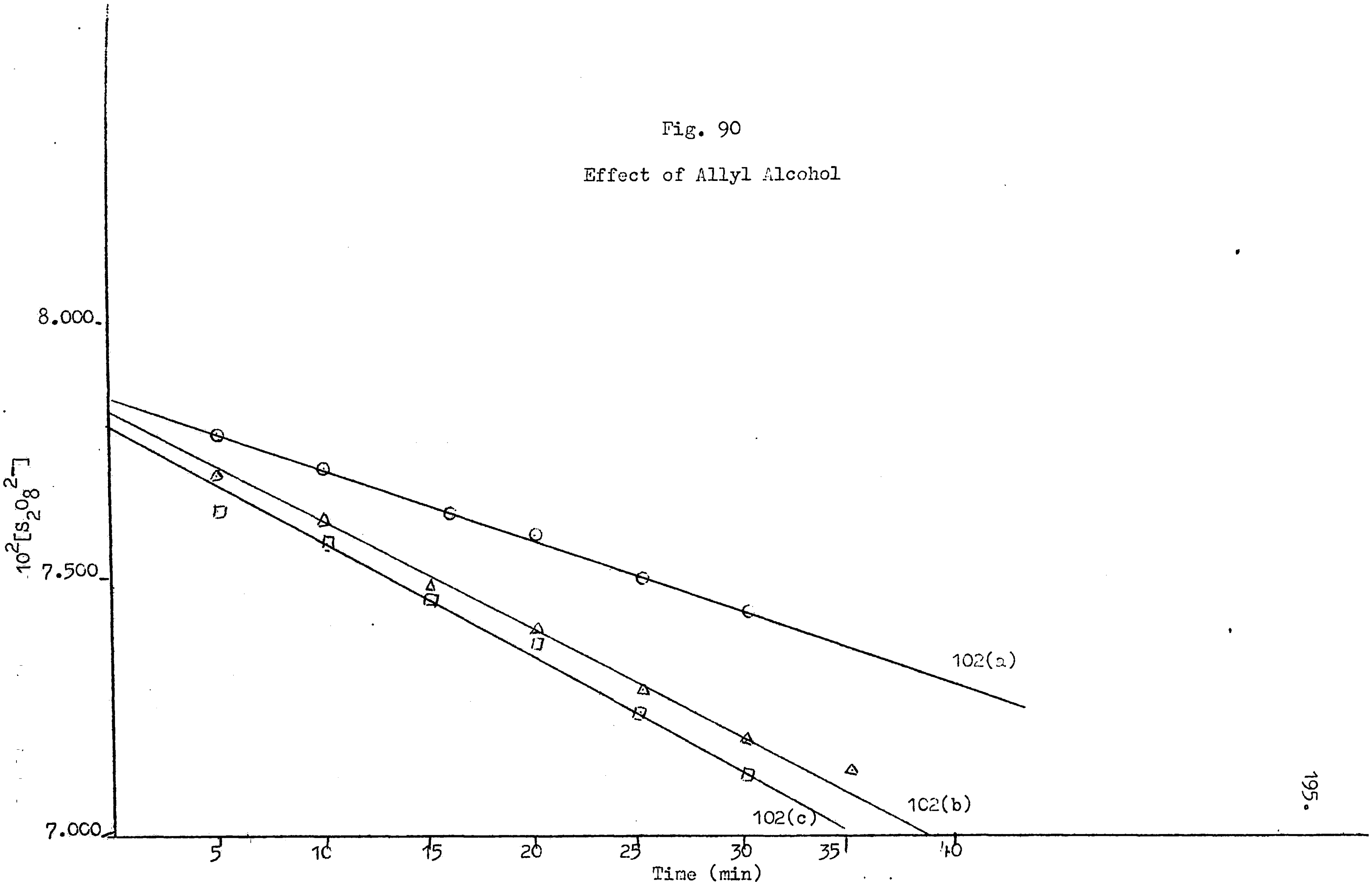


Fig. 90

Effect of Allyl Alcohol

RESULTS AND DISCUSSION

The results of the study of peroxodisulphate nitrite reaction can be summarised as follows:

(1) The reaction is first order in each of the two reactants.

(2) The reaction is sensitive to added salts and the effect depends only on the nature and concentration of cation being first order with respect to it.

The catalytic effect of the three cations studied decreases in the order $Cs^+ > K^+ > Na^+$.

(3) The reaction is independent of pH in the range 8.34 - 5.79.

(4) The rate law for the reaction at constant cation concentration, pH and temperature is

$$R = k_1[S_2O_8^{2-}] + k_2[S_2O_8^{2-}][NO_2^-] \qquad \ldots\ldots \quad [112]$$

where R is the rate of disappearance of peroxodisulphate, but generally the rate law is

$$R = k_1[S_2O_8^{2-}] + \left\{ k_2^o + k_M[M^+] \right\} [S_2O_8^{2-}][NO_2^-] \qquad \ldots\ldots \quad [134]$$

which when expanded gives

$$R = k_1[S_2O_8^{2-}] + k_2^o[S_2O_8^{2-}][NO_2^-] + k_M[M^+][S_2O_8^{2-}][NO_2^-] \qquad \ldots\ldots \quad [135]$$

where k_2^o is the second order rate constant at zero cation concentration and which has the value of $(2.28 \pm 0.05) \times 10^{-3}$ l/mole/m, k_M is the catalytic rate constant for the cation of concentration $[M^+]$ which is present in the reaction mixture and k_1 is the first order rate constant for the thermal decomposition of peroxodisulphate. It was also proved that the effects of cations are additive and that if more than one cation is present in the reaction mixture k_2 is given by

$k_2 = k_2^{o} + k_M[M_1^+] + k_M'[M_2^+]$ ...... [136]

but the maximum number present in the system at the same time was three.

(5) The activation energies for the k_1 path and the k_2 path (at $[Na^+] = [K^+] = 0.500$ mole/l) are 33.5 kcal/mole and 14.0 kcal/mole respectively while the values of A (the frequency factor) are 4.38×10^{16} sec^{-1} and 9.18×10^{5} sec^{-1} respectively.

(6) The stoicheiometry ($S_2O_8^{2-}/NO_2^-$) is variable but under experimental conditions which are more or less similar to those of the actual kinetic runs the stoicheiometry is always greater than 1.100. However, under conditions where nitrite is present in a large excess ($[NO_2^-]/[S_2O_8^{2-}] > 20$) the stoicheiometry is almost 1.000 and this is almost the stoicheiometry of the k_2 path which can be represented as

$S_2O_8^{2-} + NO_2^- + H_2O = NO_3^- + 2SO_4^{2-} + 2H^+$ ...... [137]

Proposed Mechanisms:

From equation [135] it is seen that there are three different paths for the disappearance of peroxodisulphate, the first of which is apparently independent of nitrite while the other two are nitrite dependent.

(1) $k_1$path:

The path involves the thermal decomposition of peroxodisulphate. This as was shown in Chapter I produces oxygen according to the mechanism

$S_2O_8^{2-} \longrightarrow 2SO_4^-$ ...... [5]

$SO_4^- + H_2O \longrightarrow SO_4^{2-} + H^+ + OH$ ...... [6]

$OH + S_2O_8^{2-} \longrightarrow HSO_4^- + SO_4^- + O$ ...... [8]

$OH + SO_4^- \longrightarrow HSO_4^- + O$ ...... [9]

$O + O \xrightarrow{\text{solvent}} O_2$ ...... [10]

It was also argued in the previous chapter that the most likely encounter of SO_4^- is with the solvent which leads to equations [6]. However, OH radicals may proceed to react according to equations 8-10 but the simplest reaction that it can undergo in the presence of a reducing agent is to accept an electron to form the stable OH^- ion. Hence

$$OH + NO_2^- \longrightarrow NO_2 + OH^- \qquad \ldots\ldots [138]$$

followed by the disproportionation of NO_2 according to the stoicheiometry

$$2NO_2 + H_2O \longrightarrow NO_3^- + NO_2^- + 2H^+ \qquad \ldots\ldots [139]$$

and formally

$$OH^- + H^+ \longrightarrow H_2O \qquad \ldots\ldots [39]$$

Therefore it is likely that in the presence of nitrite at least some OH radicals do not end up forming oxygen and this may explain why it was not possible to account for all the peroxodisulphate used up in the k_1 path by oxygen measurement.

(2) k_2^o path:

In this path the rate determining step is the bimolecular reaction between peroxodisulphate and nitrite according to either of the schemes (a) or (b).

(a)

$$S_2O_8^{2-} + NO_2^- = [S_2O_8NO_2]^{3-} = NO_2^+ + 2SO_4^{2-} \text{ slow} \qquad \ldots\ldots [140]$$

$$NO_2^+ + OH^- = NO_3^- + H^+ \quad \text{fast} \qquad \ldots\ldots [141]$$

or possibly

$$NO_2^+ + H_2O = NO_3^- + 2H^+ \quad \text{fast} \qquad \ldots\ldots [142]$$

(b)

$$S_2O_8^{2-} + NO_2^- = [S_2O_8NO_2]^{3-} \quad \text{slow} \qquad \ldots\ldots [143]$$

followed by a fast reaction involving water and resulting in a partial breakdown towards the same products as in (a);

$$H_2O + [S_2O_8NO_2]^{3-} \xrightarrow{fast} \text{products} \qquad \text{......} \quad [144]$$

and possibly (see (1) above)

$$SO_4^{-} + H_2O \longrightarrow HSO_4^{-} + OH \qquad \text{......} \quad [6]$$

$$OH + NO_2^{-} \longrightarrow NO_2 + OH^{-} \qquad \text{......} \quad [138]$$

Both mechanisms (a) and (b) give the rate as

$$\text{Rate} = k[S_2O_8^{2-}][NO_2^{-}] \qquad \text{......} \quad [145]$$

where k can either be k_{140} or k_{143} respectively and this equation is similar to the second term on the right hand side of equation [135].

(3) k_M path:

This path probably involves the cation and the two reacting anions or species derived from them in the rate determining step. The first step would be for the cation and peroxodisulphate, (which is a divalent negative ion in contrast to the monovalent nitrite), to form an ion-pair and this is naturally a fast equilibrium.

$$S_2O_8^{2-} + M^{+} \underset{}{\overset{Ke}{\rightleftharpoons}} MS_2O_8^{-} \qquad \text{......} \quad [146]$$

The ion-pair could well react with nitrite much faster than the non-ion-paired peroxodisulphate ion - because of the reduced charge and hence the reduced repulsion (and see below) - and the resulting activated complex breaks down into NO_2^{+}, SO_4^{2-} and MSO_4^{-}

$$MS_2O_8^{-} + NO_2^{-} \longrightarrow [S_2O_8MNO_2]^{2-} \longrightarrow NO_2^{+} + SO_4^{2-} + MSO_4^{-} \quad \text{slow}$$

$$\text{......} \quad [147]$$

followed by

$$NO_2^{+} + OH^{-} \longrightarrow NO_3^{-} + H^{+} \qquad \text{fast} \qquad \text{......} \quad [141]$$

or one of the other alternatives given before.

$$\text{Rate} = k[MS_2O_8^{-}][NO_2^{-}] \qquad \text{......} \quad [148]$$

but

$$Ke = \frac{[MS_2O_8^{-}]}{[S_2O_8^{2-}][M^{+}]} \qquad \text{......} \quad [149]$$

Therefore

$$[MS_2O_8^-] = Ke[M^+][S_2O_8^{2-}] \qquad \ldots\ldots \quad [150]$$

and hence $[MS_2O_8^-]$ is linearly related to $[M^+]$ at constant $[S_2O_8^{2-}]$.

Substituting [150] in [148] gives

$$\text{Rate} = kKe[M^+][S_2O_8^{2-}][NO_2^-] \qquad \ldots\ldots \quad [151]$$

and provided Ke is not large, not much peroxodisulphate is present in ion-paired form, equation [151] is similar to the third term on the right hand side of equation [135] when k_M is set equal to kKe.

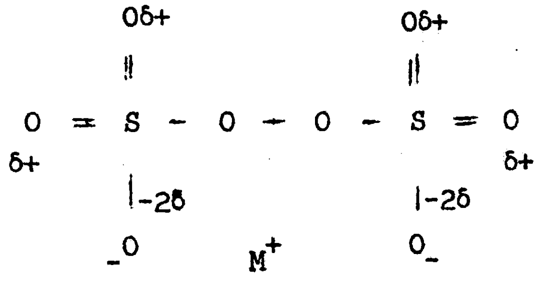
$$k_M = kKe \qquad \ldots\ldots \quad [152]$$

The maximum value of Ke which could lead to this situation would be about 1 (see below).

Under the experimental conditions of the kinetic runs the k_M path is the more dominant and the catalytic effect of the cation may be due to two reasons:

(a) The presence of the cation as part of the activated complex reduces the Coulombic force of repulsion between the two anions and therefore enhances the rate of reaction.

(b) The ion-pair which is formed between the cation (M^+) and peroxodisulphate ion can be represented as follows



The presence of M^+ causes polarization of the peroxodisulphate ion creating a concentration of negative charge towards the centre of the ion and a depletion of negative charge towards the outside making the outer parts partially positive. This system, therefore, becomes a better electron acceptor than the unassociated peroxodisulphate ion(45). The transfer of electrons from nitrite to peroxodisulphate is thus enhanced by ion-pairing, resulting in the relatively low activation energy. Because of the structure of peroxodisulphate ion cations of smaller size are expected to cause more polarization than those of larger size. Although there is no direct way of measuring the radii of hydrated ions, conductivity measurements(45) and other methods (60) indicate that the radii of hydrated cations increase in the order $Cs^+ < K^+ < Na^+ < Li^+$. Therefore Cs^+ is the smallest of the three cations studied in this work while Na^+ is the largest. Hence Cs^+ causes more polarization of peroxodisulphate ion than does K^+ and this in turn causes more than Na^+. All this explains why the catalytic effect of the three cations decreases in the order $Cs^+ > K^+ > Na^+$.

The stability of the ion-pair $MS_2O_8^-$ is also related to the size of M^+. Small cations are expected to form more stable ion-pairs than large cations and therefore the stability of ion-pairs formed by the three cations should decrease in the order $Cs^+ > K^+ > Na^+$ and hence the value of Ke (equation [151]) is expected to decrease in the same order and so is the value of k_M.

The known Ke values(67) for $NaSO_4^-$, KSO_4^- and the corresponding thiosulphates are (i) correctly in order to be consistent with kinetic effect $K^+ > Na^+$, (ii) of the order of unity at the ionic strengths used here, thus satisfying the condition necessary for the validity of equation [151].

Therefore equation [152] leads to the same conclusion that the catalytic effect of the cations should decrease in the order $Cs^+ > K^+ > Na^+$ as was found experimentally.

CHAPTER IV

THE OXIDATION OF CHROMIUM(III)

CHAPTER IV

INTRODUCTION

The silver(I) catalyzed oxidation of chromium(III) - in the form of chrome alum - by peroxodisulphate was studied by Yost (see Chapter I). Frennesson and Fronaeus(61) studied the reaction in the absence of silver(I) using chromium(III) perchlorate, in an acid perchlorate medium in the pH range 0.5 - 3 at 60°C. These authors formulated the following rate law for the reaction

$$\frac{d[Cr(VI)]}{dt} = \beta \frac{[Cr(III)][S_2O_8{}^{2-}]}{1 + \gamma\,[Cr(III)]} \qquad \ldots\ldots \quad [153]$$

in which β and γ are constants. This equation however is similar to equation [24] which was proposed by Fronaeus and Ostman for the cerium(III)-peroxodisulphate reaction. The integration of equation [153] gives [154]

$$\frac{k_{obs}}{[S_2O_8{}^{2-}]_o - [S_2O_8{}^{2-}]_t} \ln \frac{[Cr(III)]_o}{[Cr(III)]_t} = \beta - \gamma\, \frac{k_{obs}\,[Cr(VI)]_t}{[S_2O_8{}^{2-}] - [S_2O_8{}^{2-}]_t} \qquad \ldots\ldots \quad [154]$$

which may be simplified into [155]

$$A = \beta - \gamma B \qquad \ldots\ldots \quad [155]$$

By calculating the quantities A and B for different values of time, t, and plotting A against B the authors obtained an approximately straight line passing roughly through points calculated for all their series of measurements.

The authors proposed the following mechanism for the reaction in which the radicals formed in the uncatalyzed decomposition of peroxodisulphate are effective in the rate determining step

$$S_2O_8{}^{2-} + H_2O = HSO_4{}^- + OH + SO_4{}^- \qquad \ldots\ldots \quad [23]$$

$$OH \longrightarrow \text{Products} \qquad \ldots\ldots \quad [156]$$

$$SO_4{}^- + Cr(III) \longrightarrow SO_4{}^{2-} + Cr(IV) \qquad \ldots\ldots \quad [157]$$

$$OH + Cr(III) \longrightarrow OH^- + Cr(IV) \qquad \ldots\ldots \quad [158]$$

$$HS_2O_8{}^- + H_2O \longrightarrow H^+ + HSO_4{}^- + HSO_5{}^- \qquad \ldots\ldots \quad [159]$$

$$H^+ + HSO_5{}^- + Cr(IV) \longrightarrow SO_4{}^{2-} + Cr(VI) + H_2O \qquad \ldots\ldots \quad [160]$$

$$HSO_5{}^- \longrightarrow HSO_4{}^- + \tfrac{1}{2}O_2 \qquad \ldots\ldots \quad [161]$$

Steps [157] and [158] are postulated to be slower than [160] in order to explain the limited dependence of rate of oxidation on pH. However, reactions [160] and [161] are not necessarily single steps.

In the present work (and this was the first reaction attempted) some of the work of these authors was repeated to see if their results could be reproduced and to find out what other species involving chromium(III) could be studied.

THE OXIDATION OF CHROMIUM(III) PERCHLORATE

Experimental and Results

Chemicals

All chemicals - unless otherwise stated - were Analar Grade.

Preparation of Solutions

(1) Chromium(III) Perchlorate: This salt was prepared by the method of Altman and King(62). Chromium trioxide and formic acid were allowed to react in the presence of conc. perchloric acid. The product which crystallised from the reaction mixture was washed with conc. perchloric acid and recryztallized twice from 0.5 mole/l aqueous perchloric acid. It was then dried under vacuum and kept in a desiccator because the compound is deliquescent A calculated amount of the solid was dissolved in an appropriate volume of distilled water to prepare a stock solution of chromium(III) perchlorate. The exact concentration of chromium(III) was determined by oxidizing a measured volume of the stock solution with potassium peroxodisulphate in the presence of silver sulphate as a catalyst at 60°C in an acidic medium and determining the concentration of chromium(VI) spectrophotometrically(61).

(2) Cerium(IV) Sulphate Solution: This was prepared from ceric ammonium nitrate(63). Cerium(IV) hydroxide was precipitated from a solution of the reagent grade salt by the addition of a slight excess of ammonia solution. The washed precipitate was dissolved in dilute sulphuric acid and made up to the required volume. It was standardized using sodium oxalate and ferrous sulphate. A concentrated solution was observed to form a precipitate on

standing for a few days. However, dilute acidified solutions were unchanged in appearance and concentration for several months.

(3) Iron(II) Sulphate Solution: This solution was standardized simultaneously with ceric sulphate solution. It was restandardized before each kinetic run or runs because its concentration tends to decrease daily by about 0.4% due to atmospheric oxidation.

Analytical Method and Results

For each kinetic run two solutions, A and B were prepared. A contained 0.720 mole/l perchloric acid and was prepared by approximately diluting a mixture of measured volumes of the stock solution of chromium(III) perchlorate and perchloric acid (12.00 mole/l). Solution B contained accurately weighed amounts of ammonium peroxodisulphate and sodium perchlorate. The perchlorate concentration was 1.000 mole/l.

Solution B was usually prepared fresh every day and was never used more than 48 hours after preparation.

The two solutions were thermostatted separately at 60°C for 30 minutes. The reaction was started by mixing 25 ml of A and 25 ml of B in a 100 ml round bottomed Quick-fit flask. Zero time was taken as the time when the pipette delivering the second reactant (B) was half empty.

5 ml samples were withdrawn at appropriate intervals, added to ice cold water to quench the reaction and analysed for chromium(VI) or peroxodisulphate. Chromium (VI) was determined spectrophotometrically, while peroxodisulphate was estimated by cerimetric titration.

Haupt et. al.(64) report that acidic solutions which are less than 4×10^{-4} mole/l in chromium(VI) obey Beer's Law between 230 and 350 nm indicating no interference from the condensation dimerization of $HCrO_4^-$ to $Cr_2O_7^{2-}$. Altman and King(62) also analyzed for chromium(VI) in acidic medium at 351 nm where the molar absorbancy indices for chromium(III) and chromium (VI) are 2-3 and 1600 respectively and where the extinction coefficients of $HCrO_4^-$ and $\frac{1}{2}Cr_2O_7^{2-}$ are similar in magnitude. This is supported by the known equilibrium constants and extinction coefficients for the acid chromate/dichromate system$^{(65)}$. Thus with an equilibrium constant $K = [HCrO_4^-]^2/[Cr_2O_7^{2-}] = 0.03$, $Cr_2O_7^{2-}$ is well over 99% hydrolysed to $HCrO_4^-$ at 3×10^{-4} mole/l.

Figure 91 shows that a solution of potassium dichromate which is approximately 2×10^{-4} mole/l and which is also about 0.05 mole/l in $NaClO_4$ and of pH about 2 has a maximum absorbancy at 350 nm. Moreover Figs. 92 -96 in which the absorbance of solutions of potassium dichromate of ionic strength and pH similar to those of kinetic runs are plotted against the respective concentrations confirm that such solutions obey Beer's Law. These plots do not pass exactly through the origin because the reference cell contains distilled water, whereas the measured beam passes through a solution containing Cr(VI) and fairly high concentrations of dissolved salts. The same measuring system was used for calibration and kinetic purposes.

For the determination of chromium(VI), the quenched sample was diluted to 25 ml (or some other known volume), thermostatted at 25°C, its absorbance at 350 nm measured using a Unicam SP.500 spectrophotometer, and the chromium(VI) concentration read from the calibration graphs.

For the determination of the concentration of peroxodisulphate, purified nitrogen gas was bubbled through the quenched sample for 10 minutes to drive out dissolved oxygen. A measured volume of standard iron(II) sulphate was added. Chromium(VI) was reduced quickly, judged by the immediate disappearance of its colour. After about 20 minutes more dilute H_2SO_4 was added and the excess iron(II) was titrated against standard cerium(IV) sulphate to a ferroin end point using a 10 ml semi-micro burette. In this way the concentration of the total oxidant was calculated and knowing the concentration of

Fig. 91

Absorbance of 1 x 10^{-4} mole/l $K_2Cr_2O_7$ (pH ≃ 2) v. λ

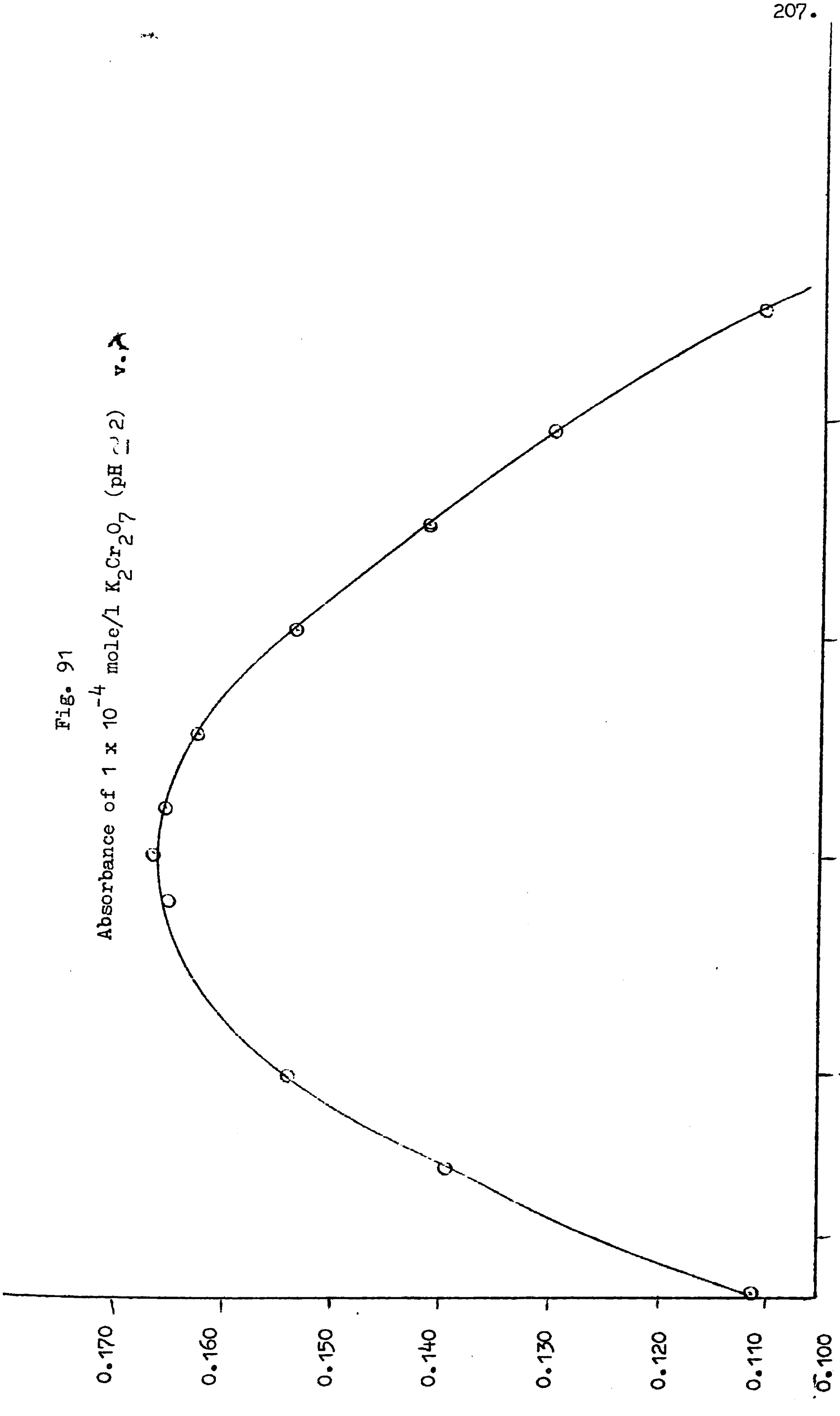


Fig. 92

Calibration Graph for the Standardization of Cr(III) Stock Solution

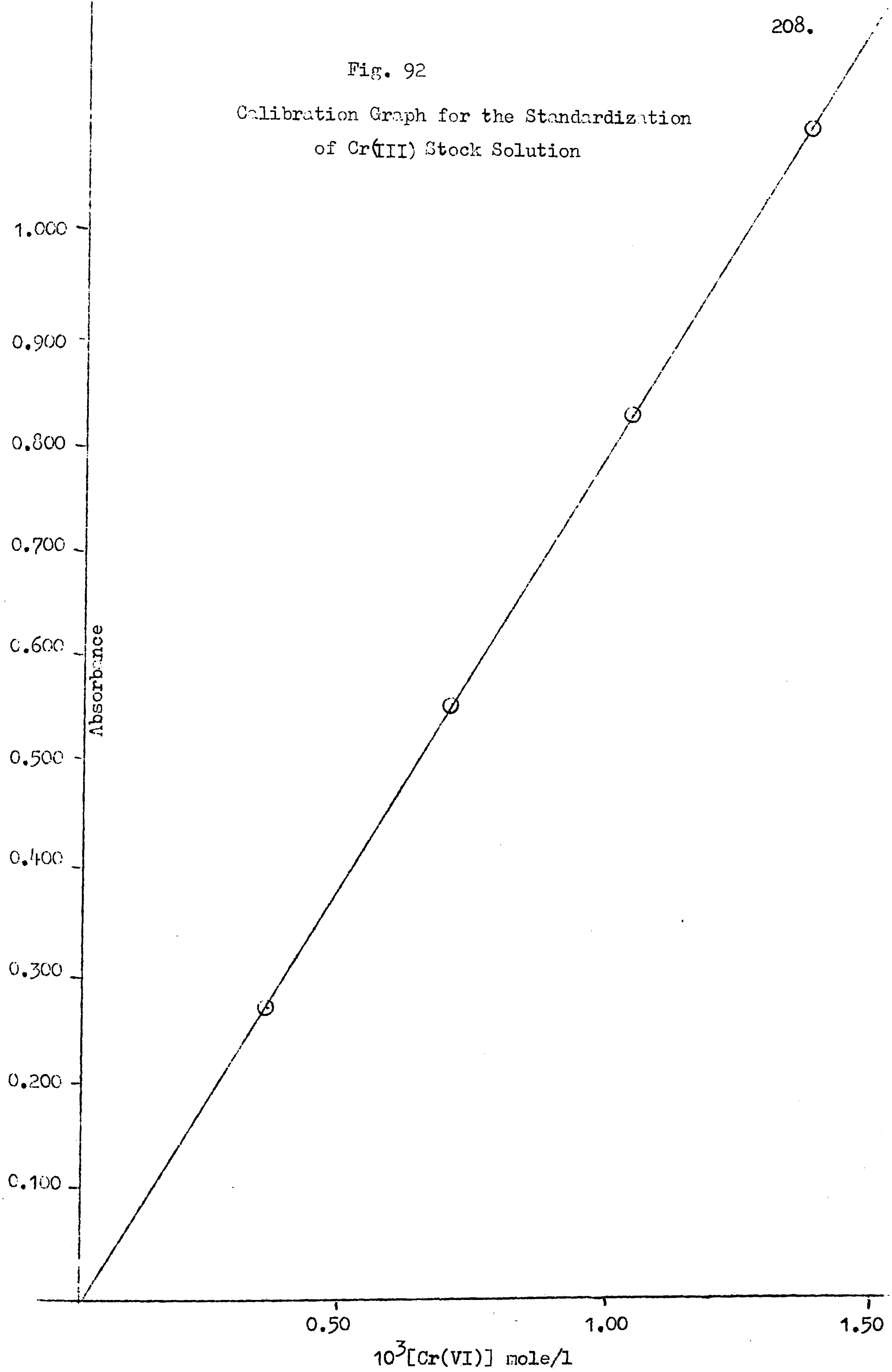


Fig. 93

Calibration Graph for 103-5, 111-2, 116-9

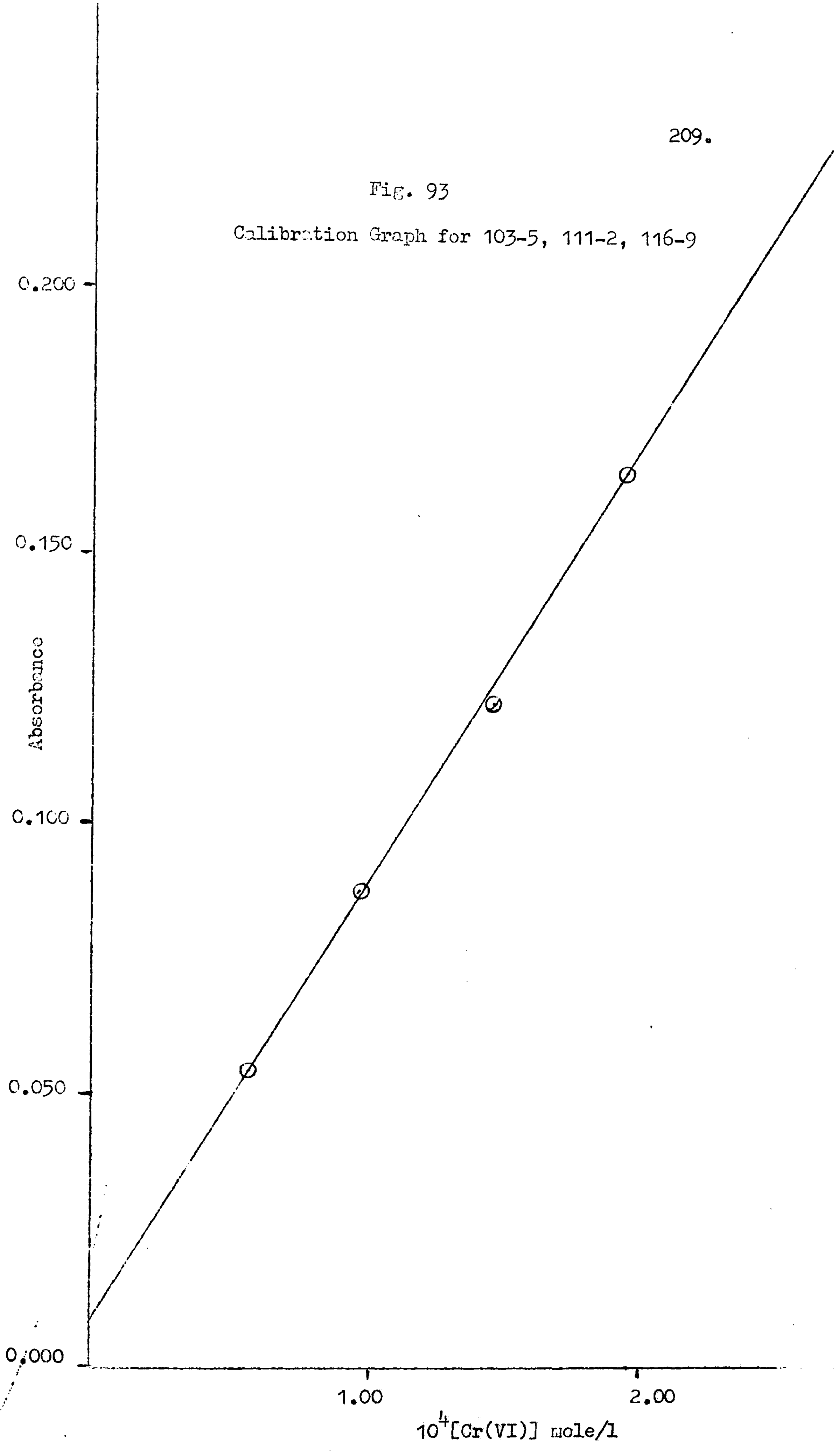


Fig. 94

Calibration Graph for 106-7 and 110

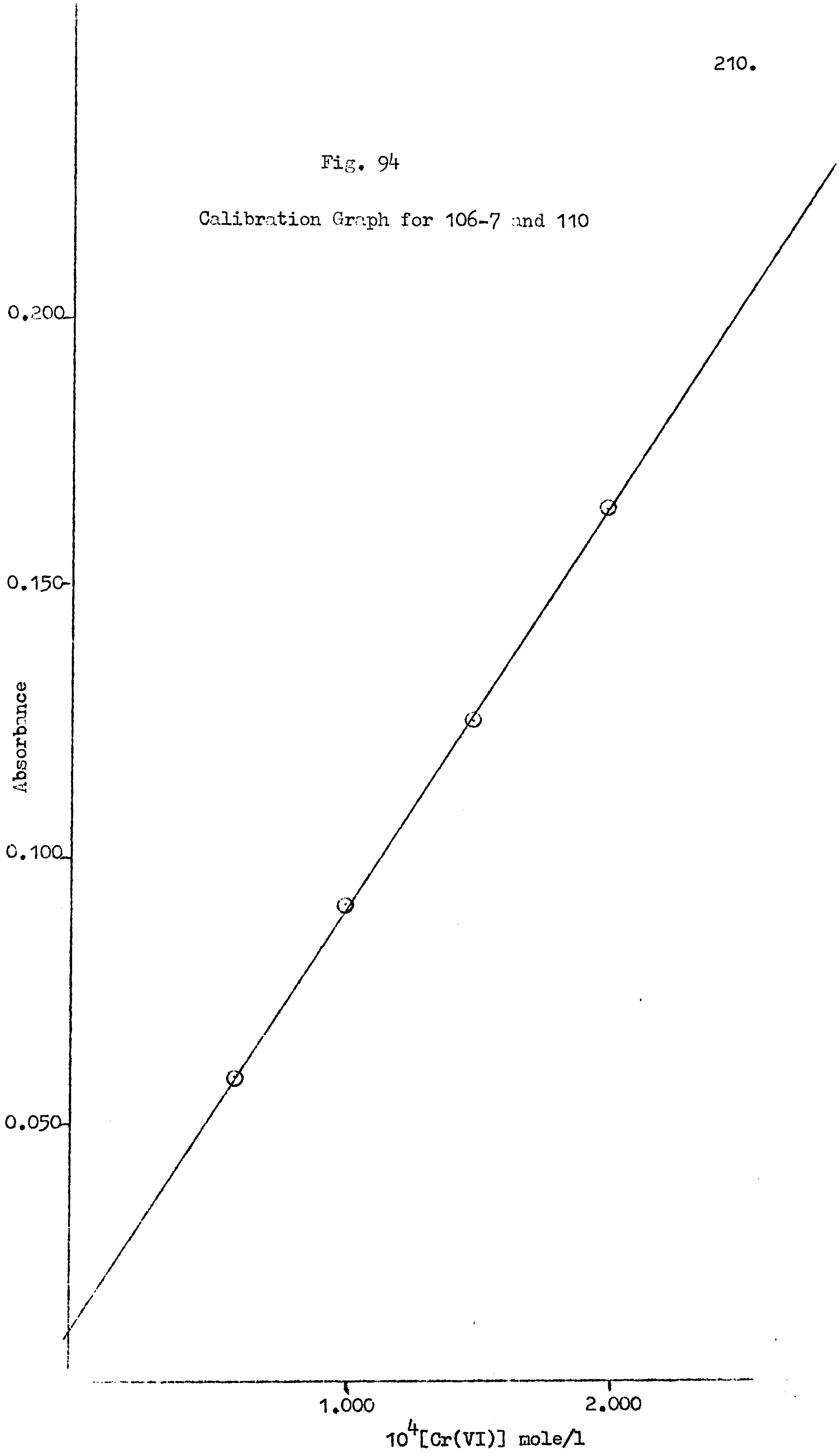
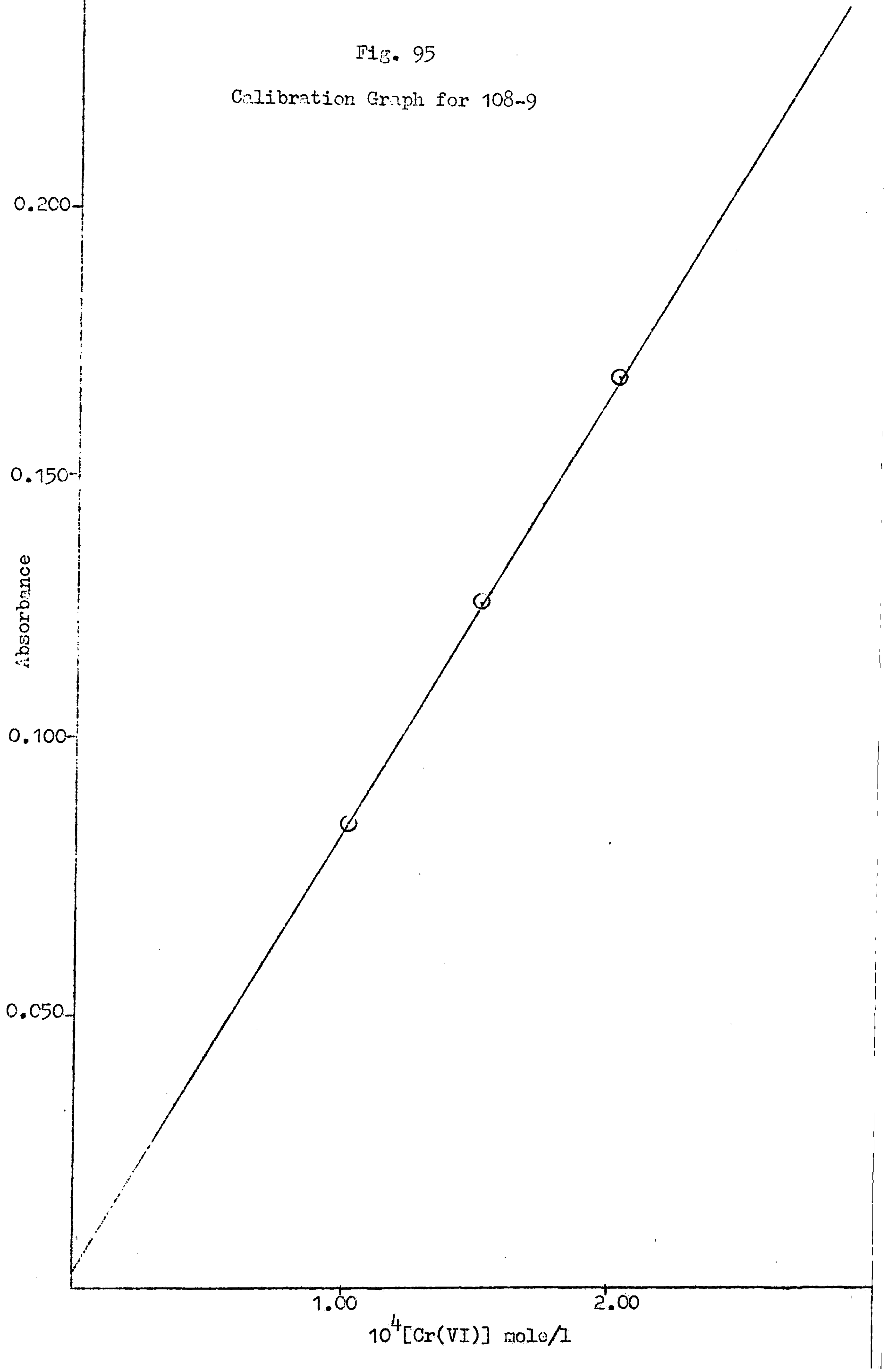


Fig. 95

Calibration Graph for 108-9



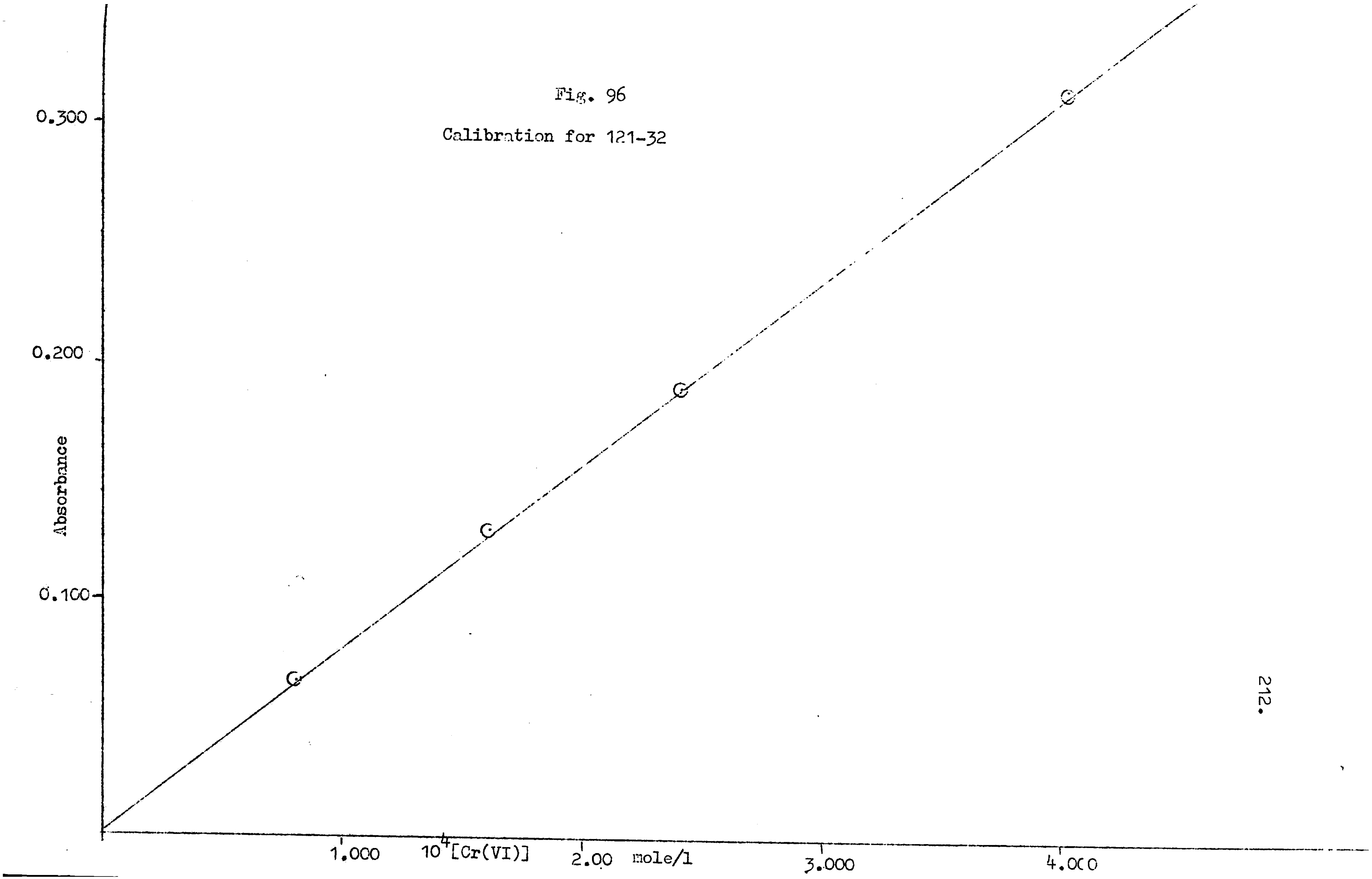


Fig. 96

Calibration for 121-32

chromium(VI), from a plot of its concentration versus time, the concentration of peroxodisulphate in the sample was calculated.

The initial rates of formation of chromium(VI) and the disappearance of peroxodisulphate were determined from a plot of the concentration of the respective ion against time after allowing for any induction period.

Tables 104-112 and the corresponding plots (Figs. 97-102) show the results of some runs made at a constant pH. A plot of initial rate of appearance of chromium(VI) versus initial peroxodisulphate concentration (Fig.103) shows that at a constant initial chromium(III) concentration of 4.000×10^{-3} mole/l the reaction is first order in peroxodisulphate with a first order rate constant of 2.75×10^{-4} min^{-1}. This value is close to the value of 2.61×10^{-4} min^{-1} which is the value of the first order rate constant for the uncatalyzed (i.e. H^+ independent) decomposition of peroxodisulphate at 60°C reported elsewhere in this work. Therefore it looks possible that the reaction under these conditions has its rate determining step in the uncatalyzed decomposition of peroxodisulphate. The plot of $\log[S_2O_8^{2-}]$ versus time gives an overall observed first order rate constant of the order of 10^{-3} min^{-1}, depending on the initial concentration of peroxodisulphate. This constant is defined by equation [18] of Kolthoff and Miller

$$K_{obs} = k_1 + k_H[H^+] \qquad \ldots\ldots \quad [18]$$

In Table 115 the calculated values of A and B of equation [155] **at different t values** (Table 114) are reported and in Fig. 104 A is plotted again B for two representative runs. A look at this plot and the Table 115 shows that the rate law given by equation [153] is obeyed above t values of 100 minutes. Moreover the two plots are almost parallel to each other rather than a continuation of one another as was suggested by Frennesson and Fronaeus.

The following experimental conditions apply for Tables 103-115.

All concentrations in units of mole/l.

$[HClO_4]$ = 0.360
$[NaClO_4]$ = 0.500
Temperature = 60.0°C

Table 103

$[Cr(III)]_o = 4.000 \times 10^{-3}$
$[S_2O_8^{2-}]_o = 3.000 \times 10^{-2}$

5 ml sample diluted to 50 ml for spectrophotometric measurements.

Time (min)	Absorbance	10^3[Cr(VI)]
60	0.029	0.26
120	0.069	0.77
180	0.106	1.24
240	0.136	1.62
300	0.151	1.81
360	0.168	2.03
420	0.181	2.19
480	0.193	2.34

Table 104

$[Cr(III)]_o = 4.000 \times 10^{-3}$
$[S_2O_8^{2-}]_o = 2.000 \times 10^{-2}$

5 ml sample diluted to 50 ml

Time (min)	Absorbance	10^3[Cr(VI)]
60	0.023	0.19
120	0.036	0.35
180	0.054	0.58
240	0.062	0.68
300	0.070	0.78
360	0.074	0.83
420	0.084	0.96
480	0.084	0.96
450	0.091	1.05

Table 105

$[Cr(III)]_o = 4.000 \times 10^{-3}$
$[S_2O_8^{2-}]_o = 4.000 \times 10^{-2}$

5 ml sample diluted to 50 ml.

Time (min)	Absorbance	10^3[Cr(VI]
60	0.052	0.54
120	0.106	1.23
180	0.148	1.77
240	0.175	2.12
300	0.201	2.45
360	0.224	2.75
420	0.230	2.83
480	0.239	2.94
540	0.251	3.10

Table 106

$[Cr(III)]_o = 4.000 \times 10^{-3}$
$[S_2O_8^{2-}]_o = 0.5000 \times 10^{-2}$

Time (min)	Absorbance	10^3[Cr(VI]
120	0.029	0.13
180	0.040	0.20
240	0.044	0.23
300	0.054	0.29
360	0.059	0.325
420	0.066	0.365
480	0.068	0.385
540	0.072	0.405

Table 107

$[Cr(III)]_o = 4.000 \times 10^{-3}$
$[S_2O_8^{2-}]_o = 1.000 \times 10^{-2}$

Time (min)	Absorbance	$10^3[Cr(VI)]$
60	0.029	0.13
120	0.055	0.30
180	0.082	0.465
240	0.092	0.54
300	0.113	0.665
360	0.126	0.745
420	0.135	0.805
480	0.150	0.90

Table 108

$[Cr(III)]_o = 4.000 \times 10^{-3}$
$[S_2O_8^{2-}]_o = 7.500 \times 10^{-2}$

5 ml sample diluted to 50 ml

Time (min)	Absorbance	$10^3[Cr(VI)]$
10	0.020	0.110
20	0.047	0.465
30	0.052	0.535
40	0.073	0.810
50	0.093	1.01
60	0.107	1.26
70	0.122	1.46
80	0.137	1.67
90	0.152	1.84

Table 109

$[Cr(III)]_o = 4.000 \times 10^{-3}$
$[S_2O_8^{2-}]_o = 10.00 \times 10^{-2}$

5 ml sample diluted to 50 ml

Time (min)	Absorbance	$10^3[Cr(VI)]$
10	0.019	0.19
20	0.042	0.46
30	0.069	0.76
41	0.090	1.04
50	0.107	1.24
60	0.123	1.43
70	0.141	1.64
80	0.157	1.84
90	0.170	2.00

Table 110

$[Cr(III)]_0 = 4.000 \times 10^{-3}$

$[S_2O_8^{2-}]_0 = 2.000 \times 10^{-2}$

$[Fe(II)] = 0.07800$ (10 ml)

$[Ce(IV)] = 0.07597$

Time (min)	Absorbance	$10^3[Cr(VI)]$	Titre (ml)	$10^2[S_2O_8^{2-}]$	$2 + \log[S_2O_8^{2-}]$
30	0.035	0.17	-	-	-
60	-	0.33	7.84	1.795	0.2541
90	0.085	0.485	-	-	-
120	-	0.61	7.88	1.722	0.236
180	-	0.875	8.045	1.556	0.1920
330	-	1.40	8.385	1.210	0.0828
360	0.244	1.50	-	-	-

Table 111

$[Cr(III)]_0 = 4.000 \times 10^{-3}$

$[S_2O_8^{2-}]_0 = 3.000 \times 10^{-2}$

$[Fe(II)] = 0.07825$ (5 ml)

$[Ce(IV)] = 0.04219$

Time (min)	Absorbance	$10^3[Cr(VI)]$	Titre (ml)	$10^2[S_2O_8^{2-}]$	$2 + \log[S_2O_8^{2-}]$
30	0.027	0.15	-	-	-
60	-	0.46	2.82	2.654	0.4239
90	0.076	0.84	-	-	-
120	-	1.02	3.22	2.400	0.3802
150	0.105	1.22	-	-	-
240	-	1.72	-	-	-
270	0.154	1.85	-	-	-
300	-	2.00	4.51	1.710	0.2330
360	0.185	2.24	-	-	-

Table 112

$[Cr(III)]_o$ = 4.000×10^{-3}
$[S_2O_8^{2-}]_\infty$ = 4.000×10^{-2}
[Fe(II)] = 0.07825 (10 ml)
[Ce(IV)] = 0.04219

Time (min)	Absorbance	$10^3[Cr(VI)]$	$10^3[Cr(III)]$	3 + log[Cr(III)]	Titre (ml)	$10^2[S_2O_8^{2-}]$	2 + $\log[S_2O_8^{2-}]$
30	0.036	0.33	3.67	0.5647	-	-	-
60	-	0.66	-	-	0.637	3.545	0.5496
90	0.088	0.98	3.02	0.4800	-	-	-
120	-	1.28	-	-	1.36	3.147	0.4979
150	0.132	1.56	2.44	0.3874	-	-	-
240	-	2.15	-	-	11.96	2.457	0.3902
270	0.193	2.35	1.65	0.2175	-	-	-
300	-	2.50	-	-	3.54	2.044	0.3104
360	0.227	2.79	1.21	0.0828	-	-	-

Table 113

$[Cr(III)]_o$ = 4.000×10^{-3}

$10^2[S_2O_8^{2-}]$	10^5 R* mole/l/min	10^3 k_{obs} min^{-1}
0.500	0.875	
1.000	2.79	
2.000	3.25	
3.000	8.00	
4.000	10.99	
7.500	22.10	
10.000	27.60	
2.000	5.43	1.68
3.000	8.40	1.86
4.000	10.93	2.06

*R = initial rate of Cr(VI) formation

** From log $[S_2O_8^{2-}]$/time plots

Table 114

*Ref (Table)	Time (min)	$10^2[S_2O_8^{2-}]_o$	$10^2[S_2O_8^{2-}]_t$	$10^3[Cr(III)]_o$	$10^3[Cr(VI)]_t$	$10^3[Cr(III)]_t$	$10^3\ k_{obs}$
		2.000	-	4.000	-	-	1.680
110	40	-	1.900	-	0.220	3.780	-
	60	-	1.850	-	0.330	3.670	
	100	-	1.755	-	0.550	3.450	
	150	-	1.638	-	0.800	3.200	
	200	-	1.518	-	1.050	2.950	-
	300	-	1.280	-	1.520	2.480	-
	360	-	1.138	-	1.245	2.255	-
		4.000	-	4.000	-	-	2.060
112	40	-	3.680	-	0.420	3.58	
	60	-	3.542	-	0.645	3.355	-
	100	-	3.285	-	1.09	2.91	-
	150	-	2.955	-	1.56	2.44	
	200	-	2.640	-	1.93	2.07	-
	300	-	2.090	-	2.52	1.48	-
	360	-	1.820	-	2.79	1.21	-

* The first column in this Table and Tables 115, 133 and 134 refers to the original tables (and the corresponding plots) from which these quantities have been obtained.

Table 115

Ref (Table)	Time (min)	10^4 B (min^{-1})	10^2 A (l/mole/min)
110	40	3.70	9.54
	60	3.68	9.64
	100	3.77	10.15
	150	3.71	10.35
	200	3.67	10.60
	300	3.55	11.15
	360	3.40	11.25
111	40	2.71	7.13
	60	2.89	7.92
	100	3.13	9.22
	150	3.07	9.72
	200	2.92	9.96
	300	2.72	10.7
	360	2.63	11.30

Hydrogen ion effect

In the following set of runs the effect of varying the concentration of hydrogen ion on the rate of the reaction was studied. The hydrogen ion concentration was varied by adding calculated amounts of standard perchloric acid. At low concentrations of acid(lower than 0.01 mole/l) the pH of the solution was measured by a Dynakap pH meter. Tables 116-119 and Figs. 105-107 give the results of these runs. In Fig. 108 the initial rates of disappearance of peroxodisulphate and the appearance of chromium(VI) are plotted against hydrogen ion concentration.

It can be seen from Fig. 108 that the formation of chromium(VI) shows very little dependence on hydrogen ion concentration. It increases rather slowly till it reaches a maximum at about $[H^+] = 0.06$ mole/l above which there seems to be a slight negative effect. However, the rate of decomposition of peroxodisulphate increases almost linearly to about $[H^+] = 0.1$ mole/l and deviates from linearity at higher hydrogen ion concentration or it may be that k_H assumes a lower value when the oxidation of Cr(III) becomes independent of H^+ concentration and thus the curve may be seen as two straight lines.

The intercepts at zero hydrogen ion concentration give the values of 0.860×10^{-5} mole/l/min and 0.720×10^{-5} mole/l/min for the rates of disappearance of peroxodisulphate and appearance of chromium(VI) respectively. Dividing 0.860×10^{-5} mole/l/min by the initial concentration of peroxodisulphate (3.000×10^{-2} mole/l) gives the first order rate constant for the redox reaction at zero hydrogen ion concentration as 2.87×10^{-4} min^{-1} compared to the value of $(2.3 \pm 0.2) \times 10^{-4}$ min^{-1} reported by Frennesson and Fronaeus. The present k value, however, conforms to the general trends of peroxodisulphate reactions in that it is higher than the k_1 value for the thermal decomposition of the ion, whereas the value obtained by Frennesson and Fronaeus is lower.

The following experimental conditions apply for Tables 116-119, all concentrations being in units of mole/l.

$[S_2O_8^{2-}]_o = 3.000 \times 10^{-2}$

$[Cr(III)]_o = 4.000 \times 10^{-3}$

$[NaClO_4] = 0.500$

Temperature = 60.0°C

Table 116

$[HClO_4] = 0.1000$

$[Fe(II)] = 0.07706$

$[Ce(IV)] = 0.04219$

Time (min)	Absorbance	$10^3[Cr(VI)]$	Titre (ml)	$10^2[S_2O_8^{2-}]$	$2 + \log[S_2O_8^{2-}]$
30	0.0275	0.24	-	-	-
60	-	0.60	2.39	2.753	0.4398
90	0.0815	0.92	-	-	-
120	-	1.18	2.52	2.613	0.4171
180	0.152	1.82	-	-	-
240	-	2.36	2.925	2.265	0.3551
270	0.215	2.62	-	-	-
300	-	2.95	3.12	2.094	0.3209
330	0.263	3.22	-	-	-

Table 117

[$HClO_4$] = 0.0500
[Fe(II)] = 0.07706
[Ce(IV)] = 0.04219

Time (min)	Absorbance	10^3[Cr(VI)]	Titre (ml)	$10^2[S_2O_8^{2-}]$	$2 * \log[S_2O_8^{2-}]$
30	0.0225	0.18	-	-	-
60	-	0.52	2.23	2.834	0.4524
90	0.0715	0.80	-	-	-
120	-	1.06	2.32	2.715	0.4338
180	0.137	1.64	-	-	-
240	-	2.10	2.57	2.454	0.3899
270	0.195	2.36	-	-	-
300	-	2.60	2.625	2.355	0.3720
330	0.230	2.82	-	-	-

Table 118

[$HClO_4$] = 0.220
[Fe(II)] = 0.07673
[Ce(IV)] = 0.04219

Time (min)	Absorbance	10^3[Cr(VI)]	Titre (ml)	$10^2[S_2O_8^{2-}]$	$2 + \log[S_2O_8^{2-}]$
30	0.024	0.20	-	-	-
60	-	0.50	11.45*	2.767	0.4420
91	0.074	0.84	-	-	-
120	-	1.13	2.71	2.523	0.4019
150	0.121	1.43	-	-	-
180	-	1.68	2.94	2.344	0.3699
240	0.177	2.14	-	-	-
270	-	2.36	3.48	2.014	0.3040
300	0.210	2.56	-	-	-

* 10 ml Fe(II)SO_4

Table 119

[$HClO_4$] = 0.0022
[Fe(II)] = 0.07673
[Ce(IV)]= 0.04219

Time (min)	Absorbance	10^3[Cr(VI)]	Titre (ml)	$10^2[S_2O_8^{2-}]$	$2 + \log[S_2O_8^{2-}]$
30	0.018	0.12	-	-	-
60	-	0.34	2.17	2.869	0.5478
90	0.052	0.56	-	-	-
120	-	0.67	11.4*	2.763	0.4414
180	0.087	1.00	-	-	-
240	-	1.35	2.20	2.704	0.4320
270	0.135	1.61	-	-	-
360	-	1.706	2.31	2.606	0.4160
365	0.143	1.71	-	-	-

* 10 ml Fe(II)SO_4

Table 120

Hydrogen Ion Effect

$[H^+]$	10^5 R	10^5 R'
0.0022	0.732	0.910
0.0500	1.088	1.970
0.1000	1.092	2.900
0.220	1.040	3.580
0.360	9.680	4.260

R ≡ initial rate of formation of chromium(VI) in mole/l/min.

R' ≡ initial rate of disappearance of peroxodisulphate in mole/l/min.

THE OXIDATION OF CHROMIUM(III) SULPHATE

In the following set of runs the oxidation of chromium(III) - in the form of chromic sulphate - by peroxodisulphate is investigated and the reaction medium is changed to sulphuric acid - sodium sulphate instead of perchloric acid - sodium perchlorate. Under these conditions plus the relatively high temperature (60°C) at which the reaction is studied the sulphate ion tends to enter the inner coordination sphere of chromium(III) to form complexes(68). The aim of this set of runs is therefore to see if complexed sulphate has any effect on the rate of the redox reaction. SO_4^{2-} is one of the few ligands which can be used for this purpose in this reaction, most ligands themselves being susceptible to the extremely strongly oxidising conditions prevailing in acidic peroxodisulphate mixture at elevated temperatures.

Reagent grade chromic sulphate was weighed accurately and dissolved in water containing a calculated volume of standard sulphuric acid to make up a stock solution. The exact concentration of chromium(III) was determined spectrophotometrically as before.

Fig. 97

[Cr(VI) v. Time

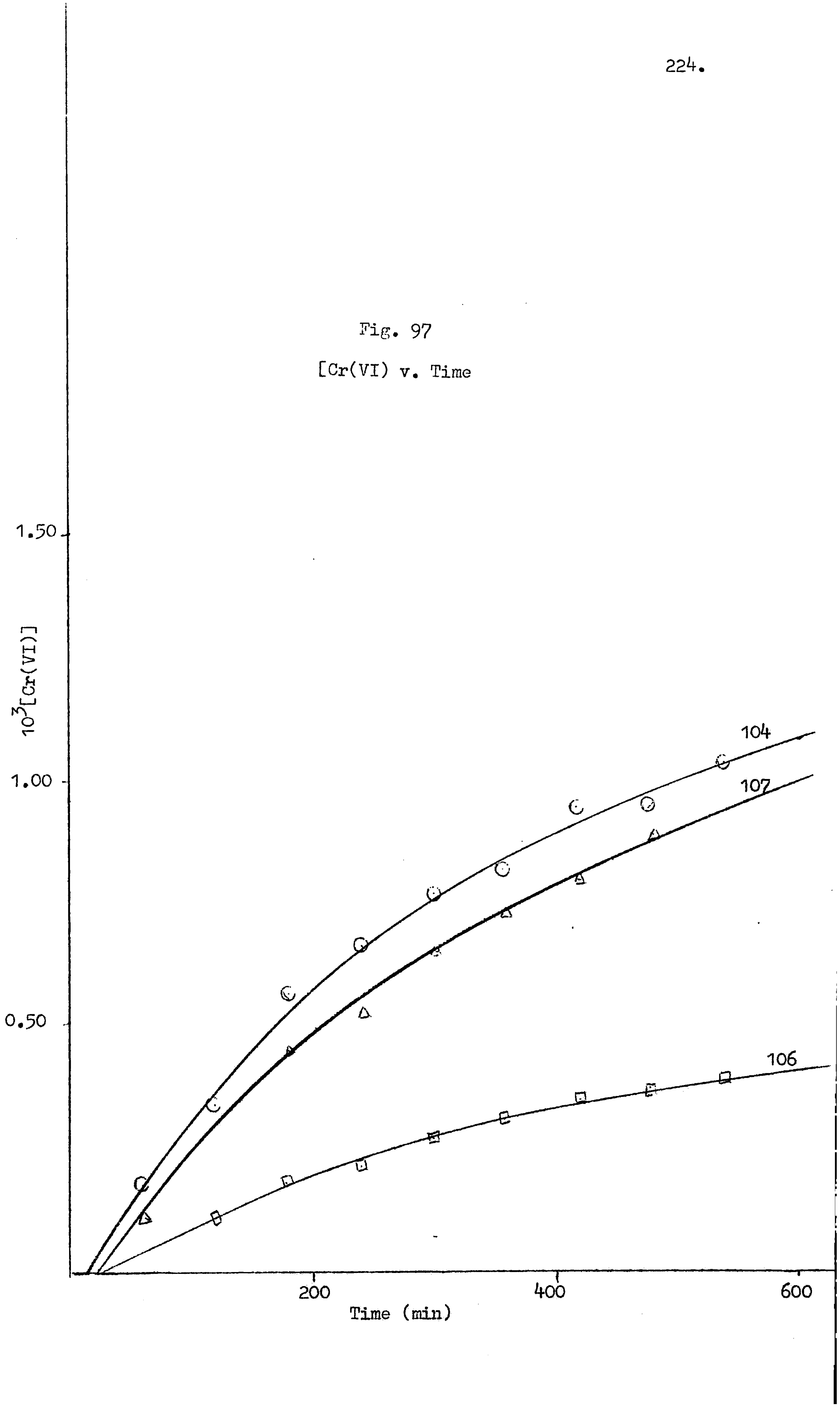


Fig. 98

[Cr(VI)] v. Time

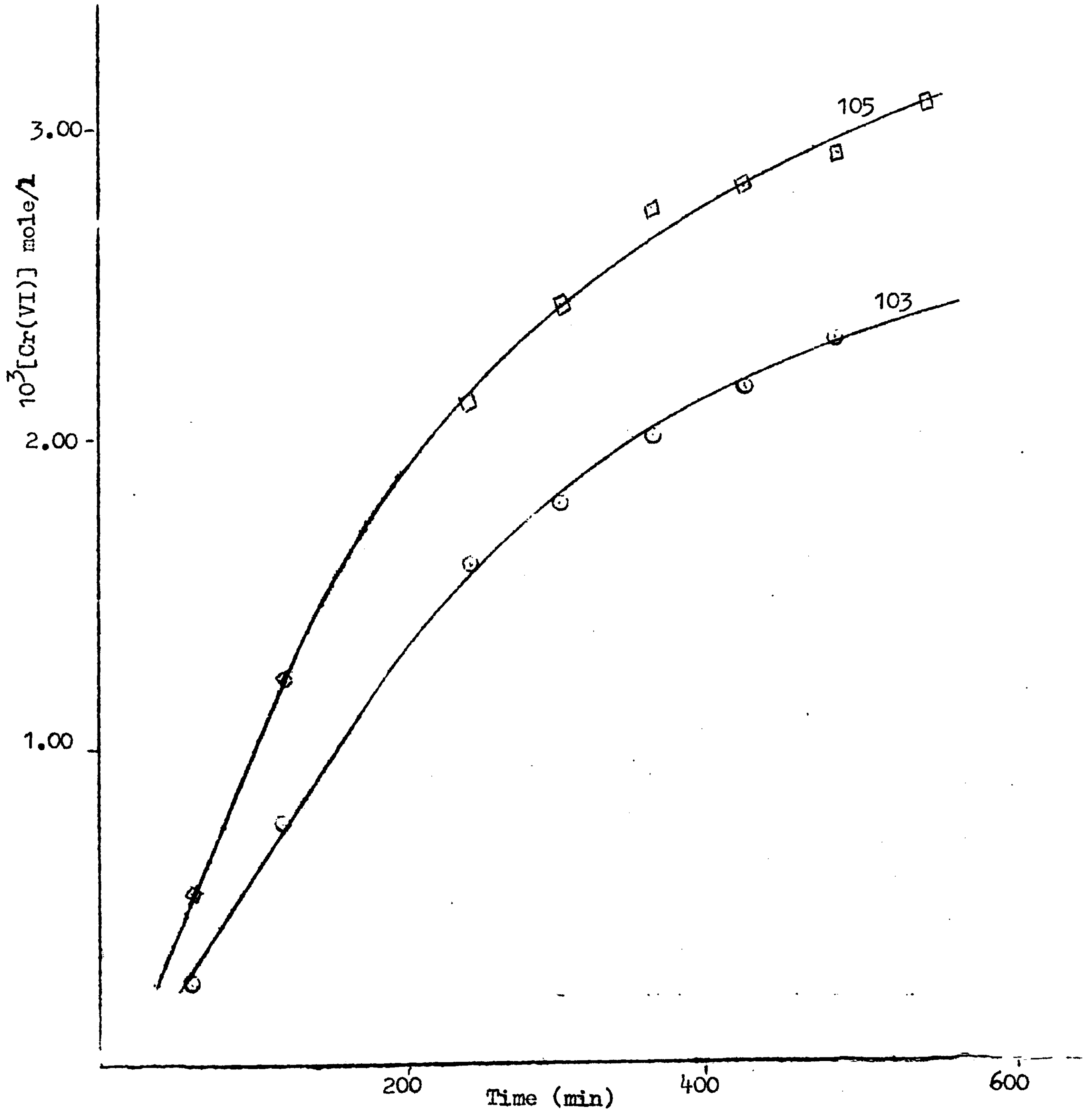
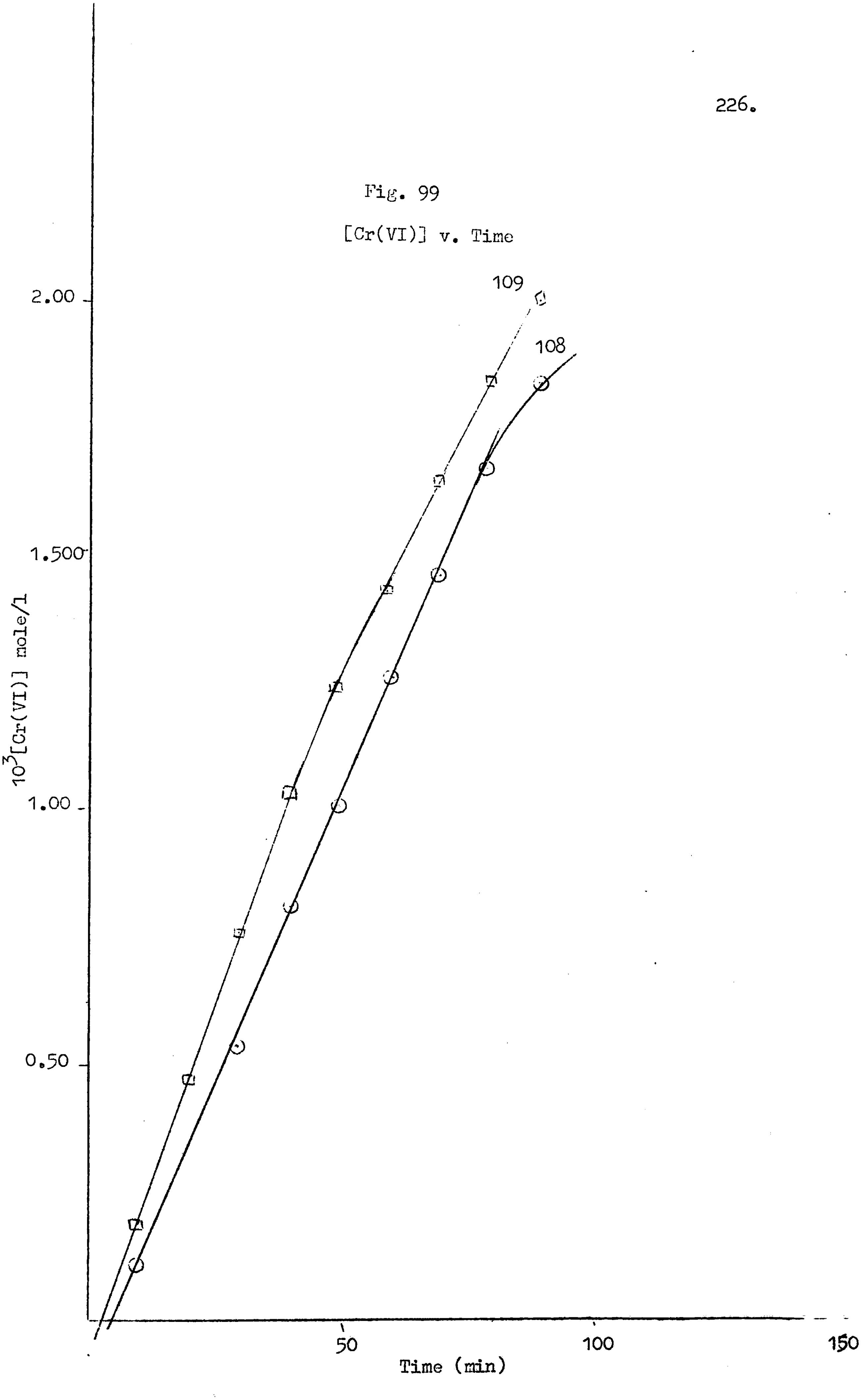


Fig. 99

[Cr(VI)] v. Time



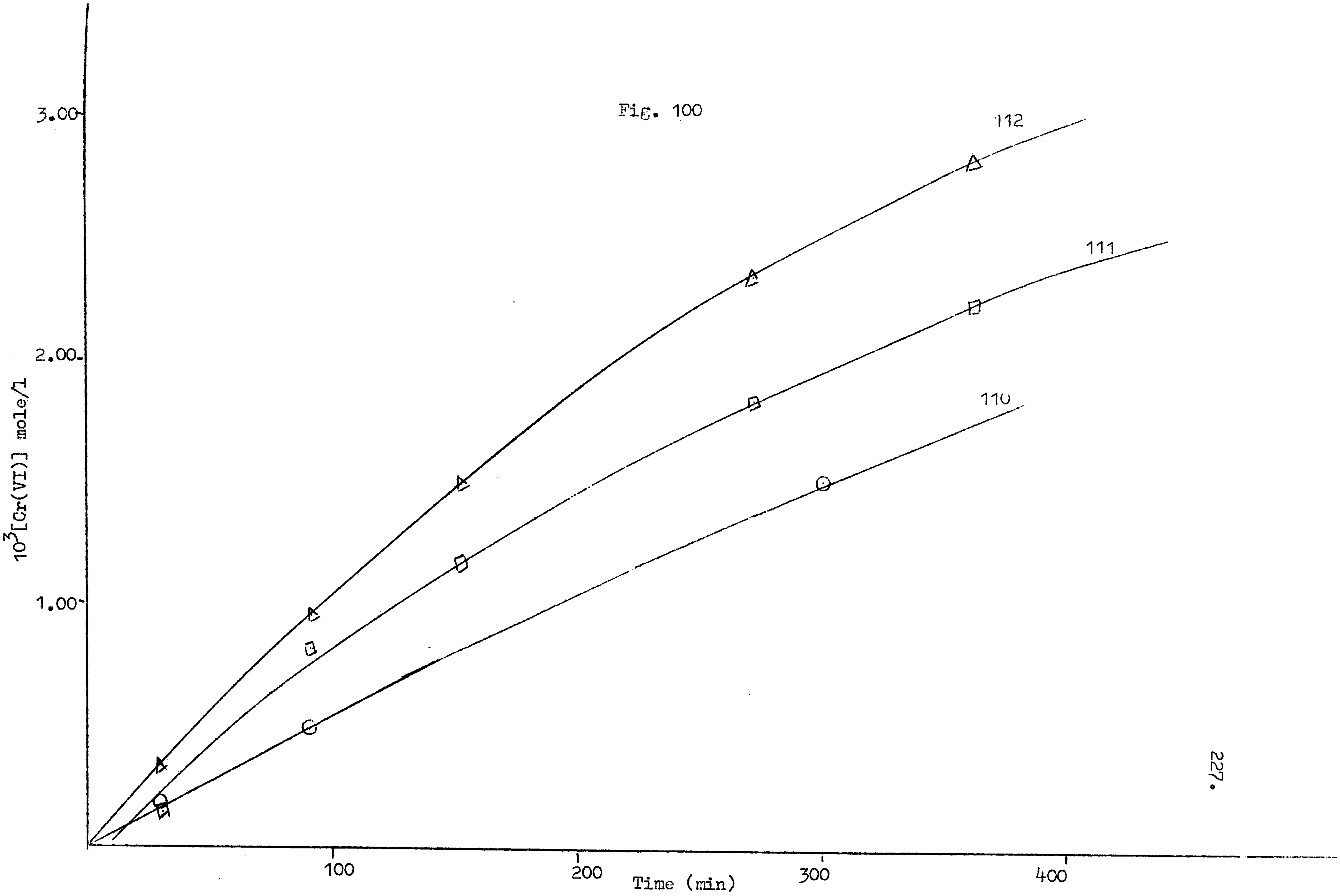


Fig. 100

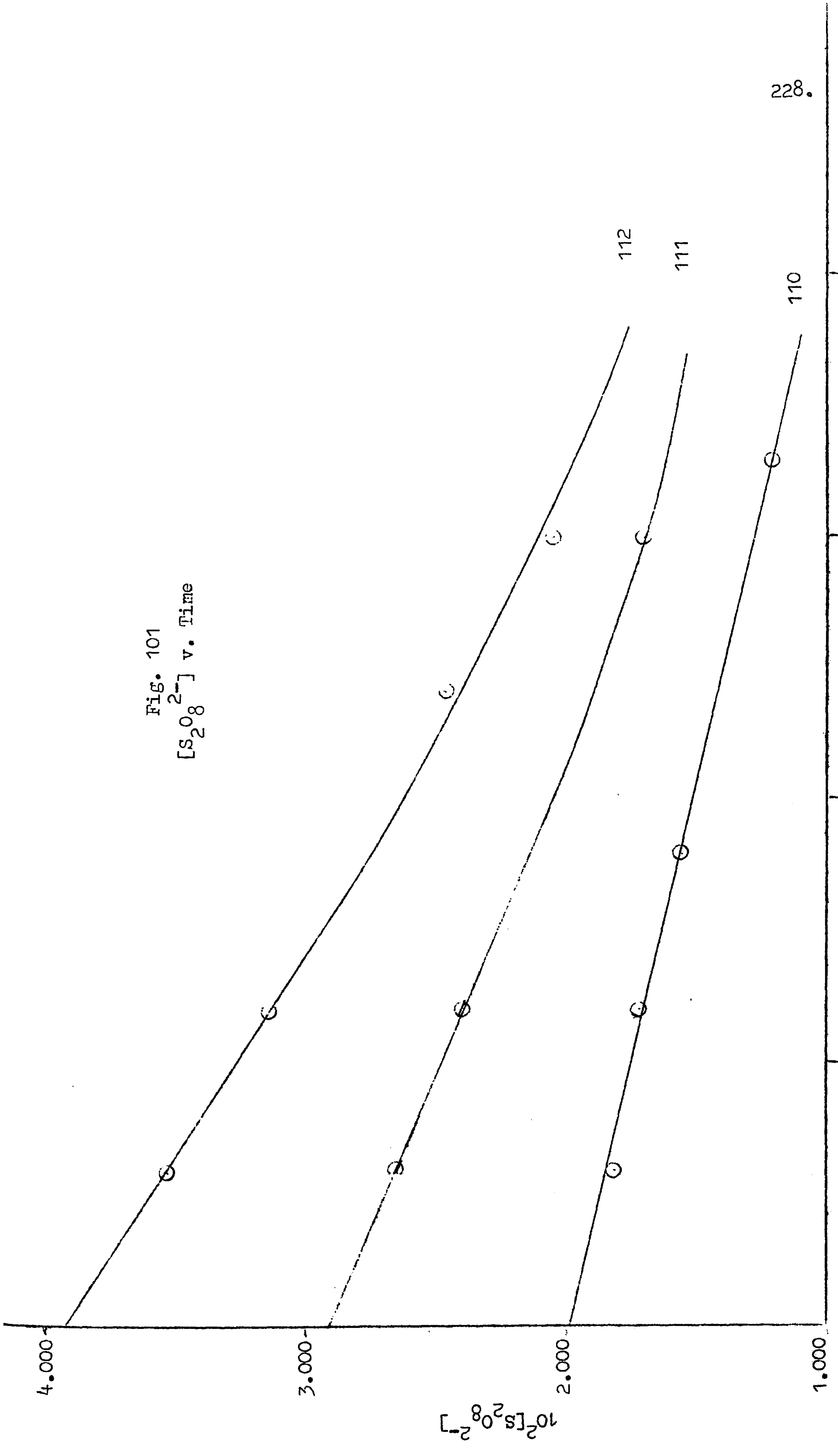
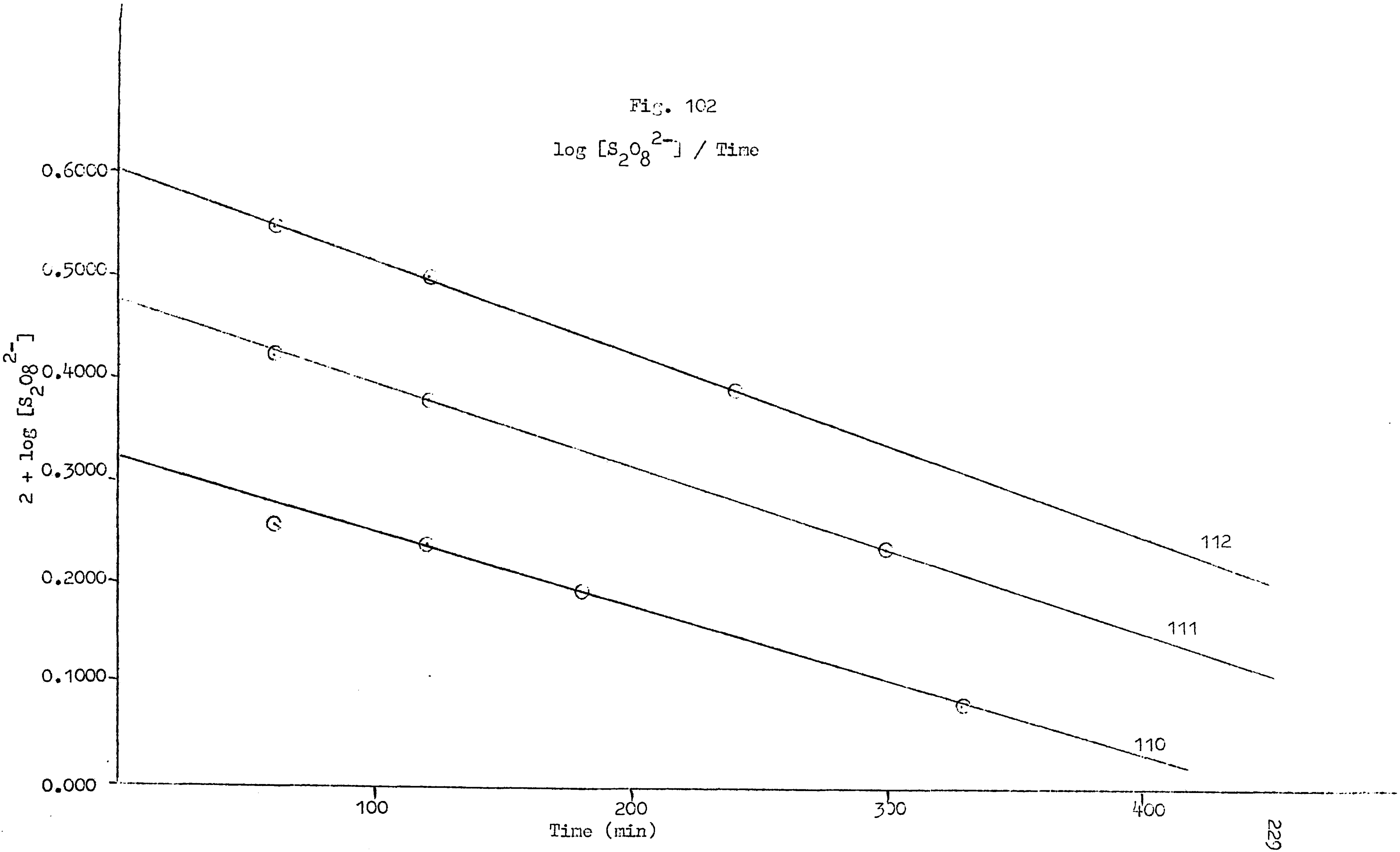


Fig. 101
$[S_2O_8^{2-}]$ v. Time

Fig. 102

log $[S_2O_8^{2-}]$ / Time



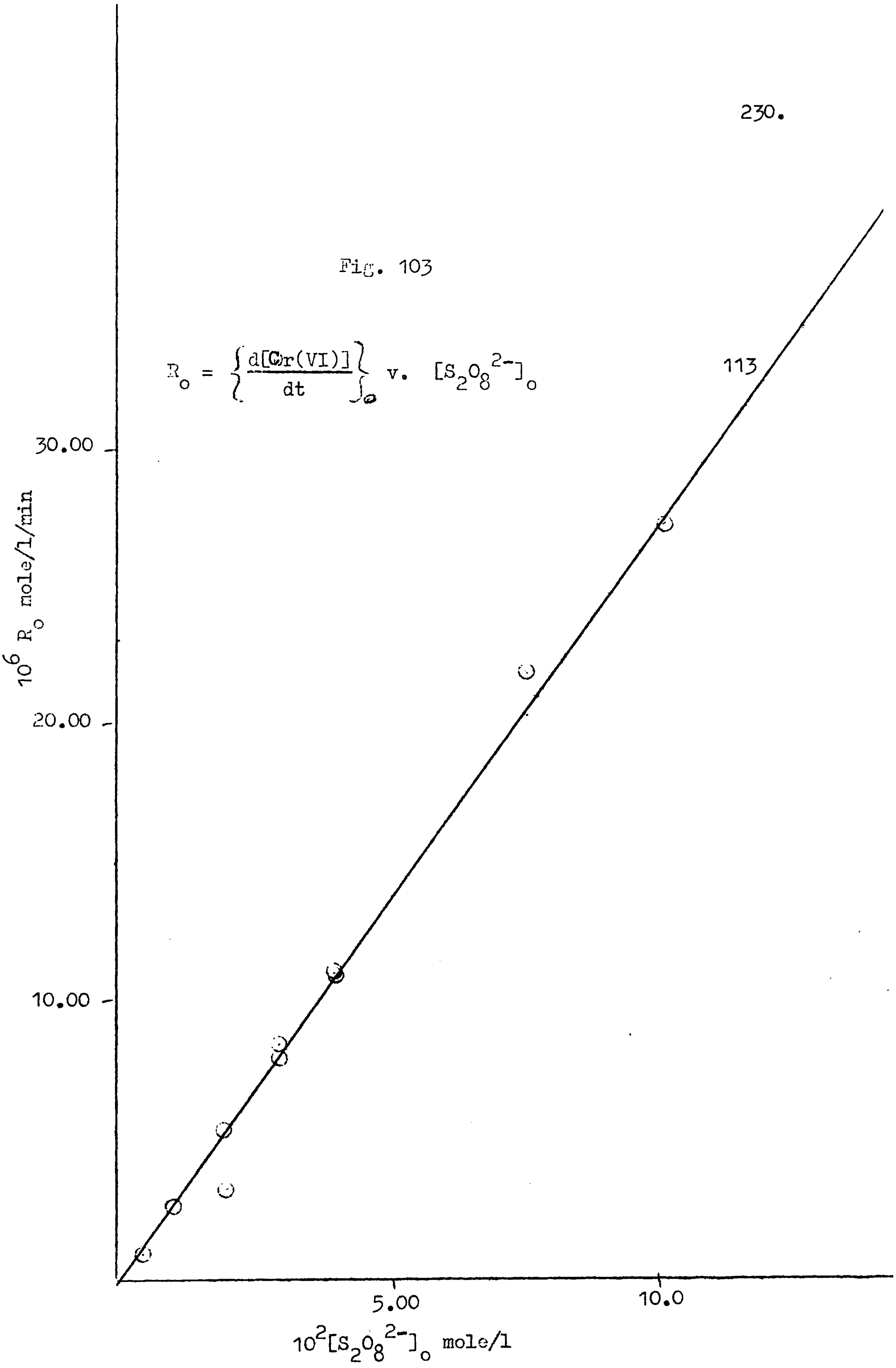


Fig. 103

$R_o = \left\{\frac{d[Cr(VI)]}{dt}\right\}_0$ v. $[S_2O_8^{2-}]_0$

Fig. 104

Oxidation of $Cr(ClO_4)_3$

A v. B

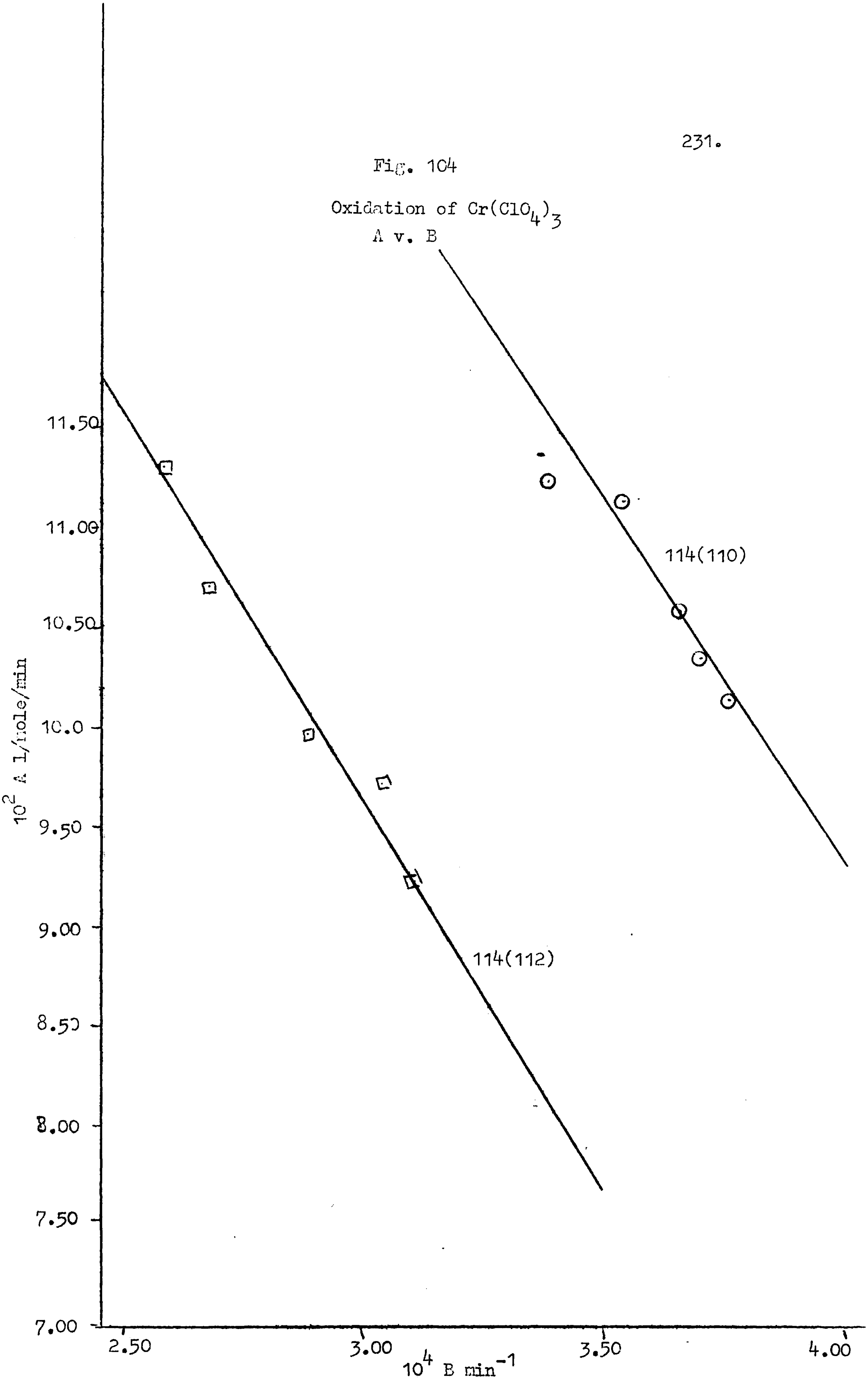


Fig. 105

Hydrogen Ion Effect

[Cr(VI)] v. Time

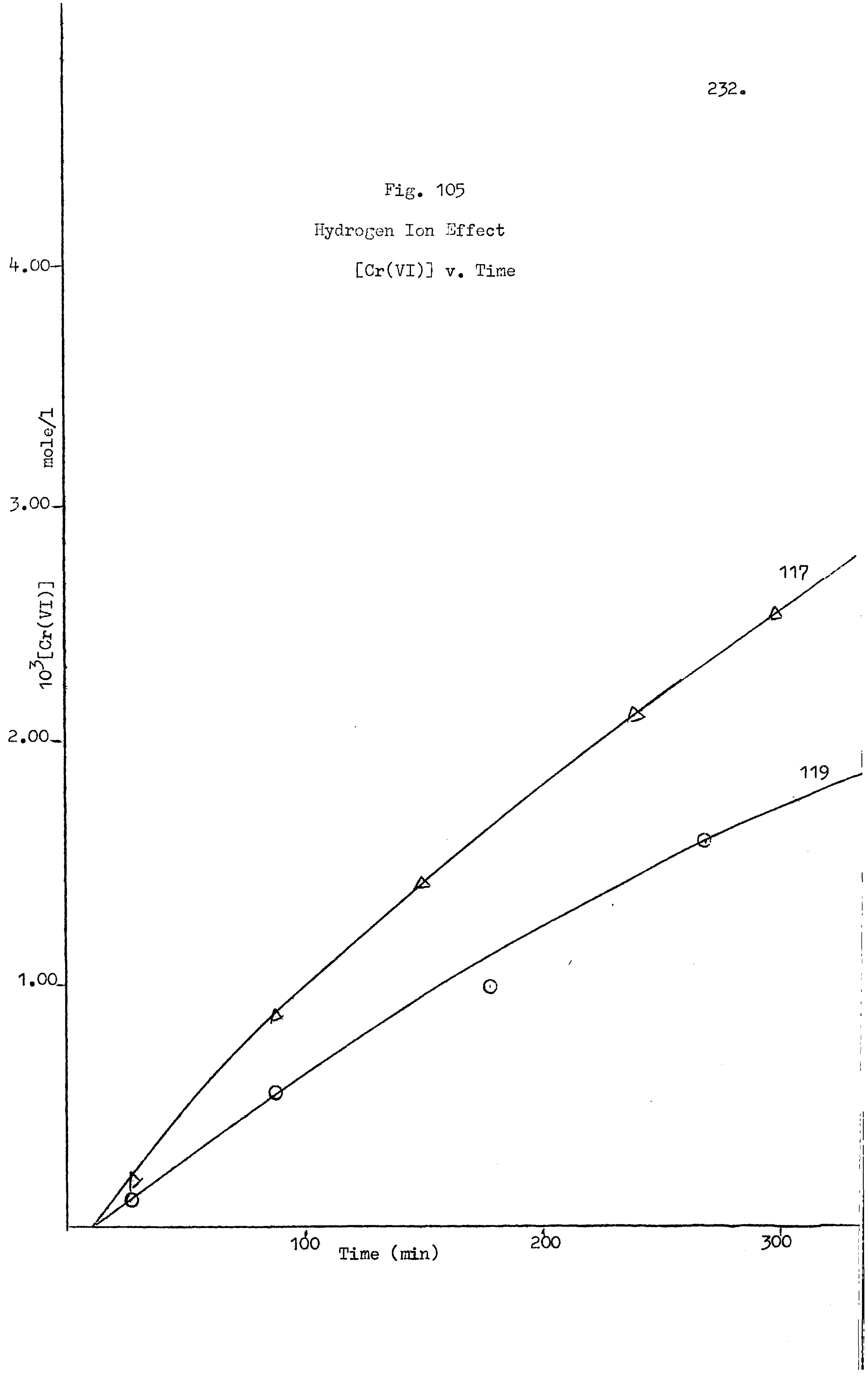
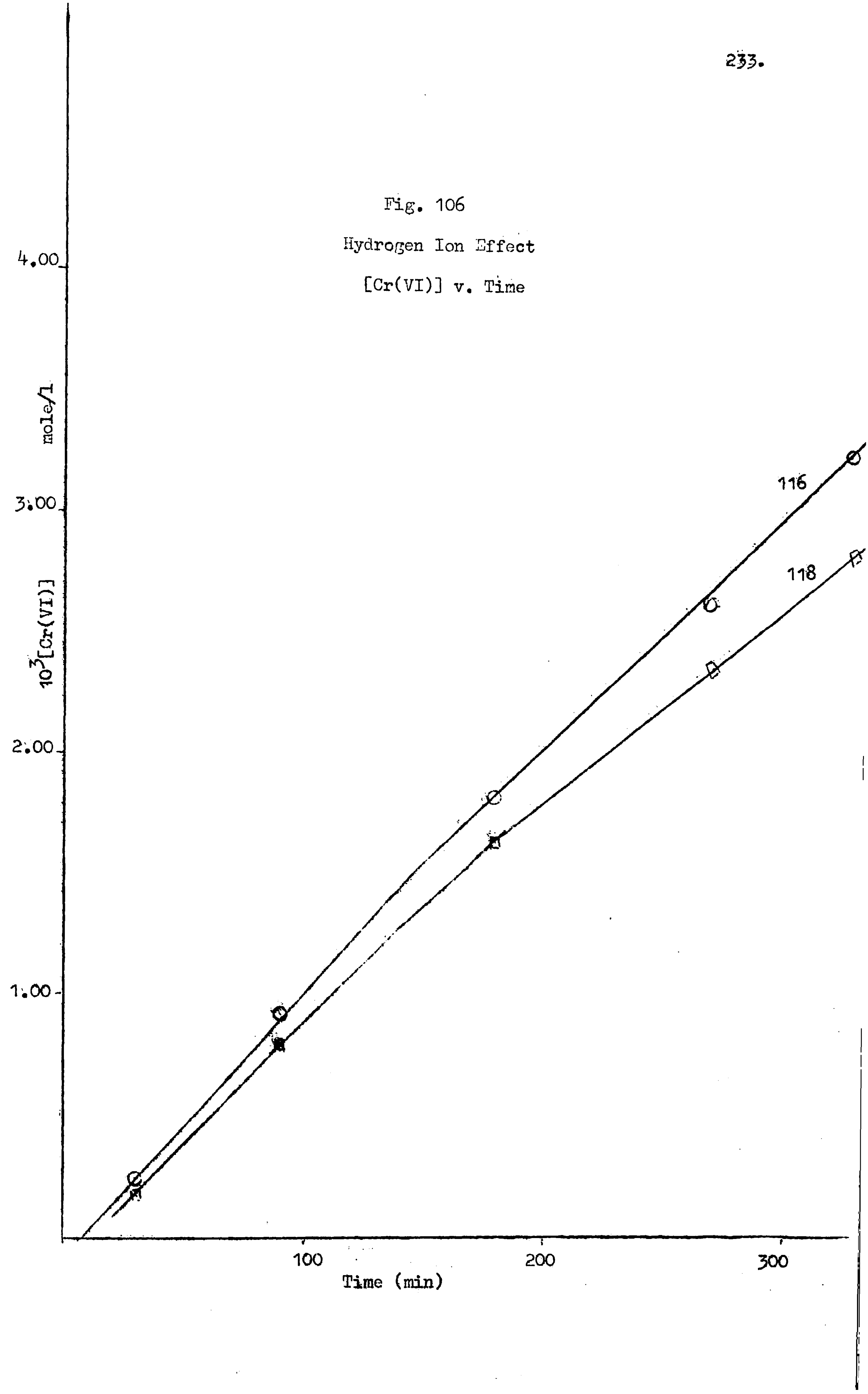


Fig. 106

Hydrogen Ion Effect

[Cr(VI)] v. Time



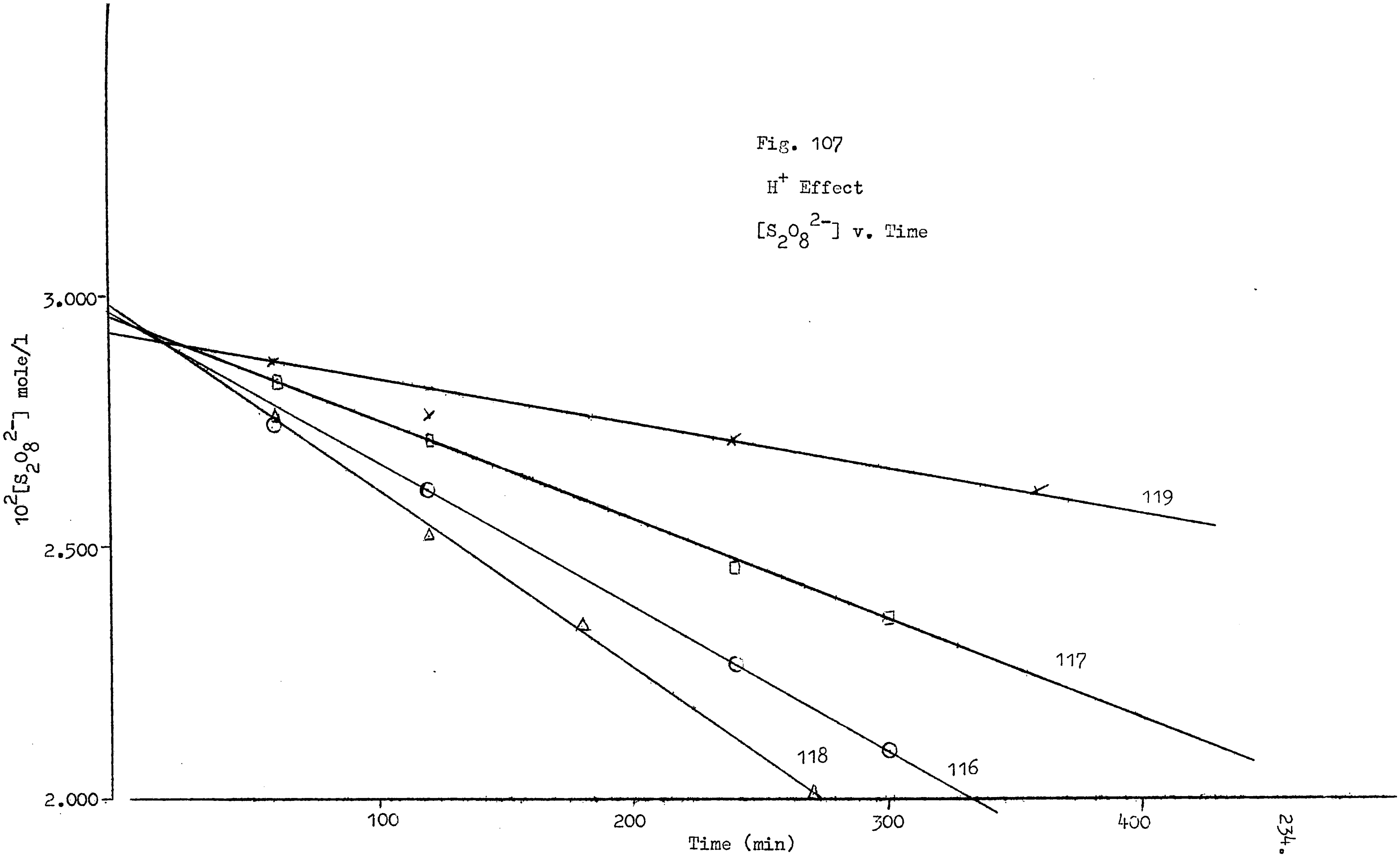


Fig. 107

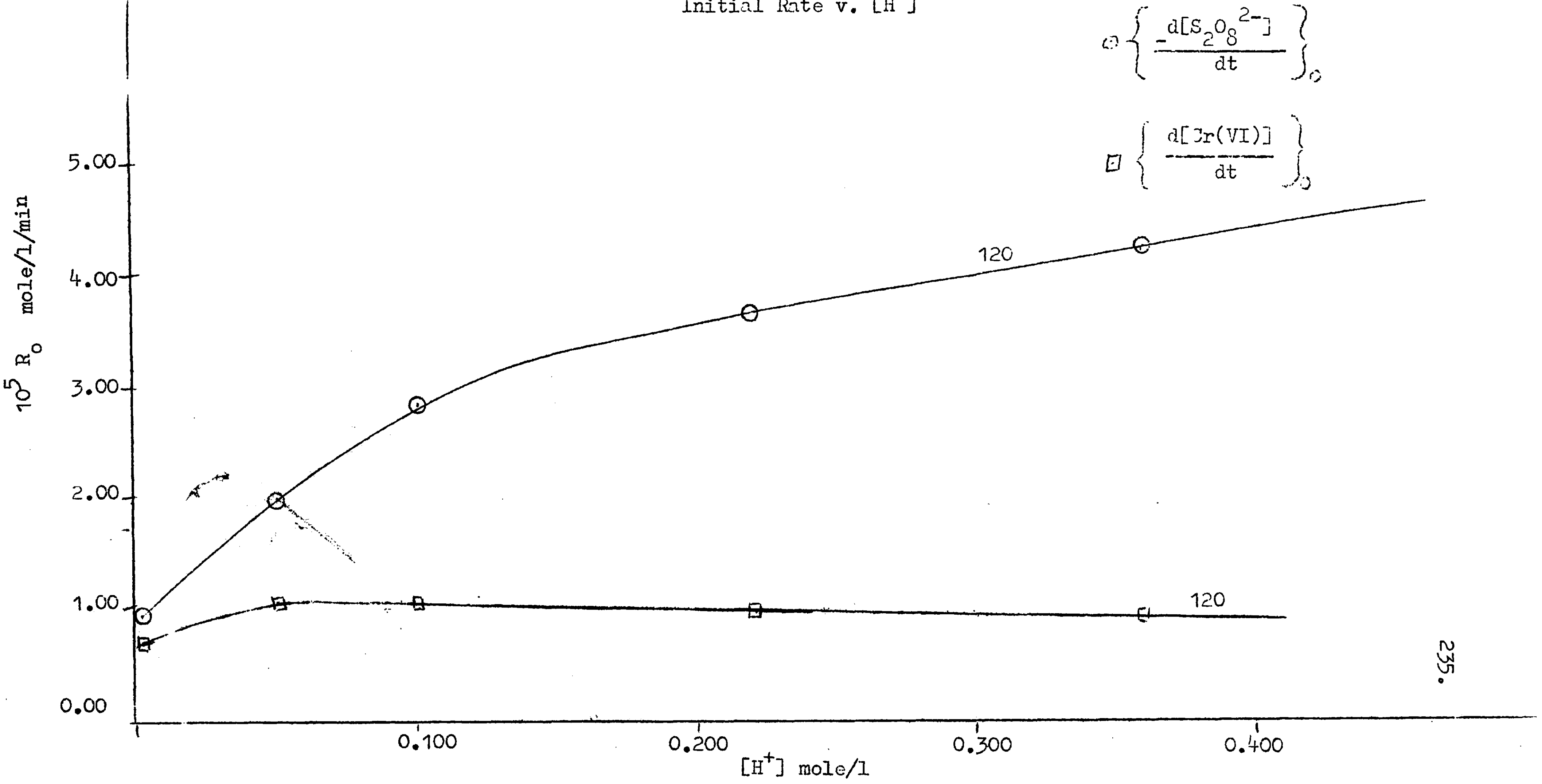
H^+ Effect

$[S_2O_8^{2-}]$ v. Time

Fig. 108

Hydrogen Ion Effect

Initial Rate v. $[H^+]$



The analytical method used to follow the reaction was the same as that used for the chromium(III) perchlorate.

Results

Table 121 - 134 and the corresponding figures give the results of some typical runs. A plot of initial rates of formation of chromium(VI) and disappearance of peroxodisulphate (Fig.127)against the initial concentration of peroxodisulphate shows that the reaction is again first order in peroxodisulphate. However, it can be seen from Figs. 109-111 and 120 that the order with respect to chromium(III) varies between zero and (probably) one; a high ratio of $[S_2O_8^{2-}]/[Cr(III)]$ making the reaction independent of chromium(III) concentration.

A comparison of Figs. 127 and 103 shows that the rate of oxidation of chromium(III) to chromium(VI) is faster in a sulphate medium (slope = 3.58×10^{-4} min^{-1}) than it is in a perchlorate medium (slope 2.75×10^{-4} min^{-1}). Thus it seems that the presence of sulphate - probably in the inner coordination sphere of Cr(III) - enhances the transfc of electrons from chromium(III) to peroxodisulphate.

An attempt to apply the rate law postulated by Frennesson and Fronaeus-equation [154] - failed to give any meaningful plot (Tables 133-134) probably indicating that this rate law does not hold at least in the case of chromic sulphate.

The following conditions apply to all runs reported in this section. All concentrations are in units of mole/l. In all runs 5 ml samples were diluted to 50 ml (or any other specified volume) for spectrophotometric measurements.

$[Na_2SO_4]$ = 0.1667
$[H_2SO_4]$ = 0.250
Temperature = 60.0°C

Table 121

$[Cr(III)]_0$ = 4.00×10^{-3}

$[S_2O_8^{2-}]_0$ = 0.5000×10^{-2}

$[Fe(II)]$ = 0.05899

$[Ce(IV)]$ = 0.03890

5 ml sample diluted to 25 ml for spectrophotometric measurements

Time (min)	Absorbance	$10^3[Cr(VI)]$	Titre (ml)	$10^3[S_2O_8^{2-}]$
30	0.015	0.065	-	-
60	-	0.09	21.47*	4.835
90	0.017	0.080	-	-
150	-	0.225	-	-
210	0.053	0.315	-	-
270	-	0.400	6.63	4.104
330	0.078	0.48	-	-
390	-	0.53	14.28	2.643
400	0.088	0.54	-	-

* 15 ml $Fe(II)SO_4$

Table 122

$[Cr(III)]_0$ = 4.000×10^{-3}

$[S_2O_8^{2-}]_0$ = 1.000×10^{-2}

$[Fe(II)]$ = 0.05899

$[Ce(IV)]$ = 0.03890

5 ml sample diluted to 25 ml for spectrophotometric measurements

Time (min)	Absorbance	$10^3[Cr(VI)]$	Titre (ml)	$10^3[S_2O_8^{2-}]$	$3+\log[S_2O_8^{2-}]$
30	0.021	0.105	-	-	-
60	-	0.20	12.81*	8.859	0.9473
90	0.052	0.31	-	-	-
150	-	0.50	5.45	7.544	0.8776
212	0.106	0.66	-	-	-
270	-	0.87	5.69	6.134	0.7878
330	0.167	1.05	-	-	-
390	-	1.66	5.78	5.271	0.7219
400	0.186	1.175	-	-	-

* 10 ml $Fe(II)SO_4$

Table 123

$[Cr(III)]_0 = 4.000 \times 10^{-3}$ $[S_2O_8^{2-}]_0 = 2.000 \times 10^{-2}$

$[Fe(III)] = 0.05882$ $[Ce(IV)] = 0.03890$

Time (min)	Absorbance	$10^3[Cr(VI)]$	Titre (ml)	$10^2[S_2O_8^{2-}]$	$2 + \log[S_2O_8^{2-}]$
30	0.017	0.160	-	-	-
60	-	0.445	2.87	1.758	0.2450
95	0.062	0.745	-	-	-
150	-	1.08	3.20	1.534	0.1858
210	0.118	1.47	-	-	-
270	-	1.83	3.62	1.258	0.0997
300	0.158	1.99	-	-	-
330	-	2.18	3.75	1.150	0.0626
360	0.185	2.34	-	-	-

Table 124

$[Cr(III)]_0 = 4.000 \times 10^{-3}$ $[S_2O_8^{2-}]_0 = 2.500 \times 10^{-2}$

$[Fe(III)] = 0.05882$ $[Ce(IV)] = 0.03890$

Time (min)	Absorbance	$10^3[Cr(VI)]$	Titre (ml)	$10^2[S_2O_8^{2-}]$	$2 + \log[S_2O_8^{2-}]$
30	0.032	0.36	-	-	-
60	-	0.58	1.54	2.255	0.3533
90	0.071	0.865	-	-	-
150	-	1.39	1.86	2.009	0.3029
210	0.148	1.86	-	-	-
270	-	2.36	2.55	1.604	0.2052
300	0.193	2.44	-	-	-
330	-	2.68	2.76	1.465	0.1659
360	0.229	2.90	-	-	-

Table 125

$[Cr(III)]_0 = 4.000 \times 10^{-3}$ $[S_2O_8^{2-}]_0 = 3.000 \times 10^{-2}$

$[Fe(II)] = 0.05848$ $[Ce(IV)] = 0.03890$

10 ml $Fe(II)SO_4$ solution used for SO_8^{2-} determination.

Time (min)	Absorbance	$10^3[Cr(VI)]$	Titre (ml)	$10^2[S_2O_8^{2-}]$	$2 + \log[S_2O_8^{2-}]$
30	0.038	0.435	-	-	-
60	-	0.66	7.91	2.672	0.4268
90	0.080	0.98	-	-	-
120	-	1.26	8.22	2.471	0.3929
150	0.125	1.56	-	-	-
182	-	1.86	8.58	2.231	0.3485
240	0.189	2.40	-	-	-
300	-	2.90	9.10	1.873	0.2725
320	0.242	3.08	-	-	-

Table 126

$[Cr(III)]_0 = 4.000 \times 10^{-3}$ $[S_2O_8^{2-}]_0 = 4.000 \times 10^{-2}$

$[Fe(III)] = 0.05848$ $[Ce(IV)] = 0.03890$

10 ml of $Fe(II)SO_4$ solution used for $S_2O_8^{2-}$ determination

Time (min)	Absorbance	$10^3[Cr(VI)]$	Titre (ml)	$10^2[S_2O_8^{2-}]$	$2 + \log[S_2O_8^{2-}]$
30	0.041	0.47	-	-	-
60	-	0.92	5.33	3.637	0.5607
90	0.104	1.3	-	-	-
120	-	1.78	5.74	3.348	0.5247
150	0.170	2.4	-	-	-
180	-	2.50	6.22	3.053	0.4847
240	0.243	3.09	-	-	-
300	-	3.15	7.155	2.592	0.4136
320	0.289	3.68	-	-	-

Table 127

$[Cr(III)]_0 = 4.000 \times 10^{-3}$ $[S_2O_8^{2-}]_0 = 7.500 \times 10^{-2}$

$[Fe(II)] = 0.05800$ $[Ce(IV)] = 0.03890$

20 ml $Fe(II)SO_4$ solution used for $S_2O_8^{2-}$ determination

Time (min)	Absorbance	$10^3[Cr(VI)]$	Titre (ml)	$10^2[S_2O_8^{2-}]$	$2 + \log[S_2O_8^{2-}]$
30	0.065	0.78	-	-	-
60	-	1.54	12.02	6.693	0.8256
90	0.188	2.38	-	-	-
150	0.289	3.68	-	-	-
180	-	3.82	14.05	5.562	0.7453
210	0.300	3.83	-	-	-
240	-	3.86	15.24	5.093	0.7070
270	-	3.88	15.88	4.841	0.6849

Table 128

$[Cr(III)]_0 = 4.000 \times 10^{-3}$ $[S_2O_8^{2-}]_0 = 10.00 \times 10^{-2}$

$[Fe(II)] = 0.05800$ $[Ce(IV)] = 0.03890$

20 ml $Fe(II)SO_4$ solution for $S_2O_8^{2-}$ determination

Time (min)	Absorbance	$10^3[Cr(VI)]$	Titre (ml)	$10^2[S_2O_8^{2-}]$	$2 + \log[S_2O_8^{2-}]$
30	0.088	1.08	-	-	-
60	-	2.14	-	-	-
90	0.253	3.22	-	-	-
120	-	3.60	7.33	8.207	0.9142
150	0.297	3.79	-	-	-
180	-	3.82	9.06	7.503	0.8753
210	0.299	3.82	-	-	-
240	-	3.84	10.65	6.881	0.8377
270	-	3.84	11.35	6.609	0.8201

Table 129

$[Cr(III)]_0$ = 1.000 x 10^{-3} $[S_2O_8^{2-}]_0$ = 2.000 x 10^{-2}

$[Fe(II)]$ = 0.05252 $[Ce(IV)]$ = 0.03890

5 ml sample diluted to 50 ml for spectrophotometry

Time (min)	Absorbance	$10^3[Cr(VI)]$	Titre (ml)	$10^2[S_2O_8^{2-}]$	$2 + \log[S_2O_8^{2-}]$
30	0.012	0.096	-	-	-
60	-	0.41	16.95*	1.748	0.2425
90	0.052	0.615	-	-	-
120	-	0.765	2.36	1.593	0.2022
180	0.074	0.90	-	-	-
210	-	0.93	2.79	1.401	0.1464
240	0.077	0.94	-	-	-
300	-	0.94	3.21	1.236	0.0920
310	0.077	0.94	-	-	-

* 16 ml $Fe(II)SO_4$

Table 130

$[Cr(III)]_0$ = 1.000 x 10^{-3} $[S_2O_8^{2-}]_0$ = 3.000 x 10^{-3}

$[Fe(II)]$ = 0.05236 $[Ce(IV)]$ = 0.03890

10 ml $Fe(II)SO_4$ used for $S_2O_8^{2-}$ determination

Time (min)	Absorbance	$10^3[Cr(VI)]$	Titre (ml)	$10^2[S_2O_8^{2-}]$	$2 + \log[S_2O_8^{2-}]$
30	0.022	0.225	-	-	-
60	-	0.57	7.77*	2.655	0.4240
90	0.072	0.88	-	-	-
120	-	0.925	8.08*	2.497	0.3974
150	0.074	0.90	-	-	-
180	-	0.94	7.22	2.286	0.3591
210	0.078	0.955	-	-	-
240	-	0.955	7.63	2.125	0.3273
260	0.077	0.94	-	-	-

* 11 ml $Fe(II)SO_4$

Table 131

$[Cr(III)]_0$ = 1.000 x 10^{-3} $[S_2O_8^{2-}]_0$ = 1.000 x 10^{-2}

$[Fe(II)]$ = 0.05127 $[Ce(VI)]$ = 0.03890

Time (min)	Absorbance	$10^3[Cr(VI)]$	Titre (ml)	$10^3[S_2O_8^{2-}]$	$3 + \log[S_2O_8^{2-}]$
30	0.015	0.065	-	-	-
60	-	0.165	4.25	8.854	0.9471
90	0.040	0.23	-	-	-
120	-	0.335	4.40	8.018	0.9040
150	0.071	0.43	-	-	-
180	-	0.50	4.53	7.262	0.8610
210	0.095	0.59	-	-	-
270	-	0.715	4.68	6.256	0.7963
290	0.120	0.75	-	-	-

Tables 132a - 132b show the results of two duplicate runs with the following conditions:

$[Cr(III)]_o = 2.000 \times 10^{-3}$ $[S_2O_8^{2-}]_o = 1.000 \times 10^{-2}$
$[H_2SO_4] = 0.250$ $[Na_2SO_4] = 0.1667$
$[Fe(II)] = 0.04814$ $[Ce(IV)] = 0.03890$

(a) 5 ml sample diluted to 50 ml for spectrophotometric measurements, except for the samples taken at 10 minutes which were diluted to 25 ml;

(b) for $S_2O_8^{2-}$ determination 5 ml $Fe(II)SO_4$ solution was used as usual.

Table 132a

Time (min)	Absorbance	$10^3[Cr(VI)]$	Titre (ml)	$10^3[S_2O_8^{2-}]$	$3 + \log[S_2O_8^{2-}]$
10	0.005	0.005	-	-	-
20	-	0.025	3.70	9.638	0.9840
40	-	0.06	3.79	9.233	0.9654
60	0.014	0.12	-	-	-
90	-	0.20	3.81	8.949	0.9517
150	0.038	0.43	-	-	-
210	-	0.575	4.02	7.569	0.8790
240	0.053	0.63	-	-	-

Table 132b

Time (min)	Absorbance	$10^3[Cr(VI)]$	Titre (ml)	$10^3[S_2O_8^{2-}]$	$3 + \log[S_2O_8^{2-}]$
10	0.005	0.005	-	-	-
20	-	0.015	3.73	9.538	0.9795
30	0.007	0.03	-	-	-
40	-	0.05	3.74	9.446	0.9750
60	0.014	0.12	-	-	-
90	-	0.205	3.82	8.907	0.9497
150	0.038	0.44	-	-	-
210	-	0.645	3.95	7.735	0.8885
240	0.061	0.73	-	-	-

Table 133

Ref (table)	Time (min)	$10^2[S_2O_8^{2-}]_o$	$10^2[S_2O_8^{2-}]_t$	$10^3[Cr(III)]_o$	$10^3[Cr(VI)]_t$	$10^3[Cr(III)]_t$	10^3k
122		1.000		4.000			1.763
	60		0.883		0.200	3.80	
	100		0.826		0.326	3.674	
	200		0.689		0.642	3.358	
	300		0.580		0.959	3.043	
123		2.000		4.000			1.560
	60		1.760		0.415	3.585	
	100		1.655		0.691	3.309	
	200		1.402		1.382	2.618	
	300		1.200		2.000	2.000	
124		2.5000		4.000			1.606
	40		2.320		0.440	3.560	
	60		2.260		0.605	3.395	
	100		2.135		0.922	3.078	
	200		1.820		1.775	2.225	
	300		1.530		2.475	1.526	
125		3.000		4.000			1.498
	40		2.760		0.550	3.450	
	60		2.682		0.695	3.305	
	100		2.538		1.080	2.920	
	200		2.170		2.038	1.962	
	300		1.865		2.905	1.095	
126		4.000		4.000			1.409
	40		3.740		0.608	3.392	
	60		3.640		0.885	3.115	
	100		3.446		1.440	2.560	
	200		2.950		2.720	1.280	
	300		2.790		3.550	0.450	

Table 133 (continued)

Ref (table)	Time (min)	$10^2[S_2O_8^{2-}]_o$	$10^2[S_2O_8^{2-}]_t$	$10^3[Cr(III)]_o$	$10^3[Cr(VI)]_t$	$10^3[Cr(III)]_t$	10^3k
127		7.500		4.000			
	40		6.860		1.040	2.95	1.546
	60		6.680		1.580	2.42	
	100		6.300		2.650	1.35	
128		10.00		4.000			1.454
	40		9.160		1.250	2.730	
	60		8.920		2.15	1.830	
	100		8.450		3.56	0.440	
130		3.000		1.000			1.343
	40		2.775		0.338	0.652	
	60		2.705		0.552	0.448	
	100		2.565		0.935	0.0550	
	200		2.223		0.950	0.050	
129		2.000		1.000			1.449
	40		1.798		0.184	0.816	
	60		1.748		0.355	0.645	
	100		1.647		0.675	0.325	
	200		1.417		0.910	0.090	
131		1.000		1.000			1.667
	40		0.9110		0.096	0.904	
	60		0.8850		0.157	0.843	
	100		0.831		0.278	0.722	
	200		0.696		0.557	0.443	
	300		0.600		0.758	0.242	

Table 133 (continued)

Ref (table)	Time (min)	$10^2[S_2O_8^{2-}]_o$	$10^2[S_2O_8^{2-}]_t$	$10^3[Cr(III)]_o$	$10^3[Cr(VI)]_t$	$10^3[Cr(III)]_t$	10^3k
132		1.000		2.000			1.214
	40		0.940		0.054	1.946	
	60		0.920		0.120	1.880	
	100		0.880		0.260	1.740	
	200		0.780		0.605	1.395	

Table 134

Ref.(table)	Time (min)	10^4B (min^{-1})	10^2A l/mole/min
122	60	3.01	7.69
	100	3.32	8.63
	200	3.64	9.99
	300	4.02	11.45
123	60	2.69	7.12
	100	3.13	8.58
	200	3.61	11.08
	300	3.91	13.50
124	40	3.93	10.35
	60	4.06	11.05
	100	4.07	11.55
	200	4.22	13.80
	300	4.61	15.95
125	40	3.43	9.26
	60	3.27	9.02
	100	3.50	9.77
	200	3.67	12.42
	300	3.83	17.12
126	40	3.28	8.92
	60	3.47	9.80
	100	3.66	11.36
	200	3.66	15.30
	300	4.14	25.40
129	40	1.32	14.62
	60	2.04	25.20
	100	2.77	46.20
	200	2.26	59.80
131	40	1.80	18.9
	60	2.28	26.30
	100	2.75	32.20
	200	3.06	44.75
	300	3.16	59.20
132	40	1.09	55.6
	60	1.82	93.8
	100	2.63	140.8
	200	3.33	215.0

Table 135

The Oxidation of Chromium(III) Sulphate

$10^2[S_2O_8^{2-}]_o$	$10^3[Cr(III)]_o$	10^5R	$10^5R'$	$10^3\ k_{obs}$
0.5000	4.000	0.144	-	-
1.000	4.000	0.315	1.45	1.76
2.000	4.000	0.690	2.56	1.56
2.500	4.000	0.839	3.13	1.61
3.000	4.000	0.960	3.70	1.50
4.000	4.000	1.39	4.94	1.41
7.500	4.000	2.68	9.40	1.55
10.00	4.000	3.56	11.9	1.45
1.000	1.000	0.303	1.33	1.67
2.000	1.000	0.873	2.55	1.45
3.000	1.000	1.08	3.50	1.34
1.000) 1.000)	2.000) 2.000)	0.346	1.00	1.21 ± 0.07

R ≡ Initial rate of formation of Cr(VI) in mole/l/min.

R' ≡ Initial rate of disappearance of $S_2O_8^{2-}$ in mole/l/min.

k_{obs} = The overall first order rate constant from $\log[S_2O_8^{2-}]$/time plots in units of min^{-1}.

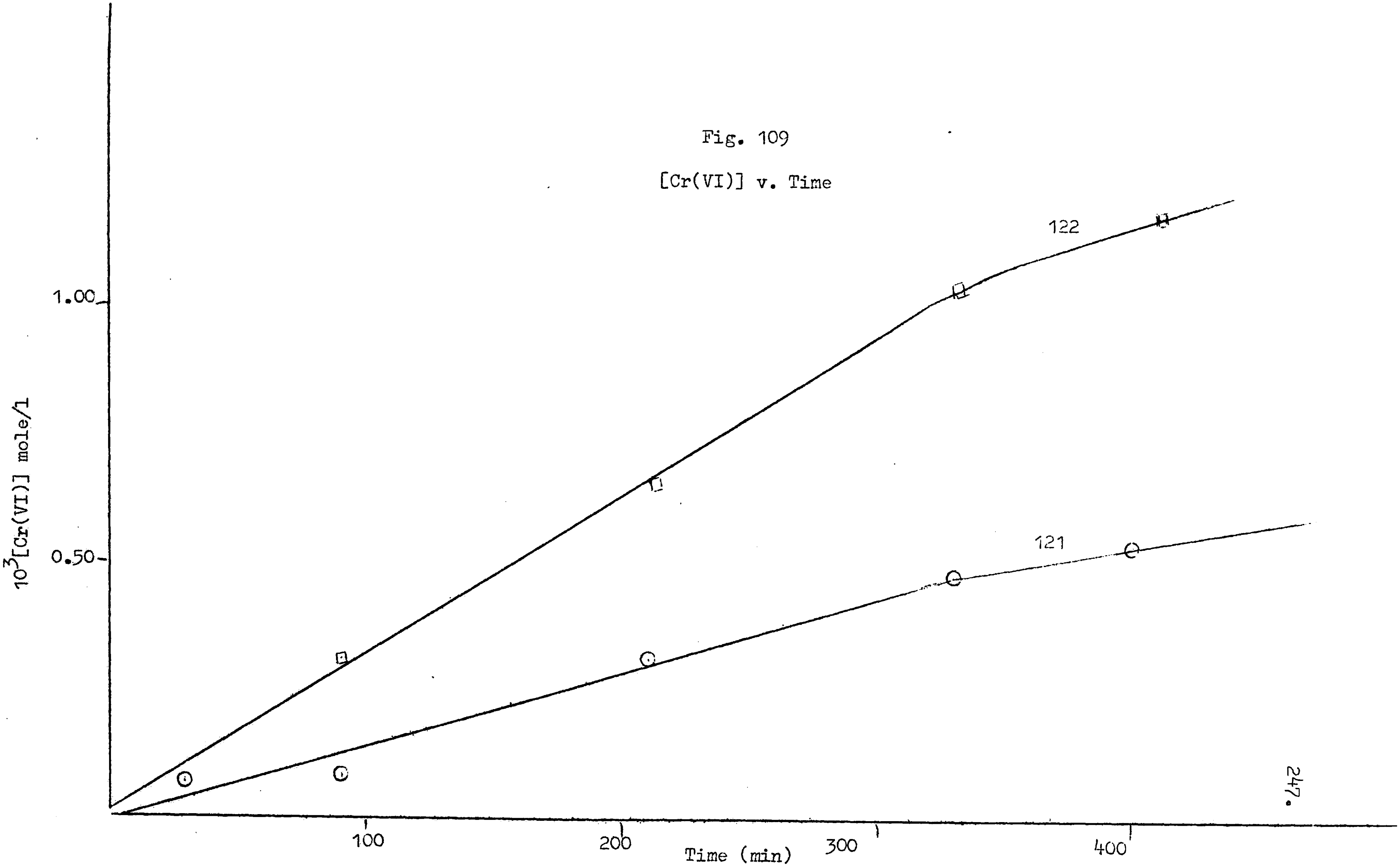


Fig. 109

[Cr(VI)] v. Time

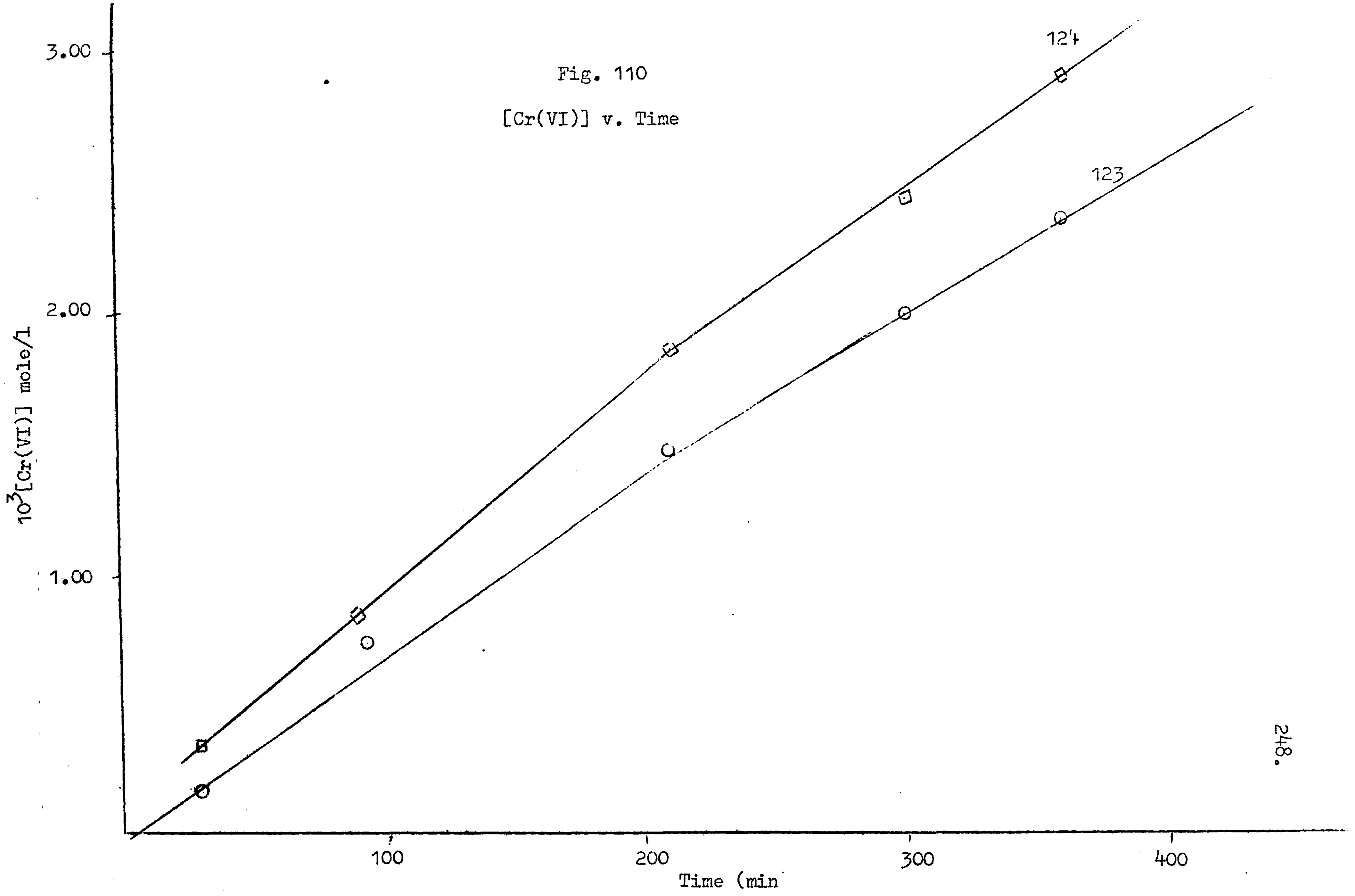
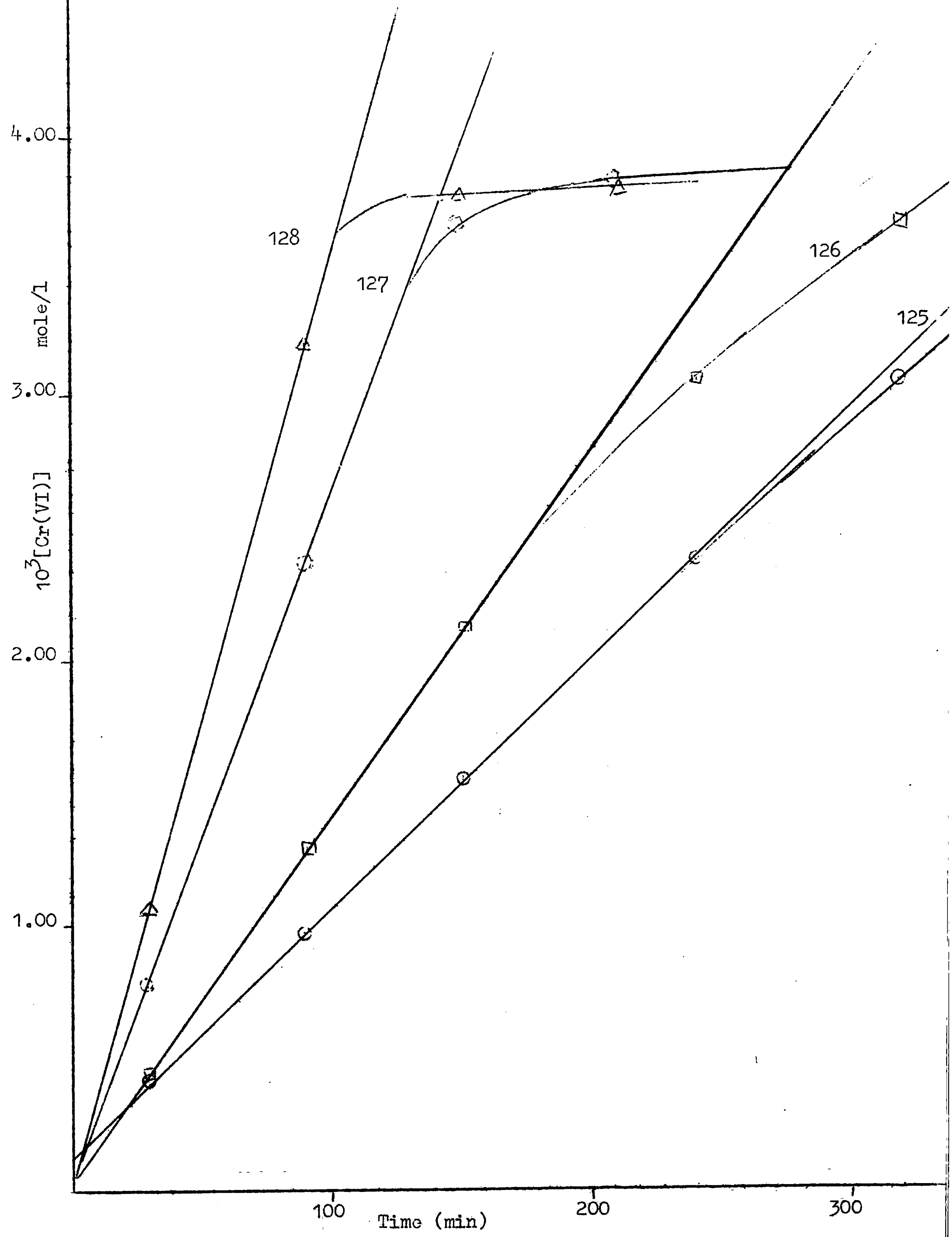


Fig. 110

[Cr(VI)] v. Time

Fig. 111

[Cr(VI)] v. Time



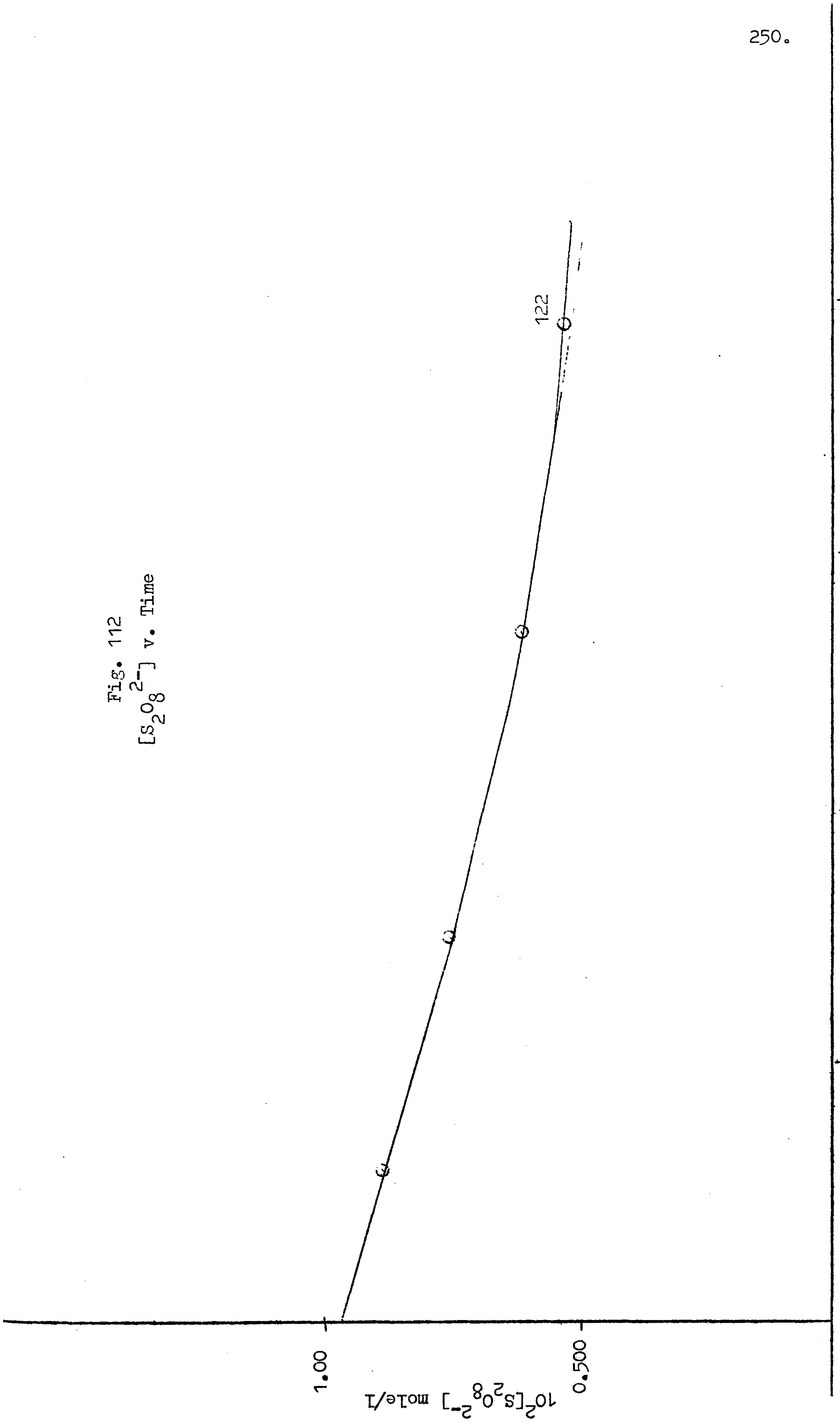


Fig. 112

$[S_2O_8^{2-}]$ v. Time

Fig. 113

[$S_2O_8^{2-}$] v. Time

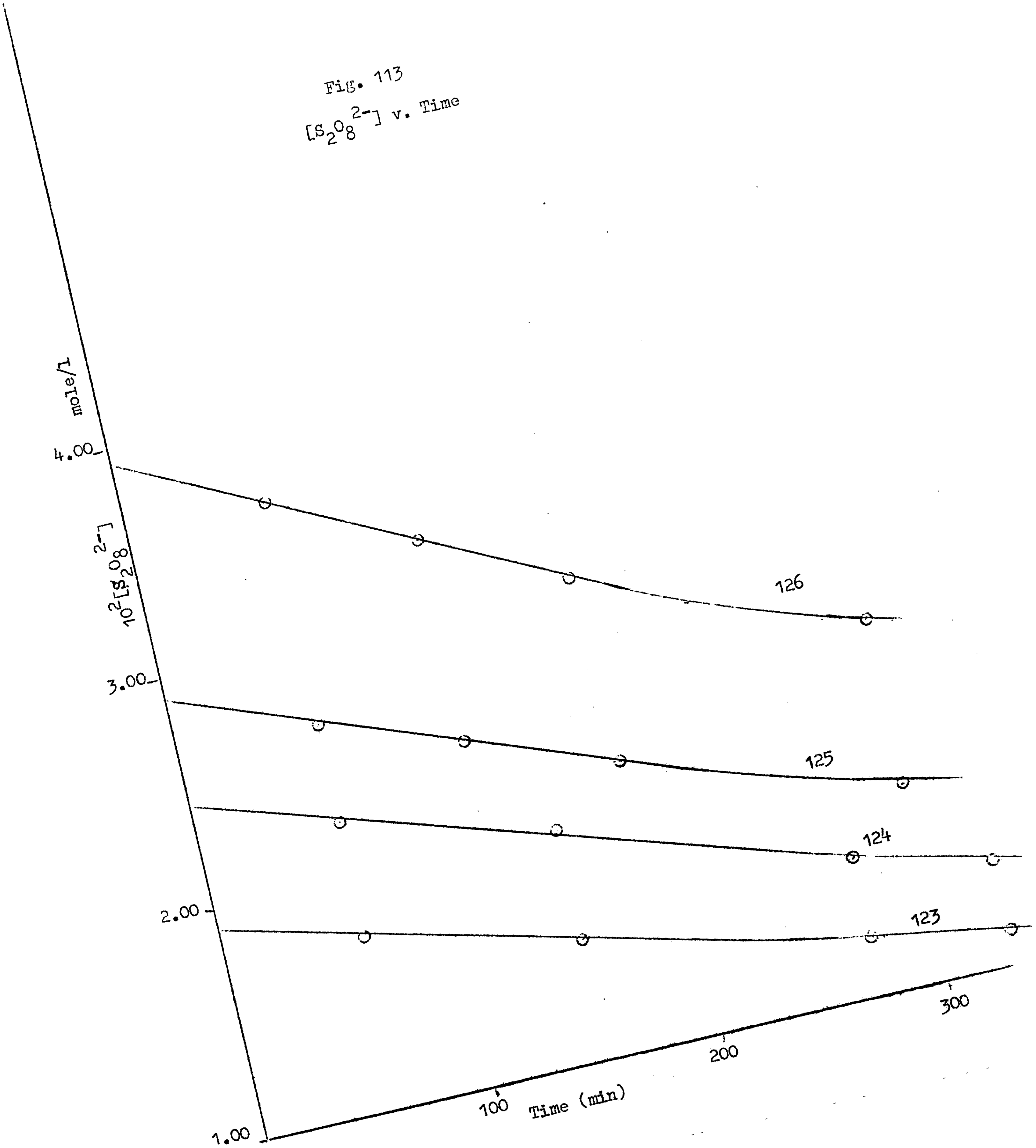


Fig. 114

$[S_2O_8^{2-}]$ v. Time

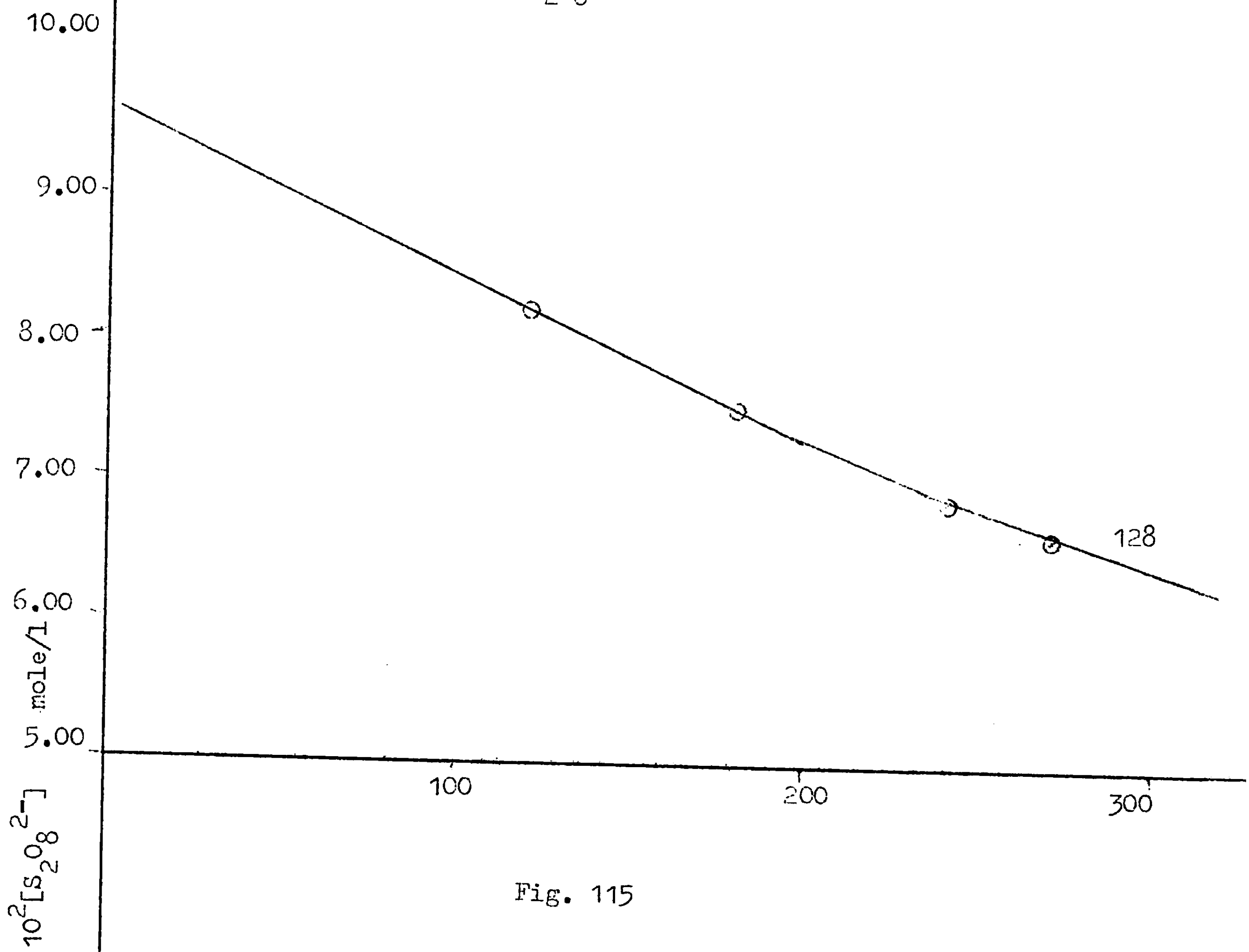
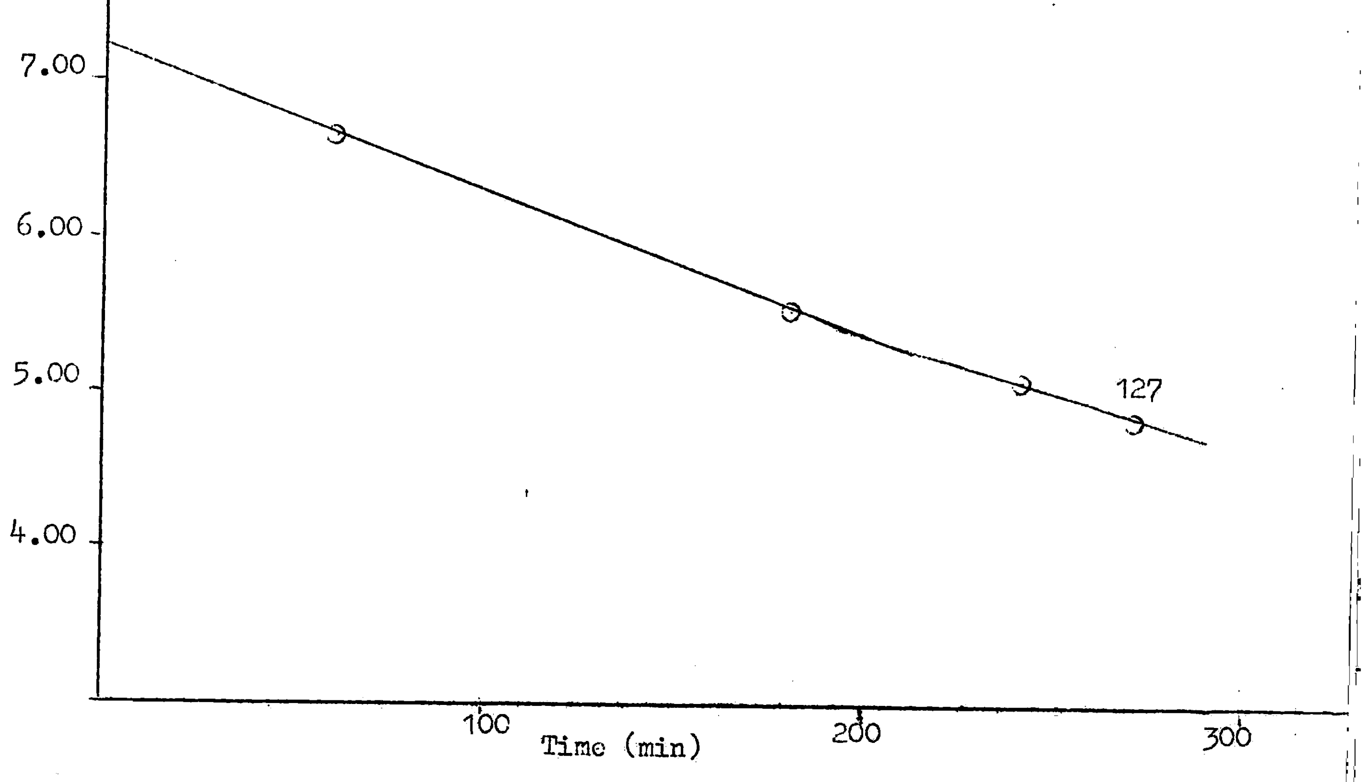


Fig. 115



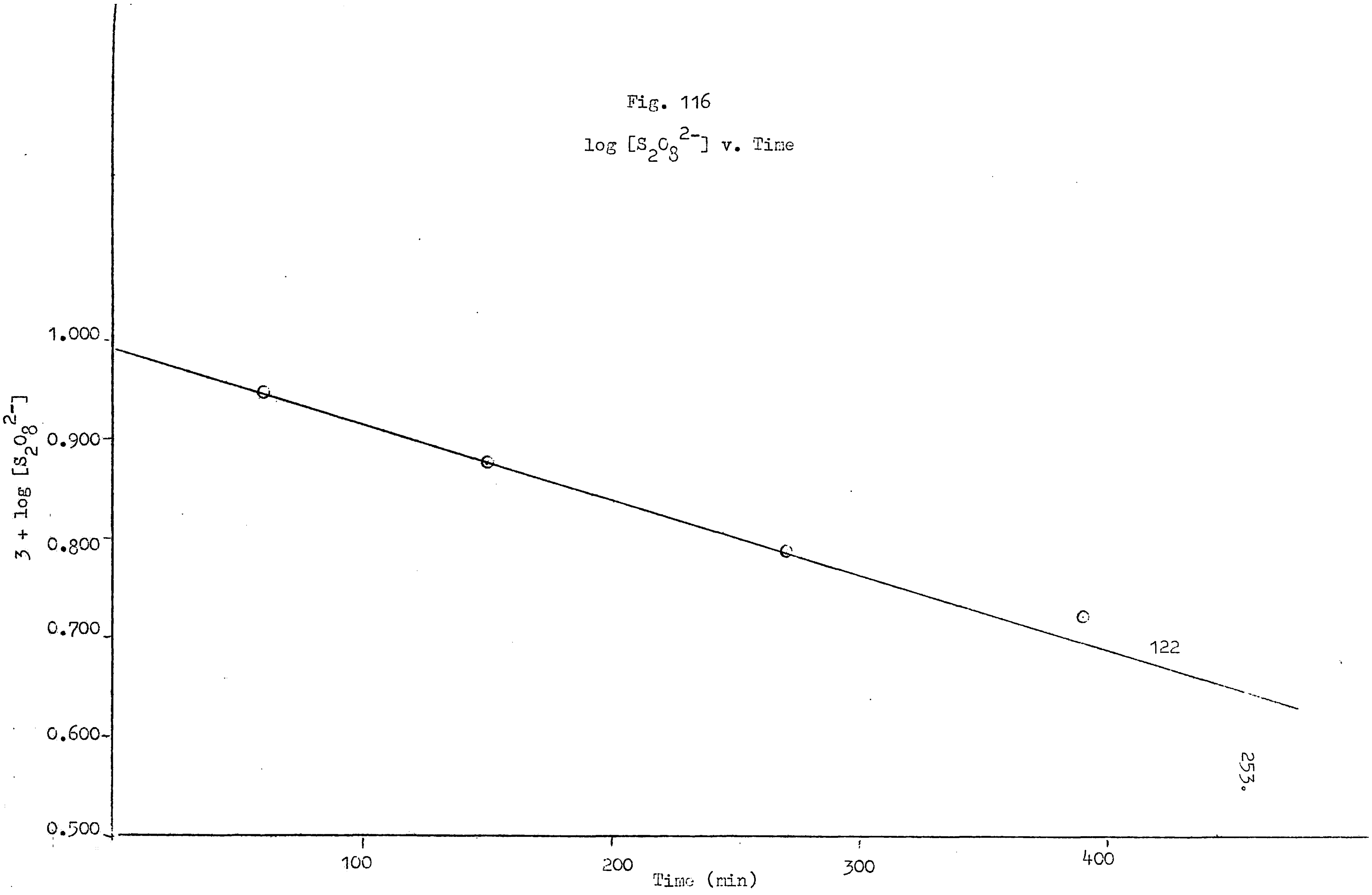


Fig. 116

log [$S_2O_8^{2-}$] v. Time

Fig. 117

$\log [S_2O_8^{2-}]$ v. Time

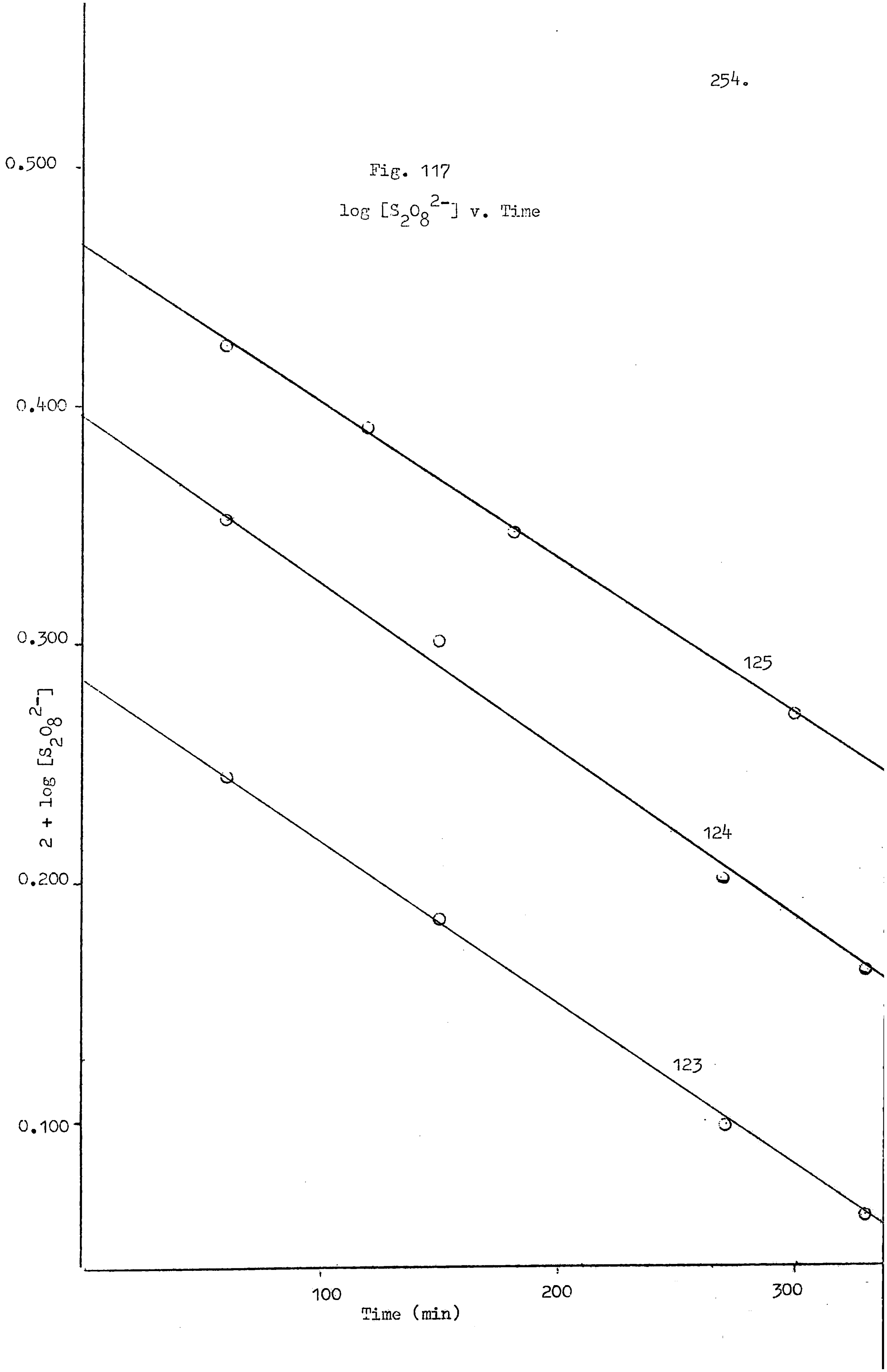


Fig. 118

log $[S_2O_8^{2-}]$ v. Time

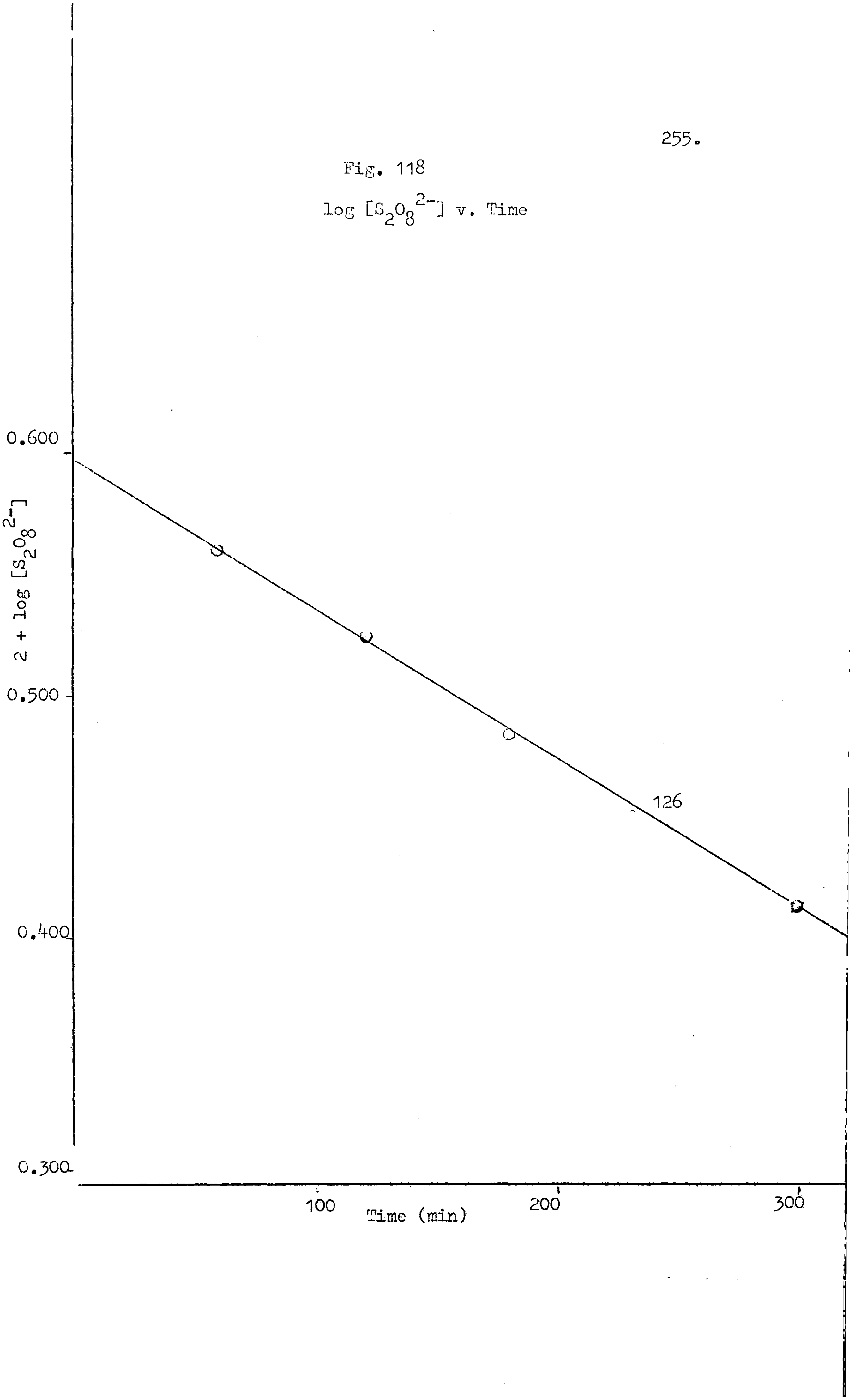


Fig. 119

log [$S_2O_8^{2-}$] v. Time

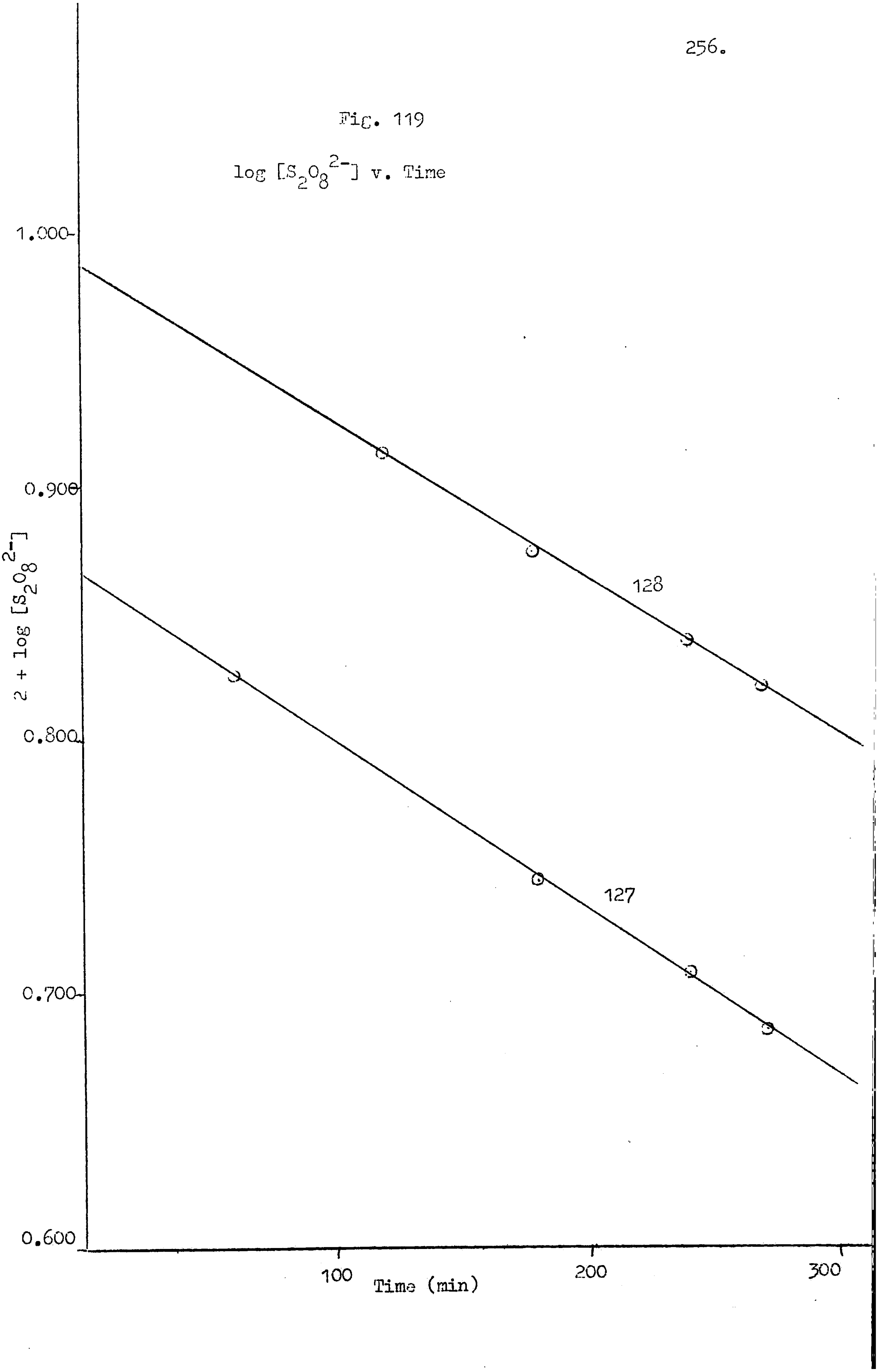


Fig. 120

[Cr(VI)] v. Time

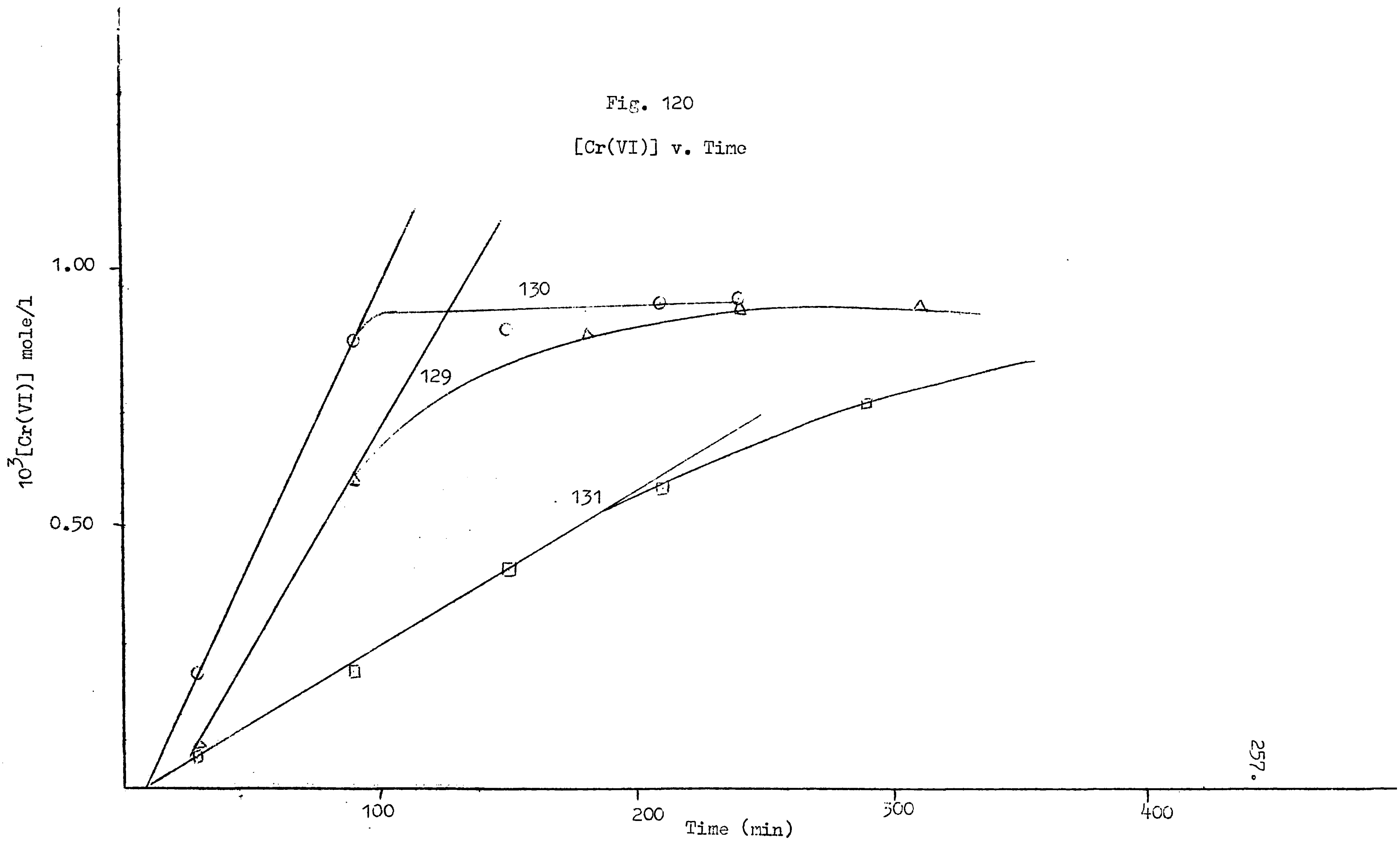


Fig. 121

$[S_2O_8^{2-}]$ v. Time

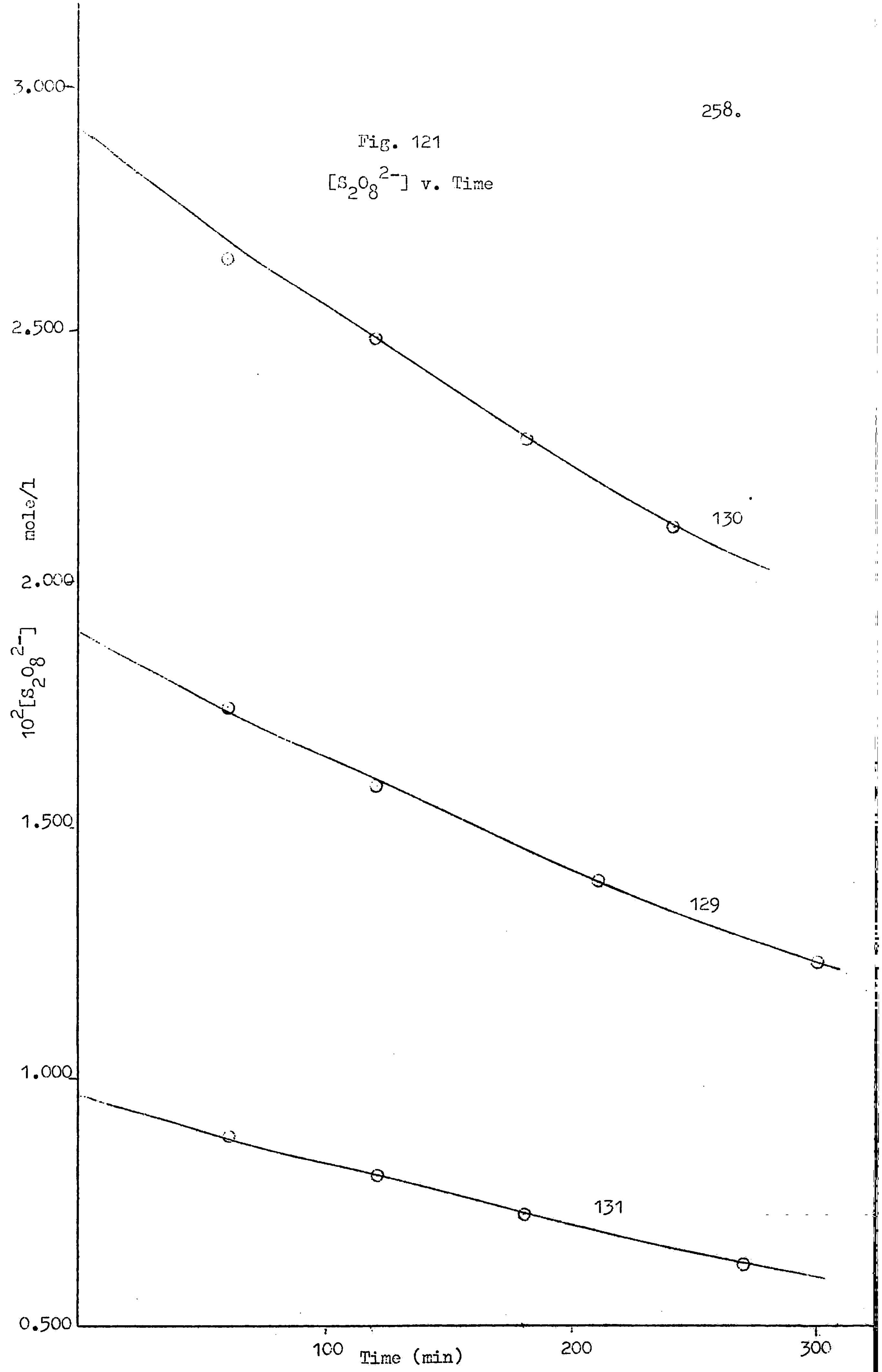


Fig. 122

log $[S_2O_8^{2-}]$ v. Time

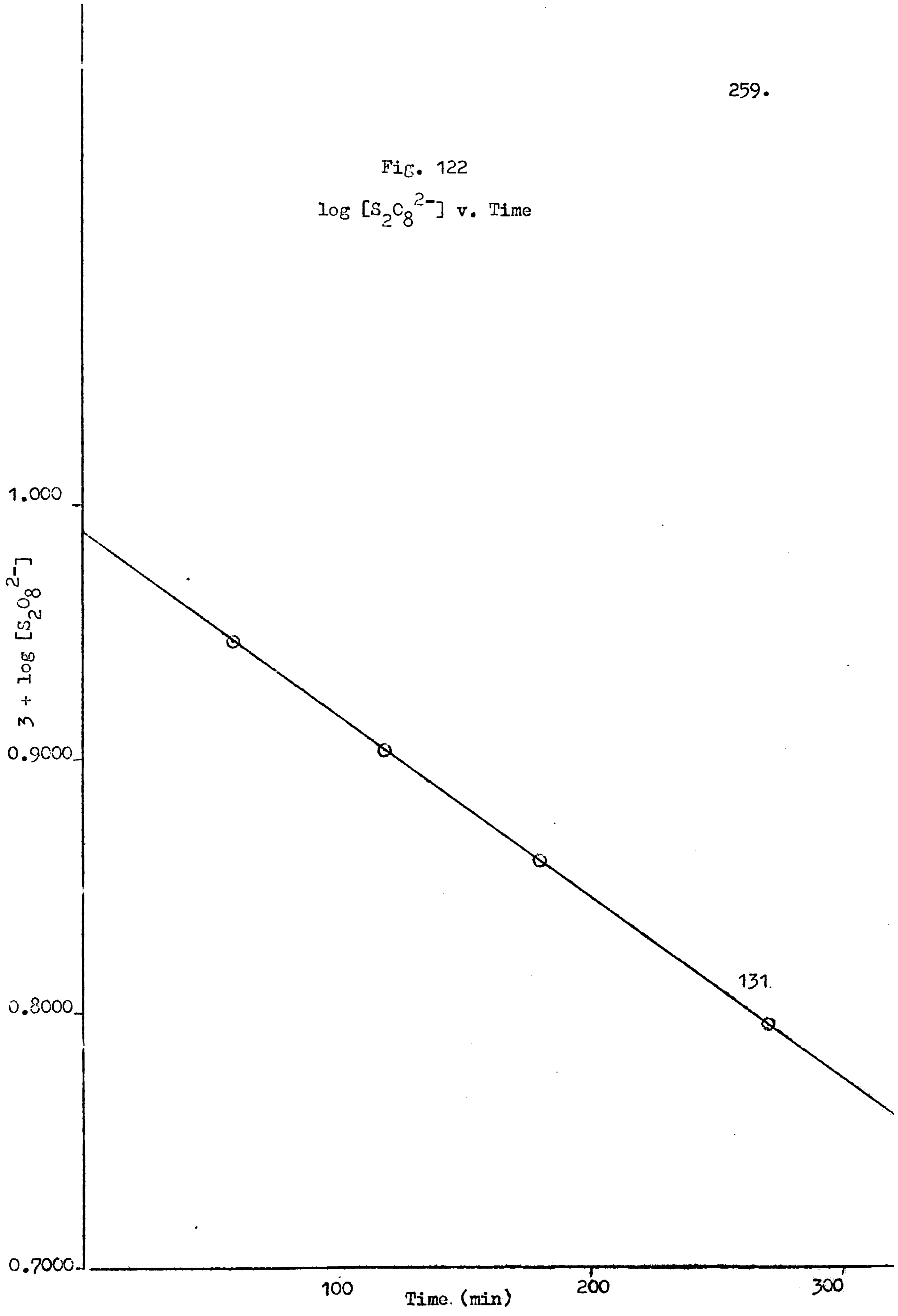
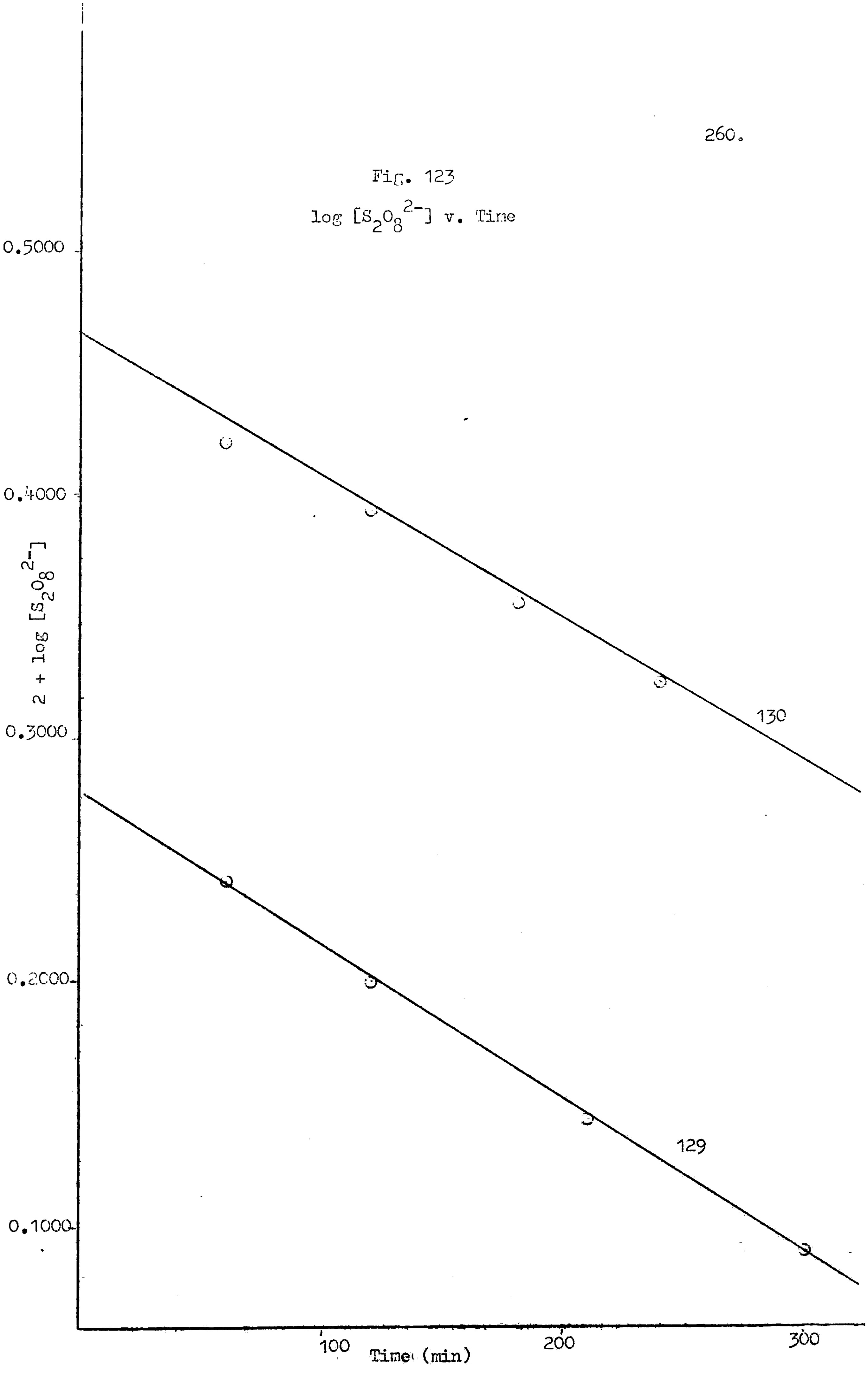


Fig. 123

log $[S_2O_8^{2-}]$ v. Time



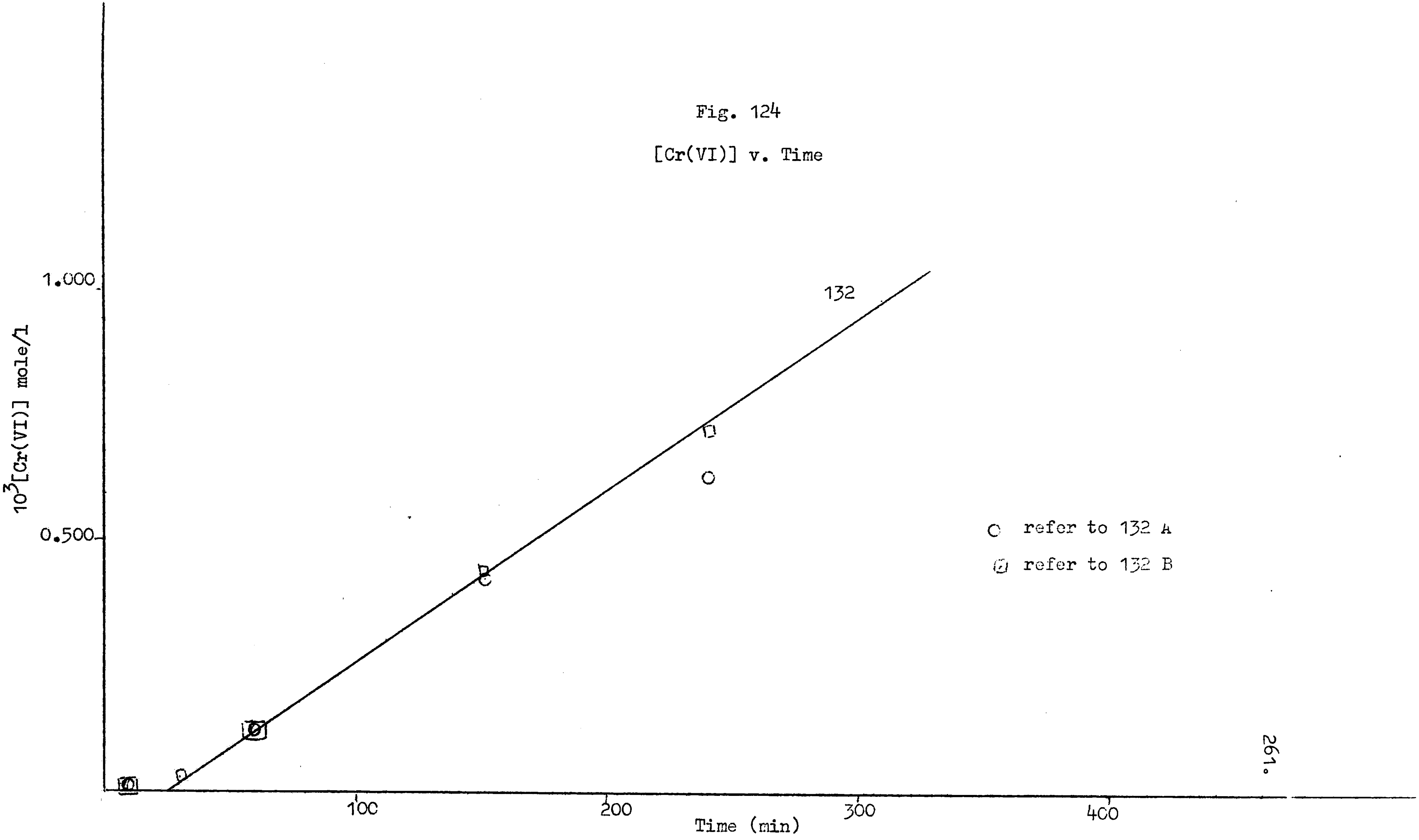
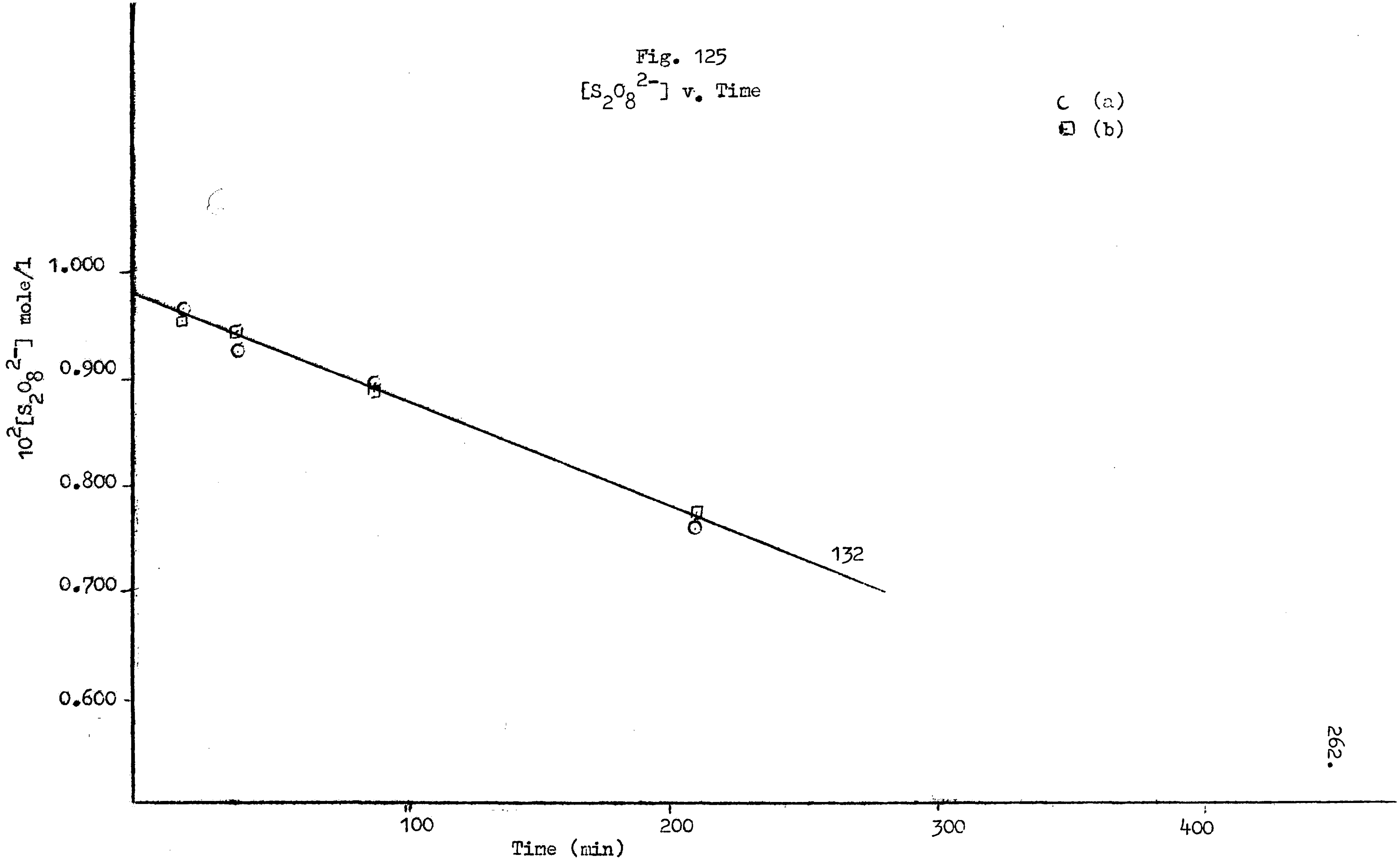


Fig. 124

[Cr(VI)] v. Time

Fig. 125

$[S_2O_8^{2-}]$ v. Time



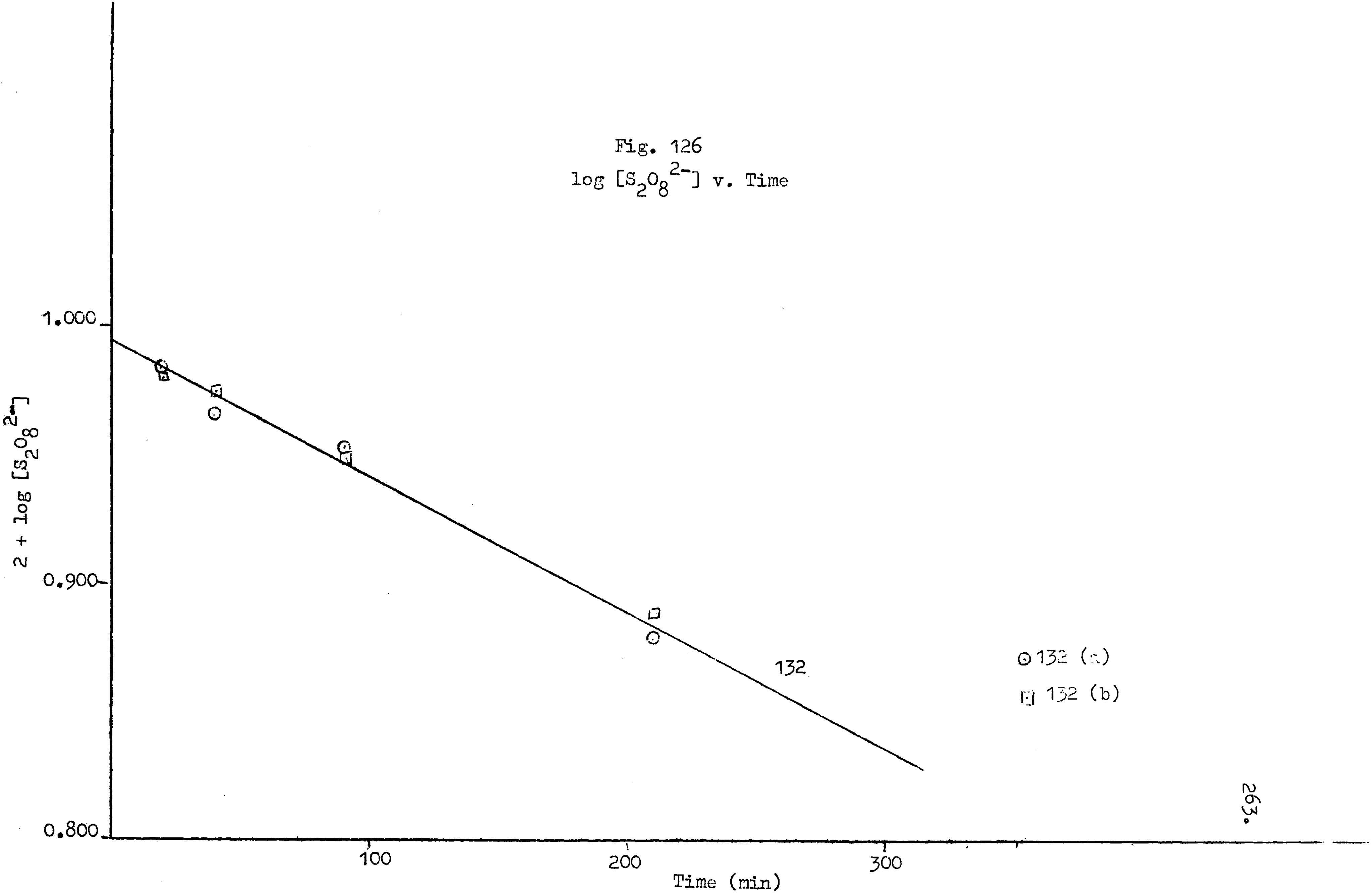


Fig. 126
log $[S_2O_8^{2-}]$ v. Time

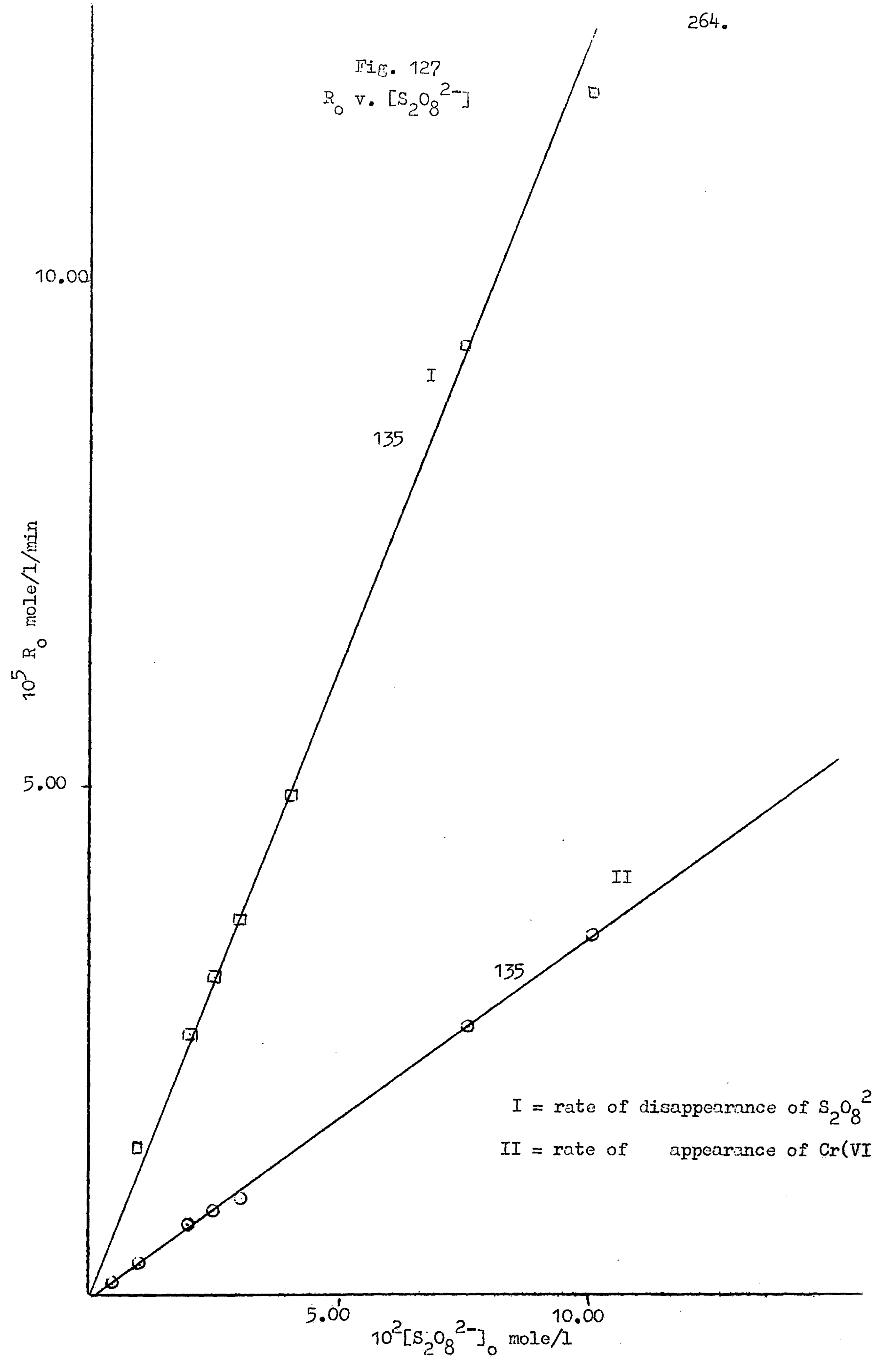


Fig. 127
R_o v. $[S_2O_8^{2-}]$

COMMENTS

The kinetics of the oxidation of chromium(III) perchlorate and sulphate by peroxodisulphate seem to have some common features. The two reactions are first order in peroxodisulphate while the order with respect to chromium(III) is variable in both cases depending on the ratio $[S_2O_8^{2-}]/[Cr(III)]$, and approaching zero as this ratio increases.

The two reactions, however, differ in that the redox reaction in a sulphate medium is faster than that in a perchlorate medium. This suggests as was mentioned earlier, that the complexed sulphate makes the process of electron transfer from chromium(III) to peroxodisulphate easier. Moreover, the observed overall first order rate constant for the decomposition of peroxodisulphate at constant initial chromium(III) concentration, increases with increasing peroxodisulphate concentration (Table 113) in the case of chromium(III) perchlorate oxidation as was also observed by Frennesson and Fronaeus, but we find that this is not the case in the oxidation of chromium(III) sulphate in which the rate constant tends to decrease slightly with increasing peroxodisulphate concentration (Table 135). Frennesson and Fronaeus attributed the increase in the k_{obs} values in their case of perchlorate media to the formation of cationic complexes between chromium(III) and peroxodisulphate and that such complexed peroxodisulphate will undergo the decomposition via the hydrogen ion catalyzed path much more slowly than the free ion. The opposite effect in sulphate media confirms that the explanation of these authors is satisfactory because in these media the sulphate ion probably enters the inner coordination sphere of chromium(III) in preference to the bulkier peroxodisulphate ion thus leaving the latter free. The slight decrease in k_{obs} values with increasing peroxodisulphate is normal for peroxodisulphate decompositions and is probably due to an ion-pairing effect on the k_1 path for the decomposition of the ion.

An attempt to apply equation [154] to the chromium(III) sulphate reaction failed to give any meaningful plot whereas in the case of chromium(III) perchlorate straight lines parallel to each other were obtained although there was a difference between our plot and that of Fronnesson and Fronaeus. However, on examination of their only plot involving this equation shows that although different sets of points lie in an approximate straight line, individual sets of points belonging to individual runs are clustered together except for one case out of twelve runs. However, the same rate law which was originally formulated by Fronaeus and Ostman(27) for the cerium(III) - peroxodisulphate reaction results in a straight line passing through almost all the points and all the sets of points. The validity of this rate law as applied to the present reaction may therefore be rather doubtful.

The reaction betweem chromium(III) and peroxodisulphate, however, can be turned into an ordinary first order peroxodisulphate reaction by increasing the ratio $[S_2O_8^{2-}]/[Cr(III)]$, keeping the pH constant, thus making it independent of chromium(III) and in such a case and at $pH > 2$ the mechanism might not be much different from that proposed for the oxidation of manganese(II) in Chapter II.

CHAPTER V

CORRELATIONS

CHAPTER V

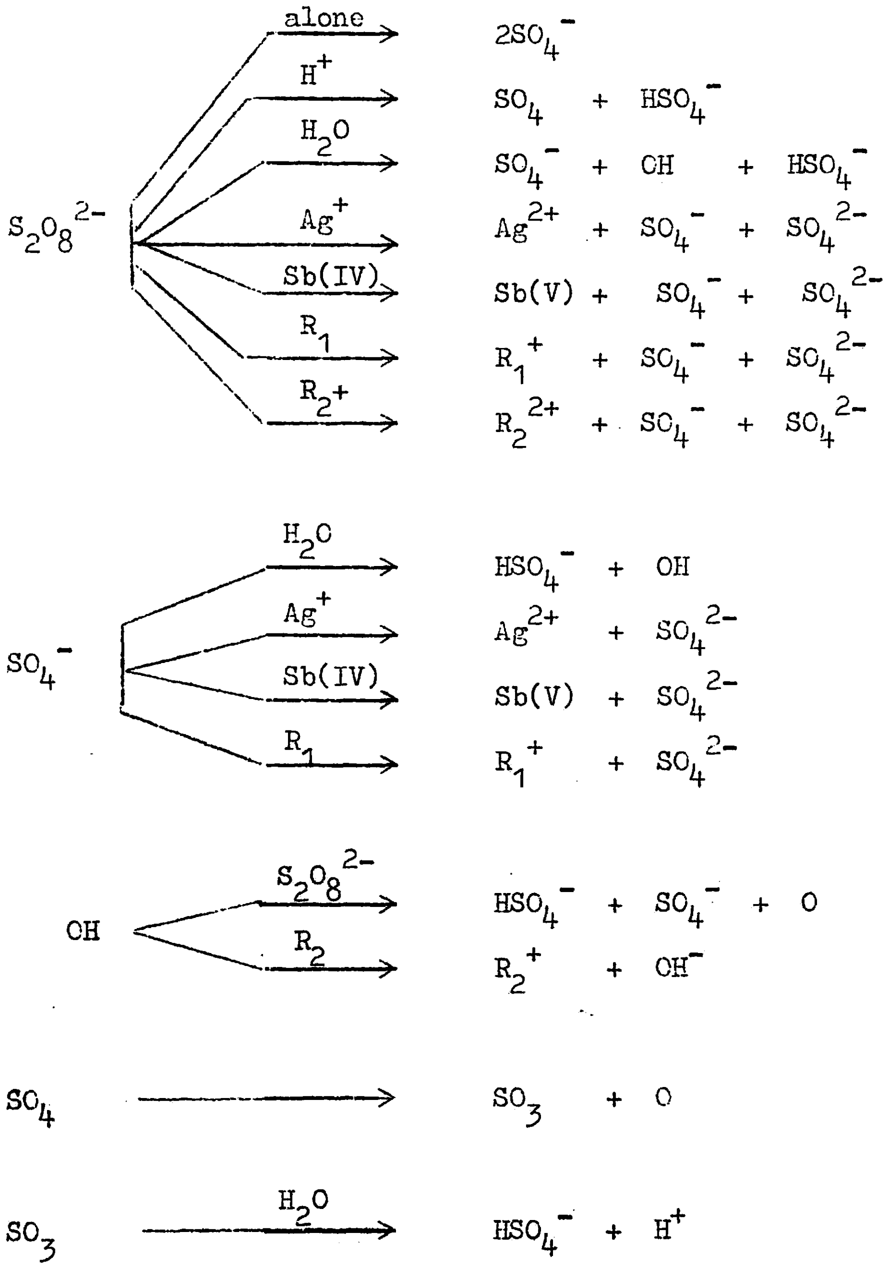
CORRELATIONS

The three reactions reported in this work seem to belong to different categories of peroxodisulphate reactions. The oxidation of manganese(II) is a first order reaction the rate of which is independent of the concentration of the reducing agent, and which shows the characteristics of a chain mechanism.

The oxidation of nitrite ion, however, is a second order reaction which is first order with respect to each reactant. The activation energy for this reaction (14 kcal/mole) is much smaller than that of the peroxodisulphate-manganese(II) reaction (31.5 kcal/mole). The mechanism seems to involve a direct reaction between the peroxodisulphate and nitrite in the rate determining step and because the two reactants are anions the reaction is catalyzed by cations.

The oxidation of chromium(III) does not seem to obey a simple rate law and the order with respect to the reducing agent is variable while the order is unity with respect to peroxodisulphate. This reaction possibly belongs to the category of 'Other Reactions' mentioned in Chapter I. The values of the initial first order rate constant for the thermal decomposition of peroxodisulphate in sulphate media (Chapter II) and phosphate media (Chapter III) whether obtained directly (Fig.64) or indirectly from the intercept of Fig.63 in which the initial rate (of disappearance of $S_2O_8^{2-}$) is plotted as a function of initial nitrite concentration, are 2.62×10^{-4} min 2.61×10^{-4} min^{-1} and 2.61×10^{-4} min^{-1}, respectively. The agreement between these values indicates that the suggestion put forward by some authors$^{(26)}$ that the thermal decomposition of peroxodisulphate shows general acid catalysis, is probably incorrect.

From what has been discussed in Chapters I - IV, the postulated kinds of reactions of peroxodisulphate and of its intermediates can be summarised as follows (if radical-radical steps are neglected).



In this scheme R_1 and R_2 are different reducing agents.

REFERENCES

1. W.L. Latimer, Oxidation Potentials, 2nd Ed., Prentice Hall Inc., N.J., 1962, p.78.

2. D.A, House, Chem. Rev., 1962, 62, 185.

3. D.M. Yost, J.A.C.S., 1926, 48, 152.

4. W.H. Cone, J.A.C.S., 1945, 78, 67.

5. A. Malaguti, Ann. Chim. (Rome), 1952, 42, 138, via C.A., 1952, 46, 8485.

6. C.E.H. Bawn and D. Margerison, Trans. Faraday Soc., 1955, 51, 925.

7. Y.K. Gupta and S. Ghosh, J. Inorg. Nuc. Chem., 1959, 11, 62

8. F. Patat and H. Proelss, Ber. Bunsenges. Phys. Chem., 1967, 71 (9-10), 1095, via C.A., 1968, 68, 43615a.

9. S.P. Srivastava and S. Ghosh, Z. Phys. Chem., 1953, 202, 191.

10. R. Schulze-Rettmer, B. Buchhein and W.Schlenter, Ber. Kornforschunsanglage Juelich, 1969, Juel 591 DE, via C.A., 1970, 72, 6549u.

11. International Union of Pure and Applied Chemistry, 1957 report of the Commission on the Nomenclature of Inorganic Chemistry, J.A.C.S., 1960, 82, 5523.

12. R.C.L. Mooney and W.H. Zachariasen, Phys. Rev., 1933, 44, 327.

13. P. Pascal, C. Duval, J. Lecomte and Pacault, Compt. Rend., 1951 233, 118, via. C.A., 1955, 46, 1908 a.

14. A. Simon and H. Richter, Naturwiss., 1957, 44, 178, via C.A., 1959, 53, 15764 h.

15. W.V. Smith, J.A.C.S., 1949, 71, 4077.

16. F.A. Bovey and I.M. Kolthoff, J. Polymer Sci., 1950, 55, 569.

17. I.M. Kolthoff, P.R. O'Conner and J.L. Hansen, J. Polymer Sci., 1955, 15, 459.

18. C. Walling, 'Free Radicals in Solution', Wiley, New York, 1957, pp. 55-56, pp. 507-8.

19. P.D. Bartlett and J.D. Cotman, J.A.C.S., 1949, 71, 1419.

20. W.V. Smith and H.N. Campbell, J. Chem. Phys., 1947, 15, 338.

21. P.C. Riesebos and A.H.W. Aten Jr., J.A.C.S., 1952, 74, 2440.

22. R.L. Eager and K.J. McCallum, Can. J. Chem., 1954, 32, 692, via C.A., 1954, 48,11887 i.

23. H. Elkeles and C. Brosset, Svensk. Kem. Tidsker, 1953, 65, 26, via. C.A., 1953, 47, 6298 d.

24. S.P. Srivastava and S. Ghosh, Z. Phys. Chem.(Leibzig), 1956, 205, 332.

25. Y.K. Gupta and S Ghosh, J. Inorg. Nuc. Chem., 1959, 11, 62.

26. I.H. Kolthoff and I.K. Miller, J.A.C.S., 1951, 73, 3055.

27. S. Fronaeus and C.O. Ostman, Acta. Chem. Scand., 1955, 9, 902.

28. S. Fronaeus and C.O. Ostman, Acta. Chem. Scand., 1968, 22, 2827.

29. S. Raman and C.H. Brubaker Jr., J. Inorg. Nuc. Chem., 1969, 31(4), 1091.

30. D.E. Pennington and A. Haim, J.A.C.S., 1968, 90(14), 3700.

31. D.H. Irvine, J. Chem. Soc., 1959, 2977.

32. V.A. Lunevok-Burmakina and A.I. Brodskii, Daklady Akad. Nauk. S.S.S.R., 1959, 129, 1335, via. C.A., 1961, 55, 26818.

33. O.A. Chaltykian and N.M. Beileryan, Izvest. Akad. Nauk. Armyan II 1958, 1, 13, via, C.A., 1958, 52, 18054.

34. J.W.L. Fordham and H.L. Williams, J.A.C.S., 1951, 73, 4855.

35. I.M. Kolthoff, A.I. Medalia and H.D. Raaen, J.A.C.S., 1951, 73, 1733.

36. J. Burgess and R.H. Prince, J. Chem. Soc., 1966, A, 1772.

37. R.A. Marcus, J. Chem. Phys., 1957, 26, 867.

38. C.V. King and O.F. Steinbach, J.A.C.S., 1930, 52, 4779.

39. C.H. Sorum and J.O. Edwards, J.A.C.S., 1952, 74, 1204.

40. A. Indelli, V. Bartocci, F. Ferranti and M.G. Lucarelli, J. Chem. Phys., 1966, 44 (5), 2069.

41. I.M. Kolthoff and R. Belcher, 'Volumetric Analysis' Vol.3, Interscience, New York, 1957, p. 288.

42. A. Indelli and J.E. Prue, J. Chem. Soc., 1959, 107.

43. B. Perlmutter-Hayman and G. Stein, J. Chem. Phys., 1964, 40(3), 848.

44. A. Indelli and E.S. Amis, J.A.C.S., 1960, 82, 332.

45. A.O. Dekker, A.H. Levy and D.M. Yost, *J.A.C.S.*, 1937, 59, 2129.

46. G.T. Morgan and F.H. Burstall, *J. Chem. Soc.*, 1930, 2594.

47. J.D. Miller, *J. Chem. Soc.*, *A*, 1968, 8, 1778.

48. W.C .E. Higginson and J.W. Marshall, *J. Chem. Soc.*, 1957, 447.

49. M.S. Tsao and W.K. Wilmarth, *Disc. Faraday Soc.*, 1960, 29, 137.

50. A.P. Bhargava and Y.K. Gupta, *Z. Phys. Chem. (Leipzig)*, 1969, 242 (5-6), 327.

51. E.P. Crematy, *Experimentia*, 1970, 26, (2), 124, via. C.A., 1970, 72, 93715 m.

52. E. Hakoila, *Ann. Univ. Turku, Ser. A.* 66, 1963.

53. Y.K. Gupta and S. Ghosh, *J. Inorg Nuc. Chem.*, 1959, 9, 178.

54. F.A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry' 2nd Ed. London, 1967, p.839.

55. N.V. Sidgwick, 'The Chemical Elements and Their Compounds' Vol.II., Oxford, 1962, p. 1272.

56. A.H. Willard and L.H. Greathouse, *J.A.C.S.*, 1917, 39, 2366.

57. C.W. Davies, 'Ion Association', Butterworth, London, 1962, p.41.

58. J.S. Laird and T.C. Simpson, *J.A.C.S.*, 1919, 41, 524.

59. M.B. Shin, *Ind. Eng. Chem., Anal.*, 1941, 13, 33.

60. C.W. Davies, *Loc. Cit.*, pp. 150-53.

61. S. Frennesson and S. Fronaeus, *Acta. Chemica Scand.*, 1966, 20, 2811.

62. C. Altman and E.L. King, *J.A.C.S.*, 1961, 83, 2825.

63. A.I. Vogel, 'Quantitative Inorganic Analysis' 2nd Ed. Longmans, London, 1958, p.302.

64. G.P. Haupt, D.C. Richardson and N.H. Coburn *Inorg. Chem.*, 1964, 3, 1779.

65. W.G. Davies and J.E. Prue, *Trans, Faraday Soc.*, 1955, 51, 1045.

66. R.E. Ball, Ph.D. Thesis, Brown University, 1967, via 'Mechanisms of Reactions of Sulphur Compounds', Vol.2., Interscience Research Foundation, Santa Monica, California.

67. The Chemical Society, London, 'Stability Constants', Special Publication No.17, 1964.

68. P.C.L. Thorne and E.R. Roberts, 'Ephraim, Inorganic Chemistry' Oliver and Boyd, London, 6th Ed., 1954, p.609 and p. 315.